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REFRACTORY MATERIALS

A SERIES OF MONOGRAPHS

John L. Margrave, Editor
DEPARTMENT OF CHEMISTRY
RICE UNIVERSITY, HOUSTON, TEXAS

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VOLUME 5. ALLEN M. ALPER, Editor
High Temperature Oxides (In Four Parts)

VOLUME 6. ALLEN M. ALPER, Editor
Phase Diagrams: Materials Science and Technology (In Three Volumes)

In Preparation
LOUIS E. TOTH
Transition Metal Carbides and Nitrides
High Temperature Oxides

Part II

Oxides of Rare Earths, Titanium, Zirconium, Hafnium, Niobium and Tantalum

Edited by

Allen M. Alper

Chemical and Metallurgical Division
Sylvania Electric Products Inc.
Subsidiary of General Telephone and Electronics
Towanda, Pennsylvania

ACADEMIC PRESS New York and London 1970
to

PROFESSOR CHARLES H. BEHRE, JR.

for the guidance and instruction he gave me in economic geology
when I was a student at Columbia University
List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

Allen M. Alper, Chemical and Metallurgical Division, Sylvania Electric Products Inc., Subsidiary of General Telephone and Electronics, Towanda, Pennsylvania (xi)*

Richard C. Anderson, Research and Development Center, General Electric Company, Schenectady, New York (1)

William J. Baldwin, Ceramic Division, National Lead Company, TAM Division, Niagara Falls, New York (167)†

M. Douglas Beals, Single Crystals, Titanium Division, National Lead Company, South Amboy, New Jersey (99)‡

LeRoy Eyring, Department of Chemistry, Arizona State University, Tempe, Arizona (41)

R. C. Garvie, Research and Development Laboratories, Corning Glass Works, Corning, New York (117)

F. Holtzberg, IBM Watson Research Center, Yorktown Heights, New York (217)

C. T. Lynch, Metals and Ceramics Division, Wright-Patterson Materials Laboratory, Wright-Patterson Air Force Base, Ohio (193)

A. Reisman, IBM Watson Research Center, Yorktown Heights, New York (217)

*Former address: Research and Development Laboratories, Corning Glass Works, Corning, New York.

†Present address: 15 Huxley Drive, Buffalo, New York.

‡Present address: Quantel Corporation, Princeton, New Jersey.
Foreword

The Refractory Materials Series was initiated in the hope of filling some serious voids in the literature available for high temperature scientists, and this new publication, *High Temperature Oxides*, edited by Dr. Allen M. Alper, will clearly perform this function. For thousands of years, men have worked with oxides at high temperatures—ceramics, cements, bricks, tiles, glazes, etc. were widely applied long before their basic chemistry and physics were understood. The application of modern methods has led to hundreds of new oxide materials and thousands of new applications as ultra-pure compounds, variable stoichiometries, and a great variety of physical and chemical properties have been measured and characterized on the basis of current theories.

In this sequence of volumes on *High Temperature Oxides*, Dr. Alper has drawn on his own experience in geochemistry, ceramics and glass technology to define the broadest coverage of this most important group of Refractory Materials yet available in the literature. His co-authors include experts from a variety of laboratories—industrial, government and academic. This group of outstanding scientists has made an extensive yet critical coverage of oxides and systems of oxides with emphasis on fundamental properties as well as the important new technological developments.

It is my hope that this publication, joined by the earlier volumes of this series, and those yet to be printed, will make the series of books on Refractory Materials an indispensable tool for the modern high temperature scientist.

*John L. Margrave*

*February 1970*
*Houston, Texas*
Preface

In the past five years, transition metal oxides have grown in technical and economic importance. They are now being widely used in chemistry and in electronic, refractory, and aerospace applications. The following are discussed: yttria, thoria, lanthanide and actinide oxides, titanates, zirconia, zirconates, zircon, hafnia and tantalum and niobium oxides.

Thoria-doped yttria ceramics are now becoming important specialty ceramics. In the past few years, these materials have been perfected into high-temperature, transparent ceramics. Lanthanide and actinide oxides are now being widely used in chemicals, phosphors, lasers, and ceramics; these oxides are discussed in depth. Titanates and some zirconates are being widely used in electronic applications. Zirconia and zirconia-containing compounds are some of the most widely used refractories. Since zirconia-containing compounds are very important in complex refractories, much work has been done to gain a better understanding of them. This work is reviewed to show the relationship of these ZrO$_2$ solid solutions and compounds to composition and temperature. The cost of HfO$_2$ is decreasing and, consequently, this very refractory oxide is becoming increasingly important. Recent research on tantalum and niobium oxide-containing compounds is also reviewed.

For information on the transitional metal oxides of Cr, Mn, Fe, Co, Ni, see Part I, entitled Magnesia, Lime, and Chrome Refractories. Those oxides were included in Part I because they are extremely important in the manufacture of steel.

Part III will discuss the properties and fabrication of the more stable oxides such as MgO, Al$_2$O$_3$, and BeO, which are widely used in ceramics and glasses.

Part IV will review the most recent research and advances that have been made in refractory glasses and glass-ceramics. Compounds containing Al$_2$O$_3$, such as mullite and spinel, are discussed, and research work on tungsten and zinc oxides is brought up to date. There is also an in-depth chapter on slip-casting ceramics.

The editor wishes to thank Prof. John L. Margrave of Rice University and Mrs. Thyrza C. Hanson and Dr. John H. Munier of Corning Glass Works. Thanks are also given to all the contributors who made this volume possible. Corning Glass Works and Sylvania Electric Products Inc. are also acknowledged for their support.

Allen M. Alper

March 1970
Towanda, Pennsylvania
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Thoria and Yttria

Richard C. Anderson

Thoria ceramics have been widely investigated during the early 1960s largely because of their great potential value to nuclear technology. Yttria, as a ceramic, was virtually unknown prior to this period. Research on its fabrication and properties may be considered a forerunner of its future use in numerous specialty applications.

This review covers investigations of the fabrication, properties, and behavior of polycrystalline ThO₂ and Y₂O₃ from the viewpoint of the ceramist. It is limited to solid solutions having the basic structure types ascribed to the pure oxides.

Recent technical progress in this area includes the development of the “Sol-gel” process for synthesizing ThO₂ powders, the advance in understanding of conductivity mechanisms of defect solid solutions, the development of processes for producing optically transparent Yttralox* and Thoralox* ceramics, and the finding that both Y₂O₃ and ThO₂ behave elastically to high temperatures. Work on sintering, creep testing, and electrical behavior indicate the need for defining the temperature dependent solution limit of CaO in ThO₂.

Ryshkewitch (1960) should be referred to for a review of ThO₂ ceramics prior to this decade. Y₂O₃ ceramics have not been reviewed previously.

I. STRUCTURAL AND CHEMICAL

A. Crystal Chemical

Thorium oxide has the fluorite-type of cubic crystal structure (after CaF₂) shown in Fig. 1 and bears many similarities to the family of stabilized zirconias having the same structure. The a₀ lattice parameter for ThO₂ is between 5.59 and 5.60 Å (see Swanson and Tatge, 1953; Kempter and

*Trademarks of General Electric Company.
Elliot, 1959) and it has a theoretical density of 10.001 gm/cm$^3$. The structure is not known to undergo any polymorphic transformation up to its melting point of 3220°C (Lamberton et al. 1953), the highest of the oxides. The thorium atom loses its $(6d)^2(7s)^2$ electrons in assuming the Th$^{4+}$ state. This quadrivalent ion has eight-fold coordination with its nearest O$^{2-}$ neighbors in the fluorite structure and a radius of 0.99 Å (Zachariasen, 1954).

Yttrium oxide has the c-type rare earth oxide structure ($\text{Tl}_2\text{O}_3$ prototype) common to the smaller cation rare earth oxides. This structure is most conveniently thought of as a modification of the fluorite structure (Wells, 1952) where Y$^{3+}$ occupies the center of a distorted cube. Figure 2 shows the idealized spatial relations for two such cubes within the unit cell. In this structure only six cube corners are occupied by oxygen ions. The unoccupied cube corners are on a face diagonal in one cube and on a body diagonal in the edge-adjacent cube. (In Chapter 2, Eyring refers to alternative possibilities for occupancy of cube corners.) This arrangement necessitates including 32 YO$_{1.5}$ groups in the unit cell, whereas only four ThO$_2$ groups are required in the fluorite structure. For Y$_2$O$_3$ this leads to an $a_0$ lattice parameter of 10.604 Å and a theoretical density of 5.03 gm/cm$^3$ (Wyckoff, 1948; Staritzky, 1956) where Y$^{3+}$ has an ionic radius of 0.91 Å (Roth and Schneider, 1960). Foëx (1966) and Sata (1966) place the melting point of Y$_2$O$_3$ at 2435 and 2376°C, respectively.

Foëx and Traverse (1966) report Y$_2$O$_3$ transforms into a hexagonal H-form at about 2270°C. Miller and Daane (1965) have prepared non-

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**FIGURE 1** Fluorite structure (after Kingery, 1960).
THORIA AND YTTRIA

FIGURE 2 Six-fold coordination in Y$_2$O$_3$.

stoichiometric samples of YO$_{1.491}$ which has the Y$_2$O$_3$ structure with no significant change in cell size. The oxygen deficiency results from the formation of O$^{2-}$ vacancies which serve as electron traps and impart an olive green color to the finely divided powder. The stability of the c-form of Y$_2$O$_3$ has been questioned by Mehrotra et al. (1966) who claim it undergoes a reversible transformation to a hexagonal or monoclinic form between 400 and 900°C.

B. Solid Solutions

ThO$_2$ forms extensive solid solutions with CaO, Y$_2$O$_3$ and the rare earth oxides, and UO$_2$. Very limited solutions are formed with other oxides. The divalent and trivalent cations substitute for Th$^{4+}$ in the fluorite structure with the formation of anion vacancies being the mechanism of maintaining electro-neutrality. With a few exceptions, the temperature dependence of solution limits for existence of the fluorite phase have not been studied in detail. The following references may be consulted for details of systems not discussed in this chapter: ThO$_2$–Yb$_2$O$_3$, Eu$_2$O$_3$, and Pr$_2$O$_3$ (Gingerich, 1961); ThO$_2$–Y$_2$O$_3$ (Hund and Metzger, 1952; Karkhanavala et al., 1965; Subbarao et al., 1965); ThO$_2$–CeO$_x$–Y$_2$O$_3$ (Hoch and Yoon, 1965); Th–O–N (Benz, 1967); ThO$_2$–CeO$_x$ (Whitfield et al., 1966); and others (Ryshkewitch, 1960).

Y$_2$O$_3$ is usually grouped with the rare earth oxides for consideration of its chemical properties (Moeller, 1963) because the size of the trivalent yttrium ion assumes a position in the lanthanide contraction very close to that of Ho$^{3+}$. The variation of ionic radii with atomic number can be seen

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in Fig. 3. Although $Y_2O_3$ is comparable in many properties with the rare earth oxides, the presence of a partially filled $4f$ electronic orbital leads to significantly different optical and magnetic behavior for the latter oxides. Figure 4 (Roth and Schneider, 1960) shows the phase stability regions for these oxides. (See also Chapter 2 by Eyring.) Schneider and Roth (1960) have examined the solid solution relationships for the rare earth oxides. A somewhat over-simplified statement of part of their findings would be that c-type rare earth oxide structures are formed when the average cation radius of the oxides in this series is about 0.93 Å or less. Using this approximate criterion it can be predicted that $Y_2O_3$ forms a continuous series of solid solutions with the oxides $Dy_2O_3$ through $Lu_2O_3$. Partial and progressively larger amounts of solution of those oxides from $La_2O_3$ through $Tb_2O_3$ are possible with $Y_2O_3$ while preserving the structural form of $Y_2O_3$. Such solutions may be formed without significant creation of Schottky or Frenkel defects if the rare earth oxide ion assumes the trivalent state. Substitution of the quadrivalent cations $Th^{4+}$ and $Zr^{4+}$ results in limited $Y_2O_3$-type solution formation accompanied by the formation of anion interstitials. Details of particular systems may be found as follows: $Y_2O_3$–CeO$_2$ (Bevan...
FIGURE 4 Stability relations of the A, B, and C polymorphic forms of the rare-earth sequioxides (after Roth and Schneider, 1960).

et al., 1965), \( \text{Y}_2\text{O}_3-\text{UO}_2 \) (Bartram et al., 1964; Aitken, 1966), and \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) (Duwez et al., 1951).

C. Stability

The elevated temperature stability of \( \text{ThO}_2 \) and \( \text{Y}_2\text{O}_3 \) is quite good as might be expected for oxides with high melting points. The free energy of formation for these and other stable oxides is shown in Fig. 5 (Grossman, 1964). Since many oxides can be driven off stoichiometry by changing oxygen pressure, may form suboxides, or may dissociate and vaporize, it is necessary to inquire beyond formation energies to define their relative stabilities. Searcy (1965) has reviewed the thermodynamic and kinetic considerations which influence high temperature reactions of ceramics. For some uses, the maximum temperature of the environment may be set by the sintering temperature used to fabricate the ceramic. At this temperature, continuing grain growth and shrinkage may alter ceramic properties.

Under neutral conditions and in contact with metals such as Ta, \( \text{Y}_2\text{O}_3 \) dissociates into the vapor species \( \text{YO}, \text{O} \), and to a lesser extent, Y. Ackermann and Thorn (1961a) give

\[
\Delta F_f^\circ (\text{Y}_2\text{O}_3, \text{s}) = -460,000 + 74.76T \text{cal/mole} \tag{1}
\]

between 1800 and 2000\(^\circ\)K, and

\[
\Delta F_f^\circ (\text{YO}, \text{g}) = -11,000 - 12.9T \text{cal/mole} \tag{2}
\]
between 2500 and 2700°K for the free energy of formation dependence of the YO gas species. The net free energy for the decomposition of $Y_2O_3$ by the reaction

$$Y_2O_3(s) = 2YO(g) + O$$

is, then, only some fraction of the total free energy of formation. Drowart et al. (1967) have determined the dissociation energy for this reaction to be 167 to 170 kcal/mole of YO gas by vaporization experiments. Also, see Walsh et al. (1960). Dissociation pressures for $Y_2O_3$ compared with ThO$_2$ and other refractory oxides are shown in Fig. 6 (Grossman, 1964).

It was mentioned above that $Y_2O_3$ loses some oxygen without undergoing a structural change at high temperatures in low oxygen pressure environments. The free energy change associated with the reaction

$$YO_{1.5}(s) = YO_{1.491}(s) + 0.009 {1\over 2}O_2$$

will be less than that associated with Eq. (3). This is a reversible reaction and the color change associated with it does not result in structural damage as when YO gas vaporizes.

Ackermann and Thorn (1961b) and Ackermann et al. (1963) have investigated the thermodynamic behavior of ThO$_2$ and find it becomes
very slightly substoichiometric (ThO$_{1.98}$) above 2800°K. The effective vapor pressure of ThO$_2$ (g) was given by

$$\log p \text{ (atm)} = 8.26 - 3.55 \times 10^4 / T$$  \hspace{1cm} (5)$$

Other values determined included

$$\Delta F_f^\circ \text{ (ThO$_2$, g)} = -138,600 + 11.4T \text{ cal/mole} \hspace{1cm} (6)$$

and

$$\Delta F_f^\circ \text{ (ThO, g)} = -10,300 - 14.4T \text{ cal/mole} \hspace{1cm} (7)$$

$$\Delta F_f^\circ \text{ (ThO$_2$, s)} = -296,000 + 46.38T \text{ cal/mole} \hspace{1cm} (8)$$

all between 2000 and 3000°K, indicating the great stability of ThO$_2$. Shchukarev and Semenov (1965) also determined the partial pressures of ThO and ThO$_2$ gas from 2000 to 2700°K.

Benson et al. (1963) have calculated the cohesive and surface energies for ThO$_2$, assuming pure ionic bonding. The cohesive energy was estimated to lie between $-2373$ and $-2413$ kcal/mole and the surface energy

FIGURE 6   Dissociation pressure for several oxides (after Grossman, 1964).
between 810 and 1150 erg/cm², with the major uncertainty being the validity of compressibility measurements.

D. Sources

Prior to the 1950s, Y₂O₃ and the rare earth oxides were not commercially available in large quantities and erroneously considered by some as “rare” in their occurrence. Today, they are still somewhat expensive by ceramic raw material standards, but commercially available in quantity at high purity levels. Moeller (1963) has discussed the chemistry of recovery and separation of the lanthanides from the cerium group minerals Monazite and Bastnaesite, and the yttrium group minerals Euxenite and Xenotime. (See Mandle and Mandle, 1964, for another review.) Monazite sand is also the principal source of ThO₂ (Kopleman, 1959). The relatively lower cost of ThO₂ stems from the ease by which it can be separated from lanthanides. The rare earth oxides, including Y₂O₃, are commercially available at purities generally in excess of 99.9 percent. The process of separation by ion exchange adds to production costs. Since a broad spectrum of lanthanides is separated from any ore body, the cost of individual oxide powers must depend in part on achieving markets for others in lesser demand.

II. ELECTRICAL

Prior to this decade, almost nothing was known about electrical conductivity mechanisms in Y₂O₃. ThO₂ was characterized as an n-type semiconductor whose conductivity was strongly affected by temperature, atmosphere, and certain compositional changes. In addition, it was presumed that oxygen ion vacancies might contribute to conductivity in a manner analogous to that established for structurally similar stabilized zirconia.

In general, pure Y₂O₃ and ThO₂ are electronic conductors whose level of conductivity is dependent upon temperature and \( p_{O_2} \) [oxygen partial pressure]. Changes in either parameter cause small deviations in stoichiometry which in turn establish a concentration of electronic charge carriers. The equilibrium charge carrier density is the principal determinant of conductivity level as the mobility of these carriers is thought to be only slightly affected by changes in temperature and \( p_{O_2} \). Since a dependence upon \( p_{O_2} \) exists, however, slight deviations in stoichiometry depend upon ionic charge transfer, which for ThO₂ and Y₂O₃ is thought to take place by oxygen ion diffusion.
A. Pure Oxides

For pure Y\textsubscript{2}O\textsubscript{3}, Tallan and Vest (1966) have established the conductivity response to oxygen partial pressure and temperature to be as shown in Fig. 7. Conductivity was shown to be better than 99 percent electronic above 1200°C. For the high \(p_{O_2}\) region a \(\frac{3}{16}\) dependence on \(p_{O_2}\) and an activation energy of 1.94 eV was calculated. They concluded that a single conductivity mechanism would account for their findings and that this mechanism most probably depended upon the presence of fully ionized yttrium vacancies and compensating holes. It was pointed out that a shift from p-type to n-type conductivity at the lower \(p_{O_2}\)'s would be expected to take the form shown in Fig. 7, but the authors did not feel their data reproducible enough to allow a concrete analysis. At temperatures below 900°C, galvanic cell and polarization measurements indicated the onset or ionic conductivity as an important contributor to total conduction, where ionic conductivity was attributed to the presence of impurities. Self-diffusion in Y\textsubscript{2}O\textsubscript{3} was measured by Berard and Wilder (1963) for Y\textsuperscript{3+} and by Wirkus \textit{et al.} (1967) for oxygen. They found the Y\textsuperscript{3+} diffusivity could be represented by \(D = 2.41 \times 10^{-4} \exp\left(-\frac{43,900}{RT}\right) \text{cm}^2/\text{sec}\) from 1400 to 1800°C, while oxygen diffusivity followed the relationship \(D = 7.24 \exp\...\)
(-58,600/RT) between 1000 and 1500°C. From these measurements it can be calculated the diffusion coefficient for oxygen in $Y_2O_3$ is two or three orders of magnitude larger than that for $Y^{3+}$ at 1400°C.

Numerous authors have contributed to our understanding of the effect of temperature, atmosphere, composition, and processing on the amount and type of conductivity exhibited by ThO$_2$. Subbarao et al. (1965) reported that “pure” ThO$_2$ shows an ionic transference of 0.05 at 1000°C increasing to 0.12 at 1400°C for measurements made in air. Lasker and Rapp (1966) recorded a $p_{O_2}^{1/4}$ dependence of conductivity for “pure” ThO$_2$ in the high oxygen pressure regions. At intermediate oxygen partial pressures, this dependence broke down and it was assumed that the ionic contribution became very significant owing to the presence of a large concentration of either intrinsic defects or impurities. The purity of ThO$_2$ used by experimenters has generally been in the 99.90 to 99.99 percent range with Ce$^{4+}$ as a major impurity. This limitation on purity has either been the cause of the development of a significant ionic contribution to conductivity at high temperatures and low oxygen pressures or at least a factor of importance in limiting the conclusions which may have otherwise been formulated concerning the intrinsic electrical character of ThO$_2$. Smith et al. (1966) determined the permeability of ThO$_2$ to oxygen, but were unable to draw conclusions regarding permeation mechanisms. It appears likely that their results were influenced by a changing value of ionic transference number over the temperatures and oxygen pressure ranges employed.

B. Anionic Conductivity

When Ca$^{2+}$ or Y$^{3+}$ is substituted for Th$^{4+}$ in ThO$_2$ a solid solution forms with anion vacancies, in the same way that it does in stabilized zirconia. For Y$_2$O$_3$, the substitution of Th$^{4+}$ or Zr$^{4+}$ for Y$^{3+}$ leads to the development of a defect solid solution with anion interstitials. In both cases, substitution at the several percent level leads to structures which exhibit a level of anionic conductivity comparable to that of the electronic conductivity plus or minus a factor of ten. The concentration of anionic vacancies (or interstitials) is now large with respect to the number of electronic charge carriers normally present in pure Y$_2$O$_3$ or ThO$_2$, and furthermore, this concentration is fixed by composition and independent of $p_{O_2}$ (to a first approximation). The mobility of these anionic charge carriers is small in comparison with that of electronic charge carriers. Their mobility is also strongly temperature dependent. Most probably, the anionic conductivity is a thermally activated process and should follow an Arrhenius relationship. The problems attendant in determining the conductivity mechanisms for these materials are...
related to sorting out ionic and electronic contributions, determining temperature, $p_{O_2}$, and crystallographic structure dependencies.

Lasker and Rapp (1966) have traced the development of our present understanding of the thermodynamic relationship between nonstoichiometry, temperature, and equilibrium gas pressure from the work of Wagner and Schottky (1930). It has been found particularly useful to treat test samples as electrolytes in oxygen concentration cells. Where electrical conduction takes place by ionic means, the standard cell potential or voltage at open circuit, is given by

$$E_0 = \frac{RT}{4F} \ln \frac{p(O_2)_1}{p(O_2)_2}$$

(9)

where $R$ is the gas constant, $T$ is absolute temperature, and $F$ is Faraday’s constant. When less than full thermodynamic voltage is measured, mixed ionic and electronic conduction is indicated and the ionic transfer number, $t_i$, is equal to the measured voltage divided by $E_0$. It is necessary to establish the reversibility or nonpolarizability of electrodes for this assumption to hold true.

C. Defect Y$_2$O$_3$ Systems

Subbarao et al. (1965) concluded that Th$^{4+}$ substituted for Y$^{3+}$ in Y$_2$O$_3$ causing the formation of an anion interstitial structure. The presence of oxygen interstitials introduced a significant ionic contribution to the conductivity as determined by oxygen concentration cell measurements. Anderson (unpublished research) concluded, also, that oxygen interstitials were created in ThO$_2$-doped Y$_2$O$_3$ based upon the comparison of x-ray calculated densities and measurements on a sample of full density. The effect of substituting 1 M/0* ZrO$_2$ into Y$_2$O$_3$ is shown in the conductivity curves of Fig. 8 (Anderson, unpublished research). ZrO$_2$ is soluble in Y$_2$O$_3$ to a level of approximately 15 M/O at elevated temperatures (Duwez et al., 1951) and is presumed to produce oxygen interstitials as does ThO$_2$. This amount of ZrO$_2$ has the effect of drastically reducing the conductivity in air of the parent Y$_2$O$_3$ structure. Since it is unlikely that the presence of ZrO$_2$ in solution would have much effect upon the mobility of the electronic current carriers, the number of electrically effective defect sites must be greatly reduced. In fact, it is possible the residual conductivity is largely n-type since a reduction in the oxygen partial pressure increases the conductivity of the substituted structure. It is presumed the substitution of Zr$^{4+}$ for Y$^{3+}$ in the cation sublattice acts to neutralize the net negative charge on the sublattice (Tallan and Vest, 1966) of pure Y$_2$O$_3$ and thereby sup-

*Mole percent.
presses the formation of positive holes responsible for p-type conduction.

The enhancement of ionic conductivity anticipated from the presumed creation of anion interstitials by the presence of Zr\(^{4+}\) in Y\(_2\)O\(_3\) is not evident in Fig. 8. However, reduced samples undergo oxidation in air at 1200°C much faster than pure Y\(_2\)O\(_3\) as evidenced by a color change from black to light. In the Y\(_2\)O\(_3\) structure (Fig. 2) it is believed the solution of ZrO\(_2\) or ThO\(_2\) leads to the introduction of anion interstitials at the two vacant cube corner sites. Such interstitials would interrupt the long range ordering of these sites. Since these interstitials see energetically equivalent sites nearby, they may enhance the mobility of the remaining vacant anion sites through a cooperative O\(^{2-}\) movement. This hypothesized mechanism of ionic conductivity would account for the ionic transference number of 0.27 measured by Subbarao et al. (1965) for a YO\(_{2.8}\) solution containing 5 M/O ThO\(_2\) in air at 1200°C. The author’s data (Fig. 9) for samples containing 10 M/O ThO\(_2\) in Y\(_2\)O\(_3\) shows conductivity to be almost independent of \(p_{O_2}\). This

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**Figure 8** Effect of 1 M/O ZrO\(_2\) on resistivity of Y\(_2\)O\(_3\).
finding is consistent with the idea that conductivity is largely ionic and fixed by composition. As is true for stabilized zirconia with a large number of $O^{2-}$ vacancies, neither the number nor the mobility of the ionic charge carriers is influenced by a change in $p_{O_2}$. For comparison, it is interesting to note that $15 M/O Y_2O_3$-stabilized zirconia has a level of ionic conductivity roughly $10^3$ times as high as that for $0.10 \text{ThO}_2 + 0.90 \text{Y}_2\text{O}_3$ at 1000°C.

### D. Defect ThO$_2$ Systems

The substitution of $Y^{3+}$ for $Th^{4+}$ in ThO$_2$ is accompanied by the creation of anion vacancies of high mobility. A number of authors have reported on the extent to which ionic conductivity is manifest in the solid solution ceramic thus formed. Hund and Meztger (1952) found that 22 to 30 mole percent $YO_{1.5}$ is soluble in ThO$_2$ at 1200°C. Because of this wide solution range and because yttrium substitutes as the relatively stable plus-three ion it makes a reasonably ideal system for which to examine the effect of introducing ionic conductivity whose number of potential charge carriers is set...
by composition. Subbarao et al. (1965) offered x-ray density calculations and measurements in support of the anion vacancy model for $Y_2O_3$ substituted ThO$_2$ solid solutions as shown in Fig. 10, as did Wimmer et al. (1967). They demonstrated by oxygen concentration cell measurements that the ionic transference number became larger with increasing $YO_{1.5}$ additions and as temperatures increased from 1000 to 1400°C in air. Numerous investigators (Steele and Alcock, 1965; Alcock and Steele, 1964; Worrel, 1965) have shown that anion defect ThO$_2$ solutions exhibit an increasing ionic transference number as oxygen partial pressure is lowered. Lasker and Rapp (1966) worked out a model for the prediction of electronic and ionic conductivity dependence on $p_{O_2}$ for $YO_{1.5}$ ThO$_2$ solutions. Figures 11 and 12 are schematic representations of this model which predicts a transition from p-type to n-type conductivity as the oxygen pressure is lowered. The effect of substituting $Y^{3+}$ (or $La^{3+}$) is to promote a large ionic contribution at intermediate oxygen pressures. The range over which ionic conductivity predomnates is extended and shifted downward in oxygen pressure as the $Y^{3+}$ substitution becomes larger within the limit of solution. The dilute solution theory which served as a basis for this model was experimentally verified for the existence of a $p_{O_2}^{-1/4}$ dependence of conductivity arising

![FIGURE 10 Densities of ThO$_2$–YO$_{1.5}$ solid solutions (after Subbarao et al., 1965).](image-url)
from the presence of holes and for the oxygen pressure independent ionic conduction up to 2 mole percent YO$_{1.5}$. At larger YO$_{1.5}$ concentrations, the mobility or fraction of participating vacancies decreased, perhaps due to a vacancy ordering effect (Tien and Subbarao, 1963) and invalidated the assumptions of the model. Figure 13 indicates the variation of ionic conductivity as a function of the percentage of vacancies. This behavior is characteristic of stabilized zirconias, as also noted by Dixon et al. (1963).

Measurements down to $p_{O_2}$'s established by the Cr–Cr$_2$O$_3$ equilibrium by Lasker and Rapp (1966) did not confirm the existence of n-type conduc-

![Figure 11](image1.png)

**FIGURE 11** Effect of YO$_{1.5}$ content on partial electrical conductivities in ThO$_2$ + YO$_{1.5}$ electrolytes at constant temperature (after Lasker and Rapp, 1966).

![Figure 12](image2.png)

**FIGURE 12** Effect of YO$_{1.5}$ content on ionic transference numbers in ThO$_2$ + YO$_{1.5}$ electrolytes at constant temperature (after Lasker and Rapp, 1966).
FIGURE 13 Ionic conductivity as a function of mole percent YO$_{1.5}$ or percent anionic vacancies at 1000°C (after Lasker and Rapp, 1966).

tion for these solutions. Using very pure starting materials, Wimmer et al. (1967) investigated the composition (0.13 YO$_{1.5}$ + 0.87 ThO$_2$) which exhibits the maximum conductivity in this solution series. They placed the upper $p_{o_2}$ limit at about 10$^{-6}$ atm and 1000°C for a 99 percent or better ionic contribution to conductivity. In agreement with others, they failed to find the development of significant electronic conductivity at very low $p_{o_2}$’s. Above 1400°C, they concluded it might not be possible to achieve less than a 1 percent electronic contribution at any $p_{o_2}$.

Wachtman (1963) conducted an interesting investigation based upon the calculation that anion vacancies in CaO–ThO$_2$ solid solutions were associated with calcium ions to a very high degree. It was predicted that calcium ion-oxygen vacancy pairs should show characteristic electrical and mechanical relaxation times on the basis of the theoretical treatment of relaxation modes. Measurements indicated the internal friction peak for 98.5 ThO$_2$ + 1.5 CaO occurred at twice the frequency as the dissipation factor peak and at the same temperature (515°C). The author calculated an activation energy of 0.93 eV for the pivoting motion of a vacancy about the Ca$^{2+}$ site and showed that no such relaxation peaks existed for pure ThO$_2$. 
III. MECHANICAL

The high melting points and chemical inertness of ThO$_2$ and Y$_2$O$_3$ make them of special interest as potential materials of construction for use at elevated temperatures. This is particularly true for ThO$_2$, which oxide has been used for many years in specialty applications. Y$_2$O$_3$ is just now being considered as a potentially attractive refractory ceramic. That Y$_2$O$_3$ has not received greater attention until this decade can be traced to its relative unavailability until the 1950s. It still ranks as an expensive material owing to the extensive purification processes necessary to achieve a 99 percent purity level.

The utility of any ceramic for use at elevated temperatures depends largely upon its mechanical response to stress induced by both applied loads and temperature gradients. Knowing only the melting points of Y$_2$O$_3$ and particularly ThO$_2$ leads one to predict they might be high strength materials which would behave elastically up to relatively high temperatures. The room temperature Young’s modulus ($E$) for ThO$_2$ containing 0.5 percent CaO has been determined to be in the range 34.6 to 34.9 × 10$^6$ psi for samples containing from 1 to 3 percent porosity. Spinner et al. (1963) calculated the zero porosity modulus ($E_0$) for pure ThO$_2$ to be 37.8 × 10$^6$ psi. The zero porosity modulus for pure Y$_2$O$_3$ was calculated to be 25.3 × 10$^6$ psi by Maust (1967) who found the relation

$$E/E_0 = 1 - 2.18P$$

(10)

to hold where $P$ is porosity. Marlowe and Wilder (1965) determined the relation

$$E/E_0 = 1 - 2.49P$$

(11)

for Y$_2$O$_3$ where the modulus at zero porosity was calculated to be 26.1 × 10$^6$ psi. They pointed out this linear relationship of modulus with porosity follows the analysis of Gatto (1950) and not the classical derivation of Mackenzie (1950) based upon closed pores in a continuous matrix. Dickson and Anderson (1968) found Young’s modulus to be 25.2 × 10$^6$ psi for a single phase, solid solution sample containing about 9 M/O ThO$_2$ dissolved in Y$_2$O$_3$. This value for a sample containing less than 1 percent pores was lower than might be calculated from a simple law of mixtures. It may be recalled, however, that ThO$_2$ and Y$_2$O$_3$ do not form a complete solid solution series.

The dependence of Young’s modulus on temperature was shown to be linear up to 1100°C (Wachtman and Lam, 1959) for ThO$_2$ samples containing 0.5 percent CaO. These results (Fig. 14), complemented by internal friction measurements, led the authors to conclude that grain boundary slip was an important factor controlling strength at elevated temperatures.
for this and other polycrystalline materials. In a review of mechanical properties of materials, Stokes (1964) pointed out that impurities may act to decrease grain boundary viscosity at elevated temperatures. It is reasonable to suspect that there may be a preferred segregation of calcium ions at the grain boundaries for CaO-doped ThO$_2$ samples. It would be interesting to know if the maximum temperature for elastic behavior of pure ThO$_2$ is significantly different from that found in this work. According to Marlowe and Wilder (1965), Young's modulus for a pure Y$_2$O$_3$ ceramic was found to decrease linearly with temperature up to about 1350°C before a non-elastic response was encountered. Their measurements for samples of several porosity levels are shown in Fig. 15. These authors also demonstrated that at room temperature, internal friction of Y$_2$O$_3$ was exponentially related to volume fraction porosity and proportional to the reciprocal of the average grain surface area.
The creep characteristics of a very pure ThO$_2$ ceramic containing about 2.5 percent porosity were investigated by Poteat and Yust (1966) between 1400 and 1800°C. They concluded viscous flow in grain boundaries resulting from ionic diffusion was the most important creep deformation mechanism encountered. An activation energy of 112 ± 7 kcal/mole was determined from this study. Although the study did not permit a strict interpretation of data in terms of Nabarro–Herring creep, diffusion coefficients for Th$^{4+}$ in ThO$_2$ were calculated using this relationship. Morgan and Hall (1966) determined that comprehensive creep rates were markedly increased by the presence of CaO in solution with ThO$_2$. Initial creep rates were found to increase as the CaO content increased, but tended to level off considerably after several hundred hours. It was suggested that exsolution of CaO between 1400 and 1500°C might play a role in determining creep behavior.

A number of strength determinations have been made for ThO$_2$ and Y$_2$O$_3$ ceramics; however, it is felt that the values reported do not have much fundamental significance. As these values are regarded as a reflection of processing and testing procedures they are mentioned in the section on processing. The fracture mode of ThO$_2$ single crystals has been studied by Edington and Klein (1966) for crystals deformed by indentation between...
room temperature and 900°C. By observation of etch pits and dislocation arrays they were able to determine that slip occurred on the \{100\} planes and fracture took place along the \{111\} planes.

The Knoop hardness under a 500 gm load of 0.5 percent CaO-doped ThO$_2$ samples was given as 640 by Lang and Knudsen (1956). Vickers hardness values of about 600 and 800 for the dense Yttralox and Thoralox ceramics, respectively, were measured by Jorgensen (1968).

The thermal expansion behavior of both ThO$_2$ and Y$_2$O$_3$ shows no anomalous behavior, as might be anticipated from knowing that neither ceramic undergoes crystallographic changes over the temperature ranges for which expansion coefficients have been measured. Authors reporting values for ThO$_2$ agree quite closely. The average coefficient of linear thermal expansion referred to the 25 to 1000°C temperature range may be taken as $9.5 \times 10^{-6}$ in/in/°C for ThO$_2$. Ohnysty and Rose (1964) have measured thermal expansion to about 2400°C and Wachtman et al. (1962) were able to extrapolate low temperature measurements to high temperature values by using the statistical mechanical treatment developed by Grüneisen (1926). The data of Curtis (1957) and Nielsen and Leipold (1964) indicate values of 8.0 and $8.3 \times 10^{-6}$ in/in/°C, respectively, for average coefficients of linear thermal expansion for Y$_2$O$_3$ referred to the 25 to 1000°C temperature range. The thermal conductivity of ThO$_2$ is low and compares with that of UO$_2$ as shown in Fig. 16.

Ryshkewitch (1960) has given the molar specific heat of ThO$_2$ as

$$c_p = 14.6 + 0.0051T(°K)$$

in cal/°C from room temperature to 1000°C. Curtis (1957) reported a mean specific heat value of 0.13 cal/gm °C for Y$_2$O$_3$ over the same range.

### IV. OPTICAL

Until recent years, technological interest in the optical properties of bulk ceramic materials was limited to reflective and absorptive behavior over a broad temperature range. The porous and/or multiphase character of polycrystalline ceramics makes them opaque to light transmission throughout the visible region because of internal reflection, refraction, and absorption phenomena. Kingery (1960) has reviewed the factors which contribute to the opacity of ceramics. It has been appreciated for some time that ceramic bodies might be fabricated as transparent, polycrystalline solids provided a pore-free state could be obtained with a single phase, cubic oxide having no significant absorption bands. This has been demonstrated for
MgO as well as for various chalcogenides and halides prepared by pressure sintering techniques. More recently, both Y$_2$O$_3$ and ThO$_2$ ceramics have been sintered to a state of optical transparency with and without the use of pressure. Brissette et al. (1966) and Lefever and Matsko (1967) have prepared dense Y$_2$O$_3$ of good optical quality by press forging. A transmission curve taken from the latter work (Fig. 17) shows the Y$_2$O$_3$ ceramic compares favorably with single crystal Y$_2$O$_3$, with appreciable transmission extending from 0.3 $\mu$m in the ultraviolet to above 8 $\mu$m into the infrared. The press forged ceramic samples had an absorbance (log I/I$_0$) of less than 0.09 throughout the visible. Figure 18 shows a transmission curve for Yttralox ceramic (Rosolowski, unpublished research) which has transmission cutoffs at 0.24 and 9.5 $\mu$m. The refractive index of this material has been measured as 1.91 at $\lambda = 0.589$ $\mu$m. The 7 M/O ThO$_2$ in solution in the Yttralox ceramic has had very little effect in altering the reported index of 1.914 (Levin, 1964) of pure Y$_2$O$_3$. Calculating out reflective losses using the Fresnel formula indicates this material absorbs less than 5 percent of the incident visible light for a millimeter-thick sample. Figure 19 shows the optical dispersion of this material. The measured Nu value of 40.0 is quite low when compared to known glasses of high refractive index. It has been observed that Yttralox ceramic can vary in coloration from gray to
slightly yellow depending upon the oxygen pressure and temperature of heat treatment.

The hemispherical spectral emittance of opaque $Y_2O_3$ was measured by McMahon and Wilder (1968). Their data show values below 0.1 up to $\sim 1000^\circ C$, which rise and approach 0.8 above the melting point.

Thorium oxide has an index refraction of 2.20, a relatively high value as oxides go. This is a consequence, in part, of its exceptionally high density and large cation size. Figure 20 indicates the optical transmission found for a theoretically dense sample of Thoralox ceramic made by Jorgensen (unpublished research) which contains $2M/O$ CaO in solution. The transmission cutoffs occur at 0.27 and 9.5 $\mu m$ for a 1.56 mm thick sample, very close to the same values found for ThO$_2$ single crystals by Linares (1967). The transmission cutoff beyond 9 $\mu m$ for $Y_2O_3$ and ThO$_2$-based ceramics extends as far into the infrared as for any known oxides which are transparent throughout the visible range.

V. NUCLEAR

The relatively sudden coming of age of nuclear energy as a competitive source of central station power during the early 1960s has served to broaden the interest in ThO$_2$ and Y$_2$O$_3$ as potentially useful reactor materials.
THORIA AND YTTRIA

Naturally occurring thorium minerals contain predominantly the $^{232}\text{Th}$ isotope, an alpha emitter with an exceptionally long half-life of $1.4 \times 10^{10}$ years (Le Roux and Glendenin, 1963). $^{232}\text{Th}$ is not directly useful as a fissionable fuel when irradiated. The fissionable isotope $^{233}\text{U}$ is formed in two steps by neutron capture and subsequent $\beta$ decay. Thus, $\text{ThO}_2$ is of potentially great value as a source of nuclear fuel, but must be cycled through a power-producing breeder reactor to yield a fissionable product. The present trend of commercial reactor design is proceeding along the line of using enriched $\text{UO}_2$ as a fuel into the 1970s with a shift to breeder reactors planned as a large enough plutonium inventory makes this economically feasible. The relative importance of the thorium cycle to the production of atomic energy is yet to be determined as its competitive position is compared to that of the uranium-plutonium cycle.

Nuclear demands for $\text{ThO}_2$ and $\text{ThO}_2-\text{UO}_2$ solid solution ceramics have been the largest single impetus for work on $\text{ThO}_2$ in recent years. Resistance to boiling water corrosion, high-melting point, and freedom from crystallographic transformations are factors which make $\text{ThO}_2$ the chemical form of $^{232}\text{Th}$ of interest to nuclear technology.

The interest in $\text{Y}_2\text{O}_3$ as a nuclear material is based on its refractoriness, very low nuclear cross-section, and ability to act as a diluent for $\text{UO}_2$ fuels or $\text{Gd}_2\text{O}_3$ poisons by forming solid solutions. Anderson (1961) lists the thermal neutron absorption of $\text{Y}_2\text{O}_3$ as 1.3 barns.

![Graph](image-url)
Ferguson et al. (1965) have described the complex Sol-gel process wherein ThO₂ and ThO₂–UO₂ powders have been prepared expressly for nuclear use. In this process a dispersed hydrosol is prepared by steam decomposition of an aqueous thorium nitrate solution. The activated ThO₂ sol dispersed in a dilute HNO₃ solution is then converted to a gel by a low-temperature evaporation. Bannister (1967, 1968) has characterized the ThO₂ gel at this stage as having a surface area of 80 m²/gm with individual crystallites on the order of 100 Å in diameter. The gel loses additional water and nitrate on heating and sinters to a density of 9.9 gm/cc between 1000 and 1150°C. At this stage grain sizes of 0.5 μ are reported. The process has been adapted to the production of microspheres (Haas and Clinton, 1966) by the organic liquid extraction of water from sol droplets. Microspheres are a useful form of ThO₂ for forming by vibratory compaction. This process has been modified to produce other oxide powders including ThO₂–UO₂ solid solutions.

Olsen et al. (1967) have presented a recent evaluation of vibratory-compacted ThO₂–UO₂ fuel prepared by the Sol-gel process. Irradiation studies indicated the superiority of ThO₂-based fuels over UO₂ fuels on
that the basis of their greater strength, high-temperature stability, and smaller swelling due to fission gas release.

Solid solutions of ThO$_2$ and UO$_2$ are potentially important as a breeder type of ceramic reactor fuel. Phase relationships in systems of which uranium oxide is one component tend to be complex owing to the tendency for UO$_x$ to assume oxidation states between the UO$_2$ and UO$_3$ limits with accompanying solution and phase changes dependent upon temperature and oxygen pressure. Several studies have shown ThO$_2$ and UO$_2$ form a complete series of solid solutions with the fluorite-type of cubic structure. There appears to be no subsolidus breakup in this system at least down to 1200°C. Mumpton and Roy (1960) have shown this solution exists into the oxygen rich region of the UO$_2$-ThO$_2$-O ternary at 1350°C out to the ThO$_2$-U$_3$O$_8$ join, except for a small area near the U$_3$O$_8$ composition. They suggested two separate cubic solid solution phases may exist in the ThO$_2$-UO$_2$-U$_3$O$_8$ ternary at lower temperatures. In the same study it was concluded less than 2 $M/O$ ZrO$_2$ could be maintained in solution with ThO$_2$ at temperatures below 1200°C.

Using thermodynamic considerations, Roberts and Markin (1967) indicated that interstitial vacancies in (U, Th)O$_{2+x}$ solutions tend to order at low temperatures and give complex superstructures. In such crystals, domains having one local structural configuration, similar to that of the next ordered phase, persist in nonstoichiometric ranges though long range order is destroyed. Hoch et al. (1967) also discussed the coexistence of two defect fluorite phases in solutions of the (U, Th)O$_{2+x}$ type from a crystal standpoint.

**FIGURE 20** Optical transmission of Thoralox ceramic 1.56 mm thick (after Jorgensen, 1967).
using oxygen activity data from Aronson and Clayton (1960, 1961). Kingery (1959) reported a drastic lowering in thermal conductivity for (U, Th)O_{2+x} solutions with a limiting value of 0.0035 cal/sec/°C/cm²/cm for Th_{0.69}U_{0.31}O_{2+x}. Karkhanavala et al. (1965) investigated the kinetics and mechanism of solution formation between U₃O₈ and ThO₂ in air. It was concluded that rapid reaction rates were obtained between 1000 and 1400°C owing to the formation of UO₃ gas which reacted with and diffused into solid ThO₂ grains.

Bartram et al. (1964) investigated phase relations in the UO₂–UO₃–Y₂O₃ system. High temperature solubility of UO₂ in Y₂O₃ was found to extend out to 14 M/O UO₂, but there was little or no solubility of UO₂ above 1000°C. Oxidation at lower temperatures produced maximum oxygen-to-metal ratios of 1.56 for the c-type rare earth oxide solution, where excess oxygen was incorporated interstitially. Aitken (1966) subsequently performed a study of the oxidation kinetics of solutions in the UO₂–Y₂O₃ system.

VI. PREPARATION

The preparation of thoria and yttria ceramics by conventional pressing and sintering methods is a relatively straightforward process. It is possible to achieve reasonably high densities, mechanical strength, and obtain elevated temperature inertness by heat treatment of commercially available powders at 1700°C or above. Research in this area can be classified by objective and usually falls into one of three categories. Investigations are aimed at (1) generating fundamental understanding of sintering mechanisms, (2) achieving lower sintering temperatures, or (3) closely approaching theoretical density.

A. Powders

Kingery (1960) has emphasized the necessity of controlling initial particle size of powders used for ceramic preparation, particularly when sintering occurs without the presence of a liquid phase. The synthesis of ThO₂ and Y₂O₃ powders as material sources for ceramic preparation has been directed toward obtaining small diameter particles of “active” powders. For purposes of sintering, this may be expressed fundamentally as attempting to maximize the surface area to volume ratio in recognition of the fact that the reduction of surface energy is the driving force in sintering. The practical result of maximizing surface energy of the starting powders may be two-fold. It often results in minimizing the temperature required to reach a useful density
level. It may also allow the attainment of a finer grain structure for a fired ceramic of given density level.

The characterization of starting powders in terms directly related to sinterability is not a precisely understood activity. Size measurements of both crystallites and dispersible particles, and surface area measurements appear to be the most useful quantitative indices by which comparisons can be made. A sintering test itself is the most direct evaluation technique available. Even so, the interpretation of a sintering test is dependent upon compaction variables and each experimenter’s concept of sinterability. Since reported work in this area is difficult of a strict interpretation the author has presented a limited review of work performed.

A prime example of achieving low sintering temperatures for ThO$_2$ is based upon development of the Sol-gel process (Ferguson et al. 1965). Since this synthesis technique has been applied principally to the fabrication of ceramics for nuclear use, it is discussed elsewhere in this chapter.

A series of investigations involving the synthesis and sintering of ThO$_2$ powders have been conducted by Moorthy and Kulkarni (1963), Moorthy et al. (1965a), Kulkarni and Moorthy (1965), and Moorthy et al. (1965b). Fine powders formed by the decomposition of tannates, oxalates, carbonates, and benzoates between 600 and 1000°C were sintered and hot pressed, and evaluated for sinterability by noting which powders underwent densification at the lowest temperature between 1000 and 1300°C. The tannate-derived powder was judged to be the most sinterable, but densification did not correlate well with measurements of particle size and surface area. An attempt was made to explain sinterability differences by degree of “crystallinity,” where deviation from this state was speculated to be an important source of energy driving the sintering process. Harada et al. (1962) studied the sintering of ThO$_2$ ceramics using powders derived from the calcination of oxycarbonate, chloride, nitrate, and oxalate sources. They were able to achieve the best results by calcining the oxycarbonate between 600 and 1000°C to yield a powder with 10 to 80 m$^2$/gm of surface area. After pressing, this powder was sinterable to between 95 and 98 percent of theoretical density by firing in air at 1500°C for 24 hours. For this density range, it might be presumed the ceramics had reached a state of residual porosity essentially of the closed-pore variety. If so, nitrogen entrapment in closed pores may have been at least partly responsible for interfering with further densification.

Y$_2$O$_3$ powders derived by the decomposition of yttrium carbonates, hydroxides, oxalates, sulfates, ammonium sulfates, and nitrates were prepared for sintering by Furlong and Dominques (1966). Sintered densities in excess of 96 percent were achieved by firing at 1600°C in air. These authors con-
cluded the particle size distribution of the powder and the pore-size distribution of the green compact were the most important parameters with respect to the sinterability of a powder for a given sintering temperature, basing their argument upon the efficacy of achieving efficient packing with sized particles. It may be noted here that many authors concerned with the problem of attaining highest ultimate densities, without regard for sintering rates, specify the ideal particle packing arrangement to be one involving uniformly sized particles with uniform interparticle spacings.

Large-scale commercial production of Y$_2$O$_3$ involves ion exchange purification of solutions for the purpose of separating the various rare earth constituents which occur in solid solution with yttrium in ore concentrates. The precipitation and thermal decomposition which are part of this process make possible close control of purity and particle size. A typical commercial powder of 99.99 percent purity examined by the author contained particles principally in the 3 to 5 μ range. Electron micrographs of replicated particles showed graininess indicating the particles are actually agglomerates of ultra-fine crystallites. X-ray line broadening measurements (Jorgensen, unpublished research) place the ultimate grain size within these agglomerates at about 500 Å. The ultrafine nature of commercial Y$_2$O$_3$ was first pointed out by Curtis (1957) who also showed a reversible weight change associated with these powders. Weight losses approaching 1 percent at 1200°C were attributed to the tendency for Y$_2$O$_3$ to form a hydrated carbonate on standing in air.

B. Sintering Y$_2$O$_3$

Schieltz and Wilder (1967) investigated the sintering of Y$_2$O$_3$ between 1200 and 1650°C in vacuum and concluded their data could be characterized by a reduced-variable sintering equation proposed by Marlowe and Wilder (1967b). The proposed sintering equation is dependent upon the concept that a temperature-dependent, end-point density exists for sintering. This analysis allowed for the calculation of an activation energy for sintering of Y$_2$O$_3$ of 23 kcal/gmole. Schieltz and Wilder (1967) were not able to correlate the time dependence of initial stage shrinkage with any proposed theoretical model. The reader is referred to Johnson and Cutler (1963) for one treatment of these theoretical models. Anderson (1966) was also unsuccessful in correlating initial stage shrinkage experiments on Y$_2$O$_3$ with proposed models. Using the reduced variable corrections developed by Johnson and Cutler (1963), the exponent $n$ in the general relationship

$$\frac{\Delta L}{L_o} = k t^n$$

(13)
was found to be 0.007 for shrinkage runs in dry H$_2$ between 1390 and 1580°C, far lower than any proposed for models based on grain boundary or bulk diffusion mechanisms. However, it was noted that proposed initial stage sintering models where grain boundary or bulk diffusion was rate controlling were based on the assumption of a single, vacancy-annihilating boundary between particles. In fact, the Y$_2$O$_3$ powders used consisted of agglomerations of ultra-fine crystallites and contained a large, randomly oriented, grain boundary surface internal to the agglomerates which could be responsible for vacancy annihilation and reduction of the driving force for shrinkage without the expected shrinkage occurring. Figure 21 shows a fracture surface for Y$_2$O$_3$ sintered to a 6 percent shrinkage value. The 3 to 5 μ diameter outlines related to the original agglomerate size are barely discernible, but clearly contain internal grains which have grown to about 0.5 μ in diameter. Marlowe and Wilder (1967a) have shown reso-

**FIGURE 21** Fracture surface of pressed Y$_2$O$_3$ powder after six percent sintering shrinkage.
nant frequency measurements can be used as a very sensitive indicator of sintering shrinkage below 1 percent. Using this technique, which is based on the elasticity-porosity relation of the material, an activation energy of 18.6 kcal/mole was calculated for Y$_2$O$_3$ for the first 1.2 percent shrinkage between 675 and 910°C.

Brissette et al. (1966) demonstrated that pure Y$_2$O$_3$ could be pressure sintered to a state in excess of 99 percent of theoretical density. Samples prepared by conventional hot pressing remained opaque while those made by press forging had a high degree of optical transparency. Press forging is similar to hot pressing except no lateral support is supplied. This technique appears to result in grain elongation perpendicular to the direction of force application, which observation is cited as evidence for plastic flow as an important mechanism of densification. Transverse bend strengths up to 42,000 psi were measured for samples which appeared to have a grain size in the 0.5 to 1.0 μ range. Lefever and Matsko (1967) prepared fully dense samples of Y$_2$O$_3$ by vacuum hot forging at 950°C and 10,000 to 12,000 psi. They used 3 to 5 wt/o LiF as a densification aid and achieved an average grain size of about 3 μ with no evidence of preferred orientation. It was concluded that grain growth did not occur in this process; however, it is felt these authors may have mistaken their determination of powder particle size for the extremely fine ultimate grain sizes known normally to exist in their starting powders.

A process for sintering a Y$_2$O$_3$-based ceramic to full density and optical transparency was developed by Anderson (unpublished research). It was found that approximately 5 to 10 M/O of either ThO$_2$, ZrO$_2$, or HfO$_2$ added to Y$_2$O$_3$ would provide the necessary inhibition of grain boundary movement during sintering such that pore-free, single phase ceramics could be obtained at 1900°C in hydrogen or vacuum. Figures 22 and 23 illustrate the process of densification for samples of pure Y$_2$O$_3$ and Y$_2$O$_3$ + 10 M/O ThO$_2$ at temperatures between 1600 and 2000°C. The limiting density for pure Y$_2$O$_3$ at 2000°C approached 98 percent of theoretical while 100 percent of theoretical density was achieved at 3 minutes for the Y$_2$O$_3$-ThO$_2$ solution sample. The presence of ThO$_2$ actually reduces the rate of densification through the intermediate stage as shown by comparison of the 1600°C curves. This effect was shown to be operative in sintering MgO-doped Al$_2$O$_3$ also by Jorgensen (1965). This finding points out the care which must be taken to distinguish between sintering aids which increase densification or shrinkage rate and those which allow for complete pore removal and may actually inhibit the kinetic phenomena associated with sintering. The mechanism of grain growth inhibition during the sintering of Yttralox

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FIGURE 22 Densification of Y₂O₃ in H₂.

FIGURE 23 Densification of Y₂O₃ + 11 M/O ThO₂ in H₂.
type ceramics was investigated by Jorgensen and Anderson (1967) who concluded the segregation of ThO$_2$ solute at grain boundaries decreased the boundary migration rate by a drag effect and set the upper limit for width of the segregated solute region at about 50 Å. Figure 24 shows the grain growth rate inhibiting effect of ThO$_2$ for samples sintered at 2000°C where the log-log slopes correspond closely to 0.5 as predicted by Burke and Turnbull (1952). Figure 25 shows the change in microhardness at the grain boundaries resulting from ThO$_2$ solute segregation. Figures 26 and 27 indicate the microstructural appearance of pure and ThO$_2$-doped Y$_2$O$_3$, respectively, after sintering.

Anderson (unpublished research) found it was possible to incorporate all of the rare earth oxides into solution for Yttralox type ceramics, or achieve full density and transparency for the smaller rare earth oxides. The limiting compositional criteria for fabricating dense solid solution ceramics of Y$_2$O$_3$ and the rare earth oxides was defined in terms of those combinations whose average cation radius ratio did not exceed about 0.93 Å. They followed quite closely the prediction of Schneider and Roth (1960) for obtaining c-type rare earth oxide solid solutions for this transitional series of oxides.

Rosolowski (1966) has measured cross-bending strengths of 17,000 psi for Yttralox ceramics with grain sizes in excess of 10 μ.

![Image](https://www.Iran-mavad.com)
C. Sintering ThO\textsubscript{2}

Morgan and Yust (1963) investigated the sintering of ThO\textsubscript{2} and CaO-doped ThO\textsubscript{2} powders by observing the densification of pressed powder compacts under several constant heating rate conditions. They concluded bulk diffusion was not the dominant material transport mechanism on the basis that densification rates did not follow the diffusion coefficient of thorium as sintering temperatures were varied. Instead, they proposed plastic flow by dislocation movement to be the probable controlling mode of material transport. Morgan and Hall (1967) found isostatic pressing of presintered ThO\textsubscript{2} compacts enhanced their further densification slightly upon resintering. This effect was explained by assuming the creation of free dislocations in the thoria grains during pressing.

Oel (1967) emphasized the numerous factors influencing the sintering of ThO\textsubscript{2} between 1700 and 1900°C.

The successful use of sintering aids for making ThO\textsubscript{2} ceramics originates from the observation of R. F. Geller in 1944 that small amounts of CaO enhanced the densification of ThO\textsubscript{2}. Johnson and Curtis (1954) first reported achieving ceramics of 99.5 percent of theoretical density by introducing
0.5 percent of CaO and sintering at 1800°C in hydrogen. Curtis and Johnson (1957) indicated that SrO also enhanced the sintering of ThO₂, but the effect of CaO was significantly diminished when samples were fired in H₂ at 1750°C. They attributed enhanced sintering to an increased diffusion flux of ions originating in the formation of oxygen ion vacancies as Ca²⁺ substituted for Th⁴⁺. Grain sizes of 60 μ in these dense ceramics were mentioned. Lang and Knudsen (1956) investigated ThO₂ containing 0.5 per-

FIGURE 26 Typical microstructure of sintered Y₂O₃ exhibiting discontinuous grain growth (×100) (after Jorgensen and Anderson, 1967).
cent CaO, producing specimens of about 99 percent of theoretical density by firing at 1800°C in an oxidizing atmosphere. Dense, sintered samples with a grain size range from 1 to 5 μm had transverse strengths from 10,000 to 15,000 psi both at room temperature and 1000°C. Little else has appeared concerning the processing of CaO-doped ThO₂ ceramics. Recently, however, Jorgensen (unpublished research) has succeeded in fabricating fully dense and optically transparent samples (Thoralex ceramics) by sintering...
at high temperatures in hydrogen. It is interesting to note the accumulated evidence suggests the use of CaO as a dopant for ThO₂ appears to enhance the sintering rate of ThO₂ under some conditions, but enables full density to be reached, as well.

VIII. APPLICATIONS

The nuclear energy field has created the only truly significant need for ThO₂ ceramics. Y₂O₃ ceramics enjoy no very important uses at this time, but Y₂O₃ as an ingredient in mixed oxide ceramics is a very important raw material. Over the last several years it has come to widespread use in the synthesis of the europium-doped yttrium orthovanadate, electronic phosphors which yield a superior red brightness for color television screens. The various fluorescent emissions found with rare earth-doped Y₂O₃ are assuming increasing importance as optical phosphors in powder form and for laser use in single-crystal form. YAG, or yttrium aluminum garnet, is an interesting laser host material owing to its good mechanical isotropy. YIG, or yttrium iron garnet, is an important material for microwave use, whose properties have been extensively modified and controlled by affecting solid solution variations. The use of Y₂O₃ to stabilize ZrO₂ has been practiced commercially for many years. Anionically conducting Y₂O₃-stabilized ZrO₂ is the first promising solid electrolyte which may be used to generate electrical power in fuel cells.

As a ceramic material, Y₂O₃ has found a few very specialized applications in nuclear technology. Grossman (1964) has considered its potential use in the construction of thermionic energy converters. In their dense, optically transparent form, both Y₂O₃ and ThO₂ are being considered for use as light source envelopes and as optical elements, particularly for infrared transmission.

Ryshkewitch (1960) discussed the use of ThO₂ as a super-refractory for melting metals and as a specialty refractory in high temperature furnace construction. Significant new uses as a refractory for these purposes are not known to the author. The Welsbach mantle, comprised of 1 percent CeO₂ in ThO₂ is still used in gas lanterns to enhance incandescent radiation. Kondratenko and Sokolov (1966) report this system catalyzes the recombination reactions of free atoms and radicals on its surface in addition to undergoing thermoluminescence.

Baskin et al. (1960) and Neimark et al. (1963) have reported on the use of Mo fibers in ThO₂ and ThO₂-UO₂ ceramics to enhance thermal conductivity and thermal shock resistance for use in nuclear applications.
Over the temperature and oxygen pressure ranges for which ThO$_2$ solutions exhibit an anionic transport number of 0.99 or better they have been used as electrolytes in galvanic cells and for coulombic titration of oxygen. At 1000°C, these cells are useful at oxygen pressures of $10^{-6}$ atm and lower where the lower limit is not yet defined, but is lower than that for which stabilized zirconia is capable. The onset of electronic conductivity above 1400°C appears to mark this as an upper temperature limit. Little is known about their operation below 800°C. ThO$_2$ solution electrolytes are not interesting for use in power producing fuel cells as they do not exhibit the high level of anionic conductivity found in stabilized ZrO$_2$.

Alcock and Steele (1964) described the use of La$_2$O$_3$–ThO$_2$, Y$_2$O$_3$–ThO$_2$, and CaO–ThO$_2$ electrolytes to measure oxygen potentials with Fe–FeO, Nb–NbO, and Cu–Cu$_2$O electrodes and cited the advantage of thoria over zirconia electrolytes because of their lower conductivity and greater thermodynamic stability. The substoichiometric stability ranges of TiO$_2$ and NbO$_2$ were investigated with thoria cells by Alcock et al. (1967). Markin et al. (1967) employed Ni–NiO and Fe–FeO reference electrodes to measure the oxygen potentials of nonstoichiometric oxides of U and Pu. These reference electrodes were preferred as being the most reliable although the accuracy of oxygen potential determinations could be limited by precision in knowledge of thermodynamic data for electrodes. The generation of gases of known oxygen potential and the coulometric titration of oxygen ions were also discussed. Readers may refer back in time from the above two references and Schmalzried (1966) to trace the recent development of this interesting use for ThO$_2$ ceramics.

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Refractory Oxides of the Lanthanide and Actinide Elements

LeRoy Eyring

1. THE LANTHANIDE OXIDES

The rare earth oxide series provides a coherent group on which to study the properties of matter. This is dramatically illustrated by the extensive work on polymorphism or magnetic properties in lanthanide sesquioxides. Not only does one observe many polymorphic forms but the trends in their formation provide a detailed set of experimental values capable of revealing subtle characteristics of chemical and physical reaction. The rare earths have been the proving ground for the theory of magnetism. In short, the rare earth oxide series provides a window through which the many facets of solid state and high temperature chemistry may be viewed.

A comparison of the lanthanide and actinide oxide systems has been made by Eyring (1967) emphasizing the interrelationships in this double series. Fluorite-type phases pervade the oxide chemistry of these 25 elements from lanthanum to californium. This structure prevails with modifications for all phases discussed in this review except for MO$_x$($x > 2.25$). In the lanthanides and most of the actinides the modifications accommodate an oxygen deficiency whereas in protactinium, uranium, and neptunium an oxygen excess is accommodated.

Exhibited among these oxides are those with regular integral valence states and some with mixed valence states but having a narrow composition range belonging to homologous series. In addition, there are single phase regions of grossly variable composition which are genuine nonstoichiometric compounds. When an understanding of the dynamics of phase transitions and chemical hysteresis, common in these systems, are added to equilibrium phase relationships much of the mystery of solid state behavior shall have vanished.

A general account of current problems in nonstoichiometry has been given by Anderson (1963, 1964) who outlines the development of ideas
with respect to defects in solids from the Schottky–Wagner theory to a consideration of grossly nonstoichiometric compounds where this theory or its descendents does not apply. He gives a consideration of the clustering of defects and calls for a great deal more careful work on specific systems. Much has been done in the interim, as shall now be indicated.

Eyring and Holmberg (1963) have presented the state of knowledge of rare earth oxide phase relationships at the beginning of the period covered by this review. The known phases are tabulated, their structures discussed in relation to the parent fluorite structure, and a new series projected from purely geometrical considerations.

A very abbreviated account of the preparation, structure, and nature of pure rare earth oxide systems is given by Topp (1965) in a short monograph. Glushkova (1967) has published an extensive review of the lanthanide oxides including preparation, phase analysis, structure, polymorphism, thermal properties, etc. The literature is reviewed up to 1965 and the booklet is especially valuable for an account of Russian contributions which are not exhaustively covered here. One may add to this a distinguished series of reviews on the structural and solid state chemistry of pure rare earth oxides by Brauer (1964, 1966, 1968) which critically reviews developments in this field over the past dozen years. In a similar way Westrum (1964, 1966a, 1967, 1968) has provided an extensive and perceptive review of the thermodynamic and magnetic properties of the rare earth oxides which parallels a similar contribution to the actinide oxides to be discussed below. These reviews have not only recalled the contributions of others but have provided a synthesis and tabular presentation of great value and should be referred to for more complete information.

In an exhaustive review, Holley et al. (1968) have brought together all the thermochemical data on rare earth oxides to compute enthalpies, entropies, and Gibbs free energies of formation over a wide temperature range (typically 50–1800°K).

A. The Lower Oxides

Occasionally in the past the monoxide (RO) of one or the other of the lanthanide or actinide metals has been reported. The last five years have produced a series of investigations which have ended in the conclusion that such phases are in fact usually ternary systems including either carbon or nitrogen or perhaps both in the oxide. A striking example is that the existence of SmO and other lower oxides of samarium previously reported seem to have been disproved (Felmlee and Eyring, 1968). A similar situation had previously been verified for gadolinium (Gambino and Cuomo, 1966).
Achard (1961, 1966a, 1966b) has continued his studies of the reduction and volatilization of the rare earth oxides using carbon or vacuum and producing lower oxides whose stability as solids may depend on the presence of carbon.

Carbon reduction of Eu(III) oxide was the preferred method of preparation of EuO by Maude and Wilkinson (1968) for europium isotopic preparation.

Achard and Albert (1966) have reduced europium oxide to Eu$_3$O$_4$ using hydrogen. The reaction began at 1300°C and was complete at 1600°C, above which temperature the Eu$_3$O$_4$ volatilized.

Among the lanthanide elements only europium seems to have well established lower oxides. Bärnighausen (1966) has suggested a new method of preparation of EuO from reduction of the oxyhalides which is useful in the preparation of Eu$_3$O$_4$ as well. The method may be represented as

$$\text{EuOX} + \text{LiH} = \text{EuO} + \text{LiX} + \frac{1}{2}\text{H}_2$$

and the pure EuO obtained has a cubic lattice constant of $a = 5.1426 \pm 0.0005$ Å. Bärnighausen further observed that oxidation of the lower oxides of europium in air at 300-400°C produces the B-form Eu$_2$O$_3$. When other salts are decomposed at these lower temperatures the C-form is normally observed.

Brauer et al. (1968) have applied this method to the oxyhalides of Nd, Sm, and Yb in the temperature range 500 to 800°C. Depending on the experimental conditions the reaction products included only metal or hydride with the sesquioxide. Neither SmO nor YbO could be prepared by careful oxidation of the metal nor could these monoxides be stabilized in a matrix of SrO or CeO.

The crystal structure of Eu$_3$O$_4$ has been reported by Rau (1964, 1966) to be orthorhombic with $a = 10.085$ Å, $b = 12.054$ Å, and $c = 3.502$ Å.

Single-phase EuO has been prepared by reacting europium metal with less than enough oxygen at low pressures, then distilling off the excess metal (Garton and Hukin, 1964). Garton and Hukin also produced EuO by low temperature decomposition of europium (II) hydroxide. Shafer (1965) suggests reduction of Eu$_2$O$_3$ by Eu as the preferred method. The reaction occurs at 800°C in an evacuated system followed by distillation of any excess metal. He finds a Curie temperature $\theta = 73^\circ$K and magnetization values $\sigma$ from 191-212 emu/gm at 4.2°K. The change of the Curie temperature with pressure and the compressibility have been measured up to 90 kbar by McWhan et al. (1966). There is a 7 percent volume decrease at 90 kbar. The Curie temperature rises to 125°K at 85 kbar.
B. The Sesquioxides

1. Polymorphism

The sesquioxides of the lanthanides and actinides have been known to belong to one or more of three types. The A-form is hexagonal in a structure where the metal atoms are seven coordinated. The B-form is monoclinic having metal atoms either six or seven coordinated and the C-form which is body centered cubic with six coordinated metals of two types. (See, for example, Eyring and Holmberg, 1963.) Because of high temperature observations by Foëx (1965a) two new types must be added—a hexagonal H-form which differs from the A-form only by a shift in the position of the lines, and an X-form of unknown structure (these were originally designated α and β modifications). Figure 1 summarizes the high temperature region recently elucidated by Foëx and Traverse (1965a, 1965b, 1966a, 1966b, 1966c) and Foëx et al. (1965a, 1965b, 1965c). Figure 1 shows the regions of temperature stability of the sesquioxides of the several forms as reported by Foëx and his co-workers.

These extensive studies into the nature of high temperature transformation in rare earth sesquioxides reveal extraordinary complexity which is

![FIGURE 1 Polymorphism in the rare earth oxides (after Foëx and Traverse, 1966c).](image)
corroborated as between thermal and x-ray analysis. In these studies the composition of the phase being observed at high temperatures has not been established. Indeed, the question of possible compositional differences between the assumed polymorphs of the rare earth sesquioxides has not finally been settled.

Glushkova and Boganov (1965), Boganov and Rudenko (1965), and Glushkova and Koehler (1967) studied phase transformations in rare earth oxides by high temperature x-ray diffraction to above 2000°C and noted copious gas evolution in the C–B transition of the lower atomic weight oxides (i.e., Nd₂O₃ and Sm₂O₃). They attributed this to a composition difference between C and A or C and B forms, respectively, or perhaps the lingering presence of water. They observed reversibility of phase transformation only above gadolinium oxide in the series.

Sastry et al. (1966a) found the transformation temperature of C-form >750°C. C-form reacts more readily both with oxygen and water at lower temperatures than A-form. A hydrate Pr₂O₃·H₂O is described and its behavior compared with Pr(OH)₃.

Chapin et al. (1965) made a study of the C- to A-type transition in PrOIr in a carefully outgassed quartz system using both high temperature and quenched sample x-ray techniques. Carefully dried PrO₁·₆ undergoes transition at 800 or 850°C depending on heating rate. Slight exposure to water at 5 × 10⁻⁴ torr at 25°C lowered the transition temperature 60°C, suggesting varying transition temperatures depend on chemical history of the sample.

Anderson and Gallagher (1963) measured chemisorption of oxygen on both C- and A-type PrOIr. Both forms chemisorbed oxygen at −196°C with little or no activation energy. C-type absorbed more oxygen per unit area of surface than A-type. Anion vacancies in C-type were credited with this greater ability for chemisorption. The adsorption on A-form is thought to measure the average “defect” coordination about praseodymium atoms on the surface. Both CO₂ and hydrogen were found to be strongly bound by PrO₁·₂ surfaces and were difficultly removed even at high temperatures. The presence of CO₂ or hydrogen on the surface blocked the chemisorption of oxygen.

Stecura (1964, 1965) used high temperature x-ray diffraction to observe the rate of phase transformation in the sesquioxides of several of the lighter rare earth oxides. A mechanism was proposed and an activation energy obtained. Kinetics of transformation were followed in some of the same materials by Mehrotra et al. (1966) using electrical conductivity measurements. They reported having prepared C-form La₂O₃ (a = 11.39 ± 0.03 Å) which was observed to transform to A-form at 590°C. The C→A transi-
tion of \( \text{Nd}_2\text{O}_3 \) occurred at 550°C and a new form of \( \text{Y}_2\text{O}_3 \) was reported tentatively as hexagonal.

Weigel and Scherer (1965) have reported the preparation of \( \text{Pm}_2\text{O}_3 \) in all three polymorphic forms. The coral red C-type \( (a = 10.99 \, \text{Å}) \) is stable to 950°C. The deep lavender A-form is formed on ignition above 1600°C \( (a = 3.802, \, c = 5.954 \, \text{Å}) \). The purplish pink B-form \( (a = 14.25, \, b = 3.66, \, \text{and} \, c = 8.93 \, \text{Å}, \, \text{and} \, \beta = 100°31' ) \) is prepared above 950°C.

Yet another study of rare earth sesquioxide polymorphism has been made by Queyroux et al. (1966) who observed reversibility in the \( \text{Gd}_2\text{O}_3 \) \( \text{B} \rightarrow \text{C} \) transition and in all heavier members of the series studied.

The effect of pressure on polymorphism of the sesquioxides has been studied by Hoekstra and Gingerich (1964) and by Sawyer et al. (1965a) and further amplified by Hoekstra (1966). These studies show that the higher coordination of metal atoms is favored at high pressure, i.e., \( \text{C} \rightarrow \text{B} \rightarrow \text{A} \) as pressure is increased. It is possible by this means to observe the B-form of the heavy oxides which do not show this modification at normal pressures. Reversals are easily observed when the pressure is released at high temperatures. Static pressures of 15 to 60 kbars were used by Hoekstra.

Ruchkin et al. (1967) prepared B-form sesquioxides of Gd, Dy, Ho, Er, Tm, Yb, Lu, and Y by explosive shock compression and studied them using refractometry, IR spectroscopy, and x-ray diffraction methods. Several peculiarities of the phase transition under these conditions were studied along with the reverse transformation to the C-form upon heating.

An early paper by Brauer and Müller (1963) on polymorphism in rare earth sesquioxides indicates the variables important in such studies. It is clear that the temperatures and rates of conversion depend on the origin and thermal history of the oxide and the atmosphere in which it is being heated. Only those studies which take scrupulous care using the purest materials prepared in a carefully described mode and completely characterized at each stage shall ease the confusion which exists.

2. Substoichiometry in the Sesquioxides

Some reports of substoichiometry in the rare earth sesquioxides have been made. Miller and Daane (1965) observed substoichiometric sesquioxides to as low an oxygen content as \( \text{RO}_{1.45} \) in one case, by weight gain on reoxidation. The reduction was accomplished by vacuum melting of the normal sesquioxide or by codistilling and comelting the rare earth metals with their respective oxides. X-ray and density measurements indicated oxygen deficient materials.
Oxygen diffusion and electrical conductivity measurements suggested to Barrett and Barry (1965) that deviations on both sides of stoichiometry are possible for $\text{Nd}_2\text{O}_3$. Eu$_2$O$_3$ was readily partially reduced by hydrogen without change in electrical conductivity.

3. Structure Analysis

There have been some new studies of the structure of the A-form sesquioxide of lanthanum and neodymium. Single crystals of lanthanum were prepared by Müller–Buschbaum and Schnering (1965) and subjected to x-ray analysis. All discrepancies in previous work are eliminated by accepting what has been termed microtwinning in which the two lanthanum atoms are distributed statistically over the four positions $\frac{1}{6}$, $\frac{5}{6}$, $\bar{z}$; $\frac{1}{6}$, $\frac{1}{2} + z$; $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{2} - z$ with $z = 0.234$ and the three available oxygens over the six positions $0$, $0$, $0$; $0$, $0$, $\frac{1}{6}$; $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{2}$; $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{2} + z$; $\frac{1}{6}$, $\frac{5}{6}$, $\frac{1}{2} - z$ with $z = 0.639$. This statistical effect is achieved by combining a number of unit cells such that equal numbers of ordered domains exist. Single crystal A-type neodymium sesquioxide has been shown by Müller–Buschbaum (1966) to be the same structure.

C-type Dy$_2$O$_3$ and Tm$_2$O$_3$ were studied by neutron diffraction by Hase (1963) and the lattice parameters redetermined.

A very provocative geometric alternative to focusing attention to the $\text{MO}_8$ cubes in the fluorite-related rare earth oxides is provided by Caro (1968) who considers rather $\text{OM}_4$ tetrahedron linkages. Such a view points up a special simplicity in certain of the oxide structures and suggests linkages important in the rare earth oxysalts such as the oxychloride and oxycarbonate where there may be inorganic polymeric complexes of rare earth and oxygen atoms.

Manning et al. (1966) have noted a decrease in Young's modulus at room temperature with increasing porosity for Dy$_2$O$_3$ and Er$_2$O$_3$. The decrease is constant between 0 and 837°C, but at 837°C the rate of decrease for Dy$_2$O$_3$ becomes much greater although no phase inversions can be detected.

C. The Higher Oxides

Not only do the lanthanide (III) oxides show polymorphism as do the actinides, but three of their number (Ce, Pr, and Tb) have complex higher oxide systems with obvious similarity to the later actinides. The high-temperature equilibrium phases over the entire composition range of both series of oxides RO$_x$ ($1.5 < x < 2.25$) are closely related to the fluorite structure. That is, the metal atom positions are very close to the normal fluorite positions for all RO$_{2-x}$ and the sublattice of oxygen gives rise to the extraordinary complexity in these systems.
During the past five years a great deal has been learned about the rare earth higher oxides. The study of oxygen dissociation pressures and phase relationships in the CeO\textsubscript{x}–O\textsubscript{2} system carried out by Bevan and Kordis (1964) at high temperatures is of fundamental importance because of the breadth of coverage in temperature, pressure, and composition. Equilibrium oxygen pressures in the CeO\textsubscript{2–x}–O\textsubscript{2} (0 < x < 0.5) systems were used to derive partial thermodynamic data and a projected phase diagram. Intermediate phases of composition CeO\textsubscript{1.818}, CeO\textsubscript{1.778}, CeO\textsubscript{1.714} as well as the end members of the series CeO\textsubscript{2} and CeO\textsubscript{1.50} were observed. In addition, wide range nonstoichiometric phases are seen to cover the composition range at high temperatures except for a miscibility gap above 1023°C. Bevan and Kordis observed that CeO\textsubscript{1.5} fully reduced at high temperature in hydrogen was stable toward oxidation in air, a fact confirmed by Shedd and Henrie (1964) for carbon reduced Ce\textsubscript{2}O\textsubscript{3} at 1300°C or hydrogen reduced CeO\textsubscript{2} in a carbon boat at 1250°C. The carbon content of their preparations is about 0.01 weight percent. Figure 2 illustrates the phase diagram suggested by Bevan and Kordis.

The greatest attention has been given praseodymium oxide, which is also the most complex, under the experimental conditions so far achieved. Hyde

![Phase diagram of cerium-oxygen system](image-url)
et al. (1964) first proposed a phase diagram consistent with extant experimental data from a wide variety of sources. This effort fitted together the end members Pr$_2$O$_3$ and PrO$_2$ including the polymorphs of the former, four or more intermediate phases of narrow composition limit, and two truly nonstoichiometric phases of wide composition range covering almost the entire composition range at high temperature.

Honig et al. (1963) reported the results of a detailed thermogravimetric study of the PrO$_2$–O$_2$ system in the low pressure region. They further clarified the existence of the ordered intermediate phases and especially the oxidation of A-type Pr$_2$O$_3$ to Pr$_7$O$_{12}$. They also discussed the thermodynamic consequences of their measurements in terms of electronic and atomic defects. The oxidation of A-type Pr$_2$O$_3$ was further studied by Faeth and Clifford (1964) and a mechanism for the reaction was proposed. They also reported extensive hysteresis effects (1963) in the PrO$_2$ system between the intermediate oxides and interpreted their results in terms of Everett’s domain theory of hysteresis.

In a continuation of the tensimetric investigation of the praseodymium oxide system, Hyde et al. (1966) employed the isobaric technique and Kordis and Eyring (1968) employed isobaric and isothermal methods to clarify the phase relationships suggested in the earlier proposed diagram (Hyde et al., 1964) and generate thermodynamic data on phase transitions which further clarify the phase diagram. A phase diagram of the praseodymia-oxygen system is shown in Fig. 3. Order-disorder peritectoidal transformations are seen to be common in the system as were hysteresis effects in all two-phase regions. The appearance of pseudophases and nonstoichiometry are explained in terms of a model involving microdomain texture. A detailed x-ray powder diffraction study was made by Sawyer et al. (1965b) on carefully annealed samples prepared with a knowledge of the phase diagram. These results confirm the loss of symmetry from cubic for the end members to rhombohedral or triclinic for the intermediate phases and reveal the complex superstructure in each phase. All x-ray information is interpreted in terms of extensive ordering of the oxygen sublattice.

Bartram (1966) has discussed the relationship between the UY$_6$O$_{12}$ structure determined from single crystal data and the iota rare earth oxide phase (R$_7$O$_{12}$).

High temperature diffraction studies on the praseodymia-oxygen system following the isobaric procedures by Burnham and Eyring (1968) confirmed the general features of the phase diagram obtained by other methods including wide range nonstoichiometry at high pressures and temperatures, hysteresis, in the two-phase regions, and ordered intermediate phases at lower temperatures. Thermal expansion information was also generated.
An isobaric study of the TbO$_x$–O$_2$ system entirely analogous to the one on the PrO$_x$–O$_2$ system (Hyde et al., 1966) was reported by Hyde and Eyring (1965). The technique proved entirely effective in revealing ordered intermediate phases of narrow composition ranges at TbO$_{1.515}$ and TbO$_{1.714}$ as well as TbO$_{1.50}$. In addition hysteresis was displayed in the two-phase regions and marked pseudophase formation as the ordered intermediate phases are approached in oxidation. These results are in agreement with data and ideas expressed for the PrO$_x$–O$_2$ and CeO$_x$–O$_2$ systems. Phase relationships are suggested in Fig. 4. The structural entity (strings of six coordinated metal atoms) responsible for the formation of the Pr$_x$O$_{2n-2}$ series is suggested and was later amplified (Sawyer et al., 1965b; Hyde et al., 1965a).

A series of investigations into the behavior of nonstoichiometric praseodymium oxides has emerged from the laboratories of Professor Marion (Wilbert et al., 1967, 1966; Delmaire et al., 1966; LeBrusq et al., 1966). From these it has been possible to sketch a free energy surface in the PrO$_{1.5-1.6}$ region (designated $\sigma$ by Hyde et al., 1966) for pressures up to one atm.
A number of studies have revealed a selective reaction of the intermediate oxides such as \( \text{Pr}_6\text{O}_{11} \) (which can be represented as \( \text{Pr}_2\text{O}_3 \cdot 4\text{PrO}_2 \)) in which the \( \text{Pr}_2\text{O}_3 \) is reacted with water, acetic acid, or hydrochloric acid to leave unreacted \( \text{PrO}_2 \). A joint report of these studies from three laboratories was made by Clifford (1964) which have had a more complete report in separate publications (Brauer and Pfeiffer, 1963; Sastry et al., 1966b; Hughes, 1964; Clifford and Hughes, 1965).

A study of the kinetics of the reaction \( \text{PrO}_{1.5-1.6} + \text{O}_2 \rightarrow \text{PrO}_2 \) was reported by Hyde et al. (1965b) in which the reaction was followed thermogravimetrically in the forward direction at 235 to 314°C and 745 torr and in the reverse direction by vacuum reduction at 242 to 347°C. The results are consistent with a phase boundary controlled mechanism.

**FIGURE 4** Phase relationships in the terbium-oxygen system (after Hyde and Eyring, 1965).
Kuznetsov et al. (1966) observed the unusually high mobility of oxygen in the fluorite CeO$_x$ (1.67 $\leq x \leq$ 2.0) system. The entropy of the solid solution resulting from possible models of their real structure was calculated. The model with indistinguishable cations and nonlocalization of the electrons agrees well with results of the thermodynamic calculations and explains the kinetic behavior of the solid solutions of CeO$_x$.

Three studies of the defect nature of CeO$_{2-x}$ have recently been reported. Hoch and Yoon (1965) discuss earlier tennimetric results (Brauer et al., 1960) from a statistical mechanical calculation of oxygen activities and conclude that a better fit is obtained if anion vacancies are assumed rather than cation interstitials. In either case, excessively high interaction energies are obtained. This may suggest the basic weakness of the assumption of interacting point defects.

Blumenthal and Laubach (1967) observed the pressure dependence of electrical conductivity of CeO$_{2-x}$ between 1 and $10^{-17}$ atm of oxygen in the temperature range 800–1500°C. An analysis of these results suggested a defect model involving quasi-free electrons and both singly and doubly ionized oxygen vacancies. At the lowest oxygen pressures at 1200–1500°C the conductivity of CeO$_{2-x}$ appears to be relatively insensitive to oxygen pressure. At these low oxygen concentrations the CeO$_{2-x}$ may behave as a degenerate semiconductor. In contrast, Kofstad and Hed (1967) analyzed the results of Bevan and Kordis (1964) in the temperature range 747 to 1169°C and oxygen pressures between $10^{-8}$ and $10^{-25}$ atm in terms of singly and doubly charged interstitial cerium atoms. According to this analysis each interstitial has six nearest neighbor cerium ions on normal lattice sites and these interstitial cations may be proposed to block 6(1 − $\alpha$) of normal cerium sites in Ce$_{1+y}$O$_2$ for occupancy by electrons (where $\alpha$ is the relative probability of a neighboring cerium site being occupied by an electron).

A neutron diffraction study of cerium-dioxide at room temperature was made by Valentine and Willis (1965). The basic structural parameters were determined, viz., the nuclear coherent scattering cross-section of cerium and the Debye–Waller factors of the cerium and oxygen atoms. There is some evidence for a small anharmonic contribution to the Debye–Waller factor of the oxygen atoms.

D. Thermochemistry

There have been many important contributions to the thermochemistry and thermodynamics of rare earth oxides during the past five years and a list of these publications is given in Table I for the sake of approaching completeness. A discussion of each is not given here since excellent coverage
LANTHANIDE AND ACTINIDE ELEMENTS

and correlation of the information has been given very recently by Holley et al. (1968), Westrum (1968), and Akopov and Poluboyarinov (1966).

TABLE I

THERMOCHEMICAL STUDIES ON RARE EARTHS

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<tr>
<td>La</td>
<td>( C_{p,r,} S_{m,} ) Justice and Westrum (1963a); ( \Delta H_f ) Fitzgibbon et al. (1965).</td>
</tr>
<tr>
<td>( \text{La}_2\text{O}_3 )</td>
<td>( C_{p,r,} ) Lounasmaa (1964a)</td>
</tr>
<tr>
<td>Ce</td>
<td>( C_{p,r,} S_{m,} ) Weller and King (1963), ( H_T, S_T ), Pankratz and Kelley (1963)</td>
</tr>
<tr>
<td>( \text{Pr}_2\text{O}_3 )</td>
<td>( C_{p,r,} ) Lounasmaa (1964b)</td>
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<tr>
<td>( \text{PrO}_1, n )</td>
<td>( H_T, S_T ), Pankratz (1966)</td>
</tr>
<tr>
<td>( \text{Nd} )</td>
<td>( C_{p,r,} ) Lounasmaa (1964b)</td>
</tr>
<tr>
<td>( \text{Nd}_2\text{O}_3 )</td>
<td>( C_{p,r,} S_{m,} ) Justice and Westrum (1963a)</td>
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<tr>
<td>Sm</td>
<td>( C_{p,r,} S_{m,} ) Justice and Westrum (1963b)</td>
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<tr>
<td>( \text{SmO}_2 )</td>
<td>( C_{p,r,} ) Lounasmaa (1964a, 1966)</td>
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<td>Eu</td>
<td>( \Delta H_r, ) Burnett and Cunningham (1964, 1965); ( C_{p,r,} ) Guerci et al. (1964)</td>
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<td>( \text{Eu}_2\text{O}_3 )</td>
<td>( C_{p,r,} H_T, S_T, ) Tsagareishvili and Gvelesiani (1965a, 1965b); ( \Delta H_f, ) Huber et al. (1964); ( \Delta H_r, ) Stuve (1965)</td>
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<td>Gd</td>
<td>( H_T, ) Dennison et al. (1966); ( C_{p,r,} ) Lounasmaa (1963); ( C_{p,r,} ) Jelinek et al. (1966); Lounasmaa and Sundström (1966)</td>
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<td>( \text{GdO}_2 )</td>
<td>( C_{p,r,} S_T, ) Justice and Westrum (1963b)</td>
</tr>
<tr>
<td>Tb</td>
<td>( H_T, ) Dennison et al. (1966); ( C_{p,r,} ) Lounasmaa and Sundström (1966); ( C_{p,r,} ) van Kempen et al. (1964)</td>
</tr>
<tr>
<td>( \text{TbO}_2 )</td>
<td>( H_T, S_T, ) Pankratz (1966)</td>
</tr>
<tr>
<td>( \text{TbO}_1, n )</td>
<td>( H_T, S_T, ) Pankratz and Kelley (1966)</td>
</tr>
<tr>
<td>Dy</td>
<td>( H_T, ) Dennison et al. (1966); ( C_{p,r,} ) Lounasmaa and Sundström (1966); ( C_{p,r,} ) Flotow and Osborne (1964)</td>
</tr>
<tr>
<td>( \text{Dy}_2\text{O}_3 )</td>
<td>( H_T, S_T, ) Pankratz and Kelley (1963); ( C_{p,r,} S_T, ) Westrum and Justice (1963)</td>
</tr>
<tr>
<td>Ho</td>
<td>( H_T, ) Dennison et al. (1966); ( C_{p,r,} ) Lounasmaa and Sundström (1966); ( C_{p,r,} ) van Kempen et al. (1964)</td>
</tr>
<tr>
<td>( \text{HoO}_2 )</td>
<td>( C_{p,r,} S_T, ) Westrum and Justice (1963); ( H_T, S_T, ) Pankratz and King (1963)</td>
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<tr>
<td>Er</td>
<td>( H_T, ) Dennison et al. (1966)</td>
</tr>
<tr>
<td>( \text{Er}_2\text{O}_3 )</td>
<td>( C_{p,r,} S_T, ) Westrum and Justice (1963); ( H_T, S_T, ) Pankratz and King (1963)</td>
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<tr>
<td>Tm</td>
<td>( H_T, ) Dennison et al. (1966); ( C_{p,r,} ) Lounasmaa (1964b); ( C_{p,r,} ) Lounasmaa and Sundström (1966)</td>
</tr>
<tr>
<td>( \text{TmO}_2 )</td>
<td>( C_{p,r,} H_T, S_T, ) Tsagareishvili and Gvelesiani (1965a, 1965b); ( H_T, S_T, ) Pankratz and King (1963)</td>
</tr>
<tr>
<td>Yb</td>
<td>( C_{p,r,} ) Lounasmaa (1963, 1966); ( C_{p,r,} ) Gerstein et al. (1964)</td>
</tr>
<tr>
<td>( \text{Yb}_2\text{O}_3 )</td>
<td>( C_{p,r,} S_T, ) Justice and Westrum (1963b); ( C_{p,r,} H_T, S_T, ) Tsagareishvili and Gvelesiani (1965a, 1965b); ( H_T, S_T, ) Pankratz and King (1963)</td>
</tr>
<tr>
<td>Lu</td>
<td>( H_T, ) Dennison et al. (1966); ( C_{p,r,} ) Lounasmaa (1964c)</td>
</tr>
<tr>
<td>( \text{LuO}_3 )</td>
<td>( H_T, S_T, ) Pankratz and Kelley (1963)</td>
</tr>
</tbody>
</table>
E. Oxygen Transport in Rare Earth Oxides

There have been a few studies of diffusion of oxygen in rare earth oxides. From oxidation studies of liquid rare earth metals and gold alloys of rare earth metals, Brett and Seigle (1966) obtained the parabolic, diffusion controlled, rate constants. They found the data insufficient to specify the variation of mobility or number of diffusing defects in the lanthanide sesquioxide as a function of atomic number or concentration gradient. Diffusion is slower in the heavier members of the series.

Wirkus et al. (1967) have determined self-diffusion of oxygen in Y\(_2\)O\(_3\) and Er\(_2\)O\(_3\) by heating the substoichiometric sesquioxides in air on a thermobalance. The diffusion coefficient for Y\(_2\)O\(_3\) in the 1000–1500°C range is

\[ D = 7.24 \exp \left( -58,600/RT \right) \]

and for Er\(_2\)O\(_3\) between 850–1250°C is

\[ D = 1.22 \exp \left( -47,800/RT \right) \]

where \( D \) = diffusivity in cm\(^2\)/sec.

Oxygen isotope exchange between the solid and gaseous phase has been used to study the high mobility of oxygen in rare earth oxides. Minachev et al. (1964) have studied the Nd\(_2\)O\(_3\)--O\(_2\) and Er\(_2\)O\(_3\) systems in the temperature range 250–325°C. The activation energy for exchange for Nd\(_2\)O\(_3\) was 13.1 kcal/mole and for Er\(_2\)O\(_3\), 15.7 kcal/mole. Minachev and Antoshin (1965) extended the study to the entire rare earth series although their materials were not very pure (98.8 percent) and not freed of water and CO\(_2\) by ignition to high temperatures. They observed that the initial mobility shows a periodicity in passing from La to Lu with maxima at Pr\(_2\)O\(_3\), and Tb\(_2\)O\(_3\). The intermediate minimum occurs at Sm\(_2\)O\(_3\) with drops in the curve at the ends. In general the Ce subgroup elements have a lower activation energy than the Y subgroup.

Sazonov et al. (1965) observed oxygen exchange between the gas and solid A-form neodymium oxide with an activation energy of 20 kcal/mole. Stone et al. (1968) have investigated self-diffusion of oxygen in neodymium and samarium sesquioxides. The coefficients observed were

\[
\text{Sm}_2\text{O}_3 (99.9 \text{ percent}) \quad D = 9.2 \times 10^{-6} \exp \left( -23.5 \pm 2 \text{ kcal/}RT \right),
\]

\[
\text{Sm}_2\text{O}_3 (99.998 \text{ percent}) \quad D = 6.0 \times 10^{-6} \exp \left( -21.3 \pm 0.5 \text{ kcal/}RT \right),
\]

and

\[
\text{Nd}_2\text{O}_3 (99.999 \text{ percent}) \quad D = 1.3 \times 10^{-4} \exp \left( -31 \pm 2 \text{ kcal/}RT \right).
\]

The freezing points of the lanthanide oxides were measured using a solar furnace by Noguchi and Mizuno (1967) and their values are compared in Table II with those observed by Mordovin et al. (1967) and Foëx (1965b). Sata (1966) has observed the melting temperatures of La\(_2\)O\(_3\) on a tungsten filament as 2304°C.

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TABLE II
MELTING POINTS (°C) OF LANTHANIDE SESQUIOXIDES

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
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<tr>
<td>La₂O₃</td>
<td>2300</td>
<td>2256</td>
<td>2217</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>—</td>
<td>—</td>
<td>2142</td>
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<tr>
<td>Pr₂O₃</td>
<td>2296</td>
<td>2183</td>
<td>2127</td>
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<tr>
<td>Nd₂O₃</td>
<td>2310</td>
<td>2233</td>
<td>2211</td>
</tr>
<tr>
<td>Pm₂O₃</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>2320</td>
<td>2269</td>
<td>2262</td>
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<tr>
<td>Eu₂O₃</td>
<td>2330</td>
<td>2291</td>
<td>2002</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>2395</td>
<td>2330</td>
<td>2322</td>
</tr>
<tr>
<td>Tb₂O₃</td>
<td>2390</td>
<td>2303</td>
<td>2292</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>2391</td>
<td>2228</td>
<td>2352</td>
</tr>
<tr>
<td>Ho₂O₃</td>
<td>2396</td>
<td>2330</td>
<td>2367</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>2400</td>
<td>2344</td>
<td>2387</td>
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<tr>
<td>Tm₂O₃</td>
<td>—</td>
<td>2341</td>
<td>2392</td>
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<tr>
<td>Yb₂O₃</td>
<td>2411</td>
<td>2355</td>
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<tr>
<td>Lu₂O₃</td>
<td>—</td>
<td>2373</td>
<td>2467</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>2435</td>
<td>2376</td>
<td>—</td>
</tr>
</tbody>
</table>

F. Rare Earth Oxide Crystal Growth

EuO crystals of good quality of centimeter size were grown by Guerci and Shafer (1966) from a melt containing an excess of europium metal. Sealed in molybdenum crucibles containing the solutions they were cooled from 1950–2000°C at a rate of 25°C per hour. The crystals had a lattice constant of 5.1451 ± 0.003 Å and a density of 8.180 ± 0.002. These experiments suggest that EuO is an incongruently melting compound. The Verneuil method was used by Popova and Zotkina (1966) to grow crystals of the monoclinic form of Sm₂O₃, Eu₂O₃, and Gd₂O₃ and the cubic form sesquioxides of Dy, Ho, Er, Tm, Yb, and Lu. X-rays did not reveal any suboxide formation. Although microhardness of the specimens were given, no information on the size or perfection of crystal grown was indicated. Attempts to grow Tb₂O₃ were unsuccessful.

Crystal growth of CeO₂ from lithium ditungstate has been accomplished by Finch and Clark (1966) and from bismuth oxide-lead fluoride and lithium molybdate by Linares (1967).

G. Dissociation Energies of Gaseous Monoxide

The dissociation energies of the gaseous monoxides of the rare earth elements have been determined by Knudsen effusion and mass spectrometric...
measurements by Ames et al. (1967). A double periodicity was seen in the variation of the dissociation energies with atomic number and these variations closely match those of the heats of sublimation of the rare earth metals. Assuming a common bound state for the monoxides $M^{2+}_2O_3^-$, it is shown that the variations in the dissociation energies in the lanthanide series correspond to the magnitude of the $4f^n \rightarrow 4f^{n-1}5d$ transitions of the divalent ions.

The vapor pressure of $Gd_2O_3$ from 2350 to 2590°C has been measured from Knudsen cell evaporation by Messier (1967). Two sets of data yielded average values of 468.7 ± 0.8 and 471.0 ± 0.5 kcal/mole for the assumed evaporation reaction

$$Gd_2O_3(s) \rightarrow 2GdO(g) + O(g)$$

The results indicate that the evaporation coefficient may be much less than one.

Semenov (1963) used a mass spectrometer to study the evaporation of various rare earth oxides and observed a decreasing stability of the gaseous monoxides with increasing atomic number. Smoes et al. (1965) calculated the dissociation energy of LaO as 191.0 ± 2.5 kcal/mole and the atomization energy of La$_2$O as 266 ± 8 and as 468 ± 11 for La$_2$O$_2$.

Trombe and Foëx (1965) have exploited evaporation property differences of the rare earth oxides to give a separation when heated by means of a solar furnace to 2500°C. Volatility coefficients were determined for various groups in the series.

**H. Magnetic Studies**

The magnetic susceptibility of the oxides of La, Nd, and Gd were measured by Smol'kov and Dobroval'skaya (1965) in the temperature range 20 to 800°C. They found satisfactory agreement with van Vleck's theoretical values obtained with a screening constant, $\sigma = 33$, and the use of the Curie-Weiss relationship.

Eu$_2$O$_3$ was observed by Arajs and Colvin (1964) to register magnetic susceptibilities in the temperature range 300–1300°K in satisfactory agreement with van Vleck's theory of magnetism and Judd's energy levels for free Eu$^{3+}$.

Holmes and Schieber (1966) found Eu$_3$O$_4$ to be antiferromagnetic with a Néel temperature of 5°K and with Curie-Weiss behavior at higher temperatures. A Curie point of 7.8°K is reported by Samokhvalov et al. (1965) who observed that the high magnetic moment and low Curie point of this oxide may serve to verify the spin-wave theory. Wang (1966), however, claimed...
that static magnetic susceptibility measurements made by the Faraday method show \( \text{Eu}_3\text{O}_4 \) to be ferromagnetic with a Curie point of 77\(^\circ\)K.

Samokhvalov et al. (1965, 1966) measured magnetization curves for ferromagnetic \( \text{EuO} \) near 4, 20, and 82\(^\circ\)K and saturation magnetization between 1.7 and 43\(^\circ\)K. Their analysis of the temperature dependence of spontaneous magnetization in terms of spin-wave theory yielded the exchange integral \( J = 0.394k \).

Stevenson and Robinson (1965) studied the shift in the ferromagnetic phase transition temperature as a function of pressure up to 10 katm at 296, 82, and 4.2\(^\circ\)K. The temperature shift was about 5\(^\circ\) higher at these pressures.

Miyata and Argyle (1967) have determined the magnetocrystalline anisotropy of single-crystal \( \text{EuO} \). The observed relationship between the magnetocrystalline anisotropy constant and the magnetization is explained by a theory of single-ion interaction with the cubic crystal potential.

The magnetic properties of rare earth element oxides capable of existing at higher oxidation states have been investigated by MacChesney et al. for oxides of praseodymium (1964) and terbium (1966). \( \text{PrO}_2 \) prepared at oxygen pressures up to 2000 atm appears to be antiferromagnetic with a Néel temperature of 14\(^\circ\)K in contrast to low pressure preparations reported by Kern (1964) not to show cooperative effects. MacChesney et al. and Kern agree on the other praseodymium oxides. MacChesney et al. (1964) made a study of the pressure dependence of the \( \text{PrO}_2-\text{PrO}_{1.83} \) phase boundary up to 5000 atm \( \text{O}_2 \).

Both terbium sesquioxide polymorphs (C- and B-types) were found to be antiferromagnets with Néel temperatures of 2 and 7\(^\circ\)K, respectively. Of the intermediate oxides \( \text{TbO}_{1.71} \) and \( \text{TbO}_{1.823} \) were observed to be ordered at 7 and 6\(^\circ\)K, respectively, while \( \text{TbO}_{1.809} \) was found not to be ordered above 1.4\(^\circ\)K. \( \text{TbO}_2 \) exhibited antiferromagnetic behavior with a Néel temperature of 3\(^\circ\)K. At higher temperatures the paramagnetic moment of terbium in each case was close to that expected for the free ion.

Bonrath et al. (1966) observed \( \text{Dy}_2\text{O}_3 \) become antiferromagnetic at 1.2\(^\circ\)K. \( \text{Tm}_2\text{O}_3 \) obeys the Curie–Weiss law between 80 and 980\(^\circ\)K according to measurements by Perakis and Kern (1965) who obtain \( \mu_{\text{eff}} = 7.56 \) Bohr magnetons.

In order to establish a correlation between the Schottky anomalies observed in the heat capacities and the corresponding cryomagnetic anomalies in the susceptibilities, Hacker et al. (1965) measured the susceptibilities of \( \text{Nd, Gd, Dy, Ho, Er, and Yb (III) oxides} \) from 4–300\(^\circ\)K. With the exception of \( \text{Gd}_2\text{O}_3 \) each of the compounds has an anomaly of the type charac-
teristic of crystalline-field splitting of the ground state in the free rare earth ion.

The noncolinear magnetic structure of $\text{Er}_2\text{O}_3$ agrees with the group theory prediction and corresponds to the identity representation of the Ia3 group according to Bertaut and Chevalier (1966).

### I. Electrical Properties

The electrical conductivity of near-stoichiometric $\alpha$-CeO$_2$ was measured by Greener et al. (1964) as a function of oxygen pressure and temperature. The data are analyzed in terms of a Ce$^{4+}$ interstitials and quasi-free electron in a conduction state although an alternative suggestion involving vacancy pairs which may dissociate is considered.

Kevane and co-workers (1963) and Holverson and Kevane (1966) have studied pure and calcia-doped CeO$_2$ and have interpreted their results in terms of oxygen transport in the solid. These measurements were frequently accompanied by voltage-time transients and non-Ohmic behavior. These effects were not observed by Blumenthal and Pinz (1967).

The division of conductivity in $\text{Gd}_2\text{O}_3$, $\text{Dy}_2\text{O}_3$, $\text{Sm}_2\text{O}_3$, and $\text{Y}_2\text{O}_3$ between electronic and ionic has been studied by Tare and Schmalzried (1964). Their measurements were in the temperature range 650–900°C at oxygen partial pressures of $1-10^{-29}$ atm.

A number of studies of electrical behavior of powder compacts of PrO$_x$ $(1.5 \leq x \leq 2.0)$ have been made. Honig et al. (1964) measured resistance and Seebeck coefficients of powder compacts in the range 600–700°C as a function of stoichiometry. They made measurements on single crystals in the composition range PrO$_{1.5}$–PrO$_{1.531}$ as a function of temperature. Their results were consistent with an electron-transfer model in which neighboring cations in different valence states exchange electrons in the 4f shell. Electrical conductivity of PrO$_x$ $(1.6 \leq x \leq 1.714)$ is studied by Wilbert et al. (1966) who used these results as a means of defining the stability regions of A-type Pr$_2$O$_3$ and the sigma phase.

Grosvald (1964) has investigated the dielectric properties of PrO$_x$ $(1.5 \leq x \leq 2)$ and observed changes which confirm the existence of an intermediate compound Pr$_6$O$_{11}$. He further considers (1965) whether an electron transfer between cations or a strong electron-phonon interaction is suggested as a tentative interpretation for the phenomena of dielectric relaxation in the higher oxides. Experiments indicate that only the latter hypothesis need be considered.

The electrical properties of rare earth oxides have been measured by Bogoroditskii et al. (1965). The oxides, compressed at 2500 kg/cm$^2$ and sintered to 1300°C, were measured in the temperature range from 240 to
1300°C. Praseodymium and terbium oxides were found to be semiconductors and Ce, Nd, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu oxides were said to be dielectrics. Dielectric loss measurements were made.

Chandrashekhar et al. (1967) have observed the electrical conductivities of the sesquioxides, dioxides, and some intermediate oxides of Pr and Tb at various temperatures. Activation energies for the conduction process have been derived. The conductivity passes through a maximum in the composition region LnO₁.₇₀–LnO₁.₈₃ and is consistent with a hopping model for these semiconductors. Their calculation of the Frolich coupling constants and transition probabilities in Pr₆O₁₁ has shown that the intermediate polaron theory is applicable to these systems.

J. Optical Properties

Optical transitions in rare earth compounds including some oxides especially as host lattices are reviewed by Gruber (1968). Gruber et al. (1966) observed and analyzed the absorption spectra, in the range 2200–10,000 Å, of large single crystals of Er₂O₃ at 10, 80, and 290°C. More than 600 transitions from all eight crystalline stark levels of the ground \(^{4}I_{15/2}\) state to over 30 excited J manifolds of the Er\(^{3+}\) ion in C\(_{2}\) sites were assigned.

Batsanov and his coworkers have used refractometry, IR spectroscopy, and x-ray methods to investigate the preparation of oxides when nitrates, oxalates, and sulfates (1965) and acetates and hydroxides (1966) are decomposed.

Reflection spectra of thin layers of Eu (II), (III) and Gd (III) oxides have been recorded in the ultraviolet region and the various peaks discussed by Sinha (1967). The diffuse reflectance spectra of eleven rare earth oxides of various structural types have been reported by White (1967). The spectra in the range 225–2700 \(\mu\)m, particularly in the near infrared, permit the use of this technique to identify rare earth ions in solid materials. The peaks in some of the spectra were tentatively assigned.

Warmkessel et al. (1968) have recorded the spectra of A- and C-type Pr₂O₅ and tentatively assigned the peaks in the UV and visible. Spectra of the ordered intermediate phases PrO₁.₇₁, PrO₁.₇₈, PrO₁.₅ₐ, PrO₁.₈₁₈, and PrO₁.₈₃₃ were observed and their relationships discussed.

Petru and Muck (1967a) have made an infrared analysis of CeO₂, Pr₆O₁₁, Nd₂O₅, and Sm₂O₃. This work was continued and the results for Eu₂O₃, Gd₂O₃, Tb₂O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, and Lu₂O₃ were presented and the force constants are calculated (Petru and Muck, 1967b).

The far IR spectra in the region 800–240 cm\(^{-1}\) have been recorded and characteristic absorption frequencies given by Baun and McDevitt (1963) for the oxides of Lu, Yb, Tm, Er, Y, Ho, Dy, Gd, Nd, Pr, La, Sm, Eu, Sc,
These studies were continued by McDevitt and Davidson (1966) in the range 700–50 cm\(^{-1}\). It is evident from these data that the crystal structure determines the frequency of the bands and clearly shows the lanthanide contraction.

McMahon (1967) has given the hemispherical spectra emittances for the sesquioxides of Y, Sm, Gd, Er, Tm, and Yb for five wavelengths in the visible spectrum over a temperature range of 1400 to 3000°K. A reflectance technique incorporating a carbon arc image furnace and a standard reflectance was used in the determinations.

II. ACTINIDE OXIDES

There is a patron of actinide oxide studies in the atomic energy commissions of the world. In particular the International Atomic Energy Agency in Vienna (IAEA) has periodically sponsored symposia and study groups to examine various facets of actinide oxide behavior. The essence of these meetings is published in the form of proceedings and technical report series.

During the past five years, several publications have originated from IAEA, Vienna (1962, 1965, 1966a, 1966b, 1966c, 1967, 1968) containing summaries, reviews, and new experimental data on oxides of importance to the nuclear energy programs, especially uranium and plutonium.

Among the general papers appearing in these publications dealing with all the oxides of the actinides is one by Westrum and Grønvold (1963) who make a critical assessment of the thermodynamic properties of all the actinide oxides which had been published to that date. These data arise principally from heat capacity measurements. Entropy data as well as a method of estimating entropies of such materials including the rare earth sesquioxides are presented.

Ackermann and Thorn (1962a) discuss the measurements on gaseous molecules at high temperatures from which thermodynamic information can be derived. A correlation of the experimental values with the entire series of monoxides and dioxides is achieved by means of a molecular orbital treatment of the gaseous molecules. The same authors (1962b) present a critical assessment of the vaporization studies on thorium, uranium, and plutonium and their oxides. Expressions for the vapor pressure as a function of temperature as well as thermodynamic data are presented. Ackermann and Thorn (1966) also give a critical review of previous vaporization studies on the actinide oxides. The results are compared and a consideration of the electronic nature of the actinide atoms and the evolution of metal oxygen interaction are given. The importance of fixing a thermodynamic state in a study is necessary since the oxides are known to exhibit a range of composition. In particular the case of UO\(_{2+\delta}\) is discussed. The total vapor pressure of the
system is least at UO$_2$ and increases as the oxygen to metal ratio changes in
either direction due principally to increased UO$_3$(g) formation at higher com-
position and to UO(g) and U(g) at lower composition. They emphasize
thereby the necessity of knowing the equilibrium oxygen pressure or the com-
position of oxide in any study of vaporization. It follows that UO$_2$ is the con-
gruently vaporizing composition, a point discussed also by Gilles (1966).

The free energies and heats of formation of the solid dioxide phase be-
comes less negative as the atomic number increases. This results in a greater
ease of vacuum reduction of the oxides. A correlative to this is that $G_{0w}$ in
these phases is considerably more negative in UO$_{2-z}$ than the corresponding
plutonium compounds.

The free energies and heats of formation of the gaseous dioxides become
less negative from ThO$_2$(g) to PuO$_2$(g) in the same direction as for the solids.
The trend for MO(g) seems to be in the opposite direction.

Roberts and Markin (1967) have discussed the thermodynamics of non-
stoichiometric oxide systems based on the fluorite structure. These phases
frequently exhibit wide ranges of stoichiometry at higher temperatures. The
thermodynamic data are seen to be compatible with and provide direct
support for the view that these nonstoichiometric phases consist of domains
having short but no long range order.

The chemistry of the actinide elements was reviewed by Cunningham
(1964) placing the oxides of these elements against the broader chemical
properties of the elements. A brief general discussion of the actinide oxides
and a comparison with the rare earth oxides has been given by Eyring
(1967).

Several papers have appeared recently describing the preparation of
actinide oxide spheres, a form preferred for many engineering and scientific
applications. Hammer and Smith (1963) described a procedure by which an
evaporated nitrate-oxide mixture was decomposed and milled and the result-
ing gel ignited.

Sol-gel techniques were used by Wymer and Coobs (1965) to produce
microspheres of ThO$_2$, UO$_2$, PuO$_2$, AmO$_2$, and CmO$_2$ of uniform size. These
materials were coated with pyrolytic carbon in a fluidized bed and found
satisfactory for fuels for high temperature, gas-cooled reactors.

There is a very large literature on this subject mainly in patents and
patent applications. No attempt has been made to summarize this work.

A. Thorium Oxides

1. Crystal Growth

Thorium oxide is one of the most stable oxides known. In addition to its
refractory properties, single crystals are of potential interest as optical mate-
rials and as a laser host. The growth of such high melting oxides in pure
form is very difficult. The growth of ThO₂ crystals from Bi₂O₃, PbF₂ melts is described by Chase and Osmer (1964). The crystals, several millimeters in extent, were colorless and appeared to be of good optical quality. Finch and Clark (1965) have grown optically transparent octahedra up to three millimeters on an edge at 1250–1350°C from molten Li₂O·2WO₃ solvent. The major impurities were < 50 ppm W and < 50 ppm Li. The method was used both for pure and rare earth doped crystals.

The growth of ThO₂ single crystals up to 10 mm on an edge has also been accomplished from PbO–PbF₂–B₂O₃, Na₂O–MoO₃–B₂O₃, and Li₂O–MoO₃–B₂O₃ among many flux systems and their transmission spectrum measured by Linares (1967).

Thoria single crystals have also been grown by vapor deposition in a solar furnace by Laszlo et al. (1967). Very pure (15 ppm Si and 5 ppm Fe) crystals three mm long and one mm in cross-section were obtained.

2. Structural Information

Using neutron diffraction from single crystals, Willis (1963b, 1963c) confirmed the fluorite structure of ThO₂ at room temperature and has given precise values for the Debye–Waller factors of the thorium and oxygen atoms and for the ratios of their nuclear scattering amplitudes. A separate study for the range from 20–1100°C yielded a Debye characteristic temperature independent of temperature above 400°C and equal to 393 K. At 1000°C the mean coordinates of the oxygen atoms are slightly displaced indicating either a disordering of the oxygen or anharmonic vibration across the normal positions.

Line broadening of x-ray reflections from thoria powders prepared in various ways have been used by Ferguson (1965) to infer average crystallite size, strain, and shape. The results are compared with those from electron microscopy and BET measurements. It is concluded that the strain energy represents only about 0.1 percent of the surface energy of the crystallites.

3. Vaporization Properties

The vaporization of thoria was studied by Ackermann et al. (1963) in the temperature range 2000–3000°C. A consistent set of thermodynamic data was derived from these and other measurements. The solid dioxide is the congruently vaporizing species at all temperatures although the phase becomes slightly substoichiometric down to ThO₁.₉₉₈ above 2800°C.

4. Transport Properties and Sintering

Doped thoria is finding increased use as an oxygen conductor in solid electrolytic cells. Lasker and Rapp (1966) have studied the mixed conduction in pure ThO₂ and in ThO₂–Y₂O₃ solutions. These studies were in the
interval 800–1100°C over a wide range of oxygen potentials. A dilute solu-
tion model was developed to predict satisfactorily the partial ionic and elec-
tronic conductivities.

In a similar way Neuimin and Pal’guev (1963) and Pal’guev et al. (1963)
studied the characteristics of conduction of ThO₂ and its mixtures. They
determined transference numbers of cations, oxygen ions, and electrons.

At temperatures between 800 and 1100°C Rapp (1967) found ThO₂ to be
an ionic conductor over a broad intermediate range of oxygen activity.
It becomes a p-type electronic conductor at higher oxygen pressures. Trace
impurities are credited with the capacity for ionic conduction.

Oel (1967) studied sintering in pure ThO₂ in the range 1700 to 1900°C
where firm and compact shaped bodies are produced. The results of this
study were compared with a simplified theoretical equation to evaluate the
importance of the great variety of factors on which sintering depends. Hep-
worth and Rutherford (1964) have reviewed some of the older literature
on thoria ceramics.

Contamination of ThO₂ by nitrogen at temperatures as low as 1550°C
was observed by Benz (1967) who concerned himself with the ternary
thorium-nitrogen-oxygen system. It is possible that some exchange of oxygen
by nitrogen in ThO₂ may occur at lower temperatures at higher nitrogen
pressures.

B. Protactinium Oxides

Nothing like a complete phase diagram for the complex protactinium-
oxygen system has been worked out; however, significant advances toward
understanding have recently been made. Stchouzkoy et al. (1964) heated
a hydrated precipitate and observed the oxide phase at various temperatures.
An amorphous oxide transforms at 500–600°C to a face centered cubic
Pa₂O₅. Between 700 and 900°C they reported the formation of a tetragonal
phase Pa₂O₅₋. Above 1100°C they obtained a hexagonal phase which they
believed to have the composition Pa₄O₉. Lattice parameters of these phases
are given in Table III.

Roberts and Walter (1966) have made a detailed x-ray study of larger
samples of PaOₓ of good purity both in oxidation and reduction. Their study
included the determination of oxygen uptake and loss which enabled them
to know their composition, assuming that Pa₂O₅ is formed when an oxide
is heated in air to 700°C. They concluded that Stchouzkoy et al. (1964)
observed only Pa₂O₅ in their experiments with no appreciable loss of oxygen.

Four phases having a composition near Pa₂O₅ have been observed as
listed in Table III. The other phases observed on oxidation or reduction are
given in Table IV.
TABLE III

THE PROTACTINIUM OXIDES

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>X-ray powder patterns (parameters in Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stchouzkoy et al. (1964)</td>
</tr>
<tr>
<td></td>
<td>Roberts and Walter (1966)</td>
</tr>
<tr>
<td>&lt;700</td>
<td>f.c.c.</td>
</tr>
<tr>
<td></td>
<td>(a = 5.446 \pm 0.002)</td>
</tr>
<tr>
<td>700–900</td>
<td>tetragonal</td>
</tr>
<tr>
<td></td>
<td>(a = 10.891 \pm 0.0001)</td>
</tr>
<tr>
<td></td>
<td>(c = 10.992 \pm 0.002)</td>
</tr>
<tr>
<td></td>
<td>(c/a = 1.009)</td>
</tr>
<tr>
<td>~1100</td>
<td>hexagonal</td>
</tr>
<tr>
<td></td>
<td>(a = 3.820 \pm 0.001)</td>
</tr>
<tr>
<td></td>
<td>(c = 13.225 \pm 0.010)</td>
</tr>
<tr>
<td>&gt;1240</td>
<td>oxygen-deficient phases</td>
</tr>
<tr>
<td></td>
<td>The hexagonal phase plus a</td>
</tr>
<tr>
<td></td>
<td>rhombohedral phase</td>
</tr>
<tr>
<td></td>
<td>(a = 5.424)</td>
</tr>
<tr>
<td></td>
<td>(a = 89.76°)</td>
</tr>
</tbody>
</table>

TABLE IV

THE LOWER PROTACTINIUM OXIDES

<table>
<thead>
<tr>
<th>Composition (O/Pa)</th>
<th>Unit cell</th>
<th>Lattice Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>f.c.c.</td>
<td>(a = 5.509 \pm 0.002)</td>
</tr>
<tr>
<td>2.18–2.21</td>
<td>f.c.c.</td>
<td>(a = 5.473)</td>
</tr>
<tr>
<td>2.33</td>
<td>tetragonal</td>
<td>(a = 5.425, c = 5.568, c/a = 1.026)</td>
</tr>
<tr>
<td>2.40–2.42</td>
<td>tetragonal</td>
<td>(a = 5.480, c = 5.416, c/a = 0.99)</td>
</tr>
<tr>
<td>2.42–2.44</td>
<td>rhombohedral</td>
<td>(a = 5.449, a = 89.65°)</td>
</tr>
</tbody>
</table>

The structures of all the lower protactinium oxides are closely related to the fluorite structure and density measurements indicate that the excess oxygen beyond \(\text{PaO}_2\) is interstitial. \(\text{PaO}_2\) forms a complete range of solid solutions with \(\text{ThO}_2\) which will take up additional oxygen.

C. Uranium Oxides

The uranium-oxygen system is at once the most complex and most studied oxide system known (perhaps the former because of the latter). For the
purposes of this discussion oxides in the range UO\(_x\)\((1.6 < x < 2.67)\) are considered refractory.

An excellent recent survey of thermodynamic and transport properties of refractory uranium oxides has been issued by IAEA, Vienna (1965). This work should be consulted for results which were "adopted" by a working group active in studies on this oxide system. Reference to much of the important older literature on the UO\(_x\)–O\(_2\) system and conclusions as to important future work are given.

1. Phase Transformations and Phase Relationships

Figure 5 is a composite diagram from Rand and Roberts (1966) who discussed some of the general features of the UO\(_x\)–U\(_3\)O\(_8\) region and from Martin and Edwards (1965, 1966) who studied the uranium-uranium dioxide phase diagram at high temperatures. Of course, the complex polymorphism of U\(_4\)O\(_9\) and especially U\(_3\)O\(_8\) and a U\(_2\)O\(_9\) phase discussed later do not appear in this diagram.

**FIGURE 5** Phase relationships in the uranium-oxygen system (after Rand and Roberts, 1966 and Martin and Edwards, 1965).
Edwards and Martin (1966) observed no phases between UO$_2$ and liquid uranium although UO has often been reported. They observed a continuing decrease in oxygen content reaching a minimum of UO$_{1.64}$ with a monotectic temperature of 2500 ± 30°C. The monotectic composition is seen to be about UO$_{1.3}$.

Amato et al. (1965) observed precipitation of uranium in phase boundaries of UO$_2$ which had been treated at 1950°C in vacuo. They attributed this to reduction by the organic binder since the effect was not observed when the binder was absent.

The melting point of UO$_2$ has recently been reported as 2805 ± 5°C determined by Hausner (1965) from a thermal arrest on cooling.

A wide variety of properties of the uranium-oxygen system has been observed over the entire composition range being considered here. Such an investigation has been reported by Deshpande et al. (1963) who conducted a DTA and TGA study of the low temperature oxidation of UO$_2$. Although a marked dependence on the source material was noticed, they interpreted their results as UO$_2$ oxidizing to U$_3$O$_8$ in a two-step process involving U$_2$O$_7$.

Stamenković and Ristić (1964) studied the formation of U$_3$O$_7$ when UO$_{2.60-2.61}$ of 3.7 m$^2$/gm or 4.3 m$^2$/gm surface area was oxidized. The first stage of the oxidation occurred with an activation energy of 24.5 kcal/mole.

A DTA study of the same region was carried out by Stamenković et al. (1966) who oxidized U$_3$O$_7$ to U$_3$O$_8$.

Sato et al. (1965) followed earlier experiments of reduction of U$_3$O$_8$ in vacuo with reduction by hydrogen. They observed a DTA curve showing three peaks which were interpreted as being due to reduction to U$_2$O$_8-x$, the nucleation of UO$_2$, and the formation of UO$_2$ in succession. Their analysis of the weak reflections in x-ray diffraction patterns of quenched samples supported this interpretation.

Imriš (1966) made a thermogravimetric study of the oxidation of particles of UO$_2$ prepared from U$_3$O$_8$ calcined under various conditions. The study was directed toward observing the effect of particle size and thermal and other history of the oxide. The samples prepared from U$_3$O$_8$ in the temperature range 610–1000°C had 1–6 m$^2$/gm surface area. An activation energy of 23.5 kcal/mole was calculated for the early part of the run before UO$_2$ was formed. All the curves showed a break at UO$_{2.33}$ and again at UO$_{2.67}$. Two types of behavior were identified depending on previous history.

The relationship between surface area of powdered UO$_2$ and its oxidation temperature was studied by Landspersky and Vachuska (1966) by observing the difference in temperature between the two-step reaction UO$_2$ → U$_3$O$_7$ → U$_3$O$_8$ for a number of samples.

Kotlar and Gerdanian (1965) studied the equilibrium properties of the uranium-oxygen system at high temperatures using CO–CO$_2$ and O$_2$–N$_2$. 

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mixtures of known oxygen content. They observed the $\text{UO}_2+x$ phase yield to a two-phase region then to a single phase $\text{U}_3\text{O}_9-y$.

A further study of the system by Kotlar et al. (1967) determined the partial pressure of oxygen in equilibrium with nonstoichiometric uranium oxides between 1080 and 1150°C and $2.19 < \text{O}/\text{U} < 2.63$. A thermobalance was used to determine the composition of uranium oxides heated in $\text{N}_2-\text{O}_2$ gaseous mixtures. Three regions of stability were seen at $\text{UO}_2+x$, $\text{U}_4\text{O}_{9-x}$, and $\text{U}_5\text{O}_{8-x}$. Phase boundaries were determined between these three regions. In the two-phase regions between $\text{U}_4\text{O}_{9-x}$ and $\text{U}_5\text{O}_{8-x}$, the thermodynamics of small systems were used to account for the shape of the log $p_{\text{O}_2}$ versus $X$ curve.

A partial phase diagram for the $\text{U}-\text{UO}_2$ system was given by Elston and Guinet (1966) in the composition range $2.0 < \text{O}/\text{U} < 2.67$ from 200–1500°C. Rachev et al. (1964, 1965) made a high temperature x-ray analysis of the uranium-oxide system in the composition range $\text{UO}_2-\text{U}_4\text{O}_{9}$. Specimens were prepared by reacting $\text{UO}_2$ and $\text{U}_4\text{O}_9$ in evacuated quartz ampules for 20 hours at 1000°C. A widening range of homogeneity of $\text{UO}_2+x$ was observed with $x$ increasing from 0.19 to 0.25 between 850 and 1150°C. The $\text{U}_4\text{O}_{9-x}$ phase was homogeneous over a narrow range and almost independent of temperature. An order-disorder transformation occurred between 1100 and 1150°C associated with a sharp increase in specific volume and coefficient of linear expansion.

Pialoux and Dode (1965) conducted an x-ray study of the uranium-oxygen system in the composition range $\text{UO}_2-\text{U}_3\text{O}_8$ at known oxygen potentials and at temperatures in excess of 1000°C. Equilibrium was observed with no further change in crystal parameters. The phase sequence observed at 1100°C and 125 ppm $\text{O}_2$ was $\text{UO}_2+x$, $\text{UO}_2+x + \text{U}_3\text{O}_9$ (after 20 hours), $\text{U}_3\text{O}_9$ (after 24 hours), $\text{U}_4\text{O}_9 + \text{U}_5\text{O}_{8-x}$ (after 24–48 hours). Lattice parameters were determined for the various phases as well as changes in the lattice parameters of $\text{UO}_2$ from 668–1400°C.

An electron diffraction study of the oxidation of $\text{UO}_2$ to $\text{U}_3\text{O}_{8-x}$ was made in transmission as the reaction proceeded on thin films of $\text{UO}_2$ by Steeb and Mitsch (1967). The film was heated between 300 and 750°C for about 20 hours in oxygen at $10^{-3}$ torr. A polycrystalline region was seen to oxidize through $\text{UO}_{2+x}$ then to $\text{U}_3\text{O}_{8-x}$ without intermediate phases being formed. The hexagonal $\text{U}_3\text{O}_{8-x}$ phase exhibited a superstructure cell with $a = 6.72$ Å and $c = 6 \times 4.105$ Å. Although the $\text{UO}_{2-x}$ lattice parameter decreased as oxidation advanced it increased again at the moment $\text{U}_3\text{O}_{8-x}$ was formed indicating a supersaturation of the $\text{UO}_{2+x}$ phase. At a pressure of $10^{-4}$ torr the monocrystalline specimens formed a superstructure with $a = 3a_{\text{UO}_{2+x}}$. When the pressure was $10^{-3}$ torr a tetragonal structure was formed with $a = 4a_{\text{UO}_{2+x}}$, $c = a_{\text{UO}_{2+x}}$ having a composition of $\text{UO}_{2.29}$ which is probably
the phase boundary at that temperature. It was suggested that the formation of \( \text{U}_3\text{O}_8 \) resulted from the long range ordering of disordered oxygen in the \( \text{UO}_{2+x} \) phase.

Phase transformations during reduction of \( \text{U}_4\text{O}_9 \) with carbon black at 700–950°C and with NH\(_3\) at 450–620°C have been studied by Zhukovskii et al. (1963) by means of x-ray diffraction. The sequence of reaction \( \text{U}_4\text{O}_9 \) to \( \text{UO}_{2+x(\text{max})} \rightarrow \text{UO}_{2+x} \) was seen including a two-phase region between \( \text{U}_4\text{O}_9 \) and \( \text{UO}_{2+x(\text{max})} \).

In the slow reduction of \( \text{U}_3\text{O}_8 \) by hydrogen below 400°C two phases were detected by Murat et al. (1966) between \( \text{UO}_{2.25} \) and \( \text{UO}_{2.60} \) but no tetragonal phases were seen. At higher temperatures cubic oxides were obtained in the composition range \( \text{UO}_{2.04} \) to \( \text{UO}_{2.25} \). In other low temperature experiments Bessonov et al. (1965b) confirmed the existence of tetragonal phases of composition \( \text{UO}_{2.33-2.37} \). A good correlation was seen among the electrical conductivity, composition, and structural changes of the samples.

Bessonov et al. (1965a) report further on the high temperature x-ray studies in the temperature region 400–800°C. The sequence of phase transformations observed was \( \text{UO}_2 \rightarrow \text{UO}_{2+x(\text{max})} \rightarrow \beta-\text{UO}_2 \rightarrow \alpha-\text{U}_3\text{O}_8 \rightarrow \beta-\text{U}_3\text{O}_8 \rightarrow \text{hexagonal U}_3\text{O}_8 \).

Ermischer et al. (1965) oxidized \( \text{UO}_2 \) in a high temperature chamber to 600°C making x-ray examinations at 50° intervals. Complete conversion to the hexagonal form \( \text{U}_3\text{O}_8 \) was observed between 150 and 200°C. The orthorhombic form reappeared upon cooling to room temperature.

Lynds et al. (1963), by means of x-ray and density studies, observed two separate linear relations for the lattice parameters as a function of oxygen content on samples quenched from 1100°C. One was characteristic of the \( \text{UO}_{2+x} \) phase with density consistent with oxygen interstitials and the other characteristic of the \( \text{U}_3\text{O}_{2.9} \) phase consistent with an oxygen vacancy model. The \( \text{UO}_{2+x} \) upper phase boundary was also mapped out.

Equilibrium information has been supposedly obtained on the \( \text{UO}_2-\text{O}_2 \) system in the temperature region 1500–2000°C by Anthony et al. (1963) from quenched specimens. These support a single phase \( \text{UO}_{2+x} \) region for \( x < 0.27 \), and for \( 0.27 < x < 0.61 \) a two-phase region is projected. Thermodynamic data are calculated from their results.

A transition in \( \text{U}_4\text{O}_9 \) near room temperature has been further studied using x-ray diffraction techniques by Naito et al. (1967). They found the transition temperature to depend on composition varying from 65 to 96°C between the oxygen-rich to oxygen-poor range. In addition they observed a sharp increase in the intensity of a superlattice reflection of \( \text{U}_4\text{O}_{n-y} \) in the same temperature range.
Sintered spheres of UO₂ were oxidized by Gašić et al. (1968) using isothermal differential thermal analysis in the temperature range 400–530°C. This relatively low surface area material was observed to oxidize in a single step to U₃O₈. The technique provided values for the heat of reaction.

The compound U₃O₈ has been reported formed upon dissolution of U₃O₈ in H₂SO₄ or by hydrogen reduction of U₃O₈. In either case a hexagonal phase with a = 3.885 Å and c = 4.082 Å was observed by Blinova et al. (1964). This same compound obtained by leaching U₃O₈ by sulfuric acid was studied by Kuz’micheva et al. (1965) by thermal analysis and x-ray diffraction with oxidation to U₃O₈ at 300–400°C. The studies suggested other metastable phases existing in this region.

Kozhina et al. (1966) studied the leaching product of U₃O₈ by sulfuric acid solution at 90°C having a composition of UO₂.5. The compound was stable in air over 1.5 months. X-ray diffraction indicated a hexagonal cell with a = 6.814 ± 0.001 KX and c = 4.118 ± 0.001 KX.

2. Structure Analysis

A neutron diffraction analysis of a polycrystalline sample of orthorhombic U₃O₈ was accomplished by Loopstra (1964). The space group is Amm2 (C₁₄) where six oxygen atoms surround the uranium atoms at distances of 2.07 to 2.23 Å and with a seventh oxygen atom at 2.44 Å for U (1) and at 2.71 Å for U (2). It was assumed that U (1) is a U⁵⁺ ion and U (2) a U³⁺.

A high temperature modification of U₃O₈ is reported by Karkhanavala and George (1966) when a=U₃O₈ was heated to temperatures in excess of 1100°C and cooled slowly. The new form was indexed on an orthorhombic cell with a = 6.70 Å, b = 12.46 Å, and c = 8.51 Å. DTA showed that δ–U₃O₈ transforms endothermically at 120°C to α–U₃O₈ with a heat of transition of 1050 ± 50 cal/gm mole.

In a series of publications during 1963 and 1964, Willis and his co-workers (1963a, 1963b, 1963c, 1964, 1965) and Rouse et al. (1963) reported significant progress in the understanding of the structure of the UOₓ system in the composition range 2.0 < x < 2.25. These studies clarify the structure of this particular system, but of greater significance, it has implications for the larger question of the nature of nonstoichiometric oxides.

UO₂ is a fluorite structure at room temperature with isotropic vibration of both U and O atoms. At high temperature there is an anharmonic contribution to the Debye–Waller factor of oxygen. This anharmonicity induces a strong anisotropic vibration of the oxygen atom while retaining its cubic point symmetry. The U atom vibrates isotropically at all temperatures up to 1100°C.
In the single phase region $UO_{2+x}$, the excess oxygens are incorporated in
the lattice interstitially producing a defect cluster consisting of two vacant
normal oxygen sites, two interstitial $O'$ and two interstitial $O''$ atoms where
the prime and double prime indicate two types of interstitial positions. The
uranium sublattice is undisturbed by the rearrangement of atoms on the
oxygen sublattice.

These 2:2:2 complexes are linked together in an ordered super-cell at
the composition $U_4O_9$ with the atomic arrangement within each complex
remaining the same as in $UO_{2+x}$. This ordering process leads to a change
of space group from face-centered $Fm3m$ to body-centered $I4_3d$, with
the symmetry remaining cubic. There are 64 fluorite-type subcells in the
$U_4O_9$ super-cell. The determination of the atomic positions in the large cell
is a very formidable and unsolved problem.

A neutron diffraction study of antiferromagnetic $UO_2$ revealed that the
unpaired electron has predominantly $5f$ character. The magnetic ordering
is such that the uranium atoms are coupled ferromagnetically with (200)
sheets and antiferromagnetically between sheets. The spin vectors lie with
the (200) sheets. A sharp transition to the paramagnetic state occurs at
30.6 K. The effective moment of the $U^{4+}$ is 1.82 Bohr magnetons.

Belbeoch et al. (1964) have recently studied, by x-ray diffraction,
quenched samples of uranium oxide in the composition range $UO_{2.00-2.25}$
which had been heated to high temperatures. Their results suggest a more
complex diagram than shown in Fig. 1. Specifically the system may become
two-phase again at high temperatures and near $UO_{2.25}$ two types of diffrac-
tion patterns are found either with or without superstructure lines showing
two polymorphic modifications.

In further x-ray studies of $U_4O_9$, Belbeoch et al. (1967) observed a
reversible cubic-rhombohedral transition at 65°C (at 20°C, $a = n a_o = n \cdot 5.4438$ A, $\alpha = 90.078^\circ$) where a lambda type anomaly with a maximum
at 330 K was observed in the heat capacity. At 1125°C a sudden increase
in lattice parameter occurs with the disappearance of superstructure lines
indicating an order-disorder transformation.

A notable study of surface reactions and configurations on $UO_{2+x}$ is
being undertaken by Ellis (1968) who has reported the surface configuration
of the (111), (110), and (100) surfaces of $UO_{2+x}$ and the effect of oxygen
absorption.

It is postulated that disordered $U_4O_9$ substructure is responsible for the
observed diffraction rings. Thermal faceting occurs on the (110) phase but
the (100) surface is stable in this respect up to $>1600$°C and does not
give fractional-order beams.
Steeb and Mitsch (1965) studied single crystal films of \( \text{UO}_2+x \) at 250-600°C by electron diffraction. A lattice of 64 uranium and 128 oxygen atoms was observed to contain 12 more oxygen atoms in groups of three not lying exactly in the ideal interstitial positions.

An analysis of the pressure dependence of the \( \text{UO}_2+x \) composition led Colombo (1964) to support the view that the structure of \( \text{UO}_2+x \) has oxygen interstitials rather than uranium vacancies.

Kingery (1965) has speculated from the solubility of \( \text{O}_2 \) in \( \text{UO}_2 \) that a molecular solution is formed. The various properties of \( \text{UO}_2+x \) are discussed in terms of a structure in which the oxygen is not in normally unoccupied positions. Some additional oxygen is associated in atomic form.

Extended defects in uranium oxide phases are beginning to be studied. Delavignette and Amelinckx (1966) have seen electron microscopic evidence for antiphase boundaries in \( \text{U}_3\text{O}_8 \) single crystal foils. These boundaries and stacking faults have been confirmed by Blank and Rouchi (1967) who observed the increased ease of formation of such gross defects as the oxygen content was increased above that in \( \text{UO}_2 \).

Point defect clusters and dislocation loops produced in bulk \( \text{UO}_2 \) by fission damage were observed by Whapham and Sheldon (1965) using transmission electron microscopy. The dynamics of growth and motion were observed.

3. Thermodynamic Properties

An important investigation of the thermodynamic data for uranium oxides between \( \text{UO}_2 \) and \( \text{U}_3\text{O}_8 \) was made by Markin et al. (1963). They reported a tensimetric study over the temperature interval 1000-1450°C and a composition of \( \text{UO}_{2+x} \) to \( \text{UO}_{2+4} \) and emf measurements in the temperature range 500-1060°C. Enthalpy, entropy, and free energy functions are given for the \( \text{UO}_{2+x}-\text{U}_3\text{O}_8 \) and \( \text{U}_4\text{O}_9-\text{U}_5\text{O}_8 \) regions. Phase relationships are considered with an attempt to place phase boundaries. One interesting result is that energy and entropy changes between \( \text{U}_3\text{O}_8 \) and \( \text{UO}_{2+x} \) of the same composition indicate a high degree of ordering in the former compared to the latter.

Rand and Kubaschewski (1963) have published their assessment of existing data on oxides including a phase diagram at higher temperatures over the composition range of interest here. Their tabulations included heats of formation, standard entropies, data on transformation, fusion and evaporation, heat capacities, vapor pressures, and free energy expressions.

Westrum (1966b) reviewed the recent developments in uranium oxide chemical thermodynamics. He noted especially the extension of cryothermal
data on $U_4O_9$ to higher temperature to show the suspected gradual, $\lambda$-type, structural transition at 348$^\circ$K associated with the displacement of the interstitial oxygen atoms. A confirmation by both heat capacity and magnetic susceptibility measurements of the antiferromagnetic-paramagnetic transition at 30.4$^\circ$K was established. A tabulation of the heat capacity, entropy, enthalpy-increment, and free energy function as a function of temperature was given for $UO_2$ and $U_3O_9$.

The $\lambda$-type thermal anomaly has been observed in $U_4O_9$ at 330$^\circ$K by Gotoo and Naito (1965) and at 348$^\circ$K by Westrum et al. (1966) and is attributed to a structural change.

Hagemark and Broli (1966) studied the equilibrium oxygen pressures over the nonstoichiometric phases $UO_{2+x}$ and $U_3O_{8-x}$ at temperatures between 900 and 1500$^\circ$C. From these measurements the phase boundaries and the partial molar free enthalpy, entropy, and enthalpy were derived. They found excellent agreement with adopted values of the IAEA panel (1965) and Rand and Kubaschewski (1963) for the $UO_{2+x}$ phase of compositions greater than $UO_{2.01}$. Their limited data for the phase $U_3O_{8-x}$ yielded partial thermodynamic quantities which did not confirm those adopted by Rand and Kubaschewski (1963) from earlier experimental measurements.

Assuming equilibrium between the oxygen in the gas phase and the crystalline $UO_{2+x}$ where the oxygen defects are not nearest neighbors, but approach one interstitial defect cluster per unit cell of $UO_2$, they fit the pressure composition relationship in the $UO_{2+x}$ region quite well simply using the mass action law.

In a continuing series of measurements Gerdanian and Dode (1965, 1966, 1968) seek direct determination of the thermodynamic quantities associated with the oxidation of $UO_2$ near stoichiometry. The first experiments at high temperature used controlled activity of oxygen by $H_2$–$H_2O$ and CO–$CO_2$ gas mixtures. The thermodynamic functions were calculated at frequent composition intervals. More recently they have made a direct measurement of the partial molar enthalpies of solution of oxygen in $UO_{2+x}$ near stoichiometry using a high temperature calorimeter of the Calvet type. They found a rapid decrease in the partial molar enthalpy from values more negative than $-200$ kcal/mole at $UO_{2.0003}$ to a minimum of about $-7$ kcal/mole for $UO_{2.0018}$ reaching a more or less linearly increasing level at $UO_{2.007}$. Their studies also allowed observations of the rate of oxygen diffusion in near stoichiometric $UO_2$.

Ogard and Leary (1968) used a drop calorimeter to determine the heat content of $UO_2$ as follows: $H_T - H_{298} = -183.9 + 8.770T + 5.824 \times 10^{-3} T^2 - 6.694 \times 10^{-7} T^3$ cal/mole in the interval 1338–2303$^\circ$K. Over a
greater range of temperature, 900–2350°C, Conway and Hein (1965) obtained: \[ H_T - H_{298} = 21.71 + 3.1 \times 10^{-2} T + 1.77 \times 10^{-5} T^2 \text{cal/g} \] \( T = ^\circ \text{C} \).

Enthalpies of solution and formation of \( \text{U}_4\text{O}_9 \) (\( \Delta H_{f298,15} = -1078.1 \pm 3.6 \text{ kcal/mole} \)) and \( \beta\text{-U}_3\text{O}_7 \) (\( \Delta H_{f298,15} = 818.4 \pm 2.8 \text{ kcal/mole} \)) have been determined by Fitzgibbon et al. (1967). Duquesnoy and Marion (1964) obtained \( \Delta H_{f298} = -1073.3 \) for the heat of formation of \( \text{U}_4\text{O}_9 \).

Hein et al. (1968a, 1968b) have recently extended their enthalpy measurements on \( \text{UO}_2 \) to above 3100°C and report the enthalpy increment of \( \text{UO}_2 \) below the melting point to be \[ H_T - H_{298} = -11,688 + 31.937T - 9.573 \times 10^{-3} T^2 + 2.577 \times 10^{-5} T^3. \] \( \text{UO}_2 \) was observed to melt at 3115°K with a heat of fusion 18.2 kcal/mole.

The enthalpy of formation of \( \text{U}_3\text{O}_7 \) has been given as \( -816.0 \pm 3 \text{ kcal/mole} \) by Stamenković et al. (1966). The standard entropy of \( \text{U}_3\text{O}_7 \) has been calculated by Stamenković (1964) as 62.39 eu.

The thermodynamic behavior of hypostoichiometric \( \text{UO}_2 \) has been studied by Aitken et al. (1966) by observing the stoichiometry and evaporation rate of the solid phase in slowly flowing hydrogen (\(-40^\circ \text{ dew point}\)) at 2400°C. They observed congruent free evaporation of a phase of composition \( \text{UO}_{1.88} \). Partial molar free energy data from their studies are shown to be consistent with the assumption that departure from the stoichiometric composition occurs with accommodation of the oxygen sublattice. Disorder occurs with the oxygen interstitials or vacancies.

Fryxell et al. (1968) made electrical resistivity measurements of \( \text{UO}_{2-x} \) and interpreted their results giving the phase boundary of this material in the temperature region 1200–1800°C in close agreement with the results of Edwards and Martin (1966). The equation \( \ln x = 3.678 - 12.675/T^\circ\text{K} \) was given for the oxygen deficiency.

The application of Anderson's formulation of the defect theory of non-stoichiometry has been made by several persons. Thorn and Winslow (1966b) argue from their results that near \( \text{UO}_2 \) differences between observers is more likely due to differing concentrations of uranium vacancies than to the failure to achieve oxygen equilibrium. The present form of the model with an interstitial site density of one per uranium site fails sharply at about \( \text{UO}_{2.08} \) rather than gradually as the oxygen content is increased from \( \text{UO}_{2.00} \). Discussion of the effects of alternate site densities is used to explain the observed values of the partial molar entropy of the oxygen in the range from \( \text{UO}_{2.02} \) to \( \text{UO}_{2.21} \).

Menzies (1966) has derived an equation of state for \( \text{UO}_2 \) covering temperatures up to 20,000°K and pressures up to 20,000 atm. The results are presented in the form of tables and empirical equations.
The cohesive energy of the UO$_2$ lattice was calculated by Olander (1965) in good agreement with that obtained from a Born–Haber cycle. Suitable potential functions were chosen and the parameters evaluated from the properties of UO$_2$.

4. Transport Properties of UO$_x$

Alcock et al. (1966) have successfully applied alpha-ray spectrometry to the determination of the self-diffusion of U in stoichiometric UO$_2$ both in single and polycrystalline form. Results using this method are compared with those obtained by a decrease of surface activity both as determined by themselves and others. They observed $D$ (cm$^2$/sec) = $4 \times 10^{-7} \exp (-70,000/RT)$ for the former and $D$ (cm$^2$/sec) = $1.2 \exp (-108,000/RT)$ for the latter.

Bates (1966) reports extensive high temperature property measurements on UO$_2$ both in and out of a reactor. He concerned himself principally with diffusion properties including fission fragment diffusion.

A correlation of thermodynamic properties and atomic transport in the uranium dioxide phase was discussed by Thorn and Winslow (1966a). They derive an equation for the diffusion coefficient by combining Rice’s local thermodynamic equilibrium theory of self-diffusion with a defect theory of nonstoichiometry and determined the parameter for UO$_2$. Thorn and Winslow (1966c), in view of their previous suggestion of a fixed, nonequilibrium concentration of uranium vacancies, reexamined the diffusion data of Auskern and Belle. The whole effect on diffusion is assumed to be due to the changed concentration of diffusion species which is a characteristic of each prepared sample. The question is further placed in the larger context of diffusion by the same authors (1967) where they gave a general discussion of chemical problems associated with lattice-defects in UO$_2$. They gave a general thermodynamic account of defect-forming reactions and then applied this directly to UO$_{2-x}$ yielding energies to form defects and interaction energies between them. In a similar way, they discussed transport processes and applied the principles specifically to UO$_2$, comparing and discussing previous measurements of diffusion and sintering.

Marin et al. (1967) have measured uranium self-diffusion in UO$_{2-x}$ at 1500°C with the result that $D$ varies proportionally to $x^{1.9}$ ($\log D = 10.8 + n \log x, n = 1.9$). Intergranular diffusion was shown to be substantial by autoradiographic examination.

Nagels et al. (1966) made an extensive study of both uranium and oxygen self-diffusion in UO$_2$. Their results for uranium self-diffusion agreed well with previous measurements by Auskern and Belle (1961) on sintered material and disagreed with the work reported above by Alcock.
The electrical conductivity of slightly oxidized and reactor irradiated UO₂ was used to observe the effect of fission-fragment damage. Pulse annealing experiments were also performed on quenched UO₂+x crystals with compositions exceeding slightly the excess oxygen-solubility limit at room temperature. Upon heating at temperatures above 110°C the oxygen interstitials start migrating and form U₄O₉ precipitates.

Electrodiffusion of oxygen in UO₂ at 900–1100°C was studied by Dornelas and Lacombe (1967a, 1967b). With a current density of 60 amperes per sq cm at 1000°C the decomposition of UO₂ resulted in diffusion of oxygen with the formation of UO₂:25 at the anode.

Lidiard (1966) studied the influence of impurities and slight departures from stoichiometry on the self-diffusion of uranium in UO₂. He (1967) has discussed radiation damage in ceramics from a general point of view with some attention to the defects present in UO₂.

The complexities of sintering behavior have been considered by numerous people in the past five years. This problem, vital to the practical use of UO₂ as a fuel, has been coped with by those who must, largely empirically. Recently the sintering behavior of UO₂ was studied as a function of many preparative variables and atmospheres by Cordfunke and Van der Giessen (1967) whose paper could be consulted for a perspective and references to the larger literature.

5. Vaporization Studies in the UOₓ System

The volatility of UO₂+x was studied gravimetrically by Chapman and Meadows (1964) in the temperature range 1100–2200°C and oxygen pressures between 10⁻⁵ and 10⁻³ torr. They suggested that UO₂ is the vapor species only over UO₂ and that UO₄ is the vapor species over UO₂+x so long as oxygen is available. They used a variety of arguments for UO₄(g) but this species has not been seen mass spectrometrically. They observed substoichiometry in UO₂(UO₁.₈₂, a = 5.4697 ± 8 A) by heating at 2000°C in vacuum.

Ackermann et al. (1965a) conducted a thermodynamic study of the U–UO₂ system from 1650 to 2500°CK. Uranium dissolved to give a composition of UO₁.₈₂ at 2500°CK. The vapor above the liquid U–UOₓ mixtures is principally UO₁ₓ with small amounts of U₁₋ₓ and UO₂₋ₓ. They observed G°(T) = −10,300 − 11.6T.

The effect of oxygen on the uranium pressure over a U–UOₓ system was studied by Ackerman et al. (1965b) and compared with previous studies.

Pattoret et al. (1968) have made thermodynamic studies on the uranium-oxygen system for hyperstoichiometric UO₂ and reported new measure-
ments on the gaseous species U, UO, UO₂, and UO₃ over different condensed phases UO₂,x. Evaporation and dissociation energies were given for each species. A detailed comparison with previous work was given with extensive reference to the literature. Above 2100°K measurements of the vapor pressure on the two-phase system U(l) + UO₂,x(s) reflect the development of gross nonstoichiometry of the dioxide. The pressure ratios of UO₂(g) over UO₂.00, congruent UO₂-x, and the limit of the UO₂-x range were given as are the compositions corresponding to these measurements. The partial pressures of oxygen and the partial thermodynamic functions for the nonstoichiometric dioxide were given as a function of composition.

The same authors (1964) earlier reviewed the thermochemical data of vaporization processes in oxides and carbides to yield a heat of sublimation of uranium in good agreement with a mass spectrographic value of ΔH°₂₉₈,₈(U) = 125.5 ± 2.5 kcal/g atom.

6. Crystal Growth

Single crystals of UO₂ have been grown by Chapman and Clark (1965) using a floating zone technique. Nagels et al. (1964) prepared single crystal UO₂ by vacuum sublimation at 2300–2500°C. From these, crystals in the composition range UO₂,x up to UO₂.25 were obtained. Numerous detailed electrical and other physical properties were studied.

Single crystals of UO₂.22, UO₂.19, and UO₂.10 have been prepared by Scott and Harrison (1965) who oxidized UO₂.0 crystals separated from fused materials.

7. Electrical Properties

A study of the variation of the electrical conductivity of some films of fused uranium oxides as a function of oxygen pressure at high temperature has been made by Duquesnoy (1965). He observed that UO₂-x is a p-type and U₃O₈ an n-type semiconductor. Some thermodynamic quantities were calculated.

The electrical properties of UO₂,x have been observed by Iida (1965a, 1965b). Substoichiometric uranium dioxide is an n-type semiconductor in the range 77–1200°K from the Seebeck voltage. Myers et al. (1964) found hyperstoichiometric UO₂ an n-type semiconductor with an activation energy of 1.3 eV at 1100–2000°C.

Bates et al. (1967) measured the electrical conductivity of nearly stoichiometric single-crystal and polycrystalline UO₂ from room temperature to
3000°K. Below 550°K an activation energy of conductivity of 0.17 eV was observed. Between 550 and 1250°K each sample behaved differently. The electrical conductivity increased rapidly above 1250°K changing from p-type to n-type. The best linear fit of the data above 1400°K gave \( \sigma = 3.57 \times 10^3 \exp(-1.5 \text{ eV}/kT) \) and above 1900°K \( \sigma = 2.10 \times 10^{2} T^{1.4} \exp(-0.916 \text{ eV}/kT) \).

The variation of the electrical conductivity of \( \text{U}_3\text{O}_8 \) as a function of oxygen pressure between 100 and 700°C as observed by Murat and Eyraud (1963) indicated n-type semiconduction.

8. Magnetic Properties

Low temperature magnetic susceptibilities of \( \text{UO}_2, \text{UO}_{2+1}, \text{U}_4\text{O}_9, \text{U}_3\text{O}_7, \) and \( \text{U}_3\text{O}_8 \) at 1.5–44°K were determined by Leask et al. (1963). All these specimens showed a maximum at 6.4°K which was larger the higher the oxygen content. The effect may be due to the defect cluster which is the same for all oxides. The magnetic susceptibility of \( \text{U}_3\text{O}_7 \) was determined by Gotoo et al. (1965) for \( \text{U}_4\text{O}_9 \) from 77–500°K. It is paramagnetic. No magnetic transition was seen near 330°K where a \( \lambda \)-type anomaly occurs in the heat capacity. The susceptibility of \( \frac{1}{3} \text{U}_4\text{O}_9 \) after correction for diamagnetism is:

\[
\chi = 420 \times 10^{-6} + 0.530/(T + 55) \text{ cm}^3
\]

Antiferromagnetism in \( \text{UO}_2 \) has been investigated by Frazer et al. (1965) in a detailed single crystal neutron diffraction study. The form factor determined indicated a \( 5f^2 \) electronic configuration with an effective moment slightly less than 1.8 \( \mu \) for the \( \text{U}^{4+} \) ion. The magnetic structure consists of alternating ferromagnetic sheets. The work reported a Néel temperature of 30.8°K.

Recent neutron diffraction studies showed that \( \text{UO}_2 \) is antiferromagnetic below 30.8°K with an effective magnetic moment of about 1.8 Bohr magnetons per uranium atom. Rahman and Runciman (1966) have made a crystal field calculation for \( \text{UO}_2 \). The electrostatic, spin-orbit, and crystal field matrices were diagonalized within the \( 5f^2 \) configuration of the \( \text{U}^{4+} \) ion in a cubic crystal field. Energy levels were calculated for a set of parameters which yielded the value of 1.8 \( \beta \) for the ground state.

Nasu (1966) measured the magnetic susceptibility of cubic \( \text{UO}_{2+x} \) over its composition range between 77 and 1100°K. It was possible to obtain the phase boundaries from breaks in the inverse susceptibility-temperature curve for the one-phase two-phase reaction. The susceptibility data of \( \text{UO}_2 \)
and \( \text{U}_4\text{O}_9 \) were discussed in terms of the ground state configuration \( j^2 \) perturbed by the crystalline field in connection with neutron diffraction results.

9. Thermal Expansion

Baldock et al. (1966) have studied the x-ray thermal expansion of near-stoichiometric \( \text{UO}_2 \) finding an average coefficient of thermal expansion of \( 10.8 \pm 0.1 \times 10^{-6}/^\circ \text{C} \) between 20–2300°\text{C}.

Room temperature elastic constants of single crystal \( \text{U}_4\text{O}_9 \) were found by de Batist (1966) to be \( c_{11} = 3.19 \times 10^{12} \text{ d.cm}^{-2} \), \( c_{12} = 1.21 \times 10^{12} \text{ d.cm}^{-2} \) and \( c_{44} = 0.41 \times 10^{12} \text{ d.cm}^{-2} \). The lattice energies of \( \text{UO}_2 \) and \( \text{U}_4\text{O}_9 \) are \(-2351\) and \(-2320\) kcal/mole, respectively, as calculated from the compressibility. The thermal expansion of \( \text{UO}_2 \) has been observed by Brandt and Walker (1967) as a function of temperature. A first order transition occurs at 30.8°K.

10. Thermal Conductivity

Thermal conductivity in \( \text{UO}_2 \) has recently been the subject of detailed discussion by persons active in the field. The state of the art and recommendations for future work are described in a report of an IAEA panel (1966c).

The thermal conductivity also shows a depression at 30.8°K, indicating a strong phonon-magnon coupling, according to measurements made by Aring and Sievers (1967). They also recorded the far IR transmission.

11. Optical Properties

The specular reflectance of uranium oxides of different oxygen content have been measured by Jones and Murchison (1965). A satisfactory correlation has been shown to exist between the \( \text{O}/\text{U} \) ratios and the optical properties.

Reflection spectra of \( \text{UO}_2 \) (and in some cases \( \text{U}_4\text{O}_9 \)) of varying particle size and history were studied by Imriš and Imriš (1965). The study was to establish the relationship between the properties and sizes of particles of \( \text{UO}_2 \) prepared under varying conditions and the reflectance spectra. It was found that the intensity of absorption bands depended on the crystalline properties of \( \text{UO}_2 \) at wavelengths of 460 and 520 nm while at 600 and 690 nm it depended on the oxygen index of \( \text{UO}_2 \).

Berman (1967) has obtained IR spectra of \( \text{UO}_2 \) and higher oxides. The complex spectrum of \( \text{UO}_2 \) is modified by an absorption particularly at shorter wavelengths in the visible and near-infrared and new peaks attributed to \( \text{U}^{3+} \) and \( \text{U}^{4+} \) or complexes containing them appear.
12. Analysis

An x-ray analytical technique for quantitative determination of a binary mixture UO$_2$–U$_3$O$_8$ is described by Conti et al. (1967). A carbon reduction method for the determination of the O/U ratio in UO$_{2+x}$ has been worked out by Nickel (1966).

Sung and Turnbaugh (1967) have calculated the temperature-dependent shear modulus of UO$_2$ which is necessary to the study of helium solubility.

D. Neptunium Oxides

The irreversible thermal decomposition of Np$_3$O$_8$ was studied, principally by x-ray diffraction, from well-crystallized samples by Roberts and Walter (1963). The samples were reduced in carbon monoxide at temperatures above 450°C to give yellow NpO$_2$. All x-ray diagrams (with the exception of a few very weak superstructure lines) could be indexed as an orthorhombic cell with $a = 6.584 \pm 0.005$ Å, $b = 4.086 \pm 0.003$ Å, and $c = 4.183 \pm 0.003$ Å and space groups C222, Cmm2, or Cmmm corresponding to Np$_3$O$_8$ or as a fluorite structure with $a = 5.432 \pm 0.002$ Å corresponding to NpO$_2$ or mixtures of the two. No intermediate phases were observed.

When ozone was bubbled through a LiNO$_3$–KNO$_3$ eutectic containing Np(V) at 150°C Cohen (1963) obtained a brown precipitate which was identified as NpO$_3$·2H$_2$O. The x-ray powder pattern was similar to that of UO$_3$·2H$_2$O.

Neptunium pentoxide (Np$_2$O$_5$) was prepared by Cohen and Walter (1964) by precipitation of NpO$_2$ from lithium perchlorate melt. The diffraction pattern was indexed as monoclinic with $a = 4.183 \pm 0.003$ Å, $b = 6.584 \pm 0.005$ Å, $c = 4.086 \pm 0.003$ Å and $\beta = 90.32 \pm 0.03$°. The pattern differs from the orthorhombic Np$_3$O$_8$ principally in the narrow, even splitting of some of the lines.

The evaporation of NpO$_2$ in vacuum was studied by Ackermann et al. (1966a) over the temperature range 1850–2475°C showing only NpO$_2$ and NpO gaseous species. The measurements revealed that the evaporating sample became single phase substoichiometric at the high temperatures but disproportionated to Np$_2$O$_3$ and NpO$_2$ when the sample was cooled. The results yielded $\Delta G_f$ (NpO$_2$, g) = $-114,000 + 3.5T$ and the dissociation energy of NpO$_2$ (g) is 14.3 ±0.3 eV and for NpO (g) 7.4 ±0.3 eV.

A neutron diffraction study of powdered NpO$_2$ was made by Cox and Frazer (1967) at 4.6°C. No long range magnetic ordering was detected although other measurements had indicated that NpO$_2$ becomes antiferromagnetic below 25°C. These results were confirmed independently by Heaton et al. (1967).
The magnetic susceptibility of NpO$_{1.94}$ was measured between 4.2 and 350°K by Ross and Lam (1967). The inverse susceptibility of the specimen is linear in temperature above 60°K with an effective moment of 2.95 $\mu_B$. A peak in the susceptibility vs temperature curve is observed at 25°K in agreement with the maximum observed in the specific heat of NpO$_2$.

E. Plutonium Oxides

During the past five years extensive work on physical, thermodynamic, and structural properties of the plutonium-oxygen system have been carried out and reviewed by Chikalla et al. (1964) at the Hanford Laboratories of the United States Atomic Energy Commission, who published a phase diagram for PuO$_{2-x}$, $0 \leq x \leq 2$, and especially by the group at Harwell (Markin et al., 1964; Markin and Rand, 1966; Gardner et al., 1965; Rand, 1966; Livey and Feschotte, 1966) whose thermodynamic and structural work is the most comprehensive to date. An invaluable guide to the thermodynamics of the plutonium-oxygen system up to the fall of 1966 is contained in IAEA (1967). In this document, the views of a panel of experts was given and the salient literature reviewed. The preparation and structural information on the oxides known was presented. Phase relationships and thermodynamic properties were discussed in detail and vaporization properties critically reviewed. The report was concluded by a brief statement of conclusion and recommended future work. More recently both Blank (1967) and Mulford and Holley (1966) on the basis of earlier work and comparison with rare earth oxide systems together with metallographic and x-ray studies suggest a modification of the phase diagram. The diagram suggested by Blank is shown in Fig. 6. Mulford and Holley’s paper is a short, valuable review of the plutonium-oxygen system which considers most of the work which has been done.

Of the many oxides which have been reported for the PuO$_x$ system, the following phases remain reasonably well established. PuO$_3$ (fluorite-type $a = 5.396 \pm 0.0003$ Å) appears to reduce discontinuously at low temperatures to PuO$_{1.5+\delta}$ (cubic, bixbyite, $a = 11.047 - 11.050$ Å space group $Ia3$) at intermediate temperatures discontinuously to PuO$_{1.0+\delta}$ (cubic b.c.c. $a = 11.00 - 11.03$ Å). At higher temperatures the PuO$_{0.5+x}$ phase has a wide temperature and composition field of existence, $1.6 \leq x \leq 2.0$. At moderate temperatures the cubic PuO$_{1.5+\delta}$ phase may decompose to the hexagonal PuO$_{1.3}$ phase ($a = 3.841 \pm 0.006$ Å and $c = 5.958 \pm 0.005$ Å space group $R\bar{3}m$) at higher temperatures the hexagonal phase is formed by reduction from PuO$_{1.0+\delta}$.

The PuO phase frequently reported appears to be a ternary phase incorporating either carbon (Mulford and Holley, 1966) or nitrogen or perhaps
both. The eutectoid composition originally reported (Chikalla et al., 1964) on the basis of electrical resistivity measurements at about PuO$_{1.7}$, has not been satisfactorily established. The more recent efforts of Livey and Feschotte (1966), to modify the phase diagram which was based heavily on that of Gardner et al. (1965), attempts to provide a miscibility gap between the PuO$_{1.0}$ and the PuO$_{2-x}$ phases, as would be expected theoretically and as is seen in the analogous rare earth oxide systems. The suggested way to accomplish this is quite different as between Blank (1967) and Mulford and Holley (1966). The phase diagram proposed by Blank is shown in Fig. 6. A comparative presentation of the rare earth and actinide oxides including plutonium oxides has recently been given by Eyring (1967).

On the basis of the older heat capacity measurements on condensed phases and the thermodynamic data obtained from high temperature galvanic cells by Markin et al. (1964), Markin and Rand (1966), Rand (1966), and Mulford and Holley (1966) summarize and compare the derived values with the phase diagram and the analogous rare earth systems.

A metallographic and x-ray investigation of the plutonium-oxygen system in the region 1.61 < O/Pu < 2.00 has been carried out by Sari et al. (1967). Specimens with composition between PuO$_{1.627}$ and PuO$_{1.69}$ are single phase b.c.c. at 650°C (called $\alpha$). Specimens with a higher oxygen content up to PuO$_{1.895}$ (called $\gamma$) invariably transformed to a two-phase mixture. These results are believed to demonstrate an eutectoidally decomposing phase at about 350°C which has a wide composition range at 650°C, but narrows.

**FIGURE 6** Suggested phase relationships in the plutonium-oxygen system (after Blank, 1967).
at lower temperatures and shows a narrow $\alpha + \gamma$ region for $1.69 \leq \text{O/Pu} \leq 1.72$. These results are included in the review by Blank (1967) cited above.

Sandenaw (1963) observed the heat capacity of PuO$_2$ below 325°K. The results were anomalous and irreproducible, especially below 100°K. This fact was attributed to the presence of metastable plutonium oxide phases at low temperatures; however, the sample was slightly substoichiometric and there may have been a slight impurity phase. Anomalies at higher temperatures were suggested due to the beginnings of radiation damage anneal.

In a review of the chemical thermodynamic properties of plutonium compounds, Oetting (1967) gives a survey of the known thermodynamic properties of each stable phase.

The evaporation behavior and a derivation of thermodynamic quantities for substoichiometric plutonium dioxide has been reported by Pardue and Keller (1964), Ackermann et al. (1966b), and Ohse and Ciani (1968). Ackermann et al. studied the system in the range $1.6 \leq \text{O/Pu} \leq 2.0$. The vapor pressures were interpreted in terms of the species PuO$_2$ (g) and PuO (g). The vapor pressure of PuO$_2$ (g) is relatively insensitive to the composition of the solid phase whereas the partial pressures of PuO (g) and oxygen show a marked dependence and become predominant near the lower and upper phase boundaries respectively. The vapor pressure of PuO$_2$ was studied by a transpiration method between 1723 and 2048°K in air, argon, or oxygen by Pardue and Keller (1964). PuO$_2$ is said to vaporize congruently or as a suboxide, depending on the conditions. The system does not seem well-defined in these experiments, but the vapor pressure appears to increase as the atmosphere becomes more reducing.

Available and derived data yield

$$\Delta G_f^\circ (\text{PuO}_2, \text{g}) = -113,100 + 4.35T$$

and

$$\Delta G_f^\circ (\text{PuO}, \text{g}) = -29,000 - 12.1T$$

The congruently vaporizing composition is calculated to vary from $1.92 \geq \text{O/Pu} \geq 1.84$ between 1600 and 2400°K. The results are compared with previous measurements of the same kind and with other thermodynamic data.

The results of Ohse and Ciani (1968) are in good agreement with those of Ackermann et al. (1966b). In the range $1.61 \leq \text{O/Pu} \leq 2.0$, a bivariant single phase region is observed. Reactions with the crucible in the lower composition ranges leave the system not well-understood in that region.

Defect equilibria in PuO$_{2-x}$ in the temperature range 1100–1600°C has been studied by Atlas and Schlehman (1966) from conductivity measure-
ments of specimens of known composition in highly reducing atmospheres. A mass-action analysis of the data suggests that the defects in PuO$_{2-x}$ are predominantly interstitial plutonium ions and at 1100, 1200 and 1600°C they are primarily in a +4 state. Between 1200 and 1300°C dissociation of the interstitials appear to be retrograde and at 1300°C an appreciable concentration of Pu$_{i}^{3+}$ occurs. As the temperature rises from 1300 to 1600°C the concentration of Pu$_{i}^{3+}$ diminishes.

From this model a general formulation of the relation between $x$, $p_{O_2}$, and $T$ is derived and $p_{O_2}$ is successfully predicted for PuO$_{1.90}$ at 100°C intervals for 1100–1600°C. The critical temperature of the two-phase region is also approximately calculated.

In sintering studies on PuO$_{2-x}$ Cina (1963) confirmed that the PuO$_{2-y}$ decomposes to PuO$_{2} + \alpha$Pu$_{2}$O$_{3}$ (PuO$_{1.67}$) where $y$ was as large as 0.20. The effect of several sintering variables and the role of impurities on decomposition are discussed.

Single crystals of PuO$_{2}$ were precipitated from a silicate glass by Phipps and Sullenger (1964) who state that from these crystals excellent atomic scattering factors for Pu$^{4+}$ may be obtained.

Manes et al. (1967) have recorded the infrared absorption spectrum of PuO$_{2}$ in the range of 4 to 50 $\mu$. A resonance frequency has been found at 360 ± 10 cm$^{-1}$ attributable to a one-phonon fundamental absorption. The spectra of PuO$_{2}$, UO$_{2}$, and ThO$_{2}$ are remarkably similar.

**F. Americium Oxides**

Few studies on the oxides of Americium have been made in recent years. This material is now becoming available in larger quantities and presumably more work will now be done.

Wallmann (1964) heated cubic, C-type Am$_{2}$O$_{3}$ on a high temperature x-ray camera and observed the transformation to the hexagonal A-type at about 800°C.

Chikalla and Eyring (1967) measured dissociation pressures of oxygen over AmO$_{x}$ using an isopiestic technique in the temperature range 866 to 1172°C and from 1 to 10$^{-6}$ atm O$_{2}$. This covered a composition interval 1.80 < O/Am < 2.00. The derived partial molal thermodynamic quantities were compared with those from other M0$_{2-x}$ systems.

The same apparatus was used to prepare specimens for phase analysis (Chikalla and Eyring, 1968). The quenched and slow cooled samples were examined by x-ray diffraction. The cubic Am$_{2}$O$_{3}$ phase was found to exist over a wide composition range. The upper boundary of this phase occurs at about AmO$_{1.07}$. Between this and AmO$_{2.00}$ at least one other phase is
thought to exist with a composition of $\text{AmO}_{1.836}$. A new polymorph of $\text{Am}_2\text{O}_3$, probably B-form, was prepared and a consideration of polymorphism in actinide and lanthanide oxides leads to the reasonableness of A-, B- and C-forms for $\text{Am}_2\text{O}_3$. The growth of the unit cell with self-radiation was studied.

Cubic $\text{AmO}$ ($a = 5.045 \pm 0.003 \text{ Å}$) has been reported prepared from a reaction of stoichiometric amounts of the elements by Akimoto (1967). The general experience has been that such phases are often ternary being stabilized by nitrogen or carbon. $\text{AmN}$ of variable lattice parameter was also observed.

### G. Curium Oxides

The increased availability of $\text{CmO}_2$ and its possible use as an isotopic power fuel has provoked support for its study. Its scientific interest and importance should provoke much more. In a comparison of actinide and lanthanide oxides the similarities of behavior are becoming very marked in the curium-oxygen system.

Wallmann (1964) prepared cubic C-form $\text{Cm}_2\text{O}_3$ ($a = 10.992 \pm 0.003 \text{ Å}$) by hydrogen reduction of the higher oxide and found it to transform spontaneously after several weeks to hexagonal A-form ($a = 3.80 \pm 0.02 \text{ Å}$, $c = 6.00 \pm 0.03 \text{ Å}$). The transformation is apparently promoted by self-radiation.

Haug (1967) heated the C-form at higher temperatures and observed partial transformation to B-form at 800°C and complete transformation at 1055°C ($a = 14.282 \pm 0.008 \text{ Å}$, $b = 3.652 \pm 0.003 \text{ Å}$, $c = 8.900 \pm 0.005 \text{ Å}$, $\beta = 100.31 \pm 0.05^\circ$, cell volume = 456.7 $\text{ Å}^3$), thus exhibiting all three forms of the rare earth type polymorphs. Whereas the C-type transforms to the A-type, the B-form is remarkably stable toward self-irradiation showing practically no change after two months.

Posey et al. (1965) have reported the influence of temperature and oxygen pressure on the composition of curium oxide using a microthermal balance. The temperature range covered was 25–1000°C and 10 to 750 torr pressure of oxygen. A continuous change in composition was observed between $\text{CmO}_2$ and $\text{CmO}_{1.5}$. An intermediate oxide $\text{CmO}_{1.72}$ was observed. No oxides beyond the limits indicated were observed although another stable intermediate oxide of composition $\text{CmO}_{1.8}$ is indicated in the curves.

More extensive measurements of this type were made by Chikalla and Eyring (1969) who studied both the heating and cooling cycle. By this means it was confirmed that intermediate oxides of compositions $\text{CmO}_{1.71}$ and $\text{CmO}_{1.82}$ are formed in reduction and oxidation with hysteresis and in
the two-phase regions and pseudophase formation in the CmO$_{1.71-\delta}$ region analogous to the praseodymium or terbium oxide systems. A phase diagram was proposed as shown in Fig. 7.

Mosley (1968) has confirmed the occurrence of three polymorphs of Cm$_2$O$_3$ by transforming the B-type to A-type reversibly at 1600°C. The B-form was observed to oxidize rapidly between 250 and 520°C but not at higher temperatures. The behavior of Cm$_2$O$_3$ should be compared to Sm$_2$O$_3$. Also confirmed was the extraordinary stability of the B-type against self-irradiation. The dioxide was observed to have the fluorite structure $a = 5.365 \pm 0.001$ Å. The intermediate oxide at CmO$_{1.82}$ indexed as fluorite, $a = 5.435 \pm 0.001$ Å and CmO$_{1.71}$ ($a = 5.455$ Å) are confirmed.

The melting point of Cm$_2$O$_3$ has been measured by McHenry (1965) and by Smith (1969). The former measurements were made on a sample of unknown purity on an iridium filament (reactive to the oxide) where a melting temperature of 1950°C was observed. Smith’s measurements were made with reasonably pure curium oxide on tungsten filaments (with Mendenhall open V-wedges where an absence of reaction was established) where a melting point of 2277°C was observed.

**FIGURE 7** Suggested phase relationships in the curium-oxygen system (after Chikalla and Eyring, 1967).
Smith and Peterson (1968) have studied the vaporization reaction of CmO_x using a conventional Knudsen cell technique. They observed that CmO_{1.50} vaporizes congruently primarily to gaseous atoms. The heat and entropy of vaporization over the range 1800–2600°K and 665 ± 13.5 kcal/mole are 167.5 ± 6.0 eu, respectively. The heat of formation of Cm_2O_3(s) at 0°K is −429 ± 14 kcal/mole. The dissociation energy of CmO(g) is less than 5.8 eV.

From the results of previous measurements the physical and thermodynamic properties of the oxides of curium and thulium are derived or tabulated by Smith et al. (1967).

H. Berkelium Oxides

The berkelium oxide system has been studied by Peterson and Cunningham (1967). The dioxide (fluorite a = 5.334 ± 0.001) is prepared by calcination in air at 1200°C. Hydrogen reduction of the dioxide at 600°C yields C-type BkO_2 (a = 10.889 ± 0.003). An analysis of lattice parameters indicates curium to give rather greater values than would be expected from an actinide contraction.

I. Californium Oxides

Green and Cunningham (1967) have prepared and studied Cf_2O_3 from a product of ignition at 1200°C. Cf_2O_3 thus prepared is the monoclinic B-type (a = 14.132 ± 0.011 Å, b = 3.592 ± 0.002 Å, c = 8.811 ± 0.007 Å, β = 100.31 ± 0.07°). The C-type Cf_2O_3 has been observed as a product of hydrolysis of CfOCl at 600–700°C (Copeland and Cunningham, 1969).

ACKNOWLEDGMENT

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Single-Crystal Titanates and Zirconates

M. Douglas Beals

1. INTRODUCTION

There is a wide variety of techniques used in the growth of single crystals although almost all of necessity are based on the ordering of atoms from some state of random disarray to some three-dimensional, regular, repeating array. Crystallization may occur from solution in which case the solute crystallizes while the solvent stays as a liquid, or directly from the liquid state in which case melt and crystal have the same composition. Crystallization may also occur from the vapor state in the presence of a carrier gas (analogous to a solvent) or directly from a vapor of the same composition as the crystal.

The driving force to induce crystallization from solution is usually either a decrease in temperature, hence a lower solubility and consequent crystallization of the solute, or evaporation of the solvent to produce supersaturation and crystallization. In the crystallization of refractory oxides a technique involving decrease in temperature is much more commonly used than solvent evaporation. Crystallization of a solid from a melt of the same composition involves normally only a scheme whereby a temperature gradient encompassing the melting point of the material being crystallized can be provided. In both cases, if growth of a single crystal is to be satisfactorily achieved, the crystallization process must proceed at a rate slow enough to avoid spontaneous nucleation in various places in the system so that only one particular crystal is permitted to grow. A detailed discussion of crystal growth is not within the scope of this chapter, but several books and review articles are available to the interested reader, e.g., Buckley (1951), Gilman (1963), Wilke (1963), White (1965), and Brice (1966), as well as Peiser (1967).

In considering specifically single-crystal titanates and zirconates, it is found that crystallization from a melt or from a solvent system are the two main processes which are used, with growth from the vapor phase playing a relatively minor role. Because of the temperatures involved, growth from a solvent is commonly referred to as growth from a flux or a
fluxed melt, and frequently the motivation behind using a fluxed melt is to permit operation at a more reasonable (lower) temperature than the melting point of the crystal being grown.

II. TITANATES

A. Rutile

Although not strictly speaking a titanate, the properties of rutile are so closely related to other titanium-containing oxides that its inclusion in a discussion of titanates seems logical.

Rutile was first grown as a single crystal by the flame fusion technique as described by Moore (1949). The powdered starting material, titanium dioxide of high chemical purity and free-flowing, is held in a container with a wire mesh bottom surrounded by a gas-tight hopper connected to the center tube of an oxygen-hydrogen burner. Two other tubes of increasingly larger diameter surround the center tube to form a three-component burner. During growth oxygen is supplied to the center tube, hydrogen to the next larger tube, and finally, oxygen to the exterior tube, to provide an oxygen-hydrogen-oxygen flame. The additional oxygen sheath (not used in the classical Verneuil burner) provides a somewhat more oxidizing environment for the crystal as it grows, for rutile has a pronounced inclination to lose oxygen at high temperature, going from the fully oxidized state represented by $\text{TiO}_2$ to a slightly reduced state, $\text{Ti}^{4+}\text{Ti}^{3+}\text{O}_{2-x/2}$.

In the early stage of crystal growth, the powdered feed material is permitted to fall through the flame to form a sintered cone on the top end of a refractory pedestal. The tip of this sintered cone is then fused and as additional feed material is added and heat is conducted away through the refractory rod a crystal grows upward, gradually widening as it increases in size. As the crystal grows upward, the pedestal is lowered so that the surface of the growing crystal, or boule, is always in the same relative position in the flame. At equilibrium then, the boule has a molten top surface, of the same composition as the crystal itself, with growth occurring at the melt-solid interface under the influence of a vertical temperature gradient. The boule is surrounded by a circular refractory furnace but with no contact between the boule and the furnace walls. A random orientation is obtained in this process unless a seed crystal is used. With a seed crystal, the upper surface of the crystal is melted in the beginning stages, after which growth proceeds in the same fashion as outlined above.
Stoichiometric rutile is an insulator but becomes a semiconductor with a color change from nearly colorless to blue as oxygen is lost. As noted earlier, rutile loses oxygen quite readily at high temperature and a rutile crystal grown by flame fusion has a blue color, characteristic of titanium dioxide that is slightly oxygen deficient. The missing oxygen may be restored by heating at temperatures of 600°C or above in air or oxygen, according to the equation below:

$$\text{Ti}^{4+}_{1-x}\text{Ti}^{3+}_x\text{O}_{2-x/2} + \frac{x}{4} \text{O}_2 \rightarrow \text{TiO}_2$$ (1)

It has been found that the addition of a small amount of aluminum oxide to the feed material leads to a crystal which is much more readily oxidized than a “pure” crystal.

This effect may be understood on the basis that Al$^{3+}$ ions occupy Ti$^{4+}$ sites; if these same sites were occupied by Ti$^{3+}$ ions the crystal would appear blue. Thus, a situation is reached in which the crystal is not blue, is an insulator, and appears fully oxidized although there are missing oxygen ions, as indicated by the formula, Ti$^{4+}_{1-x}$Al$^{3+}_x$O$_{2-x/2}$. The presence of Al$^{3+}$ ions may also increase the diffusion rate of oxygen in the crystal. These concepts, and those used later, are perhaps overly simplified but provide an extremely helpful scheme for comprehending and predicting the effect of a given impurity addition on the properties of the crystal.

Conversely, the presence of a small amount of an ion with a valence greater than four (Nb$^{5+}$, for example) leads to a rutile crystal which does not lose its blue color when subjected to oxidizing conditions because of the stabilization of the Ti$^{3+}$ ions by the Nb$^{5+}$ ions, according to the formula, Ti$^{4+}_{1-x}$Nb$^{5+}_x$Ti$^{3+}_x$O$_2$. The crystal is not oxygen deficient when related to the formula TiO$_2$, yet has the blue color and conductivity of an oxygen-deficient rutile crystal.

Drabble and Palmer (1966) have grown a number of refractory oxides by striking a d-c arc between two electrodes with the growing crystal acting as the anode and a sintered oxide rod as the cathode. Material is carried through the arc to the molten zone on the anode where crystallization takes place. A somewhat related process has been described by Holt (1965) except that rf heating was used to produce a floating zone of molten material, with single crystal growth occurring behind this zone.

Vergnoux et al. (1965) have described another modified Verneuil technique in which a solar furnace was used as a source of heat. A seed crystal was used and powdered titanium dioxide was fed from the top. One advantage claimed was the absence of a gas stream which could alter the composition of the crystal. Relatively slow cooling of the crystal after growth was also possible.
A carbon arc imaging furnace for growth of refractory crystals has been used by Kestigian et al. (1964). Two d-c carbon arcs, each backed by an ellipsoidal reflector, were set up in conjunction with a mirror (rotatable through 90°) so that the arcs could be used alternately, to compensate for the limited anode life in each arc arrangement. A feed hopper was positioned above the region of energy focus with the feed material held on a screen and with provision for the introduction of a carrier gas. Nearly stoichiometric rutile crystals were grown in this way using an oxygen atmosphere, in contrast to the reduced crystals obtained with an oxygen-hydrogen flame.

In addition to the above schemes which are related to a greater or lesser degree to the Verneuil process, oxide crystals have been grown by the Czochralski technique. The material to be grown is melted in a metal crucible by induction heating. A seed crystal is lowered to touch the surface and crystallization takes place at the seed-melt interface as heat is withdrawn through the seed and its support. As the crystal grows it is raised and frequently rotated at the same time. Nassau and Broyer (1962), in discussing the growth of calcium tungstate by this technique, commented that rutile (as well as barium titanate) had also been grown. Reed et al. (1967) have grown titanium sesquioxide in this way, using a tantalum resistance furnace as a heat source with the melt contained in a molybdenum crucible, all in an atmosphere of argon.

The growth of rutile crystals from a fluxed melt has also been examined by several investigators. For the most part crystallization is allowed to proceed by cooling a solution of titanium dioxide in a material such as sodium borate. The system is cooled slowly, with formation of acicular crystals up to perhaps 10 mm long until solidification is complete. The crystals are separated from the flux by dissolution of the flux at low temperature. As an alternative the flux may be poured off or drained away before solidification is complete, to simplify subsequent removal by leaching (Morgan and Scheffler, 1965).

Berkes et al. (1965) used fluxes of the compositions indicated by Na$_2$O·3B$_2$O$_3$ and K$_2$O·3B$_2$O$_3$. Johnson and Alley (1965) used a flux based on Na$_2$O·2B$_2$O$_3$. Russell et al. (1962) reported rutile fibers up to four inches in length through the slow cooling of a flux of the composition Na$_2$O·3B$_2$O$_3$.

An isothermal approach to the fluxed melt growth of rutile (as well as a number of other oxides) has been made by Grodkiewicz and Nitti (1966) who held a mixture of TiO$_2$ and a lead fluoride-boron oxide flux at about 1300°C so that crystals of rutile formed as the flux evaporated. The rutile was obtained in the form of slender rods, plates, and polyhedra. The larger polyhedra resembled cubes and were up to 2 mm on a side.
It is interesting to note that rutile, when growing without constraint, frequently assumes the characteristic aricular growth habit which is often observed in natural rutile (rutilated quartz). In the other growth systems which have been discussed, an arbitrary shape is imposed on the growing crystal by the geometry of the system. It appears that the rate of growth is strongly a function of orientation with the growth rate along the c axis being perhaps 20 to 30 times greater than along the a axis.

The hydrothermal growth of rutile using a variety of alkaline solutions as the solution-crystallization media has been carried out by Anikin and Rumyantseva (1964), at 500 to 600°C and pressure above 900 atm. The crystals obtained were small (0.4 to 0.7 mm) but the feasibility of the technique has been demonstrated. The possibility of taking advantage of the reversible reaction shown by the equation

\[ \text{TeO}_2 + \text{TiCl}_4 = \text{TiO}_2 + \text{TeCl}_4 \]  

has been examined by Niemyski and Piekarcyzk (1967). By proper control of temperature the direction of the reaction is controlled to produce TiCl₄ vapor at one point in a sealed quartz tube and to crystallize rutile from this vapor through reaction with tellurium dioxide at another point in the tube. A temperature gradient of 1100 to 900°C was used and crystals of up to 4 mm in size were obtained in a 90-hour period, with dislocation densities of $10^4$/cm².

One of the striking properties of rutile is its unusually high refractive index ($n_D = 2.6$ to $2.9$), and it is this high refractive index that accounts for widespread use, in the finely divided state, as a pigmented material. The index of rutile at various wavelengths of light in the visible region of the spectrum is shown in Fig. 1, and the transmission region is shown in Fig. 2. From the position of the absorption edge at about 4200 Å it can be seen that single-crystal rutile has a slight intrinsic yellowish tint.

The high refractive index and high dispersion of rutile led to one of the first usages for single-crystal rutile, i.e., as a gem stone of unusual brilliance (refractive index) and fire (dispersion). A disadvantage of rutile as a gem stone lies in its double refraction, which makes it necessary to orient the gem stone so that the table is perpendicular to either an a or the c axis. Thus, the eye views the back facets along an a or c axis; with any other viewing direction, the pronounced double refraction gives the visual effect of a double set of facets and the stone looks fuzzy.

Another drawback to rutile as a gem is the hardness, which is slightly less than quartz, and perhaps the color, if a gem which simulates a diamond is sought.

The availability of large single crystals of rutile has been quite a boon to the experimenter and a great number of fundamental investigations have
FIGURE 1 Index of refraction of rutile and strontium titanate at various wavelengths of light.

FIGURE 2 Transmission of rutile and strontium titanate at various wavelengths of light.
been carried out. Much of this work has been concerned with the semiconducting properties of rutile in the oxygen-deficient state. Rutile in the reduced state is an n-type semiconductor. It seems to be generally agreed that the blue color in the oxygen-deficient state is a result of the presence of Ti$^{3+}$. This blue color according to measurements on vacuum-reduced rutile by Carnahan and Brittain (1965) arises from an absorption maximum at 1.2 μ, somewhat in contradiction to a broad absorption maximum centered at about 1.85 μ as reported by Cronemeyer (1952) for hydrogen-reduced rutile. Whether the Ti$^{3+}$ is present on Ti$^{4+}$ sites with missing oxygen ions to preserve electroneutrality or is present interstitially without anion vacancies has been discussed extensively, with interstitial Ti$^{3+}$ apparently favored. These considerations have been discussed by Frederickse (1961), Coufova and Arend (1961), Kofstad (1962), Becker and Hosler (1963), Yahia (1963), Förland (1964), Greener et al. (1965), and Blumenthal et al. (1966, 1967). Huntington and Sullivan (1965) from diffusion and internal friction data suggest that Ti$^{3+}$ is present interstitially.

Under the influence of an applied d.c. field in the direction of the c axis, rutile becomes reduced with an increase in conductivity as noted by Harwood (1963, 1965) and Van Raalte (1965). This reduction becomes obvious by the development of a blue streak or "filaments" aligned with the c axis in the neighborhood of the electrode. Since the blue regions correspond to a change in the crystal from an insulator to a conductor, the c axis conductivity increased rapidly, depending on the time and temperature. A similar effect is not observed when the field is applied along the a axis. A similar directional effect is noticed in the oxidation of reduced rutile boules—oxidation proceeds more rapidly along the c axis than along the a axis, although Haul and Dümbgen (1965) reported that oxygen diffuses faster along the a axis than the c axis by a factor of 1.6. Wittke (1966) has reported the anisotropic diffusion of chromium, iron, cobalt, and nickel in rutile; diffusion proceeds in interstitial diffusion channels along the c axis. The anisotropic diffusion of lithium in rutile has also been observed by O. W. Johnson (1964a, 1964b) and Johnson and Krouse (1966).

Growth by the flame fusion technique leads to crystals with a relatively high dislocation density, probably resulting from the steep vertical temperature gradient existing during growth. Dislocation densities of the order of $10^8$/cm$^2$ have been measured by Nakazumi et al. (1962) on a 110 cleavage plane. The density was decreased to $10^6$/cm$^2$ by heat treatment of the crystal at 1900°C followed by slow cooling. Hirthe and Brittain (1962) found dislocation densities of about $4 \times 10^4$/cm$^2$. Annealing at 1375°C for 45 minutes decreased the density to about $1 \times 10^4$/cm$^2$. Barber and Farabaugh (1965) thinned rutile crystals chemically (sodium hydroxide at 550°C) and examined the thinned areas with the electron microscope.
The dislocation densities agreed well with those determined from etch pit measurements ($\sim 10^3$/cm$^2$).

The use of rutile as a gem because of its high refractive index has been mentioned. To a limited extent rutile has also been used as an infrared optical material. It has also been found applicable in the field of microwave amplification where it is useful as a host lattice for iron or chromium ions.

In the case of iron-doped rutile, a traveling wave maser operating at 5.4 to 5.9 Gc has been described by Morris and Miller (1965); masers operating at 34 to 36 Gc (8 mm wavelength) have been described by Arams and Peyton (1965), Nixon and Genner (1966) and deCoatpont and Robert (1967). An iron-doped rutile maser operating at 96.3 Gc has been discussed by Hughes (1962); the sample itself was used as a resonant cavity.

Chromium-doped rutile masers have been discussed by Yngvesson (1966), Schollmeier and Roth (1966), Morris and Miller (1964), and C. C. Johnson (1964).

B. Strontium Titanate

Single-crystal strontium titanate shows its relationship to rutile in several ways—it is a high index material ($n_D = 2.409$) with a high dispersion and shows the same susceptibility to reduction (semiconducting, blue in color). It is however distinguished by having a cubic structure (isotropic) at room temperature with a transmission cut-off at 0.395 $\mu$, so that it is colorless as compared with the slight yellowish tint of rutile (see Fig. 2). Some of the basic physical properties of strontium titanate are given in Table I.

To pursue the same simple concept outlined for rutile, strontium titanate can exist in the oxygen-deficient state as indicated by the formula SrTi$_{1-z}$Ti$_z$O$_{3-z/2}$. A semiconducting crystal, blue in color, can be produced by the substitution of pentavalent ions for Ti$^{4+}$ ions according to the scheme SrTi$_{1-z}$Ti$_z$Nb$_{2z}$O$_{3-z/2}$, with the additional complication that trivalent ions substituting in Sr$^{2+}$ positions produce a similar effect, that is, Sr$_{1-y}$Nd$_y$Ti$_{1-x}$Ti$_x$O$_3$. To belabor the point, the formula Sr$_{1-y}$Nd$_y$Ti$_{1-x}$Ti$_x$O$_3$ might be written. Or to return to the first case, the pentavalent ion could be compensated for by the presence of Al$^{3+}$ ions, as SrTi$_{1-z}$Nb$_z$Al$^{2+}$O$_{3-z/2}$, to provide a crystal doped with niobium but which is colorless.

Growth of strontium titanate was first carried out by the flame fusion technique by Merker (1955). Growth conditions are similar to that for rutile although the higher melting point (2080°C) requires that some modifications be made. The crystal or boule immediately after growth shows the usual dark blue color, but becomes colorless after heat treatment in air or oxygen at temperatures above 800°C.
TABLE I

PHYSICAL PROPERTIES OF SINGLE-CRYSTAL TITANATES

<table>
<thead>
<tr>
<th>Property</th>
<th>Rutile</th>
<th>Strontium Titanate</th>
<th>Perovskite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>TiO₂</td>
<td>SrTiO₃</td>
<td>CaTiO₃</td>
</tr>
<tr>
<td><strong>Crystal system (room temperature)</strong></td>
<td>Tetragonal</td>
<td>Cubic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td><strong>Unit cell parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a₀</td>
<td>4.593 Å</td>
<td>3.905 Å</td>
<td>--</td>
</tr>
<tr>
<td>c₀</td>
<td>2.959 Å</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Specific gravity</strong></td>
<td>4.26</td>
<td>5.12</td>
<td>4.10</td>
</tr>
<tr>
<td><strong>Hardness (Mohs scale)</strong></td>
<td>6.5–7.0</td>
<td>6.0–6.5</td>
<td>6.5–7.0</td>
</tr>
<tr>
<td><strong>Melting point</strong></td>
<td>1825°C</td>
<td>2080°C</td>
<td>1960°C</td>
</tr>
<tr>
<td><strong>Refractive index (nD)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ordinary ray</td>
<td>2.613</td>
<td>2.409</td>
<td>2.40</td>
</tr>
<tr>
<td>Extraordinary ray</td>
<td>2.909</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Dielectric constant</strong></td>
<td>190⁰</td>
<td>310</td>
<td>186</td>
</tr>
<tr>
<td><strong>Loss angle</strong></td>
<td>0.017⁰</td>
<td>0.0003</td>
<td>0.0003</td>
</tr>
<tr>
<td><strong>Band gap</strong></td>
<td>ca 3 eV</td>
<td>3.2 eV</td>
<td>3.4 eV</td>
</tr>
<tr>
<td><strong>Transmission range</strong></td>
<td>0.42–5.5μ</td>
<td>0.395–7.0μ</td>
<td>0.365–5.5μ</td>
</tr>
</tbody>
</table>

* Parallel to c axis.

An idea of the dislocation density can be obtained from the data of Paladino *et al.* (1965) who reported densities of about $1.4 \times 10^6$/cm². Dislocation density was reduced to about $6.6 \times 10^5$/cm² by annealing at 2000°C. Paladino (1965) and Paladino *et al.* (1965) also found that the rate at which strontium titanate could be oxidized or reduced was decreased by a decrease in the dislocation density. The oxidation is described as a diffusion controlled process in which the oxygen ion diffusion is assumed to proceed via a vacancy mechanism, with the dislocations present also playing a role.

Rhodes and Kingery (1966) found that the self diffusion of Sr²⁺ and Ti⁴⁺ ions was similarly enhanced by the presence of dislocations.

Strontium titanate crystals have been grown (or regrown) by what is called by Wolff and Das (1966) the traveling solvent method. A sandwich is made by placing a small amount of a flux between two crystals. The assembly is then heated on one side to a temperature high enough to melt the flux. Solution of strontium titanate in the flux occurs at the hotter interface with recrystallization taking place at the cooler interface. As solution and crystallization proceed, the flux or solvent “travels” toward the heat source, leaving in its wake a recrystallized structure. The dislocation density has been decreased by at least an order of magnitude in this way.

Strontium titanate is considered to be a cubic crystal at room temperature, although Lytle (1964) proposed and Rupprecht and Winter (1967) support...
a $c/a$ ratio of 1.00008. Some residual strain is normally present in flame fusion single-crystals viewed in polarized light and whether or not there is a correlation between the $c/a$ ratio noted and strain is not obvious.

Below room temperature as the crystal is cooled the structure changes to tetragonal at 110°K ($c/a = 1.00056$), to orthorhombic at 65°K ($a:b:c = 0.9998:1:1.0002$) and finally to possibly rhombohedral with further cooling (Lytle, 1964). A Curie temperature of 32°K has been reported by Cowley (1962) but is not necessarily indicative of a change to a ferroelectric state as is the case with barium titanate at about 130°C. Kikuchi and Sawaguchi (1964) found a rather large temperature change ($\Delta T = 0.3°K$) when an electric field was applied in the 110 direction at 11°K and suggested that the effect might be utilized to achieve low temperatures.

In the reduced state strontium titanate is an n-type semiconductor with the conductivity dependent on the degree of reduction. Fully oxidized strontium titanate has a specific conductivity of about $10^{-13}$ ohm$^{-1}$cm$^{-1}$ while a reduced strontium titanate with an oxygen vacancy calculated as $1.3 \times 10^{19}$/cm$^3$ showed a conductivity of about 15 ohm$^{-1}$cm$^{-1}$ at room temperature, according to Rupprecht et al. (1962). The electron mobility in semiconducting strontium titanate has been recently discussed by Tuft and Chapman (1967). Work by Walters and Grace (1967) on the conductivity and thermoelectric power of single crystal strontium titanate at elevated temperatures has shown that an oxygen vacancy defect model is applicable.

Strontium titanate was found to be a superconductor at temperatures near absolute zero by Schooley et al. (1964). The samples were reduced in hydrogen and the superconducting transition occurred at about 0.25°K. Additional work on this phenomenon in strontium titanate has been described by Schooley and Thurber (1966) and Ambler et al. (1966).

One of the first usages of strontium titanate was as a gem stone. Because of its high refractive index (see Fig. 1), it has been frequently compared with a diamond. Strontium titanate has a considerably higher dispersion with a consequent greater "fire" or color play than a diamond and the two are easily distinguished by the practiced eye for that reason. Strontium titanate has a hardness of 6.0 to 6.5 on Mohs scale comparable to that of rutile although both are considerably softer than diamond.

As can be seen from Fig. 2, strontium titanate transmits well into the infrared region. This infrared transmission combined with a high refractive index (2.31 at $1\mu$, 2.12 at $5\mu$, according to Herzberger and Salzberg, 1962) has given rise to use as an optical element in the infrared. A hemispherical lens fabricated from strontium titanate has been used as the light gathering element in infrared detecting devices (Beals and Merker, 1960).
Strontium titanate has not been used as a laser host material to any appreciable extent to date. One of the reasons perhaps is the sharp cut-off at 0.395μ so that a pumping light of a wavelength less than 0.395μ is strongly absorbed and unavailable for electron excitation.

A recent discussion by Bosomworth and Gerritsen (1968) has indicated that strontium titanate single crystals when doped with either iron plus molybdenum or nickel plus molybdenum are photochromic, darkening when exposed to 4000 Å radiation and bleaching when exposed to radiation between 4500 and 7500 Å. Their use in thick hologram storage was studied.

C. Barium Titanate

The literature on barium titanate, particularly on polycrystalline materials, is voluminous although the data on growth and properties of single crystals are less so. Barium titanate is tetragonal at room temperature with a Curie point in the neighborhood of 130°C, where it undergoes a transition on heating to cubic. The Curie temperature is frequently reported as 120°C, but measurements by C. J. Johnson (1965) on a crystal of high purity indicate a Curie temperature of about 132°C. He further commented that the Curie temperature is not a fixed material property but shows some dependence on sample history and environment, as well as purity.

There are factors which make the growth of barium titanate from a melt of the same composition as the crystal rather difficult. The stable crystal form at the melting point is hexagonal and this form persists metastably to room temperature. If the cubic form, which undergoes transition to tetragonal at the Curie point, is to be obtained, a small amount of strontium in solid solution replacing barium must be present (Basmajian and DeVries, 1957). If such an addition is made to the starting material in flame fusion growth, the cubic form is obtained. On cooling to the Curie temperature the crystal transforms to tetragonal but because of the strain present a strongly domainated crystal results. If, at a temperature near the Curie point, a strong enough electric field is applied to polarize the crystal to a single domain, the crystal invariably cracks. Careful annealing might lead to single domain crystals but such a study does not seem to have been carried out.

Barium titanate crystals were grown directly from the melt (with the addition of 1.5 percent SrTiO, to avoid the formation of the hexagonal phase) by Brown and Todt (1964). In their procedure a rod of sintered barium titanate was slowly drawn through a gas-oxygen ring burner. A seed crystal was fused to the rod and as the assemblage was passed through the
burner fusion of the rod followed by crystallization on the seed took place. The crystal was withdrawn into an auxiliary heating furnace held at a temperature between 1300 and 1500°C. Barium titanate ingots, 2.5 cm long by 0.32 cm diameter, were grown in this way.

The classical technique for the growth of barium titanate crystals is that of Remeika (1954) in which barium titanate is dissolved in a potassium fluoride flux in a platinum crucible at about 1200°C after which the melt is cooled slowly to effect crystallization of barium titanate. Excess flux is poured off or decanted at about 1000°C and the crystals are cooled slowly to room temperature. The solidified potassium fluoride is removed from the crystals by leaching with hot water. The chief drawback to crystals prepared in this way is the presence of platinum as a contaminant as well as fluoride ions substituting for oxygen ions in the crystal, with an accompanying substitution of K⁺ ions for Ba²⁺ ions, as shown by Baₓ₋ₓKₓTiO₃₋ₓFₓ (Arend et al., 1967). A modification of the Remeika technique in order to obtain crystals with less platinum contamination has been described by Bradt and Ansell (1967).

Barium titanate crystals have been grown in a similar fashion by Waku (1962) but with barium chloride as the flux. The dislocation density of the crystals was reported as 10⁴/cm².

Barium titanate crystals have been grown by the Czochralski technique by Horn (1962). An iridium crucible, not attacked by molten barium titanate, was used to hold the melt. Growth was carried out in a carbon dioxide atmosphere and the crystals were only slightly reduced. The hexagonal phase was obtained, although tetragonal crystals could be grown by the addition of 5 to 6 percent CaTiO₃ or TiO₂ to the starting material.

DeVries (1964) has experimented with the growth of barium titanate crystals in the solid state by what is called exaggerated grain growth. Crystals that were obtained were small, however, with a relatively high porosity. Thin single-crystal films of barium titanate on a platinum substrate have been produced by DeVries (1962) by the evaporation of potassium fluoride from KF–BaTiO₃ melt.

Linz et al. (1964) have utilized the eutectic (1317°C) between barium titanate and titanium dioxide to grow barium titanate crystals from a TiO₂-rich BaO–TiO₂ melt. By this scheme the problem of the formation of hexagonal barium titanate is avoided and a platinum crucible can be used. The BaTiO₃–TiO₂ mixture is melted, a seed crystal is placed in contact with the surface, and the temperature of the crucible is slowly lowered. The process, called the top seeded technique, is similar to normal growth from a fluxed melt except that crystallization is controlled by the presence of the seed crystal rather than occurring spontaneously as in the Remeika
The process has a further advantage in that the crystal may be removed from the flux once it has reached the desired size so that flux removal and leaching after cooling are unnecessary. The same process has been utilized by Sasaki (1965).

The possibility for oxygen deficiency in barium titanate also exists and a technique for the determination of the oxygen nonstoichiometry has been described by Novak and Arend (1964). The effect of this oxygen loss on the formation of anion vacancies has been discussed by Arend et al. (1967). The formation of these vacancies is complicated by the fact that the crystals which were used contained K\(^+\) and F\(^-\) ions in solid solution.

By analogy with strontium titanate it is not surprising that a semiconducting crystal results when Nb\(^{5+}\) ions are substituted for Ti\(^{4+}\) ions in barium titanate. Semiconducting ceramics doped with Nb\(^{5+}\) (for Ti\(^{4+}\)) or with La\(^{3+}\) (for Ba\(^{2+}\)) exhibit a positive temperature coefficient of resistivity in the neighborhood of the Curie point. In the same way, niobium-doped barium titanate crystals exhibit an increase in resistivity with increase in temperature at the Curie temperature (Brown and Taylor, 1964). Thus, the effect observed in a ceramic is believed to result, at least in part, from a fundamental property of the lattice and cannot be described solely to grain boundary effects.

The \(n_D\) value for barium titanate has been measured by Lawless and DeVries (1964) for the ordinary ray as about 2.37 with essentially little change with temperature over the range 10 to 100°C. Calculated values (from birefringence data) for \(n_D\) for the extraordinary ray ranged from about 2.31 at 10°C to about 2.33 at 100°C. Above the Curie point in the cubic region the two indices coincide \((n_D = 2.40)\).

The fundamental absorption edge for barium titanate was measured at 406 m\(\mu\) (3.05 eV) by Cox et al. (1966). In addition to the direct transition an indirect transition at 455 m\(\mu\) (2.63 eV) was measured. Considering that the crystals were grown in a platinum crucible using titanium dioxide of 99 percent purity, the indirect transition may be associated with a platinum or other impurity in the crystal. The 3.05 eV band gap is comparable to the absorption edge of 385 m\(\mu\) (3.22 eV) found for strontium titanate.

The growth of single-crystal barium titanate was motivated by the possibility of its use as a storage element for digital computers. Good rectangular hysteresis loop material was obtained but has not been as satisfactory as ferrite materials (switched magnetically) apparently because of the comparative slowness with which barium titanate switches or because of aging effects, or both.

Interest has been recently shown in the electrooptical effect in barium titanate (Johnston, 1965; Zook and Casselman, 1966).
D. Other Titanates

The third alkaline earth titanate which has been grown is calcium titanate (perovskite) by Merker (1962) using flame fusion. Calcium titanate grown by the normal flame fusion process invariably fractured during cooling. By use of an auxiliary furnace, it was possible to provide in situ annealing of the boule after growth and to permit slow cooling to room temperature. Boules prepared in this way were unfractured, but exhibited an intense lamellar twinning pattern. A further annealing step (1700°C for six hours) was required to eliminate this twinning.

Calcium titanate is quite similar to strontium titanate in its physical properties (see Table I), although it has a fundamental absorption edge at a shorter wavelength (365 μm versus 395 for strontium titanate).

Van Uitert and Egerton (1961) reported the growth of bismuth titanate (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>) from a Bi<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> melt (excess of Bi<sub>2</sub>O<sub>3</sub>) held in a platinum crucible and cooled slowly from 1200°C. Sheet-like crystals of bismuth titanate were obtained and were separated from the intervening layers of bismuth oxide by dissolving the bismuth oxide in strong mineral acid solutions. Resistivity values of $3 \times 10^{12}$ ohm-cm were measured; the dielectric constant and loss tangent at 1 kc were found to be about 112 and 0.0029, respectively. The crystal was ferroelectric. Ferroelectric domains were observed in bismuth titanate grown by the same technique by Cummins (1966). The switching behavior has been discussed further by Cummins and Cross (1967), who determined the crystal to be monoclinic, and by Pulvari and de la Paz (1966).

Bismuth titanate was found to transmit in the infrared region to nearly 12 μm, although this measurement was made on a 0.002 inch thick sample; the calculated transmission for sapphire at this thickness was to about 9 μm, and it was felt that bismuth titanate might find application as an infrared material (Galasso and Darby, 1965).

Several rare earth titanates of the general formula R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> where R is a trivalent rare earth ion, have been grown by flame fusion for determination of transmission and refractive index by Merker and Herrington (1964). Transmission data indicate that the crystals are transparent to about 7 μm (with polished specimens 1 mm thick), with the characteristic absorption of the particular rare earth quite evident. The crystals which were grown and examined together with their refractive indices ($n_D$) are as follows:

La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (1.99), Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (2.34), Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (2.10), Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (1.85) and Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (2.22).

Although not strictly a titanate, crystals of barium titanium phosphate (Ba<sub>2</sub>TiP<sub>2</sub>O<sub>9</sub>) [m.p. 1197°C] were grown by Harrison and Tiller (1962).
using the Bridgman technique. The twinning habit and growth mechanism were discussed.

III. ZIRCONATES

The experimental work carried out on the synthesis of zirconates is markedly less extensive than for titanates. Part of the problem is probably the higher temperatures which are involved and, in the case of zirconium oxide, the troublesome inversion (accompanied by a large volume change) from tetragonal to monoclinic as zirconium oxide cools from its melting point (near 2700°C). Single-crystal growth is to a degree influenced by motivation and if a sufficient need or desire develops many zirconates could probably be synthesized with the crystal growth techniques (or modifications thereof) that are currently available.

A. Zirconium Oxide

Using the carbon arc image furnace described earlier, Kestigian et al. (1964) prepared “cubic” zirconium oxide. The best crystals were obtained by the addition of 12 mole percent calcium oxide to stabilize the cubic form (actually a CaO–ZrO₂ solid solution).

Monoclinic zirconium oxide crystals have been grown by Anthony and Loc (1965) and by Chase and Osmer (1966a) by utilizing the eutectic between zirconium oxide and lead fluoride. The fluxed melts were slow cooled from a temperature of about 1100°C and so that the crystals formed below the monoclinic-tetragonal transformation temperature. The crystals were small but apparently of good quality.

The growth of zirconia stabilized with calcium oxide by means of a plasma torch has been described by Reed (1961). The boule which was obtained showed cracks but contained relatively large single-crystal regions.

B. Zircon

Zircon crystals were grown by Ballman and Laudise (1965) by cooling sodium molydate or lithium molydate solutions saturated with silica and zirconia at a rate of 2°C per hour from 1400 to 900°C. Platinum crucibles, with covers crimped in place to prevent volatilization of the solvent as much as possible, were used to contain the melt; crystals up to 7 mm in size were obtained.

A similar technique was used by Chase and Osmer (1966b) to grow zircon crystals both pure and doped with various lanthanides or uranium.
The lanthanide ions change the growth habit of the crystals, increasing the size of the 111 faces and decreasing the size of the 110, indicating a decrease in growth rate in the <111> direction, while uranium had no effect. Crystals up to 7 mm in size were obtained.

C. Lead Zirconate

Lead zirconate, of interest because it is an antiferroelectric, was prepared by Jona et al. (1955) in the form of small crystals by slow cooling of lead zirconate–lead fluoride melt; crystallization occurred apparently as a result of the evaporation of the lead fluoride.

D. Other Zirconates

An attempt was made by Nestor (1965) to grow barium zirconate (because of its potential interest as a laser host) by the Czochralski technique. The material was melted by induction heating in which the barium zirconate itself acted as its own susceptor; the melt was held in a container made of the compound itself. Although the material could be melted, the pulling of barium zirconate crystals was not successful.

REFERENCES

Zirconium Dioxide and Some of Its Binary Systems

R. C. Garvie

A recent article by Tatnall (1967) published in a ceramics trade journal commented that the sales volume of a major zirconia manufacturer almost quadrupled since 1960. This vigorous commercial growth has been matched by an ever accelerating research effort on this interesting and useful material. For example, a conference solely devoted to zirconia research-in-progress was convened in 1962. The combined properties of chemical inertness and refractoriness render zirconia and certain of its binary systems particularly useful in such areas as heat exchangers, crucibles and pouring nozzles for molten metals, etc. The stabilized zirconia phases are selectively permeable to oxygen ions at 1000°C and thereby find application as high temperature solid state electrolytes in fuel cells and induction furnaces.

Research in the field of zirconia technology is characterized by paradox and controversy. For example, the high temperature tetragonal phase of ZrO₂ cannot be retained by quenching; yet, this phase persists indefinitely at room temperature in zirconia prepared by calcining a zirconium salt at moderate temperatures. Another example is the monoclinic-tetragonal phase transformation which appears to violate Gibbs’ classical phase rule. Again, many scientists have studied the subsolidus equilibria in the CaO–ZrO₂ system, each one contributing his own diagram, quite different from all the others. Although this state of affairs is challenging to the scientist, it is detrimental to the practical application of zirconia ceramics. Some light has been shed on these difficulties and a critical review at this time is appropriate. The discussion is limited to ZrO₂ and the binary systems MgO–ZrO₂ and the CaO–ZrO₂. The reason is that much more is known in these areas; also, it is more interesting to discuss a small number of systems in depth, rather than present one more shallow survey covering a larger number of systems. My approach has been to try to dig out the underlying physical causes of the various phenomena and paradoxes. In certain areas, such as the peculiar thermal conductivity behavior of stabilized zirconia, only a plausible mechanism can be suggested. Hopefully, such speculations may stimulate further work and discussion. Other useful reviews which discuss additional stabilizer systems are those of Ryshkewitch (1960) and Weber (1964).
I. ZIRCONIA

A. Monoclinic Zirconium Dioxide

1. Structure

There are three well-defined polymorphs of pure \( \text{ZrO}_2 \), namely, the monoclinic, tetragonal, and cubic structures. The monoclinic phase is stable up to about 1100°C and then transforms over a 100°C temperature range to the tetragonal phase. Both these structures are related to the fluorite structure. Finally, at approximately 2370°C, the compound adopts the cubic fluorite structure. The fact that \( \text{ZrO}_2 \) crystallizes in the fluorite structure (or derivatives of it) is inexplicable in terms of modern crystal chemistry. For example, Wells (1962) asserts that the rutile structure is the stable form of binary ionic compounds of the type \( \text{RX}_2 \) when the radius ratio is in the range 0.414–0.732; but the radius ratio of \( \text{ZrO}_2 \) is 0.57, well within the rutile field. Obviously, the stable structure is governed by considerations other than the simple radius ratio; Bendoraitis and Salomon (1964) have suggested that there is appreciable covalent bonding in \( \text{ZrO}_2 \). McCullough and Trueblood (1959) contributed the first accurate crystal structure analysis of monoclinic \( \text{ZrO}_2 \). They obtained the following crystallographic data.

<table>
<thead>
<tr>
<th>Space group</th>
<th>( P2_1/c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>5.169 Å</td>
</tr>
<tr>
<td>( b )</td>
<td>5.232 Å</td>
</tr>
<tr>
<td>( c )</td>
<td>5.341 Å</td>
</tr>
<tr>
<td>( \beta )</td>
<td>99°15’</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>142.36 Å³</td>
</tr>
<tr>
<td>Density</td>
<td>5.826 gm/cc</td>
</tr>
</tbody>
</table>

The R-value of the determination was about 12. The zirconium ions are in seven-fold coordination, sandwiched on one side by oxygen ions in tetrahedral coordination (\( \text{O}_{11} \)) and on the other side by oxygen ions in triangular coordination (\( \text{O}_3 \)). A somewhat idealized picture of the coordination polyhedron is given in Fig. 1. Smith and Newkirk (1965) refined the crystal structure, thereby reducing the R-value to about 9. Their atomic coordinates are given in Table I along with those of McCullough and Trueblood, for comparison.

2. Properties

The optical energy gap of monoclinic \( \text{ZrO}_2 \) was found to be 4.99 eV by Bendoraitis and Salomon (1965). The infrared absorption spectra were
FIGURE 1 The Zr coordination polyhedra in baddeleyite (idealized) [McCullough and Trueblood, 1959].

<table>
<thead>
<tr>
<th>Zr</th>
<th>O_1</th>
<th>O_11</th>
</tr>
</thead>
<tbody>
<tr>
<td>McCullough and Smith and Trueblood</td>
<td>Smith and Newkirk</td>
<td>McCullough and Smith and Trueblood</td>
</tr>
<tr>
<td>X</td>
<td>0.2758</td>
<td>0.069</td>
</tr>
<tr>
<td>Y</td>
<td>0.0404</td>
<td>0.342</td>
</tr>
<tr>
<td>Z</td>
<td>0.2089</td>
<td>0.345</td>
</tr>
</tbody>
</table>

reported by McDevitt and Baun (1964) who detected nine bands in the region 800 to 200 cm\(^{-1}\). These authors made no assignments. Cubic stabilized zirconia gave only one broad band in the same region. This difference in spectra might be developed into a useful analytical procedure for phase identification in zirconia systems. Weber (1963) contributed some empirical findings on luminescent phenomena displayed by various forms of zirconia. The monoclinic phase emitted yellow-white fluorescence, whereas lime-stabilized zirconia showed only violet fluorescence.

Vest et al. (1964) reported on the electrical properties and defect structure of monoclinic zirconia which was shown to be an amphoteric semiconductor at 1000°C. The transition from n-type to p-type occurred in the neighborhood of $10^{-16}$ atm of oxygen partial pressure. Their data are summarized in Fig. 2. The predominant defect in the range $10^{-6}$ to 1 atm was completely ionized zirconium ion vacancies. The hole mobility at 1000°C has the very low value of $1.4 \times 10^{-6}$ cm\(^2\)/volt-sec.
FIGURE 2 Oxygen pressure dependence of conductivity of monoclinic zirconia (Vest et al., 1964).

High temperature elastic constants for zero porosity, polycrystalline monoclinic ZrO₂ were calculated by Smith and Crandall (1964) from sonic data. The data were fitted by an equation of the following form:

\[ E = E_0 \exp(-b_1 \rho) \]  

(1)

where

- \( E_0 \) = Young’s or shear modulus at zero porosity
- \( E \) = Young’s or shear modulus at some porosity \( p \)
- \( b_1 \) = an empirical constant
- \( p \) = fractional porosity

Typical data are given in Table II.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( E_0 ) (psi ( \times 10^{-6} ))</th>
<th>( G_0 ) (psi ( \times 10^{-6} ))</th>
<th>( b_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>35.43</td>
<td>13.96</td>
<td>3.544</td>
</tr>
<tr>
<td>1000</td>
<td>22.19</td>
<td>9.58</td>
<td>3.037</td>
</tr>
</tbody>
</table>

The axial thermal expansion of zirconia was first measured by Campbell and Grain (1962). Figure 3 shows the axial dilation as a function of tem-
Temperature. These data yielded the values for the axial thermal expansion coefficients and the angle $\beta$ shown in Table III.

### TABLE III

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$a$ axis</th>
<th>$b$ axis</th>
<th>$c$ axis</th>
<th>$\beta$ angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>99°14'</td>
</tr>
<tr>
<td>264</td>
<td>$8.4 \times 10^{-6} , ^\circ \text{C}^{-1}$</td>
<td>3.0</td>
<td>14.0</td>
<td>99°11'</td>
</tr>
<tr>
<td>504</td>
<td>$7.5 \times 10^{-6} , ^\circ \text{C}^{-1}$</td>
<td>2.0</td>
<td>13.0</td>
<td>99°3'</td>
</tr>
<tr>
<td>759</td>
<td>$6.8 \times 10^{-6} , ^\circ \text{C}^{-1}$</td>
<td>1.1</td>
<td>11.9</td>
<td>98°58'</td>
</tr>
<tr>
<td>964</td>
<td>$7.8 \times 10^{-6} , ^\circ \text{C}^{-1}$</td>
<td>1.5</td>
<td>12.8</td>
<td>98°42'</td>
</tr>
<tr>
<td>1110</td>
<td>$8.7 \times 10^{-6} , ^\circ \text{C}^{-1}$</td>
<td>1.9</td>
<td>13.6</td>
<td>98°43'</td>
</tr>
</tbody>
</table>

Lang et al. (1965) also measured the axial thermal expansion of monoclinic $\text{ZrO}_2$ and obtained good agreement with the data given in Fig. 3.

Domagala and McPherson (1954), using classical metallographic techniques, proved that the monoclinic phase displayed a wide range of non-stoichiometry. The metal-rich phase boundary extended from $\text{ZrO}_{1.75}$ at 1900°C to $\text{ZrO}_{1.90}$ at 700°C. The partial pressure of oxygen in equilibrium
with the nonstoichiometric phase was measured by Aronson (1961). Livage and Mazieres (1965) prepared black nonstoichiometric ZrO₂ in vacuum.

**B. Tetragonal Zirconium Dioxide**

1. Structure

The monoclinic structure is stable up to about 1100°C when it begins to transform to a tetragonal form. The transformation occurs over a 100°C temperature interval; its mechanism will be discussed in a later section. The crystal structure determination was made by Teufer (1962) who obtained the following data:

- **Space Group:** P4₂/2
- **a** = 3.64 Å at 1250°C
- **c** = 5.27 Å

With the origin at 4 M2, the Zr and O items are located in positions similar to those found in the fluorite structure:

- 2Zr (a) O, O, O; 1/2, 1/2, 1/2
- 4 O (d) O, 1/2, z; 1/2, O, z; O, 1/2, 1/2 + z; 1/2, O, 1/2 − z

where \( z_0 = 0.185 \). For the fluorite structure, the parameter \( z = 0.25 \). Tetragonal ZrO₂ is isostructural with red HgI₂.

2. Properties

Vest and Tallan (1965) discovered that tetragonal ZrO₂ exhibited mixed electronic and ionic conductivity over wide ranges of temperature and oxygen partial pressure. The n-type electronic conductivity which occurred at high temperatures and low oxygen partial pressures (1400°C, \( 10^{-13} \text{ atm} \)) was attributed to fully ionized oxygen vacancies. Hoch (1964) evaluated the pairwise interaction energy of the vacancies in the oxygen lattice and obtained a value of \(-4.6 \text{ kcal/mole}\), where the negative sign indicates the vacancies attract each other. Figure 4 shows the axial thermal expansion of tetragonal ZrO₂ as measured by Lang (1964). The axial mean thermal expansion coefficients in the range 1150–1750°C are \( a: 13.3 \times 10^{-6} \text{°C}^{-1}; c: 15.2 \).

C. Metastable Tetragonal Zirconia

Tetragonal ZrO₂ cannot be retained on quenching, yet, surprisingly, it can exist indefinitely at room temperature, if the zirconia is prepared either by calcining a salt such as the chloride or nitrate at low temperatures. The
usual explanation of this phenomenon is that the high temperature structure is stabilized by water or anions. For example, see Cypres et al. (1963). Such speculations are untenable because of two experiments. The first was performed by Clearfield (1964) who aged an amorphous precipitate of hydrous ZrO$_2$ in distilled water under reflux. The following sequence of phases was observed in the precipitate:

amorphous $\rightarrow$ tetragonal $+$ monoclinic $\rightarrow$ monoclinic

Obviously, water can play no role in the stabilization of tetragonal ZrO$_2$. The second experiment was performed by Mazdiyasni et al. (1966) who observed the tetragonal phase at room temperature in ultra-high-purity zirconia prepared by thermal decomposition of zirconium alkoxides. Clearly, minor amounts of impurities cannot stabilize tetragonal ZrO$_2$. The formation of metastable tetragonal ZrO$_2$ must be a fundamental property of the material itself. Garvie (1965) suggested that the occurrence of the metastable
phase was a crystallite size effect because this occurrence was always associated with finely divided zirconia. Figure 5 shows the sequence of phases observed at room temperature in two series of zirconia powders, one derived from the hydrous oxide (precipitated oxide) and one from the nitrate (calcined oxide). Figure 6 gives data on the crystallite size of the tetragonal phase as a function of temperature. These data show that the critical crystallite size above which the tetragonal phase is unstable is about 300 Å. Furthermore, this value is essentially independent of the method of preparing the zirconia powder. If the monoclinic and tetragonal phases are in equilibrium at the critical size of 300 Å, then their free energies must be equal. This is expressed in the following equation:

$$G_m + V_m A_m = G_t + V_t A_t$$

where $G$ = the molar free energy of ZrO$_2$ in the form of a large single crystal  
$V$ = the surface energy  
$A$ = the molar surface  

A schematic free energy diagram is given in Fig. 7. Upon inserting experimental data into the above equation, it turns out that if the surface free energy of ZrO$_2$ increased from 770 to 1130 erg/cm$^2$ upon passing from the tetragonal to the monoclinic structure, then the occurrence of metastable zirconia could be accounted for as a crystallite size effect.

![Diagram](image)

**FIGURE 5** The phases present at room temperature in active powders of zirconia heated to various temperatures (Garvie, 1965).
FIGURE 6 Experimental values of the mean crystallite size of metastable tetragonal zirconia as a function of temperature (Garvie, 1965).

FIGURE 7 Schematic free-energy diagram of monoclinic and tetragonal zirconia (Garvie, 1965).

Clearfield (1964) and Mazdiyasni et al. (1966) have reported on the existence of metastable cubic ZrO₂ in finely divided powders. It is difficult to accept these accounts for the following reason. Metastable tetragonal
HfO₂ cannot be prepared. Tetragonal hafnia is stable at 1690°C. These facts imply that the free-energy versus crystallite size curves for the monoclinic and tetragonal structures intersect at such a small value of the crystallite size that only an amorphous phase can be observed. Cubic zirconia is only stable at 2370°C and it seems likely there would be insufficient free surface energy available for its stabilization, as is the case with tetragonal HfO₂.

D. Mechanism of the Monoclinic-Tetragonal Transformation

The first significant research on this interesting problem was contributed by Wolten (1963). He clearly described the diffusionless, isothermal nature of the transformation, along with the fact that it constituted an apparent violation of the classical Gibbs' phase rule; the transformation occurred over a considerable temperature interval rather than at a sharply defined temperature. Wolten's data are summarized in Fig. 8 in which the marked hysteresis of the inversion is apparent. Wolten commented that the well-known martensitic phase transformations which occur in metals display features similar to those encountered in the zirconia inversion; he coined the phrase, “brittle-martensite” transformation to describe the zirconia inversion. According to Wolten's views the following crystallographic orientation relationships should prevail during the transformation: The c axes in both structures should be parallel; the monoclinic b axis should remain parallel to one tetragonal a axis while the other tetragonal a axis should be inclined 9.2° to the monoclinic a axis. Wolten (1964) succeeded in cycling

![FIGURE 8 Monoclinic-tetragonal transformation in zirconia (Wolten, 1963).](image_url)
a monoclinic crystal mounted on a single crystal orien ter through the inver- 
sion. Rather complicated relationships were observed; only the monoclinic 
axis was found to be parallel to a tetragonal axis. The cycled crystal 
consisted of slightly misoriented blocks, parallel in the direction, but 
rotated out of register in the plane over a range of °. A point of 
confusion now enters the discussion in that Wolten used an enlarged face-
centered cell to illustrate his argument rather than the conventional body-
centered cell. It is not clear from the text to which cell he is referring when 
he discusses axial relationships.

Smith and Newkirk (1965) next commented on the transformation 
mechanism, noting that the conversion could take place by rotation of the 
triangular coordinated oxygen ions in the (100) planes. The largest distance 
any oxygen ion need move is only 1.2 Å. The crystallographic relationship 
between the two structures is given in Fig. 9. This mechanism implies the 
following orientation relationships:

\[
\begin{align*}
(001)_m & \parallel (001)_t \\
(100)_m & \parallel (110)_t
\end{align*}
\]

![Diagram](https://example.com/diagram.png)

**FIGURE 9** A: projection of zirconia onto (001) showing pseudo body centered cell. B: projection of tetragonal zirconia onto (001). Dashed lines in A show dimensions of the true cell (Grain and Garvie, 1965).
These relationships were observed by Bailey (1964), although it is necessary to correct for the fact that he used the large face-centered cell rather than the conventional cell.

The next phase in the clarification of the mechanism was contributed by Grain and Garvie (1965) who offered an interpretation based on Ubbelohde’s (1956) theory of continuous phase transformations. According to this theory, whenever a crystal of monoclinic ZrO$_2$ is heated to a temperature within the transition region, domains of the tetragonal phase form in the monoclinic matrix. The domains are oriented so as to fulfill the relationships presented above. During the transformation, the system is described as a hybrid single crystal in which the two phases coexist, intimately coupled. This state of affairs arises because the high and low structures are very closely related. Gibbs’ classical phase rule is necessarily violated because it is based on the fundamental postulate that phases in equilibrium must be distinct and separate. The transformation is associated with considerable strain energy because the domain boundaries are coherent and there is an appreciable volume difference between the two phases; thus, a strain energy term must be added to the free-energy description of the system, thereby allowing an additional degree of freedom; the phase rule violation is then only apparent. The strain energy arising from the coexistence of both phases brings the reaction to a halt at any given temperature within the transition region; to bring about any further change in the amount transformed, the temperature must be changed. In ZrO$_2$, the strain is too great to permit perfect coexistence, so that, upon cycling the crystal through the transformation, it breaks up into a relatively few blocks of crystallites that are highly oriented about the original crystal axes. The strain involved in accommodating a monoclinic domain in a tetragonal matrix is not the same as the strain arising from a tetragonal domain in a monoclinic matrix; this situation would give rise to hysteresis. Clearly, all the features of the ZrO$_2$ inversion have been accounted for by the domain theory. However, this description of the transformation is similar to the “brittle martensite” picture advocated by Wolten. Now, a domain is a homogeneous unit of matter of more or less constant size. For example, the width of magnetic domains in iron is about $3 \times 10^{-3}$ cm. Again, Kennedy et al. (1953) estimated the crystallographic domains formed during the transformation in potassium nitrate to be of the order of $10^{-6}$ cm. If the domain theory of the ZrO$_2$ inversion is correct, then the nature of the transformation must change markedly at some critical crystallite size which must be equal to, or less than, a single domain. In such a finely divided ZrO$_2$ powder, coexistence phenomena would not be possible. An analogous situation occurs in magnetic materials where one observes a dramatic increase in coercivity as the particle size decreases to the dimensions of a single
domain (Kittel, 1966). Experimental proof for the correctness of the domain theory was obtained and is presented in Figs. 10 to 14. Figure 10 shows the usual athermal kinetics obtained with well crystallized zirconia. The reaction, at any given temperature, is time independent. Figure 11 shows the rate of transformation for finely divided ZrO$_2$; the rate is now time-dependent and obeys the following law:

$$q = k \log (1 + t) + b$$

where

$q =$ the fraction of monoclinic phase transformed

$t =$ time

$k, b =$ constants

Semilog plots of the transformation rate are given in Fig. 12 where the crystallite size has been introduced as a parameter. Figure 13 shows that the rate constant is a linear reciprocal function of the crystallite size. The rate constant becomes zero when the crystallite size is about 1150 Å so that the domain size is of the order of $10^{-5}$ cm. Figure 14 shows the results of differential thermal analysis experiments on the transformation of well-crystallized and finely divided ZrO$_2$. The heat of transformation of the finely divided sample is much less than that for the well-crystallized material. This is due to the fact that no strain energy occurs in the transformation of finely divided ZrO$_2$. The heat of transformation consists of two contributions, one arising from the chemical difference of the two structures and one arising from the strain energy associated with the transformation. The chemical contribution amounts to 622 cal/mole and the strain contribution, 798 cal/mole.

**FIGURE 10** Fraction of monoclinic phase transformed versus time; sample pre-heated 1500°C (Grain and Garvie, 1965).
Twinning occurs when ZrO$_2$ is cycled through the transformation, the twin plane being (100). This phenomenon is commonly encountered in mineralogy and is called by Buerger (1951), transformation twinning. The high and low forms of a crystal which suffer a continuous transformation have related symmetries. The space group of monoclinic ZrO$_2$ ($P2_1/c$) is a
subgroup of the tetragonal space group \((P4_2/nmc)\). In other words, the monoclinic structure can be derived from the tetragonal structure by suppressing certain symmetry elements of the latter. During the reverse transformation from tetragonal to monoclinic, monoclinic domains come into contact as the reaction proceeds; they will be in parallel or different orientation. Those which meet in different orientation are in twinned orientation with respect to one another. The twin individuals can be brought into self-coincidence by one of the operations of the tetragonal spacegroup which vanished in the formation of the monoclinic structure. McCullough and Trueblood (1959) as well as Smith and Newkirk (1965) discuss twinning in ZrO\(_2\) in greater detail.
In summary, the transformation of monoclinic ZrO$_2$ proceeds via small motions (i.e., less than an interatomic distance) of oxygen ions in triangular coordination in the (100) plane. The transformation develops by means of domains of the tetragonal form growing in monoclinic matrix. The domain boundaries are coherent and so cause the transformation to be athermal and display hysteresis. The formation of a domain need not be nucleated. Grain and Garvie (1965) showed that the maximum average amplitude of the (100) oxygen ions was 0.4 Å at 1066°C. If one allows a Boltzmann distribution of the thermal energy, then a significant fraction of the ion population will always have amplitudes great enough to cause spontaneous formation of a tetragonal domain, when the temperature is within the transition region.

E. Cubic Zirconia

Smith and Cline (1962) first reported direct evidence for the existence of cubic zirconia by means of high temperature x-ray diffraction experiments. The structure was fluorite and the tetragonal-cubic reversible inversion was placed at 2285°C. (The inversion temperature has since been corrected to 2370°C; see Viechnicki and Stubican, 1965.) The cubic phase could not be retained by quenching. Wolten (1963) confirmed these results, also using high temperature x-ray diffraction. Weber (1964) pointed out that these results were obtained under conditions in which the zirconia samples probably lost oxygen and became contaminated with metal from the diffractometer furnace; he raised the question of whether the cubic structure could exist in pure stoichiometric ZrO$_2$. The relationship between the nonstoichiometry of ZrO$_2$ and its tetragonal-cubic inversion was further explored by Ruh and Garrett (1967). Their work, summarized in Fig. 15, is consistent with the existence of a high temperature cubic form of stoichiometric ZrO$_2$. In fact, it is impossible to construct a reasonable phase diagram for the Zr–O system without allowing a tetragonal-cubic inversion at the stoichiometric composition.

II. THE MgO–ZrO$_2$ SYSTEM

A. Phase Equilibria

There have been five recent contributions to the problem of phase equilibria in the MgO–ZrO$_2$ system. The data are summarized in Figs. 16 to 20. All the diagrams generally agree that the cubic field is v-shaped, terminating in the neighborhood of 1400°C. However, these data differ considerably concerning the precise location of the phase boundaries. Table IV compares
FIGURE 15 Proposed zirconia-rich portion of the system, Zr–O (Ruh and Garrett, 1967).

FIGURE 16 Phase diagram of the system, ZrO₂–MgO (Duwez et al., 1952).
FIGURE 17 Phase diagram of the system ZrO₂–MgO (Cocco and Schromek, 1961).

FIGURE 18 Phase diagram of the system ZrO₂–MgO (Dietzel and Tober, 1953).
FIGURE 19 Phase diagram of the ZrO₂–MgO system (Viechnicki and Stubican, 1965b).

FIGURE 20 Phase diagram of the ZrO₂–MgO system (Grain, 1967a).
the phase boundaries (in MgO mole percent) for the 1600°C isotherm obtained by the various contributors.

### TABLE IV

<table>
<thead>
<tr>
<th>Tetr.-Cubic + Tetr.</th>
<th>Cubic + Tetr.-Cubic</th>
<th>Cubic-Cubic + MgO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>10.7</td>
<td>15.6</td>
<td>Grain (1967a)</td>
</tr>
<tr>
<td>10.0</td>
<td>21.0</td>
<td>28.0</td>
<td>Duwez (1952)</td>
</tr>
<tr>
<td>–</td>
<td>9–10</td>
<td>16–17</td>
<td>Cocco (1961)</td>
</tr>
<tr>
<td>–</td>
<td>10.0</td>
<td>17–18</td>
<td>Dietzel (1953)</td>
</tr>
<tr>
<td>2.0</td>
<td>12.0</td>
<td>25.0</td>
<td>Viechnicki (1965)</td>
</tr>
</tbody>
</table>

The work of Grain (1967), Cocco (1961), and Dietzel (1953) are in fair agreement. But the latter two diagrams do not show a tetragonal solid solution region which must be present since there is no phase transformation for pure ZrO$_2$ at the eutectoid temperature. In the present author’s opinion, these experimental discrepancies arise from a poor choice of experimental techniques and reagents. For example, the fact that Viechnicki and Stubican (1965) obtained a cubic field considerably larger than the others is probably related to the fact that their reagents were co-precipitated gels, which would decompose to produce very reactive oxide powders. There is some evidence that such reactive powders cause the cubic phase to be formed at lower temperatures and concentrations of stabilizer than would be the case if well-crystallized oxides were used (Garvie, 1968). There are three techniques for determining phase boundaries in subsolidus studies, namely, the lattice parameter method, the x-ray disappearing phase method, and the petrographic microscope technique. Grain (1967a) held the opinion that the lattice parameter approach was most sensitive. He compared results for the 1600°C isotherm obtained by the different methods, as shown in the following table.

### TABLE V

<table>
<thead>
<tr>
<th>Method</th>
<th>Tetr.-Cubic + Tetr.</th>
<th>Cubic + Tetr.-Cubic</th>
<th>Cubic-Cubic + MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter</td>
<td>–</td>
<td>10.7</td>
<td>15.6</td>
</tr>
<tr>
<td>X-ray disappearing phase</td>
<td>1.0</td>
<td>9.8</td>
<td>17–21</td>
</tr>
<tr>
<td>Petrographic microscope</td>
<td>2.5</td>
<td>10–11</td>
<td>14.0</td>
</tr>
</tbody>
</table>

In summary, it appears that the phase diagram presented by Grain is the most reliable in view of the fact that he used well-crystallized pure oxide reagents and the sensitive lattice parameter technique. It is worth noting
that of all the diagrams only that of Grain's shows agreement with independent data, obtained by electrical conductivity studies, on the solubility of MgO in monoclinic and tetragonal ZrO$_2$ (Kauer, 1959).

B. Decomposition of the Cubic Phase

The first scientific investigation of the decomposition of cubic solid solutions in the MgO–ZrO$_2$ system was made by Viechnicki and Stubican (1965b). They synthesized 100 percent cubic solid solutions by rapidly quenching powders derived from co-precipitated gels. Samples were then isothermally decomposed between 1000 and 1400°C; the course of the reaction was monitored by x-ray diffractometry. Electron probe and optical microscopic studies on pressed pellets showed that MgO precipitated preferentially in grain boundaries and intergranular voids. Data showing the amount decomposed ($\alpha$) as a function of time for various temperatures is given in Fig. 21. The ($\alpha$, $t$) curves are sigmoidal, indicating a nucleation and growth mechanism. According to Viechnicki and Stubican, the curves were fitted by an empirical function of the form:

$$(1 - \alpha) = C \exp(kt)$$

where $C$ and $k$ are constants. Two sets of values for each of the constants were necessary; one for the acceleratory period and one for the deceleratory

![FIGURE 21](image-url)  
**FIGURE 21** Effect of temperature on the decomposition of solid solutions of 80 mole % ZrO$_2$–20 mole % MgO. Solid solutions were prepared by heating for 1 hour at 1520°C and then were decomposed at (A) 1000°C, (B) 1075°C, (C) 1150°C, (D) 1250°C, (E) 1350°C, and (F) 1375°C (Viechnicki and Stubican, 1965b).
period. The authors commented that the exponential law may indicate that
the rate of nucleation is rate determining. However, the present author
found that the rate data were fitted over the entire extent of reaction by the
following generalized topokinetic equation developed by Erofeyev (1948):

$$\alpha = 1 - \exp(kt^2)$$

The plot is given in Fig. 22. The fact that the exponent of time is two
implies that the reaction is initiated by flat nuclei, growing in two dimen-
sions. Grain (1967b) stated that this implication is supported by an exami-
nation of the x-ray diffraction profiles of the cubic material as decomposition
proceeds. The profiles suffer asymmetrical line-broadening in the direction
of low angles, as shown in Fig. 23. This phenomenon may be the result of
a plate-like precipitate of MgO causing intense scattering about the main
diffraction lines of the matrix material. Similar effects have been noted in
age-hardened Al–Cu alloys (Guinier, 1963).

The rate constant in the exponential term was directly proportional to the
time of heating the solid solution at the temperature of preparation.
Viechnicki and Stubican attributed this phenomenon to an ordering process
occurring in the solid solution. They offered as evidence an x-ray diffraction

![Graph showing the Erofeyev equation for the 1375°C isotherm.](image-url)
pattern of the cubic phase showing extra faint lines. Their data are presented in the first three columns in Table VI. The present author discovered that all the lines but one can be indexed on a superlattice with a lattice constant four times that of the disordered cell. The reported d-value of the unindexed line is probably incorrect. Tien and Subbarao (1963a) observed a similar ordering process in the CaO–ZrO₂ system.

The rate constants passed through a maximum when plotted as a function of temperature, as shown in Fig. 24. This was interpreted on the basis of the following equation, developed by Zener (1946):

$$V_1 \approx (\Delta T)^2 e^{-Q/RT}$$

where

- $V_1$ = the velocity of the reaction interface
- $\Delta T$ = the amount of undercooling

and $e^{-Q/RT}$ is the proportional to the diffusion coefficient. The velocity is small at small amounts of undercooling, owing to the small concentration difference which drives the reaction. It is also very small for large amounts
of undercooling because of the slow rate of diffusion at lower temperatures. An intermediate amount of undercooling exists at which $V_1$ is a maximum.

### TABLE VI

*X-ray Diffraction Lines for a Solid Solution of 75 Mole % ZrO$_2$–25 Mole % MgO, Heated at 1500°C for 100 Hours*

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>$d_{obs.}$</th>
<th>$l$</th>
<th>$h^2 + k^2 + l^2$</th>
<th>$d_{calc.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>3.0258</td>
<td>VW</td>
<td>45</td>
<td>3.0297</td>
</tr>
<tr>
<td>200</td>
<td>2.9317</td>
<td>VS</td>
<td>48</td>
<td>2.9335</td>
</tr>
<tr>
<td>–</td>
<td>2.5376</td>
<td>S</td>
<td>64</td>
<td>2.5405</td>
</tr>
<tr>
<td>–</td>
<td>2.3283</td>
<td>W</td>
<td>76</td>
<td>2.3313</td>
</tr>
<tr>
<td>–</td>
<td>2.2720</td>
<td>W</td>
<td>80</td>
<td>2.2723</td>
</tr>
<tr>
<td>19597</td>
<td></td>
<td>VW</td>
<td>108</td>
<td>1.9557</td>
</tr>
<tr>
<td>220</td>
<td>1.7962</td>
<td>VS</td>
<td>128</td>
<td>1.7964</td>
</tr>
<tr>
<td>–</td>
<td>1.5755</td>
<td>VW</td>
<td>166</td>
<td>1.5774</td>
</tr>
<tr>
<td>311</td>
<td>1.5782</td>
<td>VS</td>
<td>176</td>
<td>1.5320</td>
</tr>
<tr>
<td>222</td>
<td>1.4662</td>
<td>M</td>
<td>192</td>
<td>1.4668</td>
</tr>
<tr>
<td>–</td>
<td>1.4275</td>
<td>W</td>
<td>203</td>
<td>1.4265</td>
</tr>
<tr>
<td>400</td>
<td>1.2708</td>
<td>M</td>
<td>256</td>
<td>1.2703</td>
</tr>
<tr>
<td>–</td>
<td>1.2193</td>
<td>VW</td>
<td>278</td>
<td>1.2190</td>
</tr>
<tr>
<td>331</td>
<td>1.1677</td>
<td>S</td>
<td>304</td>
<td>1.1657</td>
</tr>
</tbody>
</table>

**FIGURE 24** Plot of $\ln k_2$ versus reciprocal temperature. Solid solution, 80 mole % ZrO$_2$–20 mole % MgO were prepared by heating at 1520°C for (A) 1 hour, (B) 5 hours and then were decomposed between 1000 and 1375°C (Viechnicki and Stubican, 1965b).
C. Properties

1. Thermal Properties

The chief difficulty with property measurements in the MgO–ZrO$_2$ system is that specimens cannot be characterized properly because of the decomposition reaction. This situation is beautifully illustrated in Fig. 25 which shows thermal expansion data for successive runs, obtained by Burdick and Hoskyns (1963) on zirconia stabilized with 15.5 mole percent MgO. As each cycle is completed, the system suffers further destabilization and the characteristic thermal expansion curve of unstabilized zirconia is more and more evident. Figure 26 summarizes thermal diffusivity data obtained by the same authors during successive runs on zirconia stabilized with 15.5 mole percent MgO. The large increase in thermal diffusivity with each cycle is due to progressive decomposition of the cubic phase as discussed above. Poluboyarinov and his colleagues (1963) studied the effect of the amount of stabilizer on the thermal expansion in the MgO–ZrO$_2$ system. Their data, given in Fig. 27, displays an interesting feature, namely, that

![FIGURE 25 Thermal expansion of ZrO$_2$ + 15.5 mole % MgO (Burdick and Hoskyns, 1963).](image-url)
an increase in MgO content in the cubic phase considerably increases the thermal expansion; this effect may be the result of increasing the vacancy concentration as discussed in Sec. III, C, 2.

2. Mechanical Properties

Ryshkewitch (1953) reported the compressive strength of zirconia stabilized with 11.2 mole percent MgO as a function of porosity. The data were fitted by the following function:
\[ S = S_0 e^{-bp} \]

where

- \( S \) = strength of the porous test body
- \( S_0 \) = strength of the body at zero porosity
- \( b \) = an empirical constant
- \( p \) = porosity.

\( S_0 \) and \( b \) amounted to \( 3 \times 10^4 \text{ gm/cm}^2 \) and 7, respectively. Trostell (1962) in a similar study using a stabilized zirconia of unspecified composition obtained \( 7 \times 10^4 \text{ gm/cm}^2 \) for \( S_0 \) and 6.4 for \( b \). The compressive strength, Young’s modulus, and tensile strength of zirconia stabilized with an undisclosed amount of MgO were obtained as a function of temperature by Ryshkewitch (1960). Burdick and Hoskyns (1963) observed the temperature dependence of Young’s modulus of zirconia stabilized with 15.5 mole percent MgO as shown in Fig. 28. Kalliga and Lyutsareva (1964), in one of the more interesting contributions in this field, showed the effect of the stabilizer concentration on various mechanical properties. Their work is presented in Fig. 29. The optimum value of the properties occurs in the neighborhood of 10 mole percent MgO. Useful data relating the initial softening temperature to MgO concentration were obtained by Lukin and Poluboyarinov (1963). The data are given in Table VII.

<table>
<thead>
<tr>
<th>Composition (Mole % MgO)</th>
<th>Bulk Density (gm/cm³)</th>
<th>Initial Softening Temperature (°C; Load, 2kg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.26</td>
<td>2,100</td>
</tr>
<tr>
<td>8</td>
<td>5.37</td>
<td>2,250</td>
</tr>
<tr>
<td>10</td>
<td>5.34</td>
<td>2,270</td>
</tr>
<tr>
<td>12</td>
<td>5.28</td>
<td>2,300</td>
</tr>
</tbody>
</table>

The worth of all these data is questionable in view of the marked changes observed in the thermal properties data during successive cycles. Presumably similar phenomena occur with successive measurements of a mechanical or any other property. A prospective user of MgO–ZrO₂ ceramics would be well advised to limit his application such that little or no thermal cycling is involved.

### III. THE CaO–ZrO₂ SYSTEM

#### A. Phase Equilibria

There have been five major studies in the CaO–ZrO₂ system which can be divided into two groups. The first group consists of contributions in which
FIGURE 28 Elasticity of ZrO₂ + 15.5 mole % MgO (Burdick and Hoskyns, 1963).

FIGURE 29 Change in properties of ZrO₂, stabilized with MgO and calcined at 1710°C in relation to the amount of stabilizer added. (1) Bulk density; (2) apparent porosity; (3) bending strength, σ_{bend}; (4) residual bending strength, σ_{bend, r}, after heat cycle, 1300°C-air; (5) microhardness (Kalliga and Lyutsareva, 1964).
no compound was reported in the cubic field. The range of existence of the cubic phase in this group is given in Fig. 30. Consider any pair of matched lines in this diagram; in between the lines lies the cubic field as defined by that particular study; outside the lines are the two-phase regions. The second group of diagrams, shown in Fig. 31, consists of contributions in which a compound was reported at the composition, 20 mole percent CaO. Each group will be discussed in turn.

Duwez et al. (1952) reported the field to be between two almost vertical straight lines, one at 18.5 and the other at 28 mole percent CaO. The cubic phase, according to their work, extends from 2000°C down to room temperature. However, the data were obtained by annealing (reheating at various lower temperatures) samples which previously had been heated to 2000°C. This technique is bound to give erroneous results in view of the reported metastable existence of the cubic phase, as reported by Roy et al. (1964) [see also Sec. III, C]. Duwez and his co-workers used the relatively insensitive disappearing-phase method. This is surprising when one considers the excellent array of back reflection lines in the fluorite x-ray diffraction pattern which renders this system particularly suitable for the sensitive lattice-parameter technique of establishing phase boundaries. Dietzel and Tober (1953) presented a much smaller cubic field composed of sloping boundary lines which intersected at about 1200°C. This version

![FIGURE 30 Cubic fields in the CaO-ZrO2 system which show no compound formation (Garvie, 1968).](image-url)
probably reflects the fact that they approached equilibrium from the heating side. These workers also used the disappearing-phase method. They reported a large mysterious region of uncertainty or "unsharpness" at the low CaO boundary which is not given in Fig. 30. Roy et al. (1964) contributed the third version of the cubic field in the first group. These workers used the lattice parameter method and mixed nitrates as reagents. However, the phase diagram was mapped from only three isotherms, 1800, 1600, and 1100°C. The 1100°C isotherm was approached from the cooling side, using water as a catalyst to decompose the originally 100 percent cubic material.

In the second group of contribution, Fernandes and Beaudin (1963) presented a new discovery in this system, namely the compound CaZr$_2$O$_9$, occurring at 20 mole percent CaO. In this contribution, the cubic field was described as being formed by the solution of ZrO$_2$ in CaZr$_2$O$_9$. The existence of such a compound is certainly consistent with the fact that cubic zirconia stabilized with CaO is far more stable than the material stabilized with MgO in which apparently no compound is formed. These authors used both the disappearing-phase and the lattice-parameter methods. The reagents were CaCO$_3$ and ZrO$_2$. The final contributor, Barbariol (1965), also reported a vertical line at 20 mole percent CaO, indicating compound formation. He used the disappearing-phase method and the same reagents as the previous authors.
In the discussion so far, it is apparent that no two workers agree exactly on the nature or the range of existence of the cubic phase in the CaO–ZrO₂ system. Moreover, none of these studies involved a careful, detailed, and definitive investigation using simultaneously the lattice-parameter method and well-crystallized pure oxide reagents. Garvie (1968) attempted such a study. His x-ray data are given in Fig. 32. An analysis of the instrumental sources of error in the lattice-parameter technique showed that the standard deviation to be expected amounted to $2.4 \times 10^{-4}$ Å. The experimentally determined deviation was $2.8 \times 10^{-4}$ Å; such close agreement insured that this work was free of such errors as lack of attainment of equilibrium, poor mixing of reagents, etc. Lattice parameters obtained from samples at 12.0 and 13.2 mole percent CaO for the 1600, 1700, and 1765°C isotherms are seen to be above the sloping line by an amount exceeding the experimental precision. The points displaying discrepancy all lie near the phase boundary. This fact suggests that the anomaly may arise from a very fast decomposition reaction which occurs while the sample is being quenched. The fact that all the points for 20 mole percent or more CaO from the 1305 to 1600°C isotherms lie on a common horizontal line indicates compound formation. The point of intersection of the horizontal line with the sloping line yields the formula CaZr₄O₉ for the compound, agreeing with the work presented in Fig. 31.

Pyatenko (1963) deduced the existence of a compound in the CaO–ZrO₂ system at 20 mole percent CaO by an ingenious crystal chemical argument, apparently without the benefit of any experimental evidence. He considered

![Figure 32](https://www.Iran-mavad.com)

**FIGURE 32** Lattice parameter versus composition isotherms for the CaO–ZrO₂ system.
the three-dimensional stacking of truncated cubes and whole cubes (Pauling polyhedra) which would fill space. Truncated cubes contain zirconium as the central cation in seven-fold coordination, a common value for zirconium compounds. The truncated cubes automatically provide the oxygen ion vacancies which constitute the charge compensation mechanism in this system. It turns out that the packing conditions are exactly fulfilled at the composition, 20 mole percent CaO—80 mole percent ZrO₂. The cubic field then may be described as originating from a solid solution series between cubic ZrO₂ and CaZrO₄. Further support for the existence of CaZrO₄ was discovered in the CaO–HfO₂ system by Delamarre and Perez y Yorba (1965) who reported the compound CaHfO₄. Detection in this case was straightforward because this substance is monoclinic below 1450°C. Pyatenko (1967) proved that the structure of CaHfO₄ is based on a cell of the fluorite type which has undergone extremely slight rhombohedral deformation. The ordered structure of the compound is constructed from Ca-polyhedra with eight apices and Hf-polyhedra with seven apices, which together form a staggered three-dimensional motif, as required by the fluorite structure. Pyatenko further commented that it would be possible to miss both the splitting of the cubic maxima and the superlattice lines in x-ray diffraction powder diagrams if the angle, α, of the rhombohedral subcell differs by only a very small amount from 90°, because of the much smaller differences in the magnitude of the scattering powers of the Zr and Ca atoms compared to the Hf–Ca system.

There is a discontinuity in the 1700°C isotherm at the high CaO boundary, as indicated in Fig. 32, which is possibly the result of a phase transformation in CaZr₄O₉, resulting in a larger unit cell. For example, if the defect structure changed from the anion vacancy model to cation interstitial, one might observe an increase in the lattice parameter due to the interstitial ions. Diness and Roy (1965) presented evidence for this kind of transformation at high temperatures in the CaO–ZrO₂ system. No change in the diffraction patterns of samples quenched from 1700°C could be observed, other than the line shift. The compound may be tentatively described as alpha-CaZr₄O₉ below about 1650°C and beta-CaZr₄O₉ above this temperature. The phase diagram implied by the results of Fig. 32 is presented in Fig. 33. The cubic field appears to terminate somewhere in the vicinity of the monoclinic-tetragonal transformation of ZrO₂. This diagram is similar to that of Fernandes and Beaudin (1963), although their cubic field extends to lower values of temperature and composition than is the case in the present work. This discrepancy is possibly due to the fact that Fernandes and Beaudin (1963) used CaCO₃ as a reagent. As the salt decomposes, an active intermediate oxide would form causing the irreversible, metastable formation of the cubic phase. Some support for this idea is given in Fig. 34.
FIGURE 33 Phase diagram of the CaO-ZrO$_2$ system (Garvie, 1968).

FIGURE 34 1400°C isotherm in the CaO-ZrO$_2$ system showing the effect of reagent material (Garvie, 1968).

A portion of the 1400°C isotherm was rerun, using CaCO$_3$ as a reagent. The results do indicate that a larger field is created relative to that obtained using CaO. No experimental work was done in the regions bounded by
dashed lines in Fig. 33 because the reaction rates were too slow. However, Roy et al. (1964) showed that if the cubic phase were heated in the presence of water vapor (which is assumed to be a catalyst), it decomposed into the phases indicated in Fig. 33. There is an apparent violation of the phase rule because one too many phases was observed. The violation is only apparent if one takes into account the peculiar monoclinic-tetragonal transformation in ZrO₂, as discussed in Sec. I, D. In conclusion, it appears that the version of the cubic field offered by Garvie is the most reliable because well-defined oxide powders were used, along with the sensitive lattice-parameter technique for establishing phase boundaries.

B. Decomposition of the Cubic Phase

This discussion is based on the premise that the cubic field is generated by a solid solution series between cubic ZrO₂ and CaZrO₃. There are two main aspects to the problem of destabilization of the cubic phase. The first is concerned with the intrinsic thermodynamic instability of the cubic phase and may be conveniently subdivided into two secondary categories, namely, precipitation of ZrO₂ from solid solution and decomposition of the cubic phase. Sukharevskii (1961) and his co-workers provided evidence for the precipitation of ZrO₂ from solid solution by observing the decrease in the quantity of cubic phase (ΔC) in slowly cooled specimens compared with those quenched after ignition at 1750°C. Their data are summarized in Fig. 35. The amount of destabilization is obviously a function of the degree of supersaturation in the cubic phase. It is worth noting that these data are difficult to interpret in terms of the conventional description of the cubic phase as a solid solution of CaO in ZrO₂. If one considers ZrO₂ to be the solute (dissolved in CaZrO₃) it is clear that high degrees of supersaturation can only occur at low CaO compositions, which is what is observed. Decomposition of the cubic phase according to the reaction, cubic phase = ZrO₂ + CaZrO₃, occurs at temperatures below about 1200°C and is therefore probably exceedingly slow. Roy (1964) and his colleagues observed this reaction using water as a catalyst.

The second main aspect of destabilization is concerned with chemical attack of the cubic phase by impurities, consisting of acidic oxides which combine with CaO. This mode of decomposition is best described as corrosion rather than destabilization.

Buckley and Wilson (1963) reported that the amount of cubic phase in commercial (i.e., impure) partially stabilized zirconia refractories, used in a heat exchange furnace, decreased from 80 percent to 58 percent after 47 thermal cycles between 870 and 1090°C. Smoot and Whittemore (1963) duplicated the work in a laboratory experiment with pure oxides and found little or no destabilization.
FIGURE 35 Decrease in amount of cubic phase in slowly cooled samples as a function of composition (Sukharevskii, 1961).

C. Properties

1. Electrical Properties

The electrical conductivity of the cubic phase is quite high at temperatures equal to or greater than 1000°C; for example, the cubic material has been used to make furnace elements and solid-state electrolytes in fuel cells. The results of conductivity measurements, by many investigators, at the constant composition of 15 mole percent CaO and at 1000°C, are summarized in Table VIII.

<table>
<thead>
<tr>
<th>Conductivity, $\Omega^{-1}\text{cm}^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 10^{-8}$</td>
<td>Trombe and Foëx (1953)</td>
</tr>
<tr>
<td>$2.7 \times 10^{-7}$</td>
<td>Volchenkova and Pal’guev (1961)</td>
</tr>
<tr>
<td>$2.2 \times 10^{-6}$</td>
<td>Hund (1952)</td>
</tr>
<tr>
<td>$2.3 \times 10^{-6}$</td>
<td>Kingery et al. (1959)</td>
</tr>
<tr>
<td>$2.6 \times 10^{-6}$</td>
<td>Rhodes and Carter (1962)</td>
</tr>
<tr>
<td>$3.3 \times 10^{-6}$</td>
<td>Tien and Subbarao (1963a)</td>
</tr>
<tr>
<td>$2.8 \times 10^{-6}$</td>
<td>Ezerskii et al. (1966)</td>
</tr>
</tbody>
</table>

Kingery et al. (1959) established that the electrical conduction was mainly due to oxygen ion transport. Proof of this lay in the fact that the Nernst-
Einstein equations were satisfied. Figure 36 shows the agreement obtained between the oxygen ion diffusion coefficients, as measured directly, and those calculated from the conductivity data. The electrical conductivity of the cubic phase was measured as a function of CaO concentration in the range, 12–22 mole percent CaO by Tien and Subbarao (1963a). Their data were fitted between 500 and 1100°C by an equation of the form:

$$\sigma = A \exp (-Q/kT)$$

where

- $\sigma =$ the electrical conductivity, $\Omega^{-1} \text{cm}^{-1}$
- $A =$ the pre-exponential factor
- $Q =$ the activation energy, eV
- $k =$ Boltzmann's constant, erg/°K
- $T =$ Temperature, °K

The data obtained are shown in Table IX.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Conductivity ($\Omega^{-1} \text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 mole % CaO</td>
<td>$1.26 \times 10^5 \exp (-1.11/kT)$</td>
</tr>
<tr>
<td>15 mole % CaO</td>
<td>$1.52 \times 10^5 \exp (-1.17/kT)$</td>
</tr>
<tr>
<td>16 mole % CaO</td>
<td>$2.17 \times 10^5 \exp (-1.26/kT)$</td>
</tr>
<tr>
<td>18 mole % CaO</td>
<td>$1.71 \times 10^5 \exp (-1.30/kT)$</td>
</tr>
<tr>
<td>20 mole % CaO</td>
<td>$1.37 \times 10^5 \exp (-1.35/kT)$</td>
</tr>
</tbody>
</table>

**FIGURE 36** Comparison of directly measured diffusion coefficients with the curve calculated from electrical conductivity data (Kingery et al., 1959).
Tien and Subbarao offered the following interpretation to account for conductivity being inversely proportional to the CaO content. The oxygen ions must pass between two metal ions in order to reach an adjacent vacancy. At high Ca$^{2+}$ concentrations, there is a higher probability that the two metal ions would be Ca$^{2+}$ ions. The larger radius of the Ca$^{2+}$ ions implies that they would impose a higher activation energy on the conduction process. An alternative interpretation is that pairing of the Ca$^{2+}$ ions and vacancies occurs, thereby reducing the number of carriers. This suggestion was rejected on the basis of work by Lidiard (1956), who found that the number of free carriers increased with increasing Ca$^{2+}$ concentration, although the degree of association also increased. However, Kroger (1966) opines that most of the Ca$^{2+}$ ions are present at neutral calcium ion-oxygen vacancy pairs or clusters. His opinion is supported by the fact that relatively small amounts of donors (e.g., 2 mole percent vanadium plus 1.4 mole percent aluminum) promote n-type electronic conduction even in the presence of a large concentration of calcium, which is an acceptor. Kroger estimated the enthalpy of pairing to be $-2.7$ eV. If the entropy of conduction could be estimated independently, then comparison between the free energy of pairing and the activation energy of conduction might help decide the issue. Ezerskii et al. (1963) obtained data similar to that of Tien and Subbarao and drew similar conclusions.

Tien and Subbarao (1963a) and Subbarao and Sutter (1963) observed ordering phenomena in the cubic phase. Samples annealed for a long time at 1000°C produced extra weak lines in the x-ray diffraction pattern which were indexed with a superlattice cell four times larger than the basic cell. The ordering process was reversible, the lines appeared and disappeared as the sample was cycled between 1000 and 1400°C. Conduction in the ordered state was about one-half that in the disordered state. The kinetics of the process were consistent with a cation migration of only a few atom jumps and were too fast to permit phase separation.

Tien (1964) measured the electrical conduction in the CaO-ZrO$_2$ system over the CaO composition range 5 mole percent to 50 mole percent. The data could be divided into three distinct categories and were interpreted on the basis of the microstructure of the sintered specimens.

Region 1 (0–12 mole percent CaO). Two phases were present, ZrO$_2$ and the stabilized cubic phase. The conductivity increased rapidly with increasing CaO content reaching a maximum value at the cubic phase boundary. Initially, at low CaO concentrations, the conducting cubic grains were surrounded by insulating ZrO$_2$ grains. As the CaO content increased, the insulating layer disappeared.

Region 2 (12–22 mole percent CaO). Only one phase was present, cubic stabilized zirconia. The electrical conduction in this region has been discussed above.
Region 3 (22–38 mole percent CaO). Again, two phases were present, cubic stabilized zirconia and CaZrO$_3$. Up until 38 mole percent CaO, the conductivity decreased slowly. In this region, the nonconducting CaZrO$_3$ was located mainly at triple points. At higher compositions, the CaZrO$_3$ became the continuous phase coinciding with a marked decrease in conductivity.

2. Thermal Properties

One of the most interesting thermal properties from the ceramic point of view is thermal conductivity. Kingery et al. (1954) and Mirkovitch (1965) have shown that the thermal conductivity of calcia stabilized zirconia is low and nearly temperature independent. The following data are typical (Kingery, 1960):

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Thermal Conductivity, cal/sec/cm/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>4.7 × 10$^{-3}$</td>
</tr>
<tr>
<td>1000°C</td>
<td>5.5 × 10$^{-3}$</td>
</tr>
</tbody>
</table>

This behavior is not typical of refractory oxides and resembles the conductivity of a glass. The reason for this is probably due to the peculiar defect structure of this material. The presence of gross concentrations of anion defects would present unusual resistance to phonon transport, resulting in a low thermal conductivity. Consider the following equation for thermal conductivity in a solid:

\[
k = \frac{1}{3} C U \lambda
\]

where

- \( k \) = the thermal conductivity, cal/sec/cm/°C
- \( C \) = the heat capacity/unit volume, 0.527 cal/cc (King and Coughlin, 1950)
- \( U \) = the speed of sound, 5.22 × 10$^3$ cm/sec (Lang, 1960)
- \( \lambda \) = the phonon mean free path length, cm

The phonon mean free path length may be estimated in the following way. Consider a stabilized zirconia of the composition, Ca$_{0.14}$Zr$_{0.86}$O$_{1.86}$. It is assumed that the anion vacancies are the most efficient phonon scatterers. There is some justification for this assumption in the light of recent work by Schwarz and Walker (1966), who appear to have observed phonon scattering by lattice vacancies in KCl doped with as little as 200–300 ppm of divalent chlorides. The mean free path then, in CaO–ZrO$_2$ compositions, will be the mean distance between anion vacancies. For the composition under discussion, the vacancy concentration amounts to 4.14 × 10$^{22}$/cc. Suppose now that the crystal is divided into a great number of tiny cubes, each containing just one vacancy. The phonon mean free path length will
be the distance from the center of a given cube to the center of its nearest neighbor cube; i.e., one cube edge. Therefore, the phonon mean free path = \((10^{-21}/4.14)^{1/3} = 6.23 \times 10^{-8}\) cm. When the appropriate values are inserted into the above equation, \(k\) amounts to \(6.0 \times 10^{-3}\) cal/sec/cm/°C, in fair agreement with the experimental values. This analysis implies that the conductivity is proportional to the reciprocal cube root of the CaO concentration.

The thermal expansion of fully stabilized zirconia is quite high and is mainly responsible for the poor thermal shock resistance of this material. The high thermal expansion can also be rationalized in terms of the vacancy concentration. The magnitude of the thermal expansion depends on the degree of asymmetry present in the interionic potential well. It is reasonable to suggest that with increasing numbers of vacancies, the asymmetry would also increase. The only data showing the effect of the amount of stabilizer on the thermal expansion were obtained by Poluboyarinov et al. (1963). Their data are given in Fig. 37 where the expected increase in expansion with stabilizer content is indeed observed. Curtis and Johnson (1957) noted a similar effect in the CaO-ThO\(_2\) system. The addition of as little as one percent CaO increased the thermal expansion from \(96.7 \times 10^{-7}/°C\) for pure ThO\(_2\) to \(99.3 \times 10^{-7}/°C\) for the temperature range 100–1230°C.

This discussion leads to interesting speculations on the possibility of improving the thermal shock resistance of zirconia refractories. If the vacancies could be removed, the thermal conductivity would increase and the thermal expansion would decrease, resulting in an improvement in the thermal shock resistance. This can be accomplished by employing mixed stabilizers containing three and five valent cations; the average stabilizer valence is four so that no vacancies would form. Indeed a patent was granted to DuPont (1965) for just such a material:

\[
\text{Ln}_2\text{Nb}_2\text{Zr}_{1.2}\text{Ca}_{0.8}\text{O}_2
\]

**FIGURE 37** Curves of thermal expansion of fired bodies stabilized with CaO: (1) 8 mole %; (2) 10 mole %; (3) 12 mole % (Poluboyarinov et al., 1963).
Ln is a rare-earth element having an atomic number from 64 to 71 inclusive or Yttrium and \( x \) has a value from 0.015 to 0.15 inclusive. The patent claimed superior thermal shock resistance for this material compared to conventional stabilized zirconia ceramics.

3. Mechanical Properties

Mechanical property measurements have been determined on poorly characterized relatively impure materials, just as in the case of the MgO–ZrO\(_2\) system. Wachtman and Lam (1959) determined the Young’s modulus as a function of temperature using commercial (i.e., impure) ZrO\(_2\) stabilized with 10 mole percent CaO. Their data are summarized in Fig. 38. The density of the test specimens was 4.93 gm/cc. These authors commented that the rapid, nonlinear decrease in Young’s modulus (accompanied by an increase in the internal friction) indicated that grain boundary slip was an important factor governing mechanical properties in the high temperature range. However, one must recognize that the materials used in this work may very well have gross concentrations of impurities, at the given boundaries, possibly forming a liquid phase at high temperatures which would adversely affect mechanical properties. Burdick and Hoskyns (1963) measured Young’s modulus on a sample stabilized with about 15.5 mole percent CaO. Their data are also given in Fig. 38 and show a roughly linear decrease with temperature. Lang (1960) measured some mechanical

![FIGURE 38 Young’s modulus as a function of temperature.](image-url)
properties on material stabilized with 10 mole percent CaO. He obtained the following values at room temperature:

\[
\begin{align*}
\text{Density} & \quad 4.97 \text{ gm/cc} \\
\text{Young's Modulus} & \quad 1493 \text{ kbar} \\
\text{Shear Modulus} & \quad 584 \text{ kbar} \\
\text{Poisson's Ratio} & \quad 0.279 \\
\text{Bulk Modulus} & \quad 1125 \text{ kbar}
\end{align*}
\]

The variation of mechanical properties with stabilizer content was measured by Kalliga and Lyutsareva (1964) as shown in Fig. 39. Again, just as in the MgO–ZrO₂ system (Sec. II, C, 2) the properties pass through a maximum value in the neighborhood of 10 mole percent CaO (Fig. 29). [Hague, 1966, who measured the flexural strength as a function of CaO content confirmed this finding.] Lukin and Poluboyarinov (1963) reported the data appearing in Table X on the initial softening temperature as a function of composition.

<table>
<thead>
<tr>
<th>Composition (Mole % CaO)</th>
<th>Bulk Density (gm/cm³)</th>
<th>Initial Softening Temperature (°C; Load, 2kg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.19</td>
<td>2090</td>
</tr>
<tr>
<td>8</td>
<td>5.38</td>
<td>2260</td>
</tr>
<tr>
<td>10</td>
<td>5.29</td>
<td>2285</td>
</tr>
<tr>
<td>12</td>
<td>5.09</td>
<td>2250</td>
</tr>
</tbody>
</table>

**TABLE X**

**FIGURE 39** Change of properties of ZrO₂ stabilized with CaO and calcined at 1710°C in relation to the amount of stabilizer added. (1) Bulk density; (2) apparent porosity; (3) bending strength, \(\sigma_{\text{bend}}\); (4) residual bending strength, \(\sigma_{\text{bend}}\) after heat cycle of 1300°C-air; (5) microhardness (Kalliga and Lyutsareva, 1964).
IV. SINTERING AND TRANSPORT PROPERTIES OF THE CUBIC PHASE

Cubic stabilized zirconia is not easy to sinter, as shown by the data in Table XI obtained from material of the composition, Ca$_{0.16}$Zr$_{0.84}$O$_{1.84}$ (Tien and Subbarao, 1963b).

<table>
<thead>
<tr>
<th>Sintering Temperature, °C</th>
<th>Time, hours</th>
<th>Theoretical Density, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>1900</td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>2000</td>
<td>8</td>
<td>94</td>
</tr>
</tbody>
</table>

The poor rate of sintering is probably related to the properties of mass transport in the CaO–ZrO$_2$ system. Rhodes and Carter (1966), using the sectioning technique, measured the self-diffusion coefficients of the cations in a material of similar composition. Their data were fitted by the following equations:

\[ D_{\text{Ca}} = 0.444 \exp (-100,200)/RT \text{ cm}^2/\text{sec} \]
\[ D_{\text{Zr}} = 0.035 \exp (-92,500)/RT \text{ cm}^2/\text{sec} \]

where the symbols have their usual meanings. These authors attributed the low sintering rates of cubic stabilized zirconia to these low values of the cation diffusion coefficients. Kingery et al. (1959) measured the oxygen ion diffusion rate, using exchange measurements with O$^{18}$. They assumed an infinite rate of exchange at the surface. Their data fitted the following equation:

\[ D_o = 1.02 \times 10^{-2} \exp (-28,000)/RT \text{ cm}^2/\text{sec} \]

Simpson and Carter (1966), who also measured the oxygen ion diffusion, pointed out an inconsistency in the contribution by Kingery and his co-workers and suggested the previous equation should be changed to:

\[ D_o = 1.0 \times 10^{-2} \exp (-30,500)/RT \text{ cm}^2/\text{sec} \]

Simpson and Carter employed the conventional sectioning technique which took account of a finite rate of exchange at the surface. It was shown that this rate was indeed finite and could not be ignored if accurate results were desired. The surface exchange coefficient obeyed the following law:

\[ = 0.078 \exp (-22,800)/RT \text{ cm}^2/\text{sec} \]

The oxygen ion diffusion coefficient data were fitted by the following equation:

\[ D_o = 0.018 \exp (-31,200)/RT \text{ cm}^2/\text{sec} \]
The data on cationic and anionic diffusion in the cubic phase show that the rate of diffusion of the former is about five orders of magnitude less than the latter. In a recent paper, Reynen (1968) showed that for maximum sintered density the following relation should hold:

$$D_c C_c = D_o C_o$$

where

- $D$ = the vacancy diffusion coefficient
- $C$ = the vacancy concentration

The subscripts $c$ and $o$ refer to cation and anion vacancies, respectively. At high values of the stabilizer concentration, $D_c C_c \ll D_o C_o$, implying that one would obtain low densities. At low values of the stabilizer concentration, Reynen’s relation is more nearly satisfied and one would expect higher densities. Hague (1966) determined the sintered densities of cubic materials as a function of stabilizer content, as shown in Fig. 40, where it is seen that the density is a strong reciprocal function of the CaO concentration. It is tempting to speculate that at lower CaO concentrations there are fewer oxygen ion vacancies resulting in a higher density in accord with Reynen’s discussion. Tentative support for this speculation was found in a contribution of Smith et al. (1966). They measured the oxygen permeability of a stabilized zirconia tube of the composition, $\text{Ca}_{0.06}\text{Zr}_{0.92}\text{O}_{1.92}$. Their diffusion data were fitted by the following equation:

$$D_o = 185 \exp\left(-\frac{57,600}{R T}\right)$$

**FIGURE 40** Sintered density as a function of composition (Hague, 1966).
Apparently, decreasing the CaO content by one-half has resulted in a two-fold increase in the activation energy of oxygen-ion diffusion. Admittedly, these speculations are somewhat at odds with the electrical conductivity data which actually increase within the cubic field as the composition approaches the low CaO boundary.

Tien and Subbarao (1963) measured grain-growth in Ca$_{0.10}$Zr$_{0.84}$O$_{1.64}$ and obtained the following results:

$$D = (kt)^{0.4}$$

where

- $D$ = the grain diameter
- $k$ = a constant
- $t$ = time

The activation energy of grain-boundary migration was 80 kcal/mole, in fair agreement with the activation energy of cation diffusion.

V. PARTIALLY STABILIZED ZIRCONIA CERAMICS

Useful ceramic articles, such as pouring nozzles for molten metals, are commonly made from compositions in the two-phase region, to the left of the cubic field. Such compositions are commonly referred to as partially stabilized zirconia ceramics and consist of both the monoclinic and the cubic phases. These materials are supposed to have superior thermal shock resistance compared to the fully stabilized material. Very little data on the physical and chemical properties of partially stabilized zirconia ceramics exist. Figure 41 shows the thermal expansion of a partially stabilized zirconia, as measured by Whittmore and Ault (1956). The curve is about midway between those found for pure ZrO$_2$ and the cubic phase. King and Yavorsky (1967) recently made some interesting observations and comments on unusual phenomena occurring in partially stabilized zirconia systems. Figure 42 shows an inclusion of monoclinic ZrO$_2$ embedded in the center of a cubic grain. Three sets of slip have been generated around the inclusion to relieve the differential strain which occurred during heat treatment. The tetragonal-monoclinic transformation which occurs in the range 1050 to 600°C produces a very large increase in volume of the inclusion during cooling of the ceramic. King estimated the stress sustained by the cubic phase to be about 400,000 psi. This stress has obviously exceeded the yield stress of the matrix at 1050°C and the material has yielded. If ZrO$_2$ did not have this capability for stress relief by means of a deformational mechanism, the grain would have fractured. It is interesting to speculate on a possible mechanism for the observed stress relief. King noted that, petrographically, almost all of the monoclinic phase has disappeared.
FIGURE 41 Thermal expansion of partially stabilized and 100% cubic zirconia (Whittmore and Ault, 1956).

FIGURE 42 Inclusion of monoclinic ZrO$_2$ embedded in cubic zirconia. Three sets of slips are shown (King and Yavorsky, 1968).
at a composition of 2.82 percent MgO. Yet, the material actually contains 68 volume percent of the monoclinic phase. According to King, “the cubic and monoclinic mixture is occurring together within single grains and are acting in a grossly mechanical sense as a single phase. These grains are probably composed of mixed crystals of alternating cubic and monoclinic domains with a regular structural relation between them.” This description is precisely the same as that given by Grain and Garvie (1964) during the monoclinic transformation. Hart and Chaklader (1967) observed superplasticity in pure ZrO₂ during the inversion. It is suggested that it is this superplasticity of the monoclinic domains in the monoclinic-cubic hybrid phase which is responsible for the stress-relief phenomena, observed by King. The cubic phase alone cannot possess stress-relieving mechanisms because it becomes quite brittle as the monoclinic phase disappears with increasing stabilizer content. This is shown by microhardness data plotted as a function of MgO content in Fig. 43. “Center” refers to data obtained at the center of a grain and “boundary” denotes data obtained at the grain boundary. Clearly, partially stabilized zirconia is a most interesting material whose properties have only begun to be investigated.

VI. INFLUENCE OF IMPURITIES ON PROPERTIES OF STABILIZED ZIRCONIA

Weber (1963) commented that acidic oxide impurities such as SiO₂ and TiO₂ should be avoided in commercial zirconia because they combine with the basic stabilizers, MgO and CaO. Keler and Andreeva (1958) recommended that TiO₂ and SiO₂ should be less than 0.5 and 1.0 percent, respectively, in commercial zirconia. An interesting quantitative study of the effect of various impurities (Fe₂O₃, TiO₂, Al₂O₃, SiO₂, P₂O₅) on some thermo-mechanical properties of stabilized zirconia was made by Voronin and his colleagues (1963). The impurities were added in the amount 1, 2, and 5 weight percent to a composition consisting of ZrO₂ and 22 mole (%) percent CaZrO₃. The product, with no impurities, consisted of 80 percent cubic material and 20 percent monoclinic. Data on the effect of the additives on the compressive strength are given in Fig. 44. Additions of Al₂O₃ greatly increased the compressive strength, although the thermal shock resistance decreased until 5 weight percent Al₂O₃ was added. The increase in thermal shock resistance noted at this composition was attributed to microcracks. Additions of P₂O₅ also enhanced the compressive strength; the thermal shock resistance, however, continually decreased with increasing P₂O₅ concentration. The authors concluded that commercial zirconia should contain minimum amounts of P₂O₅, Fe₂O₃, and SiO₂.
FIGURE 43 Microhardness of ZrO$_2$ stabilized with MgO, as a function of stabilizer concentration (King and Yavorsky, 1968).

FIGURE 44 Effect of impurities on compressive strength of stabilized zirconia (Voronin et al., 1963).
REFERENCES

Zircon and Zirconates

William J. Baldwin

I. ZIRCON

A. Introduction

The mineral zircon or zirconium silicate, generally designated as ZrSiO$_4$, or ZrO$_2$·SiO$_2$, has proven of definite interest as a refractory and opacifying material for many years, such interest being in part due to (1) the commercial availability of zircon in relatively pure and controlled quality, (2) its chemical and physical properties, and (3) the many technological changes which have occurred in industry as a result of expanded research. It is the prime source for zirconium oxide which in turn is a source of the products designated as the zirconates.

B. Occurrence and Beneficiation of Zircon

Zircon is widely distributed as an accessory mineral in acidic igneous rocks. Through weathering of these rocks, the zircon appears in sediments as small crystals or sand grains which because of their high specific gravity are subject to concentration with other heavy minerals on beaches or similar wind- and water-swept areas. The heavy mineral deposit comprising the minerals zircon, rutile, ilmenite, monazite, sillimanite, kyanite, staurolite, garnet, tourmaline, and epidote are physically relatively hard and chemically resistant to earth acids and weathering. Tidal action, ocean currents, and intermittent changes in land level has over many thousands of years resulted in a greater enrichment of these heavy sands as beach deposits which represent the commercial ore now exploited. The beach sands of Queensland and New South Wales, Australia and the Tranancore Coast of India are major foreign sources for zircon, the former being of primary interest as a supply for consumption in the United States at the present time. Deposits near Jacksonville, Florida were extensively developed for domestic consumption in the States until 1966 when operations were suspended.
Zircon deposits occur in Alaska, California, and the Northwestern states of the U.S., but mining operations are considered uneconomic at the present time according to Kaufman and Holt (1965).

The heavy sand concentrates as found in the world are quite similar with respect to the type of minerals found, differing only in the percentage of each present and in that the zircon values of those sand deposits are separated from the less dense minerals by gravity equipment. Ilmenite and garnet which are moderately magnetic and monazite which is weakly magnetic are magnetically separated. Rutile is removed by electrostatic separators. While technically suitable zircon is obtained in this fashion, a calcining operation generally follows to remove any possible organics. In some instances the zircon is leached with sulfuric acid to obtain a lower iron content. A procedure for the production of a high purity zircon which involves calcining of the zircon with 1–4 weight percent of sodium chloride or sodium fluoride singly or with combinations of the two salts at a temperature of 1200°C has been reported by Bitossi (1964).

Zircon sand as obtained from the separation of the other minerals analyses approximately 98–99 percent zircon. A typical chemical analysis of Australian zircon is shown in Table I.

Zircon sand as processed is comprised of granules which are for the most part between 100 and 200 mesh. A typical screen analysis is shown in Table II.

Reduction to finer sizes is accomplished by the methods usual in the ceramic industry, such as milling accomplished by classification. Particle sizes as fine as 3 μ maximum are commercially available.

C. Properties

Zircon has a chemical composition corresponding to the formula ZrO₂·SiO₂ containing theoretically 67.23 percent ZrO₂ and 32.77 percent SiO₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrSiO₄</td>
<td>98.5–99.0</td>
<td>SnO₂</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.15</td>
<td>Nb₂O₅</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>HfO₂</td>
<td>1.30</td>
<td>WO₃</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.37</td>
<td>Cr₂O₃</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.05</td>
<td>NiO</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.001</td>
<td>TiO₂</td>
<td>0.25</td>
</tr>
<tr>
<td>PbO</td>
<td>0.003</td>
<td>CaO</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table I

Typical Chemical Analysis of Australian Zircon

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TABLE II

Typical Screen Analysis of Granular Zircon

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>+50</td>
<td>0.00</td>
</tr>
<tr>
<td>-50 + 70</td>
<td>0.92</td>
</tr>
<tr>
<td>-70 + 100</td>
<td>9.97</td>
</tr>
<tr>
<td>-100 + 140</td>
<td>40.25</td>
</tr>
<tr>
<td>-140 + 200</td>
<td>46.20</td>
</tr>
<tr>
<td>-200 + 270</td>
<td>2.65</td>
</tr>
<tr>
<td>-270</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The crystal structure is tetrahedral, the value of $a$ being 6.60 Å and of $c$, 588 Å. The density of zircon, obtained by beneficiation, averages 4.6. Hardness of zircon according to the mineralogical scale after Mohs is 7.5 which is between quartz and topaz. Zircon has a very high refractive index, with a birefringence of positive character, the values of both indices being $E = 2.01$ and $W = 1.95$.

Chemically, zircon is very stable, particularly at lower temperatures. With the exception of concentrated hydrofluoric acid, zircon is not generally attacked by organic or inorganic acids even at highly elevated temperatures. According to Ryshkewitch (1960) zirconium-oxyfluoride, $\text{ZrOF}_2\cdot2\text{HF}$, aqueous and silicon tetrafluoride are formed on reacting zircon with concentrated hydrofluoric acid.

Zircon is readily attacked at elevated temperatures by basic materials and such reactions are utilized in the decomposition of zircon to form zirconia and/or zirconium salts. When equal molecular weights of zircon and sodium or potassium carbonate are heated at 950 to 1000 °C, the corresponding alkali zirconium silicate is formed. With an excess of 5 to 15 percent of the alkali carbonate, the corresponding alkali zirconate is formed together with the alkali silicate. Treatment of this reacted product with hydrochloric acid and subsequent filtration yields soluble zirconium oxychloride. With the addition of ammonium hydroxide to the solution of zirconium oxychloride, hydrous zirconia is precipitated which upon filtering, drying, and calcining yields zirconium oxide.

The degree of decomposition of zircon when reacted with an excess of sodium carbonate was investigated by Kuleshov and Schmanenkova (1962). Mixtures of zircon and sodium carbonate when heated at 900 °C for one hour showed 24.8 percent decomposition of the zircon as compared to 100 percent decomposition when heated for four and one-half hours. The rate of decomposition was increased by additions of sodium fluoride or calcium fluoride.
With the exception of calcium carbonate no intensive investigations have been made on the reaction of the alkaline earth oxides with zircon. The reaction of calcium carbonate and zircon when mixed in equi-molecular proportions and calcined at 1600–1760°C to form calcium silicate and zirconia has been previously reported and a patent was granted to Schoenlaub (1946) for the preparation of zirconia by this procedure. The system CaO·ZrO₂·SiO₂ was recently investigated by Kordyuk (1963) who reports two ternary compounds. Ca₃ZrSiO₉ and Ca₂ZrSi₄O₁₂ are found in this system melting incongruently at 1600 and 1400°C, respectively.

Zircon has no true melting point as it dissociates before melting. Dissociation begins very slowly at 1538°C (2800°F) and increases very rapidly as the temperature is increased. The first liquid is formed at approximately 1677°C (3050°F) when all the zircon is dissociated and molten silica is in equilibrium with solid zirconia. The products of dissociation are monoclinic zirconia (at room temperature) plus silica or zirconia plus glass depending upon the temperature. The eutectic point in the ZrO₂–SiO₂ system occurs at approximately 1677°C (3050°F) and the composition contains less than 3 weight percent ZrO₂.

According to Langeron (1963b), confidence can be placed in the phase diagram established by Curtis and Sowman (1953). This author brings out the point that zircon cannot be in equilibrium with the liquid as shown by Geller and Lang (1964) since zircon dissociates at 1538°C and the eutectic comprising 97 percent SiO₂ and 3 percent ZrO₂ is formed at 1677°C. According to Geller and Lang the dissociation temperature of zircon is 1775°C which is above that of the eutectic 1675°C containing 4 percent SiO₂.

D. Industrial Applications

1. Refractories

The refractory industry accounts for the major consumption of zircon followed in turn by (1) the metallurgical industries and (2) the various ceramic industries other than refractories. In the preparation of zircon refractories, granular zircon sand, finely milled zircon, and high density zircon grog ranging in size from 1/4 inch and down are used, the proportions of each in the composition being dependent upon the processing involved and the end use of the refractory shape.

In those applications where high density and low porosity of the fired refractory shape are essential for resistance to glass attack and corrosion, use is made of finely milled zircon. Refractory shapes are formed by dry pressing or slip casting, the latter being used where large refractory shapes
not amenable to dry pressing are involved. Isostatic pressing of relatively large zircon blocks in sizes up to $6 \times 24 \times 36$ inches and $12 \times 18 \times 36$ inches was recently announced by A. P. Green Company of Mexico, Missouri. Refractory shapes processed by isostatic pressing are reported to show lower glass penetration and corrosion than similar shapes produced by slip casting.

Temperatures for firing zircon ware, ranging from 1400 to 1510°C (2700 to 2750°F), are generally used, the time of heating to and holding at peak temperature being dependent upon the load and furnace conditions. Using Orton cones, firing to cone 20 down is general practice.

Of the various uses for zircon as a refractory which includes crucibles, sagger, bricks, washes, ramming mixes, etc., the largest tonnage of zircon is used in refractory applications for the glass industry, such applications ranging from the use of zircon orifice rings and expendable feeder parts for borosilicate, opal and barium TV glasses to complete bottom pavings and superstructure applications in furnaces melting opal, borosilicate, and soda-lime glasses. The increasing demand for zircon refractories in the glass industry has stimulated considerable interest in the improvement of such refractories. Numerous papers have been published and patents issued within the past 5 to 7 years relative to the application of zircon refractories in the glass industry and the development of new and better zircon refractories which result in increased production, better quality glass, and lower operating costs.

On the basis of investigations conducted by Busby (1957) relative to the relationship between porosity of mullite refractories and corrosion by molten glass, Vago and Griffiths (1961) investigated the corrosion of zircon refractories by molten glass relative to porosity of the refractory and/or the concentration of the zircon dissolved in the glass. The results of their laboratory trials with commercial and laboratory prepared samples of varying porosity in a calcium alumino-borosilicate glass showed a highly significant degree of correlation between the percentage apparent porosity of the zircon refractory samples and their percentage loss in volume. Their investigations also showed that as the concentration of zircon dissolved in a calcium alumino-borosilicate or a soda-lime silicate glass was increased, corrosion rate on the zircon refractory was markedly reduced. With the calcium alumino-borosilicate glass, approximately 12.6 percent zircon was required to saturate the glass whereas with the soda-lime silicate glass, approximately 23.8 percent was required. A higher rate of attack on zircon by the soda-lime silicate glass is indicated by these tests.

Busby et al. (1962) investigated the corrosion of pressed versus slip-cast zircon refractories in borosilicate and soda-lime-silica glasses using a static
corrosion test, a simulated bottom test, and a test relative to corrosion by batch materials. Eight commercial zircon refractory materials (three pressed and five slip cast) were evaluated. In the static corrosion tests in the soda-lime-silica glass (1400°C–24 hours) corrosion was more marked with the pressed zircon ware than with the slip-cast ware. Linear corrosion measured at the fluxline as percentage of original ranged from 9.60 to 16.35 percent for the five slip-cast zircon specimens as compared to 18.10 and 64.51 percent for two of the pressed zircon specimens, the third being corroded away. In the borosilicate glass tests (1400°C–72 hours) the corrosion of pressed and slip-cast zircon was comparable with values for linear corrosion ranging from 1.53 to 3.58 percent.

In laboratory tests to simulate bottom corrosion tests, slip-cast zircon specimens were not affected by molten soda-lime-silica glass (1400°C–48 hours) whereas pressed zircon specimens under similar circumstances disintegrated completely. Under similar test conditions with a borosilicate type glass, the effect on the pressed and slip-cast zircon samples was only slight, with the latter zircon specimens showing some slight advantage. From these results it was concluded that slip-cast zircon refractories could be used successfully as a paving material in the conventional soda-lime-silica tanks.

Batch corrosion tests conducted by spraying 600 gm of sodium carbonate per hour or 600 gm of boric oxide per hour on zircon samples heated at 1450°C produced results which could be expected in view of the acidic properties of zircon. All of the zircon samples were readily attacked in the presence of sodium oxide, but with boric oxide only surface glazing was evident.

The corrosion of zircon refractories by soda-lime and borosilicate glasses was also investigated by Aldred et al. (1965) using zircon refractory samples with apparent porosity values of 6, 10, and 15 percent. Their results again showed that the corrosion rate increases with increased porosity of the zircon and that soda-lime glass is the most corrosive on the zircon refractory. High-lime borosilicate glass (21 weight percent CaO and 54 weight percent SiO₂) was found to be more corrosive to zircon refractories than the low-lime high-silica borosilicate glass (12.0 weight percent CaO and 72.1 weight percent SiO₂).

Zircon refractory used as a hearth in the manufacture of white bottle glass (soda-lime-silicate) for continuous operation over a period of 28 months was examined by Lister (1964) relative to mineral changes due to thermochemical effects. Microscopic examination of slices cut from the zircon refractory at right angles to the hot face indicated a porous layer under the glass that definitely indicated solution and attack of the zircon,
with zirconia being present in large amounts. In the cold-face zone of the zircon refractory, chemical and physical properties corresponded to those of the original unused zircon refractory. The porous layer of the zircon refractory consisting of zirconia and amorphous vitreous material resulting from the decomposition of the zircon provides a dense protective layer over which the glass flows, thus minimizing further erosion and decomposition of the zircon layer beneath it.

With increasing use of zircon refractories in glass furnace construction, problems arose which have been attributed to zircon and its reaction with the glass. The problem of outgassing at the interface between the molten glass and the refractory with the resulting formation of blisters and seeds in the glass was reported by Bossard (1959) to be eliminated through the use of a soda surface treatment and refiring of the zircon refractory. In a more recent patent, McTaggart (1965) covers the use of a zircon refractory containing 0.5 to 7.5 weight percent of a finely divided soda-zirconia-silica glass, said refractory composition being very effective in eliminating the outgassing effect.

With new installations of zircon refractories, particularly in bottom walls, reaction of the molten glass with the refractory has been considered by some operators to be the cause for frothing and foaming of the glass melt with resulting overflow of the molten glass from the tank in some instances. Flexon and Troy (1966) indicate in their patent that such problems can be overcome by applying a layer of cullet and alkali to the refractory face and prefiring same at a temperature not less than 2500°F prior to melting of the glass composition. The layer so applied should contain at least 5 weight percent of the alkali metal oxide as sodium or potassium or combinations thereof. On the basis of the investigations which resulted in the above patents, it is indicated that solution to the problems encountered may be provided to some extent by means of a controlled amount of alkali within the zircon refractory or at its surface in contact with the glass.

The application of zircon refractories for the roof and sidewalls of tunnel kiln firing bone china, earthenware, and sanitary ware is reported by Housley (1965). In 12 plants where the use of zircon refractories were evaluated, all reported definite economic advantages in spite of the higher initial cost. With the installation of zircon roof bricks versus firebricks, a marked reduction in the quantity of ware damaged by glaze droppers was noted. Zircon refractories containing no clay addition are definitely superior to those with clay addition and 10 weight percent clay is considered to be the maximum for use in preparing the zircon refractory body.

Refractory bodies with high load capacity and high resistance against corrosion and thermal shock are reported by Thomas (1963, 1964, 1965,
1967). The refractory material, according to the patents cited, is composed essentially of zircon and two different forms of alumina and in the fired state is essentially an alumina refractory bonded with a zirconia-mullite matrix and a minimum of glassy phase. Excellent corrosion and spalling resistance, good structural stability, excellent hot load bearing characteristics, and relatively low thermal conductivity are among some of the properties listed. Within recent years, this newly developed refractory, designated as ZIRMUL (a product of the Chas. Taylor Sons Co., Cincinnati, Ohio) has attained wide acceptance by glass producers in the United States and Europe.

A basic refractory, suitable for use in glass tank regenerator checker construction, composed of 60 to 90 percent dead burned magnesite and 40 to 10 percent zircon is the subject of a patent by Good and Davies (1965). Linear change on firing is less than 0.5 percent and fired shapes are characterized by excellent volume stability under cyclic temperature change as experienced in glass tank checker service. The fired refractory consists of a coarse textured periclase grain bonded by a forsterite matrix, the latter resulting from reaction of MgO and the SiO\textsubscript{2} of the zircon during firing. Magnesia stabilized zirconia is also present distributed throughout the forsterite matrix.

Development of a refractory composition consisting of a mixture of 40 to 90 percent coarse magnesite and 60 to 10 percent zircon is reported by Holt and Cash (1967). With additions of approximately 3 percent hydrated sodium silicate and 1 to 2 percent of other auxiliary agents to promote wetting, strength, etc., a chemically bonded mix is obtained suitable for ramming, gunning, or pressing into shapes, said refractory mix being virtually hydration proof under normal conditions of use and storage. Shrinkage or expansion of the fired body may be varied by means of variation in the grain size of the magnesite used. Fired refractories produced from the coarse magnesite and fine zircon show better spalling resistance and strength than refractories made from magnesia alone and are not wet as readily by slag and molten metals, such as steel, as are lime and/or magnesia refractories.

The physical properties of zircon refractories such as apparent porosity, bulk density, thermal conductivity, and cold crushing strength are dependent upon such factors as fineness of the zircon used in the refractory body, the forming methods used, and firing cycle. The physical properties of commercial zircon refractories which are presented in Table III show the variations which one may expect from the reasons cited above.

Considerable variation in the electrical resistivity of zircon is noted in the literature. A recent article by Wallace and Ruh (1967) covers the elec-
ZIRCON AND ZIRCONATES

TABLE III

PHYSICAL PROPERTIES OF SOME ZIRCON REFRACTORIES

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, lb/cu ft</td>
<td>212</td>
<td>235–245</td>
<td>255–265</td>
<td>235</td>
</tr>
<tr>
<td>Apparent Porosity, %</td>
<td>25–28</td>
<td>8–10</td>
<td>0.5–2.0</td>
<td>17.4</td>
</tr>
<tr>
<td>Reheat Change, % Linear at 3000°F</td>
<td>-0.3 to 0.7</td>
<td>-0.85</td>
<td>-0.05</td>
<td>-</td>
</tr>
<tr>
<td>Linear Coefficient of Expansion, °F (80–2600°F)</td>
<td>-</td>
<td>$2.77 \times 10^{-8}$</td>
<td>$2.77 \times 10^{-6}$</td>
<td>-</td>
</tr>
<tr>
<td>Thermal Conductivity, BTU/hr/sq ft/°F/°F (200–2800°F)</td>
<td>12–15</td>
<td>24</td>
<td>26–27</td>
<td>-</td>
</tr>
<tr>
<td>Cold Crushing Strength (psi)</td>
<td>7045</td>
<td>$&gt;50,000$</td>
<td>$&gt;50,000$</td>
<td>11,500</td>
</tr>
</tbody>
</table>


electrical resistivity of various refractories including zircon, data for which is presented in Table IV.

2. Metallurgy

Zircon sand, milled zircon sometimes designated as flour, and zircon washes have had wide acceptance in steel, iron, aluminum, bronze, and magnesium foundries. The high refractoriness and the slight chilling effect

TABLE IV

ELECTRICAL RESISTIVITY OF ZIRCON REFRACTORY

<table>
<thead>
<tr>
<th>°C</th>
<th>Electrical Resistivity (ohm cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>533</td>
<td>$2.94 \times 10^7$</td>
</tr>
<tr>
<td>592</td>
<td>$1.03 \times 10^7$</td>
</tr>
<tr>
<td>680</td>
<td>$3.53 \times 10^6$</td>
</tr>
<tr>
<td>760</td>
<td>$1.47 \times 10^6$</td>
</tr>
<tr>
<td>868</td>
<td>$4.41 \times 10^5$</td>
</tr>
<tr>
<td>971</td>
<td>$1.41 \times 10^5$</td>
</tr>
<tr>
<td>1081</td>
<td>$5.09 \times 10^4$</td>
</tr>
<tr>
<td>1192</td>
<td>$1.87 \times 10^4$</td>
</tr>
<tr>
<td>1301</td>
<td>$7.73 \times 10^3$</td>
</tr>
<tr>
<td>1478</td>
<td>$2.40 \times 10^1$</td>
</tr>
</tbody>
</table>
make zircon highly effective in combating "burning-in" and preventing metal penetration into cores and molds, thus lowering cleaning and grinding costs. The use of zircon chills has advantages over metal chills in flexibility of shape and the elimination of chill marks on castings. The chilling effect of zircon is due largely to its high thermal conductivity. The low and uniform expansion of zircon when compared with silica decreases the cracking of cores and molds during the baking and pouring cycles, tending to eliminate the formation of fins on castings.

Recent references in the literature have indicated the definite advantages of zircon over silica as mold material and as washes. Fleming et al. (1961) report that the greater heat diffusivity of zircon as compared to silica results in a more rapid cooling of an Al–4.5 percent Cu alloy. Fluidity of the alloy when cast in zircon sand is 55 percent lower at 677°C and 22 percent lower at 760°C than when cast in silica sand. Zircon molds with phenylformaldehyde resin or a furan resin as the organic binder were used successfully in casting gas face reactive metals such as titanium, uranium, aluminum, F.S. 1020 steel, and bronzes, according to Chandley (1961).

In connection with the application of the CO₂ process to the manufacture of medium/heavy steel castings, the use of zircon sand bonded with sodium silicate as mold sand for casting high-alloy, heat-resisting steels versus similarly bonded silica sand is discussed by Magee (1962). Zircon sands bonded with sodium silicate are reported as showing greater resistance to thermal shock and are definitely more dimensionally stable than silica sands bonded with sodium silicate. With the use of zircon for large enclosed cores, the resulting fired strength of the core after casting presented a problem with respect to breakdown, but it is reported that this difficulty was overcome without any appreciable deterioration of the surface finish by the addition of up to 1 percent dextrine and other similar materials.

The use of zircon as the refractory in mold washes for foundry sand molds and cores is the subject of a patent issued to Middleton and Mellon (1963). A coating of the wash comprising a suspension of 65–70 percent zircon, 1.5 percent dextrine, and 0.075 to 0.1 percent sodium alginate applied to a core at a thickness of 0.02 to 0.03 inch resisted penetration of the molten metal cast at 1600°C into the sand core.

The application of zircon as a refractory material for tundish nozzles through which molten metal passes into the mold has received considerable attention. Properties of zircon such as good thermal shock resistance, high erosion resistance, dimensional stability, and resistance to penetration and chemical reaction by the melt favor its used in this application.

Nozzles prepared from a combination of granular and milled zircon, clay and sulfite lye as the binder, formed by dry pressing and fired at
1540°C were reported by Strelets et al. (1963) to possess high erosion resistance and give a more stable casting rate for killed and uncooked steels than other types of nozzles. Reports on the preparation and use of zircon nozzles for continuous steel casting plants are also discussed by Pitak and Drizheruk (1964) and by Bobkun et al. (1966).

In shell molding and precision casting of metals, the use of zircon has been well established in view of its refractory and nonreactive properties with many metals. Investment molds produced on the pattern by application of several coats of a slurry composed of a powdered refractory with an aqueous solution containing colloidal silica and a resinous polymer, the preferred refractory for the first coat being —325 mesh zircon is covered in a patent by Erdle and Feagin (1961). No external reinforcement on the precoated mold is required to resist stress exerted by the expansion of the pattern material prior to removal by melting. For a somewhat similar application Tkachenko and Lipman (1962) found that slurries prepared with water glass from a blend of zircon, clay, cut asbestos, and bakélite and applied to patterns for facing purposes resulted in shell molds which had twice the binding strength of similar molds produced with silica sand. The advantages of zircon as a refractory for specific applications in precision casting is also reported by Operhall and Schwartz (1961) and Fischman (1967).

3. Glaze Opacifiers

In the wall tile and sanitary-ware industries, zircon as a mill-added opacifier to glazes has been used extensively in the United States and Canada for many years. Conversion from the use of tin oxide to zircon as an opacifier was based primarily on economic reasons, but other advantages such as improved abrasion resistance, improved craze resistance, and another most important factor—improved color stability—have warranted its continued use.

Within the past 5 to 10 years, considerable interest has been developed in England and European countries in the use of zircon as an opacifier particularly in the sanitary-ware industry. The bulk of information concerning the application of zircon as a glaze opacifier has been of foreign sources during the past five years with little being published by investigators in the United States or Canada.

The two major producers of zircon opacifiers in the United States are M&G Chemicals, Inc., Rahway, New Jersey, and TAM Division of National Lead Company at Niagara Falls, New York, the latter also producing the synthetic alkaline earth and zinc-type zirconium silicate products which are used as opacifier additions and for certain textural effects. Within the past
two years, zircon opacifiers produced in Japan have been introduced in competition with the domestic product. Podmore and Sons and the Zircon Division of Associated Lead Manufacturers Ltd. are producers of zircon opacifiers in Great Britain and are major suppliers of the market there and in Europe.

With the increased use of zircon as a glaze opacifier, definite improvements have been made in the control of the processing steps involved and in the production of finer milled products. Zircon opacifiers as originally introduced were milled to a maximum particle size of 15 μ, but as milling and classification techniques have been improved, finer milled zircons with a maximum particle size of 5 μ have been produced. Within the past few years a zircon opacifier (TAM EXCELOPAX, a product of TAM Division, National Lead Co.) of high purity and with a maximum particle size of 3 μ has been developed and marketed.

A review of glaze opacification using zirconia, zircon, and various zirconium-type opacifiers is reported by Jacobs (1963). The necessity of developing glaze compositions specifically designed for use with the zirconium type of opacifier is stressed. Advantages to be gained through the use of the synthetic alkaline earth zirconium silicates and zinc zirconium silicate products relative to control of viscosity and suspension of the glaze slip and fired properties of the glaze are reported. With the use of zirconia or the synthetic zirconium silicate products as opacifiers, the crystalline phase producing opacity in the fired glaze is zircon.

The advantages to be gained by use of the synthetic alkaline earth and zinc zirconium silicate products as opacifiers in glazes are also reported by Bhushan et al. (1966). In low-temperature lead-type glazes maturing at approximately 1000°C, zinc zirconium silicate as the opacifier addition produced good textured glazes and higher opacity than zircon. With glazes maturing at 1200 to 1280°C, optimum properties of the fired glaze—gloss, texture, and opacity—were obtained with the combination of zircon and calcium zirconium silicate opacifiers.

Considerable interest has been shown recently by French investigators relative to the application of zircon as an opacifier in sanitary-ware glazes to replace tin oxide. Such investigations have included comprehensive studies of glaze compositions best suited for opacification with zircon and the resulting properties of the fired glazes. Single-fired zircon opacified sanitary-ware firing at cone 9 were investigated by Lécrivain (1963). In this investigation a base composition of soda-feldspar, kaolin, zircon, and silica was used with kaolin and zircon maintained at 5 and 10 percent, respectively, the feldspar and silica varied to give silica-alumina ratios of 7, 8, 10, and 12. To these variations of the base compositions, additions
were made of various combinations of calcium, barium, and magnesium carbonates in amounts ranging from 6 to 16 percent and the properties, such as viscosity, texture, whiteness, opacity, etc., of the resulting glazes determined.

The results of this investigation indicated that silica-alumina ratios of 7–8 with alkaline earth carbonate additions of 14–16 percent produced the most satisfactory glazes. Of the alkaline earth carbonate additions, calcium carbonate was most effective in increasing the fluidity of the glaze and constituted the major portion of the alkaline earth carbonate addition in those glazes which were considered most desirable for further investigation. Mill additions of 10 to 15 percent zircon produced glazes of comparable whiteness to commercial tin oxide opacified glazes.

The molecular composition of the three glazes suggested by Lécrivain as starting points for development of commercial sanitary-ware glazes fired at 1280 ± 20°C differs considerably from the molecular compositions of sanitary-ware glazes used in the United States and Canada which are fired at approximately the same temperature. This is clearly indicated in Table V in which the molecular formulas suggested by Lécrivain are compared with the molecular formula of a typical sanitary-ware glaze used in the United

| TABLE V |
| MOLECULAR FORMULATIONS OF CONE 9 ZIRCON OPACIFIED SANITARY-WARE GLAZES SUGGESTED BY LÉCRIVAIN & TYPICAL SANITARY-WARE GLAZE Used in the United States |

<p>| | | | | | |</p>
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<tbody>
<tr>
<td>A</td>
<td>0.35</td>
<td>Na₂O</td>
<td>0.57 Al₂O₃-4.3 SiO₂</td>
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</tr>
<tr>
<td>B</td>
<td>0.42</td>
<td>Na₂O</td>
<td>0.68 Al₂O₃-5.2 SiO₂</td>
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<td></td>
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<tr>
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<td>0.28</td>
<td>CaO</td>
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<tr>
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<td>0.20</td>
<td>BaO</td>
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<tr>
<td></td>
<td>0.10</td>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.34</td>
<td>Na₂O</td>
<td>0.55 Al₂O₃-4.25 SiO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>CaO</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.32</td>
<td>MgO</td>
<td></td>
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</tr>
<tr>
<td>D</td>
<td>0.131</td>
<td>Na₂O</td>
<td>0.42 Al₂O₃-3.62 SiO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.082</td>
<td>K₂O</td>
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</tr>
<tr>
<td></td>
<td>0.563</td>
<td>CaO</td>
<td></td>
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<tr>
<td></td>
<td>0.045</td>
<td>MgO</td>
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</tr>
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</tr>
<tr>
<td></td>
<td>0.090</td>
<td>ZnO</td>
<td></td>
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</tbody>
</table>

*A, B, C: Formulas by Lécrivain. D: Typical formulation used by U.S.*
States. Formulas suggested by Lécrivain contain a considerably higher alkali content, somewhat lower calcia content, and a higher baria and magnesia content. A high percentage of feldspar in the batch formulation is indicated by the high alkali content. Batch compositions (Table VI) calculated from these molecular formulas show this to be true. For comparative purposes, the batch composition of the typical sanitary-ware glaze used in the United States is given.

Following the investigation by Lécrivain (1963) on the soda feldspar type of sanitary-ware glaze the development of zircon opacified sanitary-ware glazes based on the use of a potash feldspar was investigated by Lécrivain et al. (1965b). The plan of investigation was similar to that conducted with the soda-feldspar glazes and the results again indicated that the most interesting compositions were those with a silica-alumina ratio of approximately 8 with additions of the alkaline earth carbonates comprising 15 to 20 percent of the batch composition. Properties of the glazes produced with the potash feldspar were not considered to be comparable to those produced with the soda spar.

Using a composition composed of soda feldspar, kaolin, silica, and calcium carbonate as the base formula, Lazennec (1965) investigated the effects of such additions as calcium carbonate, lithium zirconium silicate, zinc oxide, and cryolite on opacity, whiteness, texture, and bubble formation with zircon and zirconia as the opacifier addition.

With zirconium oxide as the opacifier, Lazennec found that the silica-alumina ratio of the base glaze must be higher (8–9) than that required with the use of zircon (7–8) in order to obtain optimum fluidity. This was attributed to the fact that the solution of zirconium oxide in the glaze on

<table>
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<th>TABLE VI</th>
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<tr>
<td><strong>Batch Formulations</strong> for Zircon Opacified Sanitary-Ware Glazes</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td><strong>A</strong></td>
</tr>
<tr>
<td><strong>Feldspar</strong></td>
</tr>
<tr>
<td><strong>Silica</strong></td>
</tr>
<tr>
<td><strong>Clay</strong></td>
</tr>
<tr>
<td><strong>Calcium Carbonate</strong></td>
</tr>
<tr>
<td><strong>Magnesium Carbonate</strong></td>
</tr>
<tr>
<td><strong>Barium Carbonate</strong></td>
</tr>
<tr>
<td><strong>Talc</strong></td>
</tr>
<tr>
<td><strong>Zinc Oxide</strong></td>
</tr>
</tbody>
</table>

*A, B, C: Based on molecular formulas by Lécrivain (Table V). D: Based on molecular formula—U.S. type (Table V).*
firing with subsequent recrystallization to zircon results in a lowering of the silica content of the glaze. Decreased fluidity occurs as a result of lowering the silica-alumina ratio. Fluidity of the glaze was materially increased with the additions of lithium zirconium silicate in the range of 1 to 6 percent and with cryolite in the range of 1 to 7 percent, but as fluidity of the glaze increased, pitting of the glaze became more apparent. Additions of zinc oxide and lithium zirconium silicate at low levels improved the texture and brightness of the glaze compositions studied, but opacity was reduced. Opacity of the fired glazes was found to be increased as the fineness of the zircon opacifier was increased and with greater dispersion of the opacifier in the glaze, the latter being affected by longer milling time.

Zircon opacified sanitary-ware glazes, in view of their higher viscosity than tin oxide opacified glazes, exhibit a greater tendency for the formation of bubbles in the fired glaze layer which can result in pitting with overfiring of the glaze. The distribution of the zircon opacifier in the glaze layer was studied by Lécrivain et al. (1965b) and found to vary considerably dependent upon the milling afforded the glaze. High concentrations of zircon were generally associated in the presence of spherical gas bubbles on the walls of which zircon was present as a layer.

A comprehensive investigation on bubbles in single fired sanitary-ware glazes was made by Lécrivain et al. (1965a). Observations on the formation of bubbles and pits in such glazes are presented, but the cause and means of eliminating same are not considered in this report. Cross-sections of fired glazes showed a heterogeneous distribution of zircon with a concentration of zircon at the surface of the glaze. Electron micrograph studies indicated the size and shape of the zircon crystals which were most prevalent to be of the same order as the mill-added zircon opacifier. In certain areas, however, a cluster of fine zircon crystals was noted with particle size in the order of 0.1 to 1.0 \( \mu \) as compared to 1 to 2 \( \mu \) for the zircon opacifier. These fine crystals of zircon were attributed to recrystallization of the zircon, approximately 2 percent, which was taken into solution during the firing of the glaze. It was observed that a concentration of zircon does exist on the surface of the bubbles present in the glaze structure and a correlation does exist between this zircon concentration and the bubble formation. The presence of pits in the glaze surface is attributed to (1) the porosity of the body, (2) the formation and partial sealing over of a bubble at the surface of the glaze, and (3) the formation and contraction of a bubble in the proximity of the glaze surface.

Godron (1965) in a discussion on bubbles in glazes points out the fact that all fired glazes show the presence of bubbles, the size and number of bubbles being dependent upon the type of opacifier used, the thickness
of the glaze, and the body. Bubbles produced with zircon as the opacifier in sanitary-ware glazes were more numerous and larger when compared with tin oxide as the opacifier. Bubble formation in a tile body with zircon as the opacifier in the glaze was more numerous than in a sanitary-ware body, but of smaller size.

Mineral composition used in the preparation of glazes and bodies with their attendant gases and liquids evolved on heating are discussed as possible causes for the formation of bubbles in glazes by Deicha (1965). Coordinated research by ceramists and mineralogists is recommended as a means of attacking the problem of bubbles in glazes.

In the previous discussion on zircon opacified glazes, consideration has been given to those glazes opacified by the mill addition of zircon and/or zirconium-type opacifiers. The development of zircon opacified glaze frits which develop opacity on firing due to recrystallization of the dissolved zirconium oxide to zircon have proven of interest in England, Europe, and South America, but have not been exploited to any great extent in the United States or Canada.

Zircon, used as the opacifying agent in this type of frit will comprise from 5 to 20 percent of the batch weight. At the higher levels of zircon content (15 to 20 percent) sufficient opacity is produced in the fired glaze without the addition of milled added opacifier to the frit and clay which comprises the glaze. At the lower levels of zircon content in the frit, mill added opacifiers in the order of 3 to 5 percent may be added with the clay.

Silica, alumina, boric oxide, and zinc oxide have a favorable effect in the development of opacity in zircon opacified frits. The alkaline earth carbonates have a marked effect on reducing viscosity and play an important part in development of a satisfactory white glaze. Calcium carbonate comprises the major part of the alkaline earth carbonate additions, magnesium carbonate and/or barium carbonate additions being made at the expense of calcium carbonate where improved whiteness of the fired glaze is desired. Typical compositions of zircon opacified glaze frits are presented in Table VII and these indicate the marked variation of composition used in preparation of these frits.

Glazes prepared from zircon opacified glaze frits have a general tendency for small perforations or pinholes to appear in the glaze surface. Lowering of the clay content used to suspend the milled glaze or replacement of the clay by additions of 0.5 to 1.0 percent bentonite plus small additions 0.125 to 0.25 percent of carboxy-methyl-cellulose or sodium alginate will in many instances eliminate or reduce considerably this pinholing tendency.

The pinholing tendency of zircon opacified fritted glazes was investigated by Hennicke et al. (1965) and reduction in this characteristic defect was
TABLE VII

<table>
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<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydrated Borax</td>
<td>8.4</td>
<td>13.0</td>
<td>28.4</td>
<td>21.7</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>11.2</td>
<td>11.9</td>
<td>1.8</td>
<td>—</td>
</tr>
<tr>
<td>Flint</td>
<td>30.0</td>
<td>22.5</td>
<td>32.0</td>
<td>53.2</td>
</tr>
<tr>
<td>Barium Carbonate</td>
<td>6.0</td>
<td>9.5</td>
<td>1.6</td>
<td>—</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>14.6</td>
<td>11.8</td>
<td>—</td>
<td>12.0</td>
</tr>
<tr>
<td>Zircon</td>
<td>5.0</td>
<td>20.0</td>
<td>15.5</td>
<td>20.5</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>3.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>3.0</td>
<td>3.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>2.4</td>
<td>—</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>33.5</td>
<td>24.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Clay</td>
<td>—</td>
<td>—</td>
<td>11.3</td>
<td>4.9</td>
</tr>
<tr>
<td>Alumina Hydrate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4.0</td>
</tr>
<tr>
<td>Litharge</td>
<td>—</td>
<td>—</td>
<td>5.9</td>
<td>—</td>
</tr>
<tr>
<td>Magnesium Carbonate</td>
<td>—</td>
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<td>1.7</td>
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<tr>
<td>Fluorspar</td>
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<td>—</td>
<td>0.8</td>
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reported to result by firing of the glazes at the lowest possible temperature or firing cycle to mature the glaze. Maintenance of as high a glaze viscosity as possible in the firing range was further advocated for reduction of the pinholing tendency.

The maximum temperature for firing glazes prepared from zircon opacified glaze frits is in the range of 1000 to 1100°C. Frits used in the preparation of these glazes are smelted at approximately 1300 to 1425°C. For the production of glazes of this type maturing at higher temperatures, smelting temperature must be increased or raw additions made to the glaze to increase the maturing temperature. Development of such glazes does not appear warranted in view of the lower cost of raw glazes opacified with mill additions of zircon and/or zirconium-type opacifiers.

4. Miscellaneous Applications for Zircon

Various applications for zircon other than those previously noted have been reported recently which are indicative of the versatility of this product in industry. In the preparation of ceramic stains, Jamieson (1962a, 1962b) has utilized zircon as a component for producing salmon-pink and pink colors in fired glazes. In the preparation of pink stain, cost is materially reduced without impairment of color by substituting zircon for part of the tin oxide used in the stain formulation.
Improvement in the alkali resistance and maturing temperature of a low firing vitreous enamel used for glass decoration is reported by Hoffman (1962) to be attributed to the $\text{ZrO}_2$ in the melted composition. Use of zircon, 2 to 3 percent, in $\text{TiO}_2$ opacified vitreous enamel frit batches as a means of increasing alkali-resistance of the enamel is well known. It is assumed, therefore, that zircon rather than zirconium oxide, in view of cost, is added to supply $\text{ZrO}_2$ in the low firing vitreous enamel described by Hoffman.

The use of zircon in the preparation of a water-soluble zirconium product useful for tanning of leather at low cost is reported by Horrigan (1963). Steps involved are calcining of equimolar amounts of sodium carbonate and zircon to form sodium zirconium silicate. Reaction of one mole of sodium zirconium silicate with 1.5 to 2.2 moles of concentrated sulfuric acid results in the water soluble zirconium product designated as silicated sodium zirconyl sulfate. Reacted product contains water soluble zirconium products equivalent to approximately 24 to 30 percent and about 1 to 5 percent soluble silica.

Preparation of zirconium diboride in a submerged electrode arc furnace using zircon, commercially pure $\text{B}_2\text{O}_3$ as the boron source, and carbon as the reducing agent is described by McMullen and McKee (1965).

II. ZIRCONATES

A. Introduction

The products resulting from the reaction of zirconium oxide with the various inorganic oxides and/or their compounds have been investigated by many researchers and a very comprehensive summary of these investigations has been prepared by Langeron (1963a). Within recent years, investigations on the zirconate compounds have dwelt to a large extent with the alkaline earth zirconates (Ca, Ba, Sr). Little commercial value has resulted in their application as refractory materials in spite of their refractory properties, but as components of electrical ceramic compositions, particularly in the dielectric capacitor type of body, their application has been found to be of definite interest. Review of the literature indicates a growing interest in the properties and applications of the zirconates and these are discussed.

B. Alkali Zirconates

In the investigations on the reaction of zirconia with the alkalis, lithia and soda, no new data have been presented within the past 5–7 years.
ZIRCON AND ZIRCONATES

With lithia, the compounds $\text{Li}_2\text{ZrO}_3$, $\text{Li}_4\text{ZrO}_4$, and $\text{Li}_2\text{Zr}_2\text{O}_5$ are formed. With the reaction of sodium oxide and zirconia, only one compound $\text{Na}_2\text{ZrO}_3$ has been confirmed. The reaction of zirconia with potassium oxide has reportedly been similar to that of sodium oxide in that only one compound, $\text{K}_2\text{ZrO}_3$, is formed. Lehman and Erzberger (1959), however, claim the preparation and identification of the compound $\text{K}_2\text{Zr}_2\text{O}_5$, but according to Tournoux (1964), the compound has the formula $\text{K}_2\text{Zr}_3\text{O}_7$.

C. Alkaline Earth Zirconates

The alkaline earth zirconate compounds designated as $\text{MZrO}_3$ ($\text{M} = \text{Ca, Sr, Ba}$) are commercially prepared by solid state reaction between zirconia and the corresponding alkaline earth carbonate. Magnesium zirconate designated as $\text{MgO} \cdot \text{ZrO}_2$ is a solid solution type of zirconate and commercially is prepared with magnesium oxide.

Synthesis of barium and strontium zirconates and properties of bodies prepared from these products were investigated by Keler and Kuznetsov (1961) in view of the lack of definite information from available data. Differences in the formation rate of strontium zirconate and barium zirconate were shown by differential thermal analyses. With equimolar mixtures of $\text{BaCO}_3\cdot\text{ZrO}_2$, most of the barium zirconate was formed after 15 minutes at 1100°C. With equimolar mixtures of $\text{SrCO}_3\cdot\text{ZrO}_2$, it required 12 hours at 1100°C before equilibrium was attained. X-ray analyses showed that approximately 71 percent $\text{SrZrO}_3$ was formed at 1300°C in 15 minutes, with equilibrium being attained after one hour at that temperature. Bodies prepared from barium and strontium zirconate were reported as being highly porous even though fired at high temperatures, presumably 1500–1600°C. An effective method for lowering the sintering temperature and improving the ceramic properties of fired strontium and barium zirconate resulted from the addition of 5.2 weight percent of $3\text{SrO} \cdot \text{B}_2\text{O}_3$ to strontium zirconate and 5.9 weight percent of $3\text{BaO} \cdot \text{B}_2\text{O}_3$ to barium zirconate.

In view of the refractory characteristics of the alkaline earth zirconates, Tilloca and Perez y Yorba (1964) made a comparative study in the preparation of the zirconates of calcia, baria, and strontia from the point of view of their structure as well as their physico-chemical properties. According to these authors, the compound barium zirconate (cubic structure) is more readily formed than the calcium or strontium zirconate, both having orthorhombic structure. This greater ease in the formation of barium zirconate is attributed to the higher basicity of barium oxide as compared to calcium or strontium oxide.

Strontium zirconate was found to be the most difficult to prepare and unless fusion of the sample resulted, monoclinic zirconia was present as
another phase. In the case of calcium zirconate, they report that there is always a certain quantity of cubic solid solution present which is difficult to eliminate.

Solid solution series in the BaZrO$_3$–SrZrO$_3$ system were also studied by Tilloca and Perez y Yorba (1964) by progressive replacement of the Ba$^{2+}$ ions by Sr$^{2+}$ ions in the compound BaZrO$_3$. A definite series of solid solutions were obtained, the cubic structure of the BaZrO$_3$ changing at 55 mole percent BaZrO$_3$, 45 mole percent SrZrO$_3$ to rhombohedral. At 25 mole percent BaZrO$_3$ and 75 mole percent SrZrO$_3$, the orthorhombic structure begins to appear with traces of monoclinic zirconia. With further increase of the Sr$^{2+}$ ions at the expense of the Ba$^{2+}$ ions the orthorhombic structure identical to that of SrZrO$_3$ resulted.

In their investigations on the SrO·ZrO$_2$ system, Tilloca and Perez y Yorba (1964) reported three new compounds having the general formula Sr$_n$Zr$_{n-1}$O$_{3n-2}$ ($n = 2, 3, 4$), when an excess of SrO, 50–80 mole percent is used. These compounds correspond to the following formulae: Sr$_2$ZrO$_4$, Sr$_3$Zr$_2$O$_7$, and Sr$_4$Zr$_3$O$_{10}$. The compound Sr$_2$ZrO$_4$ is unstable and decomposes at 1350°C to form Sr$_3$Zr$_2$O$_7$ and SrO. Sr$_3$Zr$_2$O$_7$ has been obtained quite pure and is stable in the temperature range of 1330°C to 1650°C, decomposing at and above the latter temperature to form the compound designated as Sr$_4$Zr$_3$O$_{10}$ with SrO present.

In view of the high melting points of the alkaline earth zirconates (SrZrO$_3$ > 2800°C, CaZrO$_2$ – 2320°C, BaZrO$_3$ > 2600°C), consideration has been given to their possible use as refractory materials. The use of calcium zirconate as a refractory coating on graphite crucibles in the preparation of high purity products by fusion technique is reported by Monti (1962). The addition of 15 to 25 weight percent of calcium zirconate to calcium oxide bodies as a means of increasing stability to hydration and improving the mechanical and electrical properties of the body is reported by Margulis et al. (1964). Calcium zirconate or strontium zirconate as insulating bodies for Mo, W, and W–Re thermocouples in a reducing atmosphere of CO/CO$_2$ at temperatures ≤1950°C are recommended by Kamenetski and Gulko (1965). Sibert and Tsukamoto (1965) claim the use of magnesium zirconate or strontium zirconate as coatings on space vehicles whereby the relatively uniform temperature necessary to protect internal components and occupants is achieved.

The properties of strontium zirconate and its utility as a refractory material were investigated by Chang (1963). Test results on bars formed at 10,000 psi and fired in the temperature range of 2000 to 2900°F with one-half hour holding at peak temperature indicated a very critical firing range, with 2700°F firing producing the optimum results relative to such properties as percent absorption, modulus of rupture, density, and fired
shrinkage. An absorption value of 0.8 percent was obtained at 2700°F firing and this value was found to increase to 1.2 percent when firing temperature was raised or lowered 50°F. Thermal expansion value of 9.58 in/in/°C in the temperature range of room temperature to 1200°C was reported. Corrosion tests made with bars of the strontium zirconate suspended in molten glass, acid slag, and basic slag at 2500°F for 6 hours showed a high percentage of loss in area.

The use of magnesium, calcium, barium, and strontium zirconates as thermal sprayed coatings for the aerospace industry was investigated by Wheildon (1967) in comparison with stabilized zirconia. Adherence of the coatings to their substrates was considered comparable, but large differences were noted in the impact and wear abrasion resistance of the coatings with calcium zirconate producing the best results, barium zirconate the poorest, with the others intermediate. Magnesium zirconate coatings showed the highest resistance to thermal shock.

Undoubtedly the greatest application for the alkaline earth zirconates has been in the field of electrical ceramics. In the preparation of ceramic capacitor bodies, the alkaline earth zirconates comprise from approximately 5 to 20 percent of the dielectric composition, the balance being barium titanate. The function of the zirconate addition is to modify the dielectric properties of barium titanate by reducing the sharp rise in the dielectric constant at the Curie temperature (ca 118°C) and shifting same to a temperature range of 25 to 50°C.

Due to the high temperature (1500–1600°C) required to mature dielectric bodies formed from the alkaline earth zirconates, no application has been made of these products as individual components in dielectric ceramics. Because of their wide application as additives to titanate compositions, Stetson and Schwartz (1961) investigated the ceramic and electrical properties of the alkaline and rare earth zirconates as single components. The results of their tests (Table VIII) show that in the temperature range of 1450 to 1500°C, with two hours soak at peak temperature, complete vitrification (zero absorption) was not obtained with calcium, strontium, or barium zirconate. Dielectric constant values at one megacycle are 32.0 for barium zirconate, 26.5 for strontium zirconate, and 24.6 for calcium zirconate. Of the three alkaline earth zirconates, barium shows the highest Q or lowest power factor at −55°C and at +25°C. However, at +85°C barium zirconate shows a slightly lower Q (600 versus 800 to 850) or slightly higher power factor than the calcium or strontium zirconate.

Calcium and strontium zirconate show a positive temperature coefficient of capacity (P76 and P140, respectively) whereas barium zirconate exhibits a negative temperature coefficient of capacity (N = 330). Temperature coefficients of capacity of the blends of barium zirconate and strontium
<table>
<thead>
<tr>
<th>Composition</th>
<th>Firing temp. (°C) and time (hours)</th>
<th>Absorption, %</th>
<th>Specific gravity</th>
<th>Dielectric constant</th>
<th>Q values</th>
<th>Average temp. coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25°C</td>
<td>−55°C</td>
<td>+25°C</td>
</tr>
<tr>
<td>CaZrO₂</td>
<td>1500/2</td>
<td>0.46</td>
<td>4.35</td>
<td>24.6</td>
<td>1470</td>
<td>1250</td>
</tr>
<tr>
<td>SrZrO₂</td>
<td>1450/2</td>
<td>0.13</td>
<td>5.1</td>
<td>26.5</td>
<td>1180</td>
<td>1050</td>
</tr>
<tr>
<td>(0.75Sr, 0.25Ba) ZrO₂</td>
<td>1500/2</td>
<td>0.33</td>
<td>5.20</td>
<td>28.4</td>
<td>2160</td>
<td>1260</td>
</tr>
<tr>
<td>(0.6Sr, 0.4Ba) ZrO₂</td>
<td>1500/2</td>
<td>0.50</td>
<td>5.30</td>
<td>31.0</td>
<td>1430</td>
<td>1820</td>
</tr>
<tr>
<td>(0.4Sr, 0.6Ba) ZrO₂</td>
<td>1500/2</td>
<td>0.00</td>
<td>5.45</td>
<td>33.5</td>
<td>1540</td>
<td>1540</td>
</tr>
<tr>
<td>BaZrO₂</td>
<td>1450/2</td>
<td>0.13</td>
<td>5.34</td>
<td>32.0</td>
<td>2370</td>
<td>1640</td>
</tr>
<tr>
<td>La₂Zr₂O₇</td>
<td>1660/6</td>
<td>0.06</td>
<td>5.64</td>
<td>24.9</td>
<td>435</td>
<td>610</td>
</tr>
<tr>
<td>Nd₂Zr₂O₇</td>
<td>1700/5</td>
<td>0.00</td>
<td>6.34</td>
<td>23.4</td>
<td>97</td>
<td>68</td>
</tr>
<tr>
<td>Sm₂Zr₂O₇</td>
<td>1550/2</td>
<td>0.00</td>
<td>6.37</td>
<td>20.5</td>
<td>290</td>
<td>220</td>
</tr>
</tbody>
</table>

*Measured at 1 mc.  "N = negative, P = positive.*
ZIRCON AND ZIRCONATES

Zirconate should show a decrease in the positive trend as the mole percentage of barium zirconate is increased at the expense of strontium zirconate and this is evident from the data presented.

Thermal expansion data on various zirconate compounds and equimolar zirconate solid solutions of magnesium, bismuth, cerium, and zinc have been determined by Branson (1965) and are presented in Table IX. Data on the thermal expansion of the zirconates have also been reported by Krikorian (1960), but such data as reported are the results of preliminary tests and not complete.

D. Zirconates of Lead, Rare Earths, and Uranium Oxide

In the field of electrical ceramics, many references are to be found concerning lead zirconate and in combination with lead titanate, excellent piezoelectric ceramic materials, designated as LZT, are produced which find

<table>
<thead>
<tr>
<th>Material</th>
<th>Bulk density (gm/cm³)</th>
<th>Coefficient of expansion (cm/cm/°C × 10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZrO₃</td>
<td>6.73</td>
<td>23–214°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>214–324°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>324–700°</td>
</tr>
<tr>
<td>Bi₂O₃-ZrO₃</td>
<td>7.42</td>
<td>23–339°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>339–428°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>428–508°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>508–700°</td>
</tr>
<tr>
<td>CaZrO₃</td>
<td>4.95</td>
<td>23–223°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>223–333°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333–700°</td>
</tr>
<tr>
<td>CdZrO₃</td>
<td>6.38</td>
<td>23–153°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>153–302°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>302–700°</td>
</tr>
<tr>
<td>CeO₂-ZrO₂</td>
<td>6.28</td>
<td>23–181°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>181–700°</td>
</tr>
<tr>
<td>MgO-ZrO₂</td>
<td>4.11</td>
<td>23–260°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260–475°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>475–700°</td>
</tr>
<tr>
<td>PbZrO₃</td>
<td>7.42</td>
<td>Nonlinear expansion to 411°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>411–700°</td>
</tr>
<tr>
<td>SrZrO₃</td>
<td>5.00</td>
<td>23–320°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>320–700°</td>
</tr>
<tr>
<td>ZnO-ZrO₂</td>
<td>4.85</td>
<td>23–225°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>225–340°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>340–700°</td>
</tr>
</tbody>
</table>
many applications in industry. Such uses include ultrasonic cleaners, sonar devices, accelerometers, strain gauges, resonator and filter applications, and spark igniters. Preparation of such bodies is not limited, however, to the use of prereacted lead zirconate and lead titanate, the raw oxides of high purity lead, zirconia, titania plus other additives generally being employed.

Zirconates of the rare earth oxides have received some consideration within recent years relative to fundamental investigations on the formation of same. No commercial applications of these zirconates have been reported, due undoubtedly to the high cost of the rare earth oxides. A very comprehensive report on a study of the zirconia–rare earth oxide systems is presented by Perez y Yorba (1962), and on the basis of this work, equilibrium diagrams for these systems are proposed. Rare earth systems studied include La₂O₃, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃, and Yb₂O₃. In their investigations on the rare earth zirconates, Fan et al. (1964) report the melting points of La₂Zr₂O₇ and Nd₂Zr₂O₇ to be 2000 ± 30°C and 2300 ± 30°C, respectively. Perez y Yorba (1962) reports melting points of 2180°C for La₂Zr₂O₇ and 2280°C for Nd₂Zr₂O₇. Extensive phase studies of the ZrO₂–Ce₂O₃ system were made by Leonov et al. (1966) who report formation of the compound Ce₂Zr₂O₇ and formation of a cubic solid solution (5 to 17 mole percent Ce₂O₃) which is stable at high temperatures. They report that Ce₂Zr₂O₇ when heated in air decomposes into CeO₂ and ZrO₂ forming a solid solution of the fluorite type.

The results of an investigation of the UO₂–ZrO₂ relative to the development of a solid solution diluted fuel for nuclear power is reported by Wright (1965). The procedure for preparing the high density, homogeneous UO₂–ZrO₂ fuel is discussed and properties of the product such as thermal conductivity, thermal expansion, electrical resistivity, hardness, and behavior on thermal cycling are reported. Phase studies of the UO₂–ZrO₂ system studied were in good agreement with previously reported data.

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Hafnium Oxide

C. T. Lynch

1. INTRODUCTION

Hafnium oxide is one of the most stable refractory compounds known with a melting point of 2900°C. Of the oxides, only thorium oxide has a substantially higher melting point. In all chemical properties hafnium compounds are remarkably similar to those of zirconium. The oxides ZrO\textsubscript{2} and HfO\textsubscript{2} are thus expected and found to be nearly identical in chemical behavior. Differences in physical properties are of great significance, however, and increased interest has focused on some of these differences in the last few years. The high neutron absorption capacity of hafnium, for example, makes it attractive as a control rod material for water-cooled reactors. Zirconium on the other hand has such a low specific nuclear cross-section absorption that is a useful cladding material for nuclear fuels. Another such example is the improved oxidation resistance of the hafnium oxide coatings at elevated temperatures because of the higher temperature at which a deleterious phase transformation occurs in hafnium oxide compared with zirconium oxides. Differences such as these have encouraged increased attention to the experimental determination of the properties of hafnium compounds for the last five to ten years. There remain serious gaps in knowledge of behavior, high-temperature properties, and reactions, however, as becomes quite obvious in any review of the literature. Mechanical properties are particularly scarce, and high-temperature properties are often of doubtful validity for “hafnia.” The tendency to equate the properties of hafnia that are unknown with those of zirconia is a practice that should be limited to chemical behavior and generalizations on physical behavior. Two illustrations serve to emphasize this point and will be examined later in more detail. Both zirconia and hafnia undergo monoclinic to tetragonal phase transformations. The transformation range and hysteresis effect on the return transformation is broader, more pronounced, and more sluggish for zirconia than for hafnia. Important differences are observed in the partial
molar free energies and heats of formation apparently from the marked
differences in the solubility of oxygen in α-Zr and α-Hf as discussed by
Schick (1966).

II. OCCURRENCE AND PURIFICATION

Hafnium compounds are always found in nature accompanying zirconium
compounds. The principal commercial sources are baddeleyite (mixed
oxides) and zircon (mixed silicates). These minerals typically contain 1.5 to
3.0 weight percent hafnium referred to zirconium content. Commercial
grade materials contain this hafnium content as an expected and under-
stood impurity. There are some zircon-related minerals which Fleischer
(1955) observed to contain up to 17 weight percent hafnium, which have
not been found in large deposits. If commercial exploitation were possible
for such minerals the production of high purity hafnium would be greatly
enhanced. Current production is entirely dependent on the availability from
zirconium production as a by-product. Hafnium has an estimated natural
abundance according to Mason (1952) of 4.5 ppm in the earth’s crust.
This is the same abundance as reported for dysprosium, slightly greater
than for uranium, and much greater than for boron, mercury, and iodine.

Purification processes have been described by Martin and Pizzolato
(1961) in an article which contains an excellent bibliography on hafnium.
Separation and purification processes are costly and tedious because of the
great chemical similarities between hafnium and zirconium compounds.

Typically, the hydrous oxides or hydroxides of Zr and Hf are converted
to the tetrachlorides, phosphates, or other compounds and separated by
such techniques as ion-exchange, fractional crystallization, or fractional dis-
tillation. Gould (1955) points out that the addition compounds $3\text{ZrCl}_4 \cdot 2\text{POCl}_3$ and $3\text{HfCl}_4 \cdot 2\text{POCl}_3$ have been separated by distillation. The haf-
nium adduct boils at 5°C lower than the zirconium adduct. A convenient
recent separation method uses differential solvent extraction with thenoyl
trifluoracetyl acetone, a fluorinated diketone which is a strong chelating
agent.

Utilizing these fractional or differential methods zirconium compounds
are readily available with low hafnium contents, high purity zirconia usually
containing 0.2 percent or less hafnia. Spectrographic grade zirconia gen-
erally contains about 100 ppm hafnium as found by Fehrenbacher et al.
(1965). Hafnia, on the other hand, nominally contains 2 weight percent
zirconia. Spectrographic grade hafnia, however, contains less than 200 ppm
zirconium as reported by Domagala and Ruh (1965) confirming batch
analyses of commercial vendors. In the absence of confirming analyses it
must be assumed that a commercial “high purity” hafnia powder contains at least 2 weight percent zirconia. Much work on hafnia has been undertaken without such confirming analyses of zirconia content. Such analyses are difficult and time-consuming and are generally not undertaken by the investigators. Consequently most experimental work in the literature should be repeated or corrected utilizing the high purity powders of zirconia and hafnia that are obtainable today.

III. LANTHANIDE CONTRACTION

The inner transition (rare earth) elements immediately preceding hafnium in the periodic table add electrons to the inner 4f shell from \( ^{58}\text{Ce} \) through \( ^{71}\text{Lu} \). Since no outer electrons have been added to compensate for the increased nuclear charge there is a contraction in atomic size such that element 72, hafnium, is slightly smaller than element 40, zirconium, the preceding period Group IV transition element. This is the lanthanide contraction described in detail by Moeller (1952). Using the atomic radii of Pauling (1960), the effect of this contraction is shown in Table I. From Ce through Lu the atomic size decreases from 1.646 to 1.557 Å. The outer electron shells are [Kr] \( 4d^2 \text{5}s^2 \) for Zr and [Xe] \( 4f^{14} \text{5d}^2 \text{6s}^2 \) for Hf. Only the outer four electrons enter into the chemistry of these elements. Under ordinary conditions only \( \text{M}^{4+} \) ions and their derivations such as \( \text{M}^2+ \) and \( \text{MX}_2^- \) are stable. Ahrens (1952) gives the \( \text{M}^{4+} \) crystal radii as 0.79 Å for Zr and 0.78 Å for Hf. The electronegativity values given by Little and Jones (1960) are 1.22 for Zr and 1.23 for Hf. These values are indicative of the almost identical chemistry exhibited by these elements. Until the discovery of hafnium in 1923, the determinations of atomic weight of zirconium were generally too high due to the unrecognized presence of hafnium.

IV. PHYSICAL PROPERTIES

A. Tabular Values

Physical properties for hafnia have been given in Table II. In several instances earlier values such as the transformation temperature for mono-

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
<th>Mo</th>
<th>La</th>
<th>Hf</th>
<th>Ta</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.439</td>
<td>1.324</td>
<td>1.224</td>
<td>1.176</td>
<td>1.616</td>
<td>1.454</td>
<td>1.342</td>
<td>1.296</td>
<td>1.690</td>
<td>1.442</td>
<td>1.343</td>
<td>1.304</td>
</tr>
</tbody>
</table>

TABLE I

ATOMIC RADIUS AND LANTHANIDE CONTRACTION (IN Å)
### TABLE II

**PHYSICAL PROPERTIES OF HAFNIA**

<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, HfO₂</td>
<td>210.49</td>
<td>Curtis <em>et al.</em> (1954)</td>
</tr>
<tr>
<td>Melting point</td>
<td>2900°C ±25°C</td>
<td>Thomas and Hayes (1960)</td>
</tr>
<tr>
<td>Boiling point</td>
<td>&gt; 4427°C</td>
<td>Bondarenko and Tsarev (1959)</td>
</tr>
<tr>
<td></td>
<td>5400°C</td>
<td>Thomas and Hayes (1960)</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>3 × 10⁻⁸ atm at 2667°C</td>
<td>Ackermann and Thorn (1961)</td>
</tr>
<tr>
<td>Density</td>
<td>9.68 gm/cm³, monoclinic</td>
<td>Curtis <em>et al.</em> (1954)</td>
</tr>
<tr>
<td></td>
<td>10.01 gm/cm³, tetragonal</td>
<td>Curtis <em>et al.</em> (1954)</td>
</tr>
<tr>
<td></td>
<td>10.3 gm/cm³, tetragonal</td>
<td>Sardi (1967)</td>
</tr>
<tr>
<td>Lattice dimensions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>a = 5.1156 Å</td>
<td>Adam and Rogers (1959)</td>
</tr>
<tr>
<td></td>
<td>b = 5.1722 Å</td>
<td>Adam and Rogers (1959)</td>
</tr>
<tr>
<td></td>
<td>c = 5.2948 Å</td>
<td>Adam and Rogers (1959)</td>
</tr>
<tr>
<td></td>
<td>β = 99°11'</td>
<td>Adam and Rogers (1959)</td>
</tr>
<tr>
<td>Molecular volume</td>
<td>138 Å³</td>
<td>Sardi (1967)</td>
</tr>
<tr>
<td>Seven nearest neighbors</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.05–2.30 Å Hf–O distance</td>
<td>Sardi (1967)</td>
</tr>
<tr>
<td>Tetragonal phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>a = 5.14 Å</td>
<td>Curtis <em>et al.</em> (1954)</td>
</tr>
<tr>
<td></td>
<td>c = 5.25 Å</td>
<td>Curtis <em>et al.</em> (1954)</td>
</tr>
<tr>
<td>Cubic phase</td>
<td>No Data Available</td>
<td></td>
</tr>
<tr>
<td>Transformation temperatures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic-tetragonal, x-ray</td>
<td>1620–1650°C</td>
<td>Ruh <em>et al.</em> (1968)</td>
</tr>
<tr>
<td>Monoclinic-tetragonal, DTA</td>
<td>1725–1775°C</td>
<td>Ruh <em>et al.</em> (1968)</td>
</tr>
<tr>
<td>Monoclinic-tetragonal, thermal exp.</td>
<td>1650–1750°C</td>
<td>Ohnysty and Rose (1964)</td>
</tr>
<tr>
<td>Monoclinic-tetragonal, x-ray</td>
<td>1500–1600°C</td>
<td>Baun (1963)</td>
</tr>
<tr>
<td>Tetragonal-monoclinic, x-ray</td>
<td>1620–1520°C</td>
<td>Ruh <em>et al.</em> (1968)</td>
</tr>
<tr>
<td>Tetragonal-monoclinic, DTA</td>
<td>1700–1650°C</td>
<td>Ruh <em>et al.</em> (1968)</td>
</tr>
<tr>
<td>Tetragonal-monoclinic, x-ray</td>
<td>1550–1450°C</td>
<td>Baun (1963)</td>
</tr>
<tr>
<td>Tetragonal-cubic, x-ray</td>
<td>~ 2700°C</td>
<td>Boganov <em>et al.</em> (1965)</td>
</tr>
</tbody>
</table>
HAFNIUM OXIDE

Clinic to tetragonal hafnia reported by Curtis et al. (1954) have been omitted in favor of later values. What is felt are the most precise crystal structure measurements have been given. Actually the agreement is reasonably good between the tabulated values and those reported by Ruh et al. (1968) \([a = 5.119, b = 5.169, c = 5.290; \beta = 99^\circ25']\). The differential thermal analysis data (DTA) of Ruh et al. were extrapolated to the 100 percent \(\text{HfO}_2\) composition for the monoclinic-tetragonal transition. The transition temperature was likewise estimated from the linear thermal expansion curve discontinuity of Ohnysty and Rose (1964).

B. Crystal Structure

Sardi (1967) has reviewed crystal structure information on hafnia and commented on the lack of data available and discrepancies regarding interatomic distances and bond angles. Adam and Rogers (1959) have shown the marked similarity in crystal structure for monoclinic zirconia and hafnia, however, and the classic study of monoclinic zirconia by McCullough and Trueblood (1959) serves as a guide to explain the hafnia structure. The Zr-O system was found to have a sevenfold coordination with bond distances varying from 2.04 to 2.26 Å. The next nearest neighbor was at 3.77 Å, clearly indicating a distorted fluorite lattice with CN of seven. A simple idealized picture was given in which four oxygen ions are at the base of a derived cube with one oxygen at an upper corner and the other two at the mid-points of the cubic edges adjacent to the unoccupied corners. The zirconium atom is at the center of the cube. Zirconium and hafnium form \(\text{MO}_2\) structures which are intermediate to those in common rutile and fluorite structures as seen in Table III. Failure to fulfill the Pauling criteria for the ratio of cation to anion radii \((r_c/r_a)\) to exceed 0.73

<table>
<thead>
<tr>
<th>Compound</th>
<th>(r_c/r_a)</th>
<th>Structure</th>
<th>Coord. No.</th>
<th>(r_c + r_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF(_2)</td>
<td>0.47</td>
<td>Rutile</td>
<td>6</td>
<td>2.02</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.49</td>
<td>Rutile</td>
<td>6</td>
<td>1.96</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>0.51</td>
<td>Rutile</td>
<td>6</td>
<td>2.06</td>
</tr>
<tr>
<td>PbO(_2)</td>
<td>0.60</td>
<td>Rutile</td>
<td>6</td>
<td>2.16</td>
</tr>
<tr>
<td>HfO(_2)</td>
<td>0.55(_1)</td>
<td>Distorted Fluorite</td>
<td>7</td>
<td>2.18</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>0.56(_1)</td>
<td>Distorted Fluorite</td>
<td>7</td>
<td>2.17</td>
</tr>
<tr>
<td>CeO(_2)</td>
<td>0.67</td>
<td>Fluorite</td>
<td>8</td>
<td>2.34</td>
</tr>
<tr>
<td>UO(_2)</td>
<td>0.69</td>
<td>Fluorite</td>
<td>8</td>
<td>2.37</td>
</tr>
<tr>
<td>CaF(_2)</td>
<td>0.71</td>
<td>Fluorite</td>
<td>8</td>
<td>2.35</td>
</tr>
</tbody>
</table>
leads to a distorted fluorite lattice for zirconia and hafnia. Pauling (1960) reported that only ZrO$_2$ and CeO$_2$ failed to meet the criteria for forming rutile structures from substances of the unsymmetrical valence type for $r_c/r_a < 0.73$ and for fluorite structures where $r_c/r_a > 0.73$. In Table III the values of Ahrens (1952) have been employed which changes the $r_c/r_a$ ratio slightly. In giving a radius sum, $r_c + r_a$, the value of 1.40 Å is assumed for the O$^{2-}$ atom when not significantly polarized. The shrinkage reported for Ahrens (1952) for Ti–O, Pb–O, and Sn–O, has been included, reducing the respective $r_c + r_a$ values by 0.12, 0.08, and 0.05 Å. PbO$_2$ becomes a borderline case with HfO$_2$ and ZrO$_2$ with an almost identical radius sum and a smaller radius ratio. The difference in crystal structure might be postulated as due to the increased covalent character of the Pb$^{4+}$ ions with a completed 18 outer electron shell as discussed by Moeller (1952) as a polarizability factor.

C. Stabilization Parameters

The stabilization of cubic zirconia through solid solution formation with additive oxides has been investigated by Fehrenbacher et al. (1965). The importance of parameters of radius ratio and electronegativity and related factors of compressibility and bond polarization, ionic bond character, and valence were determined. Since zirconia and hafnia are so similar in size and electronegativity the results are equally applicable to hafnia. The closest packing of cations with wide latitude for anion vacancies is required for the stable fluorite (cubic) structure with a coordination number of 8. The presence of anion vacancies favors a close packed structure. Closest packing in the fluorite phase is more likely to take place with atoms somewhat larger than Zr and Hf, but close enough in size to allow free solid solution substitution. Therefore two general criteria for the formation of hafnia fluorite solid solutions are the ability of the additive oxide cation to enter into the crystal lattice and to increase the ionic character of metal-oxygen bonds. As discussed by Fehrenbacher et al. (1965) the practical requirements of stabilizing additives can be reduced to larger cation radius, more electropositive cations, larger electronic core, cation valence less than four.

The rare earth oxides and yttrium satisfy these parametric considerations. They constitute the most promising stabilizing additives and make possible the stabilization of cubic zirconia at extremely low temperatures as found by Mazdiyasni et al. (1967).

The ability of rare earth oxides to produce stable fluorite zirconia and hafnia increases with ionic size. In Table IV the comparison of size and electronegativity relationships shows the values for Y, Dy, and Yb which are almost identical. These three additives as oxides have been demonstrated by Fehrenbacher et al. (1965) and Mazdiyasni and Lynch (1965)
HAFNIUM OXIDE

TABLE IV
SIZE AND ELECTRONEGATIVITY COMPARISONS OF ZIRCONIA, HAFNIA, AND STABILIZING OXIDES

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cation r, Å</th>
<th>(\chi)</th>
<th>Electronic Structure</th>
<th>(\Delta r)</th>
<th>(\Delta \chi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO(_2)</td>
<td>0.79</td>
<td>1.22</td>
<td>[Kr] 4d(^5) 5s(^2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HfO(_2)</td>
<td>0.78</td>
<td>1.23</td>
<td>[Xe] 4f(^{14}) 5d(^6) 6s(^2)</td>
<td>—0.01</td>
<td>—0.01</td>
</tr>
<tr>
<td>LaO(_3)</td>
<td>1.14</td>
<td>1.08</td>
<td>[Xe] 5d(^6) 6s(^2)</td>
<td>+0.35</td>
<td>+0.14</td>
</tr>
<tr>
<td>CeO(_3)</td>
<td>1.07</td>
<td>1.08</td>
<td>[Xe] 4f(^2) 5d(^6) 6s(^2)</td>
<td>+0.28</td>
<td>+0.14</td>
</tr>
<tr>
<td>NdO(_3)</td>
<td>1.04</td>
<td>1.07</td>
<td>[Xe] 4f(^{14}) 5d(^6) 6s(^2)</td>
<td>+0.25</td>
<td>+0.15</td>
</tr>
<tr>
<td>DyO(_3)</td>
<td>0.92</td>
<td>1.10</td>
<td>[Xe] 4f(^{14}) 5d(^6) 6s(^2)</td>
<td>+0.13</td>
<td>+0.12</td>
</tr>
<tr>
<td>YbO(_3)</td>
<td>0.86</td>
<td>1.06</td>
<td>[Xe] 4f(^{14}) 5d(^6) 6s(^2)</td>
<td>+0.07</td>
<td>+0.16</td>
</tr>
<tr>
<td>Y(_2)O(_3)</td>
<td>0.96</td>
<td>1.11</td>
<td>[Kr] 4d(^2) 5s(^2)</td>
<td>+0.17</td>
<td>+0.11</td>
</tr>
</tbody>
</table>

\(^*\) Cation \(r\) from Ahrens (1952). \(\chi\) values from Little and Jones (1960) except for Y and La from Allred and Rochow (1958).

The properties of hafnia received little study until modern separation techniques produced zirconia and hafnia practically free from contamination by each other. The classical determination of properties of refractory...
hafnium compounds was by Curtis et al. (1954). The zirconia available to them at Oak Ridge National Laboratory contained 80 ppm hafnium and the hafnia contained an unheard-of (at that time) 2 ppm zirconium. Curtis et al. (1954) demonstrated that despite the large differences in molecular weight and density, the polymorphic behavior of hafnia appeared to be quite similar to that of zirconia. Reactions of hafnia with silica, calcia, and carbon were investigated and found similar to those of zirconia. Solid solution formation between zirconia and hafnia was observed. Definitive studies of phase equilibria in the Hf–O system were completed only in the past few years by Domagala and Ruh (1965) and Rudy and Stecher (1963). The zirconia-hafnia system was thoroughly investigated by Ruh et al. (1968).

B. The Hf–O System

The phase diagram by Domagala and Ruh is shown in part in Fig. 1 with appropriate notations for differences with the results of Rudy and Stecher. It is beyond the purposes of this article to examine critically the differences in the phase equilibria found in the 15 atomic percent oxygen region of the

![Phase diagram of Hf–O system](image)

**FIGURE 1** The hafnium-oxygen system (after Domagala and Ruh, 1965). Significant differences of Rudy and Stecher (1963) noted by ———.
Hf–O system. They are significant, however, and should be examined by further work. Equilibrium conditions at these temperatures are most difficult to obtain and contamination is particularly critical. Neither study has carried out the extensive postexperiment analytical work required to prove composition. The homogeneity range is seen to narrow at higher temperatures, approaching a line compound at the melting point. The homogeneity range determined by Domagala and Ruh is extremely narrow (no more than 2 percent) while that of Rudy and Stecher is possibly 4 percent. They found evidence that at 62 atomic percent oxygen the homogeneity range was nearly reached, contrasting with distinct evidence of the alpha phase present at 65.4 atomic percent O by Domagala and Ruh. Excellent agreement was found for lattice parameters with a gradual increase up to 20 atomic percent O and then a leveling off to indicate no intermediate compound formation. No evidence for HfO in the solid phase has been found.

C. Hafnia Transitions

Curtis et al. (1954) placed the monoclinic-tetragonal transition of hafnia at above 1700°C. The hysteresis which accompanies the zirconia transition was also observed for hafnia. It was noted by Baun (1963), however, that the transformation of HfO₂ occurred from approximately 1500 to 1600°C and the reverse transformation at 1550 to 1450°C. This is a compressed transformation curve for hafnia compared to zirconia, at approximately 400°C higher temperature for the monoclinic to tetragonal transformation. The hysteresis effect is more pronounced with zirconia and the reverse transformation thus occurs at an approximately 600°C lower temperature. Ruh et al. (1968) have obtained data by high temperature x-ray and differential thermal analysis on the entire range of zirconia-hafnia solid solutions, confirming Baun’s observation of a narrower transformation range for hafnia. Data on these transformations are summarized in Table II. Wolten (1963) and Fehrenbacher and Jacobson (1965) have established the diffusionless, athermal character of the monoclinic-tetragonal transformation in zirconia. Adam and Rogers (1959) have shown the strikingly similar monoclinic lattice parameters of hafnia and zirconia. It is quite probable that the hafnia transformation occurs by the same diffusionless mechanism found for zirconia.

Williams (1968) considers the substantial difference in transformation temperatures between monoclinic and tetragonal zirconia and hafnia as quite reasonable since hafnia has a higher lattice energy based on the attractive energy of additional electron shells for hafnium and the smaller monoclinic cell structure. The density change of 3.4 percent for hafnia compared to 7.5 percent for zirconia, and the lower expansion rate of the more stable
monoclinic hafnia should thus be expected. The practical consequences of this in fabrication and utilization of unstabilized hafnia as opposed to zirconia have not been significantly explored. The higher cost and limited availability of hafnia have apparently precluded taking advantage of its attractive refractory characteristics.

The existence of cubic \( \text{ZrO}_2 \) has been reported by Smith and Kline (1962) with a transformation from tetragonal to cubic of approximately 2300°C. High-temperature x-ray measurements are tenuous in this range and contamination is a continual problem. Ruh and Garrett (1967) have assumed 2285°C to be the reasonable value for this transformation. There is at least one report by Boganov et al. (1965), confirming the existence of cubic hafnia with a tetragonal-cubic transformation at 2700°C. One difficulty Baun (1963) points out is that oxygen deficiency and metal heater contamination occur readily in high-temperature x-ray cameras and seriously influence results.

There can be little doubt that zirconia-hafnia system shows complete solid state miscibility. Ruh et al. have found evidence of this in melting point, x-ray lattice parameter, DTA, and metallographic examination of a complete series of bracketing solid solutions. This confirms earlier x-ray work by Curtis et al. (1954) and later thermal expansion measurements by Stansfield (1965).

Based on these investigations of the Hf–O and Zr–O systems and the work of Ruh and Garrett (1967), particularly, comparisons can be made for the phase stability of the metal-oxide systems as in Fig. 2. The effect of nonstoichiometry, lowering the tetragonal to cubic transformation temperature, is seen to be pronounced for the slightly oxygen-deficient zirconia system. On this basis one might predict the same behavior for hafnia but at much higher temperatures. At elevated temperatures nonstoichiometric oxides were found to be stable by Ruh and Garrett (1967). Stability aspects of this nonstoichiometry (oxygen-deficiency) have been considered by Barker and Williams (1968).

VI. THERMODYNAMIC PROPERTIES

A recent review of the thermodynamic properties of hafnium oxides: \( \text{HfO}_2 \), \( \text{HfO}_2 \), and \( \text{HfO}_2 \) is found in the volume edited by Schick (1966). Because of experimental difficulties in high-temperature measurements much of the available thermodynamic data must be considered preliminary and unprecise. Huber and Holley (1962) point out the need for further confirmation of the heat of formation of \( \text{HfO}_2 \). The value of
HAFNIUM OXIDE

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>M=Hf</th>
<th>M=Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE 2** Some comparisons in the M–O systems for Zr and Hf.

Humphrey (1953) is thus accepted tentatively as $-266.06 \pm 4$ kcal/mole for $\Delta H_f^\circ$ at 298.15 K. The classical value quoted in earlier literature is that of Roth and Becker (1932), given as $-271.0 \pm 5$ kcal/mole.

The partial molar free energies of the hafnium-oxygen system are more positive than in the zirconium-oxygen system. Schick (1966) notes that this seems to be unexpected since the heat of formation and free energy of formation values of $\text{ZrO}_2$ are more positive than for $\text{HfO}_2$. Komarek and Silver (1962) and Silver et al. (1963) have accounted for this discrepancy as the resultant of differing solubilities of oxygen in hafnium and zirconium. These values are 30 percent for $\alpha$-Zr and 20 percent for $\alpha$-Hf.

The melting point generally accepted for pure $\text{HfO}_2$ is 2900 ± 25°C first reported by Curtis et al. (1954). This is the value given by Thomas and...
Hayes (1960) in their review on hafnium and subsequently employed in the definitive studies of Rudy and Stecher (1963) and Domagala and Ruh (1965). The melting points in the zirconia-hafnia series as determined by Ruh et al. (1968) are shown in Fig. 3. Lower melting points in the earlier literature can be ascribed in part to impurity effects. Vaporization studies of HfO$_2$ have been conducted by Ackermann and Thorn (1961), Panish and Reif (1963), and Shchukarev and Semenov (1962). The primary species involved in vaporization is HfO. The boiling point of HfO$_2$ has been given as greater than 4427°C by Bondarenko and Tsarev (1959). Thomas and Hayes (1960) quote a value based on earlier work of 5400°C. Clearly, additional data are needed. The vapor pressure of HfO$_2$ at 2667°C is given as $3 \times 10^{-5}$ atm by Ackermann and Thorn. They have reported it as the least volatile of all the oxides although its melting point is several hundred degrees below that of thorium IV oxide.

HfO$_2$ loses oxygen at relatively low temperatures to form an oxygen-deficient compound of the type HfO$_{x-\chi}$. The $x$ is variable with experimental conditions and influences the electrical conductivity as studied by Kofstad and Ruzicka (1963) at 784 to 1297°C.

Values of some thermodynamic functions for HfO$_2$ are listed in Table V. A number of these data are obtained by estimates and data interpretations that are adequately described by Schick. There are important limitations such as those caused by using the analogous case for the zirconia monoclinic-tetragonal phase transformation as done by Kelley (1960) and Brewer.

FIGURE 3 Melting points in HfO$_2$-ZrO$_2$ system.

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<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Capacity</td>
<td>$C_p^\circ$</td>
<td>14.40 cal/°K mole</td>
<td>Todd (1953)</td>
</tr>
<tr>
<td></td>
<td>$S^\circ$</td>
<td>14.188 cal/°K mole</td>
<td>Todd (1953)</td>
</tr>
<tr>
<td></td>
<td>$C_p^\circ$</td>
<td>$-0.3093 \times 10^{-3} T + 17.2346 + 2.1628 \times 10^{-3} T$</td>
<td>Schick (1966)</td>
</tr>
<tr>
<td></td>
<td>$\lambda$</td>
<td>2.5 kcal/mole</td>
<td>Schick (1966)</td>
</tr>
<tr>
<td></td>
<td>$C_p^\circ$</td>
<td>26.0 cal/°K mole</td>
<td>Pears (1963)</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_f^\circ$</td>
<td>$-266.06 \pm 4$ kcal/mole</td>
<td>Humphrey (1953)</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_f^g$</td>
<td>$-70.0 \pm 15$ kcal/mole</td>
<td>Schick (1966)</td>
</tr>
</tbody>
</table>
(1953) to calculate the heat transition for hafnia. Schick uses 1700°C for the phase transformation, which is an outdated value, and thus introduces a determinant error in the results. Low temperature heat capacity data for HfO₂ were determined by Todd (1953) from 52 to 298.15°K. Orr (1953) determined the high temperature heat content data for HfO₂ in the range of 298 to 1804°K. Pears (1963) has reported heat content data over a wide temperature range from 650 to 2888°K. These data have been treated by Schick (1966) and show a wide scatter through the transition range. They are, however, the only data in that range and can be used to estimate the heat of transition of 3 kcal/mole. A better value considering the analogous zirconia transformation studied by Kelley and Brewer appears to be 2.5 kcal/mole.

No experimental determinations of the structure and spectroscopic constants for the HfO₂ molecule have been made. Thermodynamic functions are, therefore, entirely based on estimated parameters. Brewer and Rosenblatt (1961) calculated free energy functions for HfO₂ assuming a linear molecule with an Hf-O bond distance of 1.74 Å and a vibrational frequency for HfO of 895 cm⁻¹. Their estimate of the dissociation energy for HfO₂ (g) is 360 ± 20 kcal/mole. This leads to an estimated heat of formation value of ΔHᵋ° 298.15°K = −95.962 kcal/mole. From the data of Ackermann and Thorn (1961), Schick (1966) calculates ΔHᵋ° 298.15°K = −67.774 kcal/mole. Shchukarev and Semenov (1962) observed an HfO₂⁺ ion intensity of less than 0.01 of HfO⁺ in a mass spectrometer. From this data and the reaction

\[ \text{HfO}_2(s) \rightarrow \text{HfO(g)} + \text{O(g)} \]  

Schick and his co-workers have calculated a heat of formation of ΔHᵋ° 298.15°K = −66.412 kcal/mole. This is in excellent agreement with the results derived from Ackermann and Thorn, indicating the values are reasonable. Schick then gives a “rounded” value of ΔHᵋ° 298.15°K = −70.0 ± 15 kcal/mole for HfO₂ (g).

VII. ENGINEERING PROPERTIES

Recent compilations of engineering properties of refractory materials such as those of Smiley et al. (1960) and Lynch et al. (1966) indicate the paucity of data on the thermophysical properties of hafnia and an almost total lack of data on mechanical properties. Future utilization of hafnia and its potential for various applications cannot be determined without a concerted increase in investigations of its properties.
The specific heat of hafnia has been plotted from the heat capacity data of Orr (1953) by Lynch et al. (1966). Values of 0.1 to 0.12 Btu lb$^{-1}$ °F$^{-1}$ from 1000 to 2900°F were obtained, somewhat lower than the values of 0.15 to 0.16 for zirconia. Lynch et al. report the thermal conductivity of hafnia at 1.5 Btu hr$^{-1}$ ft$^{-2}$ °F$^{-1}$ from 2000 to 3450°F. This is about the same as the values of Kingery et al. (1954) for zirconia.

The linear thermal expansion of hafnia is shown in Fig. 4. The data were obtained for yttria-stabilized and unstabilized hafnia to 4000°F by Ohnysty and Rose (1964) using a telemicroscope method and by Fulkerson (1960) on unstabilized hafnia to 2415°F using a dilatometer method.

Much can be learned about the polymorphism of hafnia and its similarity to zirconia from these thermal expansion measurements. The unstabilized hafnia shows the familiar transformation to the more dense tetragonal phase at approximately 1650-1750°C. The yttria-stabilized hafnia shows a similar (and slightly lower) coefficient of thermal expansion compared to yttria-stabilized and dysprosia-stabilized zirconia as found by Mazdiyasni et al. (1966) and Fehrenbacher et al. (1965), for fully cubic-stabilized zirconia. For both zirconia and hafnia the rare-earths and yttria afford complete stabilization and a higher thermal expansion coefficient is found for the cubic phase. No discontinuity is found in the thermal expansion curve for stabilized hafnia since no monoclinic phase remains in the stabilized material.

Room temperature bend strengths of yttria-stabilized hafnia ceramics of high porosity have been reported between 70 and 370 psi by Lange and

![FIGURE 4 Linear thermal expansion curves for hafnia.](https://www.Iran-mavad.com)
Ohnysty (1965), varying with heat treatments given to the specimens. Lynch et al. (1966) reported no data on compressive strength, tensile strength, Young’s modulus, shear modulus, Poisson’s ratio, creep, or hardness of hafnia. Hardness data have been obtained, however, by Rudy and Stecher (1963) and Domagala and Ruh (1965) in their studies of the Hf–O system. Hardness increased to 650 to 750 kg/mm$^2$ at 20 atomic percent oxygen and then leveled off until rising to the hafnia value of 1100 kg/mm$^2$ reported by Domagala and Ruh.

VIII. INFRARED SPECTRA

The infrared spectra of metal oxides have recently been studied by McDevitt and Baun (1964) [see also Baun and McDevitt, 1963]. They studied oxides of 52 metals including zirconia, hafnia, and the rare earth oxides. As with most oxides, no absorption bands were found for zirconia and hafnia in the rock salt region from 4000 to 800 cm$^{-1}$. In the medium infrared region from 800 to 300 cm$^{-1}$, using a prism-grating double beam spectrophotometer characteristic absorption spectra were found. Low frequency infrared spectra from 350 to 50 cm$^{-1}$ were also obtained on a far infrared grating-grating instrument. The spectra from 800 to 300 cm$^{-1}$ are shown in Fig. 5 and for 350 to 50 cm$^{-1}$ in Fig. 6. Characteristic absorptions for monoclinic zirconia and hafnia are listed in Table VI. Although the spectra of zirconia and hafnia are qualitatively similar, differences in band position and shape make differentiation between zirconia and hafnia quite simple. In the cubic phase, however, the band is so broad in both cases to place doubt on the use of infrared spectra to differentiate between the two oxides. The band maximum for cubic zirconia is at 490 cm$^{-1}$ and for cubic hafnia at 460 cm$^{-1}$, but it is a very flat maximum. Probably for this reason the type stabilizing agent makes little difference in the cubic spectrum for zirconia and hafnia.

The key to obtaining this type of spectrum as pointed out by McDevitt and Baun (1964) was to grind the powder without contaminating it to a 5 to 10 μm maximum size range. The concentration of oxide in a KBr pellet was generally 0.6 percent which was lower than the concentration used for organic compounds, to reduce the scatter from the solid particles. In the low frequency region two peaks were found for monoclinic zirconia at 270 cm$^{-1}$ and 230 cm$^{-1}$. The 270 cm$^{-1}$ peak was quite asymmetric and in hafnia, the spectrum had peaks at 230 cm$^{-1}$ and 250 cm$^{-1}$ with a pronounced shoulder at 260 cm$^{-1}$. Again the results are qualitatively similar but have
FIGURE 5 Infrared absorption spectra.

- Monoclinic HfO$_2$ (KBr pellet)
- Cubic HfO$_2$ (CaO stabilized) in Nujol mull

* Nujol absorption

TABLE VI
INFRARED FREQUENCIES OF ZIRCONIA AND HAFNIA
(MONOCLINIC PHASE)

<table>
<thead>
<tr>
<th>ZrO$_2$ (cm$^{-1}$)</th>
<th>HfO$_2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>745</td>
<td>755</td>
</tr>
<tr>
<td>620 s</td>
<td>645</td>
</tr>
<tr>
<td>530</td>
<td>530</td>
</tr>
<tr>
<td>450</td>
<td>450 s</td>
</tr>
<tr>
<td>420</td>
<td>425</td>
</tr>
<tr>
<td>375</td>
<td>375</td>
</tr>
<tr>
<td>360</td>
<td>350</td>
</tr>
<tr>
<td>264</td>
<td>262 s</td>
</tr>
<tr>
<td></td>
<td>251</td>
</tr>
<tr>
<td>225</td>
<td>229</td>
</tr>
</tbody>
</table>

s = shoulder
differentiating characteristics. The cubic zirconia and hafnia gave no peaks in the 300 to 50 cm\(^{-1}\) region.

The marked difference in infrared spectra for the monoclinic and cubic phases has been employed by Mazdiyasni et al. (1967) to follow the stabilization of the oxides with yttrium and rare earth oxides. In laboratories which do not possess x-ray facilities, but have a high quality infrared spectrophotometer, the routine use of this method to determine phase stabilization should be given consideration. It is rapid, simple, and inexpensive.

**IX. PREPARATION OF HIGH-PURITY HAFNIA**

**A. Alkoxy Method**

Vapor phase decomposition of metal alkoxides has been employed by Mazdiyasni et al. (1965) to obtain ultra-high-purity submicron refractory oxides, including zirconia and hafnia. In the method employed the alkoxide was vaporized in the round bottom flask and carried by a dry inert gas stream into the decomposition chamber where a preheated (platinum induc-
tion furnace heater) inert gas impinged on the alkoxide vapor providing substrateless in situ vapor phase decomposition of the alkoxide to the oxide. The fine particulate powder was collected with the assistance of an electrostatic precipitator. A representative reaction is the decomposition of hafnium tetra-tertiary butoxide to hafnium oxide. Vaporization of the alkoxide was done at 190–210°C at 760 mm Hg and decomposition at 325–500°C:

$$\text{Hf (OC}_3\text{H}_7\text{)}_4 \xrightarrow{\Delta} \text{HfO}_2 + 2\text{C}_4\text{H}_9\text{OH} + 2\text{C}_4\text{H}_8$$

(2)

The particle size of this powder was determined from an alcohol dispersion of the powder sprayed onto a carbon substrate on a copper mesh screen and viewed in an electron microscope. The average particle size was found to be 30–50 Å with evidence that the larger particles were agglomerates of individual particles of 20 Å or less. Particle size range was generally <20 Å to 200 Å with only an occasional large agglomerate particle of 0.1 to 0.5 micron (1000 to 5000 Å). The purity obtained was >99.95 percent on a continuous basis. The decomposition is completed without degradation of the alkyl group which would cause carbon contamination.

The simultaneous decomposition of two or more selected metal-organic compounds has been employed by Mazdiyasni et al. (1967) to prepare ultra-high purity submicron mixed phase particulate materials. Polycrystalline refractory bodies of high density, with fine grained, low porosity microstructures have been made from powders prepared by the simultaneous decomposition of the alkoxides. The process can be done either by hydrolytic or vapor phase methods as indicated in the following equations:

(a) hydrolytic

$$2\text{Y (OC}_3\text{H}_7\text{)}_3 + 3\text{H}_2\text{O} \rightarrow \text{Y}_2\text{O}_3 + 6\text{C}_3\text{H}_7\text{OH}$$

(3)

$$\text{Hf (OC}_3\text{H}_7\text{)}_4 + 2\text{H}_2\text{O} \rightarrow \text{HfO}_2 + 4\text{C}_3\text{H}_7\text{OH}$$

(4)

(b) thermal

$$2\text{Y (OC}_7\text{H}_{15}\text{)}_3 \rightarrow \text{Y}_2\text{O}_3 + 3\text{C}_7\text{H}_{15}\text{OH} + 3\text{Olefin}$$

(5)

$$\text{Hf (OC}_4\text{H}_9\text{)}_4 \rightarrow \text{HfO}_2 + 2\text{C}_4\text{H}_9\text{OH} + 2\text{Olefin}$$

(6)

The difference in volatilities of Hf and Y alkoxides (see Mazdiyasni et al., 1966) makes the solution decomposition preferable for the preparation of a mixed oxide such as yttria-stabilized hafnia. The precipitation is quantitative and yields a high purity powder of approximately 100–200 Å particle size.

Other organic groups may be substituted for the isoproxy (C₃H₇O−) group, and the double decomposition reaction is general for a wide variety of complex oxides. For example titanates such as BaTiO₃ and HfTiO₄.
have been prepared by Mazdiyasni et al. (1967) at >99.9 percent purity in 100–500 Å particle-size range in this manner:

$$\text{Hf} (\text{OR})_4 + \text{Ti} (\text{OR})_4 + 4\text{H}_2\text{O} \rightarrow \text{HfTiO}_4 + 8\text{ROH} \quad (7)$$

where R is an alkyl or substituted alkyl group, and the reaction is carried out in a CO$_2$-free atmosphere. The oxide product is dried and then calcined at 650–750°C in an inert atmosphere. It is in the titanate form as-calcined.

Vapor phase decomposition has been extended to prepare hafnium titanate from hafnium tetra-tertiary butoxide and titanium isopropoxide:

$$\text{Ti} (\text{OR})_4 \rightarrow \text{TiO}_2 + 2\text{ROH} + 2 \text{Olefin} \quad (8)$$

$$\text{Hf} (\text{OR})_4 \rightarrow \text{HfO}_2 + 2\text{ROH} + 2 \text{Olefin} \quad (9)$$

The reaction is carried out at 250° to 300°C in an inert atmosphere and with special attention to have a CO$_2$-free atmosphere. The as-prepared powder is calcined at 650°C in an inert atmosphere. It is in the titanate form as-calcined.

### B. Coatings of Graphite with Hafnia

The deposition of thin, dense, adherent films of hafnia on graphite substrates was accomplished by Mazdiyasni and Lynch (1965). Hafnium tetra-tertiary butoxide was vaporized in a Vycor glass chamber and carried in an inert gas vapor stream into a Pyrex chamber containing a heated graphite substrate. The decomposition reaction produced a white insulative coating with no carbon contamination with the substrate temperature maintained at 400–600°C and a deposition rate of approximately 1 mil per hour. The coatings were tested at 1000°C in still air to determine their effective protection of a commercial grade of graphite. The results are shown in Fig. 7, with an uncoated specimen for comparison. A 3-mil thick coating gave the lowest oxidation weight loss in this investigation (which included zirconia coatings) of 5 mg cm$^{-2}$ per hour at 1000°C. The protection afforded was more dependent on the coating thickness than on the character of the substrate as the results of Fig. 7 indicate.

The monoclinic forms of zirconia and hafnia have lower permeability to oxygen and lower thermal expansion rates (and better thermal shock resistance) than the cubic-stabilized modifications. Thus Kaufman et al. (1967) have been developing HfB$_2$ refractories superior to ZrB$_2$ refractories for oxidizing environments due to the superiority of HfO$_2$ over ZrO$_2$ as a protective surface layer formed in situ on the refractory. The oxidation rate for ZrB$_2$ increases at 1200°C (after the transformation) and a full 400°C or more below the similar increased rate for HfB$_2$. 

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FIGURE 7 Oxidation weight loss versus test time for RT-0029 graphite coated with HfO$_2$ and tested at 1000°C.

C. High-Pressure Hot Pressing

Preparation of high density fine grained hafnia from high purity powders at pressures of 3.8 to 30 kbars and temperatures to 1700°C has been reported by Vahldick and Lynch (1967). Cyclic high-pressure techniques were developed to produce hafnia bodies with grain sizes of 3 to 4 μ and densities of 99.8 to 100 percent of theoretical. The grain structure was characterized by smooth, rounded grains of uniform appearance. Calcia-stabilized hafnia was prepared in a similar manner to produce fine-grained cubic hafnia.

Single stage hot pressing at 5 kbars and 1700°C produced a finer grain size for hafnia of 1 to 2 μ, but the density did not exceed 99 percent of theoretical. The results indicate that a variety of high-density fine-grained hafnia
microstructures can be produced through high-pressure hot pressing of high purity powders.

**X. CONCLUSION**

Hafnium oxide represents a refractory oxide with great similarities in chemical properties with zirconium oxide. Some physical properties are also nearly identical such as atomic size and electronegativity, but important differences do occur. The greatest difference is in the high neutron absorption cross section which makes hafnium a good control material in reactors. The higher transition temperature of monoclinic to tetragonal hafnia and lower thermal expansion are among the other properties that make hafnia attractive compared to zirconia. The great lack of data on mechanical properties and the disparate limited results on phase equilibria suggest that many fruitful areas of research need investigation before considered evaluation of hafnia for other uses can be made.

**REFERENCES**


Nb$_2$O$_5$ and Ta$_2$O$_5$ Structure and Physical Properties

A. Reisman and F. Holtzberg

I. THE POLYMORPHISM OF Nb$_2$O$_5$ AND Ta$_2$O$_5$

A. Introduction

The polymorphism of Nb$_2$O$_5$, and to a lesser extent that of Ta$_2$O$_5$ has been the subject of many papers. As might be anticipated then, the status of Ta$_2$O$_5$ is fairly well, though not unanimously, agreed upon. The nature of Nb$_2$O$_5$ polymorphism is, however, less clear and open to considerable debate. The problem can be traced to several origins, some semantic, but others of more fundamental nature. Because Nb$_2$O$_5$ was subjected to intensive study by a number of workers during a relatively short time span, overlap in publication in different journals occurred. It was inevitable that differences in nomenclature should arise. Such differences, in general, can be unraveled for the most part. What is difficult to unravel is the question of when a new phase of Nb$_2$O$_5$ really is a new phase and when, for example, is it a contaminated or suboxide phase. One would expect that x-ray data would be of considerable aid in elucidating matters. Frequently, such data just adds to the confusion because phases are reported as being the same as other phases, but exhibit noticeably different patterns. Conversely, it is not always clear, because of the lack of detailed x-ray data that two phases reported as different are really separate entities. For example, much of the detailed crystallographic characterization is based on powder diffraction data. In the absence of single-crystal photographs, assignment of a crystal class and indexing of maxima is not unequivocal for these complex structures. If all that are given are lattice constants, there is no way of ascertaining whether different investigators were using the same, similar, or different powder data. We will discuss this question at greater length in Sec. II. One further point worth noting is that the complexity of the Nb$_2$O$_5$ patterns is such that it is difficult to know when only a single phase is present.

Another cause for confusion is that Nb$_2$O$_5$ appears to give rise to an inordinate number of metastable polymorphs. These can, in general, be
prepared by two very different means. The first involves formation of amorphous Nb$_2$O$_5$ via hydrolysis of either a niobium halide or a watersoluble salt followed by static heat treatment. The second involves vapor transport of the pentoxide using halogen carriers. As we shall see, the situation involving the former technique is fairly well agreed upon following several years of controversy. The situation involving the latter is still up in the air, and along with it, the status of four purported polymorphs.

Our approach in evaluation is as follows. For a phase to be considered stable at one atmosphere, it must exhibit a temperature interval of stability and must be capable of being generated thermally from two directions. In other words, two assumed stable, adjacent phases must be transformable one into the other reversibly. New phases must be shown to be uncontaminated and if they are metastable, it must be demonstrated that they are transformable thermally into a stable entity. Finally, if transformable into a stable entity, it must be shown that the melting point of this stable phase coincides with the accepted value.

It has not been a well-enough appreciated point by a number of workers in the field that Nb$_2$O$_5$ exhibits a marked affinity for SiO$_2$, Al$_2$O$_3$ and alkali metals. This may be a crucial consideration, since as already mentioned, the two primary methods used for studying Nb$_2$O$_5$ polymorphism, or forming “new” Nb$_2$O$_5$ phases expose the specimen either to a furnace ambient atmosphere containing gaseous Al$_2$O$_3$, SiO$_2$ or both, or to quartz receptacles at elevated temperatures in the presence of corrosive halide vapors. In addition, binders used in furnace chambers may contain significant alkali metal concentrations.

The marked gettering action of Nb$_2$O$_5$ for SiO$_2$ and Al$_2$O$_3$ was encountered by Reisman et al. (1956a) in studies of the Nb$_2$O$_5$--Ta$_2$O$_5$ system. Lengthy anneals at elevated temperatures were required to bring starting Nb$_2$O$_5$--Ta$_2$O$_5$ mixtures into a state of apparent equilibrium. Early in this study, it was found that, depending upon the length of sintering time, temperature, and sample size of specimens, contained in platinum or platinum 10 percent rhodium containers, new phases, detected via x-ray techniques, unlike any known Nb$_2$O$_5$ and Ta$_2$O$_5$ phases were being generated over very small composition intervals. These phases could be simulated by intentional contamination of the starting mixtures with SiO$_2$, Al$_2$O$_3$, or both. Using larger samples of the mixed oxides in lidded crucibles, no discernible changes in control samples of the pure oxides were observed, even after months of heat treatment. These pseudobinary mixtures then exhibited self-consistent changes in powder patterns which could be attributed to the actual phase relationship behavior in the system being studied. In addition, melting point progressions, starting with pure Nb$_2$O$_5$ exhibited orderly and
reproducible behavior. It is such information which detracts from the credibility of some of the extant literature on Nb₂O₅ polymorphism.

B. Nb₂O₅ Polymorphism

The first detailed examination of Nb₂O₅ polymorphism was described by Brauer (1941) in what remains a classic paper in the field. He identified three distinct phases, a low temperature phase T, a middle temperature phase M, and a high-temperature phase H. The starting point for his studies was amorphous material resulting from the hydrolysis of niobic acid. Brauer found that incremental heating resulted in a number of irreversible steps. At 500°C the amorphous material converted to the crystalline T phase. At 1000°C, the T phase transformed into the M form, and finally at 1100°C the M structure gave way to the H polymorph. Schäfer and Breil (1952) repeated Brauer's work and corroborated it with the important difference that they claimed to have observed reversibility of the T→M transformation. In a later article, however, Schäfer et al. (1954) questioned whether the M and H phases were indeed different. They did not re-examine the reversibility of the T→M transformation. Hahn (1951) had in the interim reported a new phase of Nb₂O₅. His x-ray data which coincided with many of the lines of Brauer's T form, contained several additional lines. Considering that Hahn's "pentoxide" was prepared by direct oxidation of the metal, it must be concluded that his starting material was very heavily contaminated.

In attempting to clarify inconsistencies in standard x-ray patterns of Ta₂O₅ and Nb₂O₅ powders, Frevel and Rinn (1955) presented data for two different forms of Nb₂O₅. One of these phases was commercially purchased and characterized by Frevel and Rinn as pseudohexagonal. The second material, whose method of preparation is not specifically given, but may have been prepared by direct oxidation of Nb, as was done in preparing Ta₂O₅ by them, is referred to as a low-temperature form. This phase is asserted as being isomorphic with the low-temperature form of Ta₂O₅. Upon heating the pseudohexagonal phase to 700°C, Frevel and Rinn found that it converted to the low-temperature form. This low-temperature form is presumably equated to Brauer’s T form, since Frevel and Rinn referenced his work. However, a comparison of their data with Brauer’s shows that while quite similar there exist some differences. As we shall see subsequently, Frevel and Rinn’s pseudohexagonal phase can be related to Brauer’s T form.

Lapitskii et al. (1962) studied the amorphous to crystalline transition and found it to occur exothermically at 600°C during heating cycles. Considering that such a conversion is expected to be spontaneous (and non-
reversible since the process is exothermic during heating), and susceptible to contamination as well as heating conditions, the disagreement with Brauer's observation is understandable. In 1957, as part of a study of Nb$_2$O$_5$-metal oxide interactions, the present authors and co-workers (Holtzberg et al., 1957) described a study of Nb$_2$O$_5$ polymorphism, hopefully to resolve some of the differences in the earlier literature. Amorphous Nb$_2$O$_5$ prepared in two different ways, was used as a starting material. As one starting material, NbCl$_5$, prepared from high purity Nb was hydrolyzed in water yielding hydrated Nb$_2$O$_5$, which was amorphous to x-rays. A second starting material was obtained by fusing high purity Nb$_2$O$_5$ with reagent grade K$_2$CO$_3$, dissolving the resulting mixture in H$_2$O, adding NH$_4$OH and then hydrolyzing with HCl (Reisman et al., 1956b) to obtain amorphous hydrated Nb$_2$O$_5$.

It was found, in agreement with Lapitskii et al. that either of the derived amorphous starting materials converted exothermically and irreversibly to a crystalline phase as low as 200°C when contaminated with NH$_4$Cl, and generally in the vicinity of 440°C when free of detectable contaminants. Depending on time-temperature annealing conditions, static heat treatments of amorphous Nb$_2$O$_5$ resulted in the appearance of a phase similar to Frevel and Rinn's pseudohexagonal phase, termed δ or γ' by us, or in a mixture of δ and Brauer's low-temperature phase termed γ by us, or in pure γ. The x-ray maxima of δ were quite diffuse. It was concluded that δ is a poorly crystallized γ phase since all major δ diffraction maxima occurred in the γ photographs as sharper, frequently split lines. Additional γ lines were found to be of low intensity and would not be expected to be seen in the δ pattern. Frevel and Rinn's low temperature phase (their γ analogue) may not have been sufficiently heat-treated to fully crystallize it and thereby reveal low intensity peaks and line splitting.

Upon heating statically as low as 830°C, the γ phase converted irreversibly to a mixture of Brauer's M and H forms, renamed β and α, respectively, by us. These phases remained in admixture even after 18 days at 1000°C. At 1095°C, the β–α mixture converted readily and irreversibly to the pure α form.

Based on these data, and the inability to obtain either pure β or α with sharp x-ray patterns (Holtzberg et al., 1957) it was concluded that β is an imperfectly crystallized α phase, that α is the only stable form of Nb$_2$O$_5$ at 1 atm, and concomitantly that γ is a metastable polymorph. It was also found in this study, as well as in earlier and later ones, that pure Nb$_2$O$_5$, however prepared, melted at 1491 ± 2°C. This is in good agreement with the value of 1487°C reported by Mohanty et al. (1964). Shafer and Roy (1958) proposed the existence of a new phase of Nb$_2$O$_5$, I (high) and
claimed to have found a region of stability for the $\beta$ phase. However, these authors did not demonstrate reversibility of the $\beta \rightarrow \alpha$ transformation. Furthermore, a comparison of their x-ray data with that of the $\beta$ phase, with previously reported data for this phase, showed the two materials to be crystallographically different. The new phase, I high, was reported as exhibiting an endothermic transition corresponding to the high to low transition at 1285°C. It is important to note that their study was based on Nb$_2$O$_5$ melting at only 1465°C. This heat effect could not be reproduced by us in a follow-on study of Nb$_2$O$_5$ polymorphism (Reisman and Holtzberg, 1959). This latter investigation was occasioned by the following observation. Whenever a melt of Nb$_2$O$_5$ was cooled to room temperature without seeding to induce nucleation of the $\alpha$ phase, the solidified material was found to be shattered into innumerable fragments. These fragments gave the x-ray powder pattern of $\alpha$ Nb$_2$O$_5$, but their occurrence suggested a previously undetected phase transformation during the unseeded cooling cycle. Indeed, repeated differential thermal analyses on Nb$_2$O$_5$ obtained in different ways showed, in the absence of seeding through the melting point, an exothermic anomaly below the normal melting point during which time the liquid solidified. The resulting solid, upon heating, melted endothermically at 1435°C. Upon seeding this melt with $\alpha$ Nb$_2$O$_5$, it solidified exothermically and upon continued elevation of temperature to 1491°C, the solid melted again. This behavior typifies the classical description of a monotrope, the observation of an exotherm during heating being conclusive proof of metastability. If this metastable phase, $\varepsilon$, was cooled much below 1350°C, it always converted spontaneously and exothermically to the $\alpha$ phase, shattering in the process. The process of crystallizing $\varepsilon$ from undercooled melts, followed by the cyclic treatments described could be effected readily and repeatedly on the same and fresh samples. Clearly then $\varepsilon$ is metastable relative to $\alpha$.

At about the same time, Zvinchuk (1958) re-evaluated the stabilities of $\alpha$, $\beta$, and $\gamma$ Nb$_2$O$_5$ using single crystals of Nb$_2$O$_5$ and found no evidence of reversibility, even after 2500 hour heat treatments at 600°C or 40 hour treatments at 1000°C. Shortly thereafter, Goldschmidt (1958) conducted in situ high-temperature x-ray studies of Nb$_2$O$_5$ for the first time. He supported the conclusions of Schäfer et al. (1954), and the present authors (Holtzberg et al., 1957) that $\beta$ and $\alpha$ are probably the same, and the conclusions of the present authors that $\alpha$ was the only stable polymorph. Goldschmidt employed a reversed nomenclature to that used by us, calling the high-temperature phase $\beta$, and the low-temperature phase $\alpha$. During his study of Nb–Si alloy oxidation, Goldschmidt found, contrary to the results we cited earlier, that SiO$_2$-contaminated Nb$_2$O$_5$ melts yielded only the diffraction pattern of $\alpha$ Nb$_2$O$_5$ (high-temperature form), the SiO$_2$ being present.
only in the amorphous state. It is not known, however, what contamination levels he studied, or what ours were, or how Goldschmidt cooled his samples. Our studies of the Nb$_2$O$_5$–Ta$_2$O$_5$ system, where contamination had to be contended with, were on solid state reacted samples quenched from sintering temperatures. It is possible that the two different procedures employed and/or the quantities of SiO$_2$ present account for the different observations of the effects of SiO$_2$ contamination.

What appears to be reasonably accepted at the present time is that starting with either amorphous or molten Nb$_2$O$_5$ and subjecting samples to a variety of time-temperature cycles, three different forms of crystalline Nb$_2$O$_5$ are detectable at one atmosphere pressure. These are the $\alpha$, $\gamma$, and $\varepsilon$ phases. The status of the $\delta$ phase, which exhibits marked similarities to Frevel and Rinn's pseudohexagonal phase, appears to be that of a poorly crystallized $\gamma$ phase and similarly for the $\beta$ phase relative to $\alpha$. At 1 atm pressure, there appears little question that the $\alpha$ phase is the only stable structure and that $\varepsilon$ is monotropic with respect to $\alpha$. The relationship between $\gamma$ and $\varepsilon$ is unknown, but it is not unreasonable that they are polymorphic with one another.

It is at this point that the picture becomes complicated with the advent of vapor transport growth of crystals. In 1964, Schäfer et al. (1964) reported for the first time on the growth of Nb$_2$O$_5$ polymorphs via hot to cold halogen vapor transport processes. They found three new structures which were termed P, B, and N. Depending upon the conditions employed, these phases deposited simultaneously, in isolatable crystalline form, generally further admixed with crystals of $\alpha$ and impure crystals of $\beta$. It is surprising that in a single transport reaction one is capable of obtaining codeposited crystals of pure phases, isolatable from each other but as we shall see, others apparently encountered similar behavior. The main thing that causes concern about the vapor transport derived phases is how important a role contamination plays in what is finally observed. Significantly, it was noted by Schäfer et al. that the N phase was contaminated with considerable quantities of SiO$_2$, the status of the SiO$_2$ in the lattice being unknown. Schäfer et al. do not discuss the question of SiO$_2$ contamination of the P and B forms. One would guess, however, that such contamination would be present. In this regard it is to the point that recently, Emmenegger and Robinson (1968) in a study of the dielectric properties of Nb$_2$O$_5$ reported on the formation of the B phase, also via a halogen transport process using NbCl$_5$, Cl$_2$ and a trace of H$_2$O. The resulting crystals were found to be contaminated by as much as 9000 ppm of SiO$_2$. Since the method employed is so similar to that employed by Schäfer et al., it might be concluded that the vapor transport polymorphs of Nb$_2$O$_5$ have been observed only when considerable
SiO₂ contamination is present. An interesting sidelight of Emmenegger and Robinson's report is their finding that Nb₂O₅ phases prepared by HCl and HCl/Cl₂ transport are contaminated also by Al, Mg, and Fe and that Si impurity markedly influences the resistivity and dielectric behavior of B Nb₂O₅.

Laves et al. (1965) and Petter and Laves (1965), shortly after the report of Schäfer et al., published on an η phase obtained by using iodine transport techniques. This η phase is claimed to be related to the high temperature form of Ta₂O₅, α, and is apparently the same as the P form discussed above. Unfortunately, Laves et al. do not provide interplanar spacings for their η form to enable comparison with data given for P Nb₂O₅. Of some value, however, is the observation that the η phase upon heating to 900°C converted to the α form. A determination of the melting point of this α phase plus analytical information on purity would have been of considerable value in establishing the validity of η.

Laves et al. (1964a, 1964b) had in the previous year reported on another new phase, zeta, again as a product obtained in a halogen transport process. The powder diffraction lines of this phase coincide with those presented by Schäfer et al. for the B phase. There is also a marked similarity between the ζ phase and the unexplained diffraction lines observed by Terao (1963) in the preceding year. These extra lines were attributed subsequently by Terao (1965) to a new phase γ'. The extra lines arose during extensive annealing of Nb₂O₅. Laves et al. (1964a) had noticed them in similar annealing studies starting with amorphous Nb₂O₅. Again, because of the possibility of contamination, either during extensive heat treatments or vapor transport in quartz tubes, the characterization of all of these data is suspect. An interesting speculation raised by Terao (1965) in his paper on the γ → α transformation (Terao considered the β phase as a poorly crystallized α phase) is that γ is nonstoichiometric and has the formula Nb₂₃O₆₉. This conclusion was arrived at by attempting to reconcile Helium and x-ray calculated density data. These could be made compatible with the stoichiometries Nb₂O₅ or Nb₂₃O₆₀, depending on how many formula weights were assigned to a unit cell.

The last "new phase" of Nb₂O₅ reported to date is attributable to Gruehn (1966), based again on vapor transport either with halogen or halogen-water mixtures. This phase was designated R. Gruehn found that R transforms to P at 750°C, indicating that R is less stable than P. The reverse process is not discussed nor is the possible conversion P → α considered. While this indicates, but does not prove that R and P are part of the same system, it is not conclusive that either is part of the quasi-unary Nb₂O₅ system.
In 1966, Schäfer et al. further discussed the polymorphism of Nb$_2$O$_5$ in the manner of a review. Unfortunately, this attempt has not clarified matters because it contains references to some 20 pieces of unpublished work by a number of authors, many of these references being key to the conclusions arrived at by Schäfer and his co-workers. In addition, a number of serious inconsistencies or contradictions are presented which mitigate against certain arguments. For example, in one section of the paper, the status of the $\varepsilon$ phase (that is, where it fits into the polymorphism series) is left up in the air and rightly so. Yet in another section it is implied that evidence exists that $\varepsilon$ and $\gamma$ are identical although the evidence is not specified. This change in position is confusing. More to the point, however, are the published facts (Reisman and Holtzberg, 1959) which indicate that $\varepsilon$ is extremely unstable below 1350°C. We know, however, that $\gamma$ is only slowly converted to a $\beta$-$\alpha$ mixture with heating. This evidence suggests strongly that $\varepsilon$ and $\gamma$ are different entities.

In another section, it is stated that the $\beta$ phase has been obtained as both powders and needle-like crystals. The formation of the latter would indicate that our conclusions and those of other investigators concerning the $\beta$ phase, which were based solely on powders derived from amorphous Nb$_2$O$_5$, are very likely incorrect. Yet despite this apparently conclusive evidence that $\beta$ is a real crystallographic entity, Schäfer et al. in a later section question the existence of the $\beta$ phase and imply that it should, in agreement with our conclusions, be regarded as a "less ordered precursor of the H form." Clearly, if single crystals of $\beta$ are in existence, the crystal structure of this phase should not remain unknown. Further, if single crystals are in existence then $\beta$ cannot be a two-dimensional precursor to $\alpha$.

Finally, it is argued that reversibility of the B and $\alpha$ forms was observed upon isothermal heating in an NbOCl$_3$/Cl$_2$ atmosphere. Thus heat treatment at 650°C of a mixture of B and $\alpha$ in such an atmosphere resulted only in the B form. Heat treatment of the mixture at 750°C results in only $\alpha$ Nb$_2$O$_5$. This is difficult to reconcile with the arguments that in transport reactions involving these same reagents, mixtures of $\alpha$, $\beta$, $\gamma$, N, P, and B are obtained when the deposition temperature is 750°C. Clearly, according to the arguments presented elsewhere in the paper, if $\alpha$ nuclei were present these other phases should either not have formed or should have converted to $\alpha$.

As asserted then, the credibility of vapor transport derived phases of Nb$_2$O$_5$ must remain suspect on a number of grounds. It is highly unlikely that in a single vapor transport experiment a multitude of pure single-crystal phases could arise in readily isolatable form. It is equally improbable that only one of such admixed growths is contaminated while the others are not.
Further, if we accept the contaminated phase possibility then we must also accept the possibility that what we are dealing with are pseudobinary compounds and solid solutions or ternary compounds and solid solutions. Even if the purported vapor transport phases are shown to be convertible to the α phase for which no quantitative experimental evidence has been given, the matter is not resolved in the absence of melting points and a knowledge of the system Nb–Si–O along the possible pseudobinary join Nb₂O₅–SiO₂. For example, the compounds formed may be unstable at high temperatures, and difficult to regenerate via short cooling cycles. Exsolutions may occur upon heating solid solutions and be difficult to reverse upon cooling, etc.

Thus, while obviously a number of distinguishable phases have been observed under similar experimental conditions by several independent workers, it has not been demonstrated that these phases are indeed Nb₂O₅ phases. In this respect we are not suggesting that a contaminant implies that a phase is not Nb₂O₅ since contaminants may function as catalysts in the formation of metastable phases. What is being discussed is the question of whether the combination contaminant + Nb₂O₅ → a new compound in a pseudobinary or ternary system.

In the following section we will tabulate some of the published x-ray information to enable the reader to see the nature of the problems involved in differentiating the work of different authors.

C. Ta₂O₅ Polymorphism

A number of authors appear convinced that Ta₂O₅ exists in only two modifications, a high-temperature α phase and a low-temperature β phase, both stable at one atmosphere in different temperature intervals (Reisman et al., 1956; Mohanty et al., 1964; Zaslavskii et al., 1955; Terao, 1967; Pavlovic, 1964; Lagergren and Magneli, 1952; Lapitskii et al., 1954). Moser (1965), however, claims to have detected four new, metastable low-temperature phases which he terms γ₁, γ₂, γ₃, and γ₄ with γ₂ being isostructural with γ Nb₂O₅. He claims also that the β–α phase transformation is oxygen pressure sensitive with α being stabilized by increasing p'O₂. This is interpreted by him as indicating that α is a suboxide and β is the only stable form. Shönberg (1952) has also disclaimed the existence of α Ta₂O₅ based on reduction studies. These disclaimers are discounted by the present authors based on what is known of the Ta–O system to be discussed in the section on nonstoichiometry. Since nothing further has been reported on the γ₁–γ₄ phases we can make no further comments about them.

α Ta₂O₅ melts at 1872 ± 10°C based on strip melting points (Reisman et al., 1956). This value is in good agreement with the value of 1872°C
reported by Ruff et al. (1913) and 1880°C given by Schäfer et al. (1954). The \( \alpha - \beta \) phase transformation is sluggish and occurs at 1360 ± 5°C (Reisman et al., 1956), at >1300°C according to Terao (1967), at 1320°C according to Mohanty et al. (1964) and Lagergren and Magneli (1952), and 1340°C according to Pavlovic (1964). We have found that \( \beta \) melts metastably at 1785 ± 30°C (Reisman et al., 1956).

II. X-RAY DATA AND STRUCTURE

A. Introduction

This section is divided into four parts. The first attempts to summarize the x-ray data reported for the clearly established polymorphs of \( \text{Nb}_2\text{O}_5 \), obtained generally by step-wise heat treatment of amorphous \( \text{Nb}_2\text{O}_5 \). The second part covers the information obtained on the still somewhat controversial polymorphs produced principally by vapor transport. The third contains a summary of available data on \( \text{Ta}_2\text{O}_5 \) polymorphism, and the last part presents some data on oxide-oxide systems.

B. Phase Analysis of the \( \alpha, \beta, \) and \( \delta \) Forms of \( \text{Nb}_2\text{O}_5 \) from X-Ray Measurements

The transition from the amorphous phase to the lowest temperature crystalline entity occurs at approximately 400°C. Although the lowest temperature form has been characterized by several authors (Frevel and Rinn, 1955; Terao, 1963; Holtzberg et al., 1957; Brauer, 1941; Inouye, 1953; Bridges and Fassell, 1956; Hahn, 1951; Holtzberg and Reisman, unpublished), there are two obvious problems associated with its unique identification. The first, being trivial, relates to nomenclature, the phase having been identified as \( \delta, \gamma, \text{TT}, \text{T}, \alpha, \) pseudohexagonal, etc. The second problem concerns the data itself. Table I collates the relevant powder data and reflection intensities when available. It was clear in compiling the table that the reported three decimal precision would not permit reasonable comparison and we have, therefore, rounded the \( d \)-spacings to two places. The powder data for most of the polymorphs show discrepancies, but the higher temperature phases show reasonable agreement (if we do not concern ourselves with occasional extra lines). Reproducibility for the \( \delta \) and \( \gamma \) phases is particularly poor. This probably is a consequence of the low temperature of formation, low diffusion rates, and the slow transition of the partly crystallized \( \delta \) into the \( \gamma \) phase (Holtzberg et al., 1957). To illustrate this transition, the \( \delta \) phase is shown at the left of the table and the arrows direct
attention to the splitting of lines as crystallinity increases. This scheme is continued in order to direct attention toward the lines which are reproduced by the various authors. Extra lines can arise from any of the following causes: impurities in the starting material, longer exposures may show up weaker lines (this will also lead to differences in reported intensities), simultaneous occurrence of different polymorphs depending on preparation techniques, and reporting of Kβ lines because of insufficient filtering (this most often happens for high intensity lines). A few authors (Frevel and Rinn, 1955; Terao, 1963) have indexed the powder lines and give lattice constants for their data. Since no single crystals of the δ or γ forms have been produced, none of the lattice constants have been given in the Table. The choice of unit cell based on the rather complex line spectrum is almost arbitrary and the lattice constants reported rarely even define the same crystal class.

It is quite evident from Table I that the δ → γ phase transformation is not uniquely characterized, but that there are strong correlations shown by the arrows. In moving from left to right, the number of lines increases and as we have said the γ phase appears to be a more crystalline state of δ. Certain other additional lines, such as 3.48, 2.73, 2.12, etc., appear consistently in the right-hand side of the Table. Most of these are reported as very weak lines and may belong to the pattern of a fully crystallized γ phase. Other lines appear inconsistent and possibly derive from one or more of the proposed considerations given earlier.

At approximately 800°C the transitional β phase is observed. It characteristically shows mixtures of broad diffuse lines and some sharp lines. Comparison of Debye Scherrer photographs of the β and α phases shows that the diffuse lines are precursors of the finally crystallized α pattern. In spite of this broadening (marked a in Table II) the comparison of data from different laboratories is considerably better than in Table I, and we have retained the third decimal place. Schäfer et al. (1966) have reported a number of extra lines in this pattern which they have attributed to the α phase. Since the broad lines split and shift with increasing crystallinity, tabular comparison is not as satisfying as visual film comparison. The discrepancies in these data are most probably dependent on the actual thermal history of the samples involved. Shafer and Roy's (1958) data (their II form which they describe as similar to Brauer's M form) is not included in the Table since it does not lend itself to comparison.

Both Zvinchuk (1958) and Terao (1965) have indexed the β phase powder pattern and agree that the crystal class is monoclinic. Their lattice constants are, respectively, $a = 20.28$ Å, $b = 3.83$ Å, $c = 20.28$ Å, $β = 120°$ and $a = 22.1$ Å, $b = 7.638$ Å, $c = 19.52$ Å, $β = 118° 15'$. 

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TABLE II (Continued)
INTERPLANE SPACINGS FOR $\beta$ Nb$_2$O$_5$

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Even if their results were in better agreement, it would require other evidence to establish the crystal symmetry. As stated in Sec. I, the three-dimensional crystallinity of $\beta$ Nb$_2$O$_5$ is still uncertain.

The transition of $\beta$ to $\alpha$ Nb$_2$O$_5$ is completed at 1100°C. Single crystals of the latter have been prepared in several laboratories and this powder

TABLE III
MONOCLINIC UNIT CELL DIMENSIONS OF $\alpha$ Nb$_2$O$_5$

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<th>Author</th>
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<th>$c_0$ (Å)</th>
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<td>Gatehouse and Wadsley (1964)</td>
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<td>19.35</td>
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<td>Roth (1959)</td>
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<td>Norin and Magneli (1960)</td>
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<tr>
<td>Shafer and Roy (1958)*</td>
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<td>120° 0'</td>
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*Zvinchuk's data corrected from Kx to KÂ and transformed to this setting.

$^*$: Broad Lines.
$^a$: Intensities converted to numerical scale.
$^+$: Denote $\alpha$ Nb$_2$O$_5$ lines.

Reversed.

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diffraction data is the most well-characterized of the polymorphs. Even in this case, however, there are discrepancies in literature values (Table III). Goldschmidt (1958), for example, lists powder data which is sufficiently different to exclude his results from a precise identification of the phase, but his trend of \(d\) spacings are somewhat reminiscent of the known interplanar spacings. Table IV lists the powder data of Holtzberg et al. (1957) for \(\alpha\) Nb\(_2\)O\(_5\). These data have been reindexed using the \(d\) spacings and powder diffraction intensities of Holtzberg et al. (1957), making the latter compatible with single-crystal intensities reported by Gatehouse and Wadsley (1964), as well as similar unpublished data of Holtzberg. A full crystallographic determination of the structure of \(\alpha\) Nb\(_2\)O\(_5\) has been done by Gatehouse and Wadsley starting with the assumption that there are 14 Nb\(_2\)O\(_5\) “molecules” per unit cell. Their unique solution to this structure involves the introduction of 1 tetrahedrally coordinated Nb atom out of the 28 niobium atoms per unit cell. Their rendition of the structure is shown in Fig. 1 as a ball and stick model and in an idealized drawing, Fig. 2, showing the octahedral contacts.

C. Other Phases of Nb\(_2\)O\(_5\)

With the exception of Terao’s (1965) and Shafer and Roy’s (1958) results, all the phases reported in this section have been obtained by vapor transport...
### TABLE IV

**INTERPLANAR SPACINGS FOR α Nb₂O₅**

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<th>Rel. Int.</th>
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*After Holtzberg et al., 1957.*
FIGURE 2 Idealized drawing of the structure of $\alpha \text{Nb}_2\text{O}_5$ looking down the $b_s$ axis. The upper dark shaded octahedra are $\frac{1}{2}$ unit cell above the lower light shaded octahedra with which they share edges. The tetrahedrally bonded Nb are shown as circles at the unit cell corners (after Gatehouse and Wadsley, 1964).

techniques. Table V is a summary of the x-ray powder diffraction data for the $\text{P}$ or $\eta$ phase reported by Schäfer et al. (1964) and by Petter and Laves (1965) based on a single crystal study; the $\text{B}$ ($\gamma'$ or $\zeta$) form reported by Schäfer et al. (1964), Terao (1965), and Laves et al. (1964a); and Gruehn’s (1966) $\text{R}$ form of Nb$_2$O$_5$.

Shafer and Roy’s (1958) Nb$_2$O$_5$ II, which they report as similar to Brauer’s $\text{M}$ form, is listed here because it cannot be reconciled with any of the data in Sec. II, B. Data for Shafer and Roy’s Nb$_2$O$_5$ I high form are given in Table V (see Sec. I).

The patterns of $\text{B}$, $\gamma'$, and $\zeta$ are listed in Table V, the data indicating that they are essentially the same form of Nb$_2$O$_5$.

The structure of the $\eta$ phase (Schäfer’s $\text{P}$ phase, Table V) was worked out by Petter and Laves (1965) and is shown in Fig. 3. They indexed single-crystal films on the basis of a “tetragonal” unit cell with $a = 3.896$ Å and $c = 25.43$ Å, and propose $I4$ or $I4_22$ as possible space groups. However, they say that optical data indicate that the crystal is biaxial, suggesting this may be due to submicroscopic twinning. Intensity data also show deviations from tetragonal symmetry.
FIGURE 3 The structure of $\eta$ Nb$_2$O$_5$ showing the packing of NbO$_6$ octahedra in a tetragonal unit cell (after Petter and Laves, 1965).

The data for Gruehn’s R form are listed in Table V. Gruehn says that there was some amorphous and N–Nb$_2$O$_5$ contamination of his sample, but he does not discuss other impurities.

D. Ta$_2$O$_5$ X-Ray Data

Table VI lists the data for $\beta$ Ta$_2$O$_5$. Here again, the $d$ spacings found by different authors are in general agreement, but Terao (1967), for example, has reported a significant number of weak lines, whereas Lehovic (1964) has elected to ignore these in an attempt to solve the structure. Lehovic attributes the weak lines to a superlattice which he is not able to describe. Lehovic’s conclusions are questionable since he “solves” the structure on the basis of high intensity powder lines only, and then finds the low intensity lines to be incompatible with this solution. Lattice constants for the $\beta$ Ta$_2$O$_5$ have not been given since none are based on single-crystal data. Lehovic (1964) lists as many as six unit cells obtained by different authors based on an orthorhombic unit cell, some of these being related by simple multiple axis lengths.

The differences in x-ray spacings in the high temperature or $\alpha$ Ta$_2$O$_5$ powder data given by various authors (Terao, 1967; Zaslavskii et al., 1955; Reisman et al., 1956) appear to be related to the degree of resolution of the line spectra. Only the data of Reisman et al. (1956) are given in Table VII.
TABLE V
INTERPLANAR SPACINGS FOR SEVERAL "Nb₂O₅" PHASES

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<tr>
<th>Equivalent Phases</th>
<th>Schäfer al. (1964)</th>
<th>Terao et al. (1965)</th>
<th>Laves et al. (1964a)</th>
<th>Schäfer et al. (1964)</th>
<th>Schäfer et al. (1964)</th>
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<td>( \beta \gamma'  )</td>
<td>( \xi )</td>
<td>( \rho )</td>
<td>( \eta )</td>
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<td>( \rho )</td>
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<td>( d(\AA) )</td>
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| 2  | 2.19 | vw  | 2.198 |
| 2  | 2.16 |
| 3  | 2.05 | vw  | 2.051 |
| 6  | 1.91 | w   | 1.912 |
| 2  | 1.88 | vw  | 1.885 |
| 7  | 1.80 | m   | 1.805 |
|     | w   |     | 1.724 |
|     | m   |     | 1.703 |
|     | w   |     | 1.692 |
|     | w   |     | 1.658 |
|     | vw  |     | 1.540 |
|     | vw  |     | 1.492 |
|     | vw  |     | 1.481 |
|     | vw  |     | 1.453 |
|     | vw  |     | 1.438 |
|     | vw  |     | 1.423 |
|     | vw  |     | 1.366 |
|     | vw  |     | 1.341 |
|     | vw  |     | 1.302 |
|     | vw  |     | 1.288 |

| 2  | 1.99 | 1    | 2.53 | 173 | 2.13 | 5    | 2.085 | 10   | 2.514 | 15   | 1.438 |
| 5  | 1.95 | 1    | 2.50 | 190 | 1.99 | 10   | 2.085 | 5    | 2.448 | 10   | 1.406 |
| 2  | 1.93 | 1    | 2.43 | 231 | 1.91 | 5    | 2.036 | 5    | 2.373 | 65   | 1.396 |
| 3  | 1.87 | 1    | 2.39 | 17  | 1.91 | 20   | 1.972 | 20   | 2.338 | 10   | 1.366 |
| 2  | 1.77 | 1    | 2.37 | 124 | 1.89 | 25   | 1.956 | 20   | 2.320 | 10   | 1.316 |
| 5  | 1.75 | 7    | 2.30 | 50  | 1.88 | 20   | 1.835 | 75   | 2.281 | 10   | 1.274 |
| 6  | 1.74 |     |      | 83  | 1.91 | 10   | 2.233 | 5    | 1.212 |
|     |      |     |      | 41  | 1.83 | 5    | 1.403 | 5    | 2.206 | 65   | 1.190 |
| m  | 1.703|     |      | 256 | 1.75 | 5    | 1.391 | 15   | 2.153 | 15   | 1.170 |
| w  | 1.692|     |      | 165 | 1.72 | 10b  | 1.307 | 75   | 2.096 | 10   | 1.153 |
| w  | 1.658|     |      | 66  | 1.70 | 55   | 2.049 | 5    | 1.083 |
| vw | 1.540|     |      | 50  | 1.66 |     |      |     |      |      |      |
| vw | 1.492|     |      | 140 | 1.65 |     |      |     |      |      |      |
| vw | 1.481|     |      | 91  | 1.64 |     |      |     |      |      |      |
| vw | 1.453|     |      | 66  | 1.62 |     |      |     |      |      |      |
| vw | 1.438|     |      | 17  | 1.60 |     |      |     |      |      |      |
| vw | 1.423|     |      | 50  | 1.53 |     |      |     |      |      |      |
| vw | 1.366|     |      | 74  | 1.52 |     |      |     |      |      |      |
| vw | 1.341|     |      | 58  | 1.52 |     |      |     |      |      |      |
| vw | 1.302|     |      | 17  | 1.49 |     |      |     |      |      |      |
| vw | 1.288|     |      | 50  | 1.46 |     |      |     |      |      |      |

b = broad reflections.
Laves and Petter (1964) describe three phases of \( \text{Ta}_2\text{O}_5 \) \( \alpha'' \), \( \alpha' \), \( \alpha \). These new phases are formed by annealing quenched \( \alpha \) \( \text{Ta}_2\text{O}_5 \) platelets grown by the Verneuil technique. In an optical and x-ray study they found (at room temperature) that \( \alpha'' \) \( \text{Ta}_2\text{O}_5 \) has a monoclinic-pseudotetragonal body centered cell with \( a = 3.784 \, \text{Å} \), \( b = 3.802 \, \text{Å} \), and \( \beta = 91^\circ \). In the (001) plane of the platelet, the \( a \) and \( b \) axes are parallel to the morphological crystal

### TABLE VI

<table>
<thead>
<tr>
<th>Lehovic (1964)</th>
<th>Frevel and Rinn (1955)</th>
<th>Holtzberg and Reisman (unpubl.)</th>
<th>Terao (1967)</th>
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The crystals were visibly, as well as submicroscopically, twinned.

At about 320°C the $\alpha$ $\mathrm{Ta}_2\mathrm{O}_5$ forms a monoclinic pseudotetragonal cell with $a = b = 5.365$ Å, $c = 35.85$ Å and $\beta = 91^\circ$.

After relatively long annealing at 1450°C they obtain $\alpha$ $\mathrm{Ta}_2\mathrm{O}_5$ (measured at R.T.) having a tetragonal body centered unit cell with $a = 3.795$ Å and $c = 35.54$ Å.

If this description of the transformations in $\alpha$ $\mathrm{Ta}_2\mathrm{O}_5$ is correct, it is understandable that the powder data will show variations in resolution depending on the heat treatment of the $\alpha$ $\mathrm{Ta}_2\mathrm{O}_5$ as the temperature is reduced to room temperature. Presumably the $\beta$ phase was not observed because of the low temperature at which the quenched $\alpha$ phase was annealed.

Figure 4 is a schematic representation of a proposed idealized structure of the high-temperature form of $\mathrm{Ta}_2\mathrm{O}_5$. The bonding arrangement satisfies the requirement for a basic formula $\mathrm{Ta}_2\mathrm{O}_5$. The octahedral pattern is clearly related to that of the structure proposed by Petter and Laves (1965) for $\eta$ $\mathrm{Nb}_2\mathrm{O}_5$. Laves et al. (1965) had suggested that a more complex stacking sequence than for $\eta$ $\mathrm{Nb}_2\mathrm{O}_5$ will give the required $c$-axis length in $\alpha$ $\mathrm{Ta}_2\mathrm{O}_5$.

By distorting the idealized octahedra, it should be possible to generate a series of structures which would follow a sequence of transformations similar to those described by Petter and Laves.
If one accepts the proposed structure for $\alpha$ Ta$_2$O$_5$, it is interesting to note that it provides an unusually large number of octahedral and tetrahedral holes which would readily coordinate a variety of impurity ions which could easily distort the lattice. Recently, Wolten and Chase (1969) have produced four polymorphs of Ta$_2$O$_5$ by crystallization of the pentoxide from KPO$_3$ and KVO$_3$. These polymorphs are suspect, since the fluxes employed could result in the formation of K tantalate or K tantalo-vanadates.

E. Oxide-Oxide Compounds

Tables VIII and IX list the x-ray data for 2 Nb$_2$O$_5$·Ta$_2$O$_5$ as obtained from a powder specimen which was indexed on the basis of single-crystal data (Mohanty et al., 1962). The compound crystallizes with a tetragonal unit cell having the probable space groups $I4$, $I4$, or $I4/m$ with $a = 15.77 \pm 0.01$ Å, $c = 3.84 \pm 0.01$ Å.

Waring and Roth (1964) confirm these lattice constants and claim the compound to be isomorphic with V$_2$O$_5$·9Nb$_2$O$_5$ with $a = 15.72$ Å, $c = 3.821$ Å, and V$_2$O$_5$·9Ta$_2$O$_5$ with $a = 15.66$ Å and $c = 3.820$ Å.
FIGURE 4 Proposed model of the structure of $\alpha$ Ta$_2$O$_5$. The packing of undistorted TaO$_6$ octahedra in combined corner and edge sharing yield a tetragonal unit cell with $a = b \approx 3.8$ Å and $c \approx 35.5$ Å (after Holtzberg and Reisman, unpubl.).

TABLE VIII

INTERPLANAR SPACINGS FOR 2Nb$_2$O$_5$·Ta$_2$O$_5$*

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*After Mohanty et al. (1962).
TABLE IX
LATTICE CONSTANTS FOR 2Nb₂O₅·Ta₂O₅ AND
RELATED COMPOUNDS

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<td>3.820</td>
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*aMohanty et al. (1962).*

*bWaring and Roth (1964).*

III. NONSTOICHIOMETRY

Nb₂O₅ and Ta₂O₅ being binary in nature might be expected to exhibit ranges of variable composition (nonstoichiometry) in a manner analogous to that exhibited by III–V compound semiconductors. Depending on oxygen overpressure and temperature, this nonstoichiometry would lead to regions of variable composition in which a metal excess was present and in which the pentoxides would behave as defect, n-type semiconductors. Lavrent’ev et al. (1961), for example, have reported that in the metal excess region, a composition Nb₂O₄,94 is single phase and exhibits the structure of α Nb₂O₅. They found that if the oxygen deficiency increases to a point where the composition of the system is Nb₂O₄,66, the system becomes two phase, consisting of a mixture of Nb₂O₄ and Nb₂O₅₋ₓ solid solution. Norin and Magneli (1960), on the other hand, have indicated a much smaller region of variable composition. These authors reported that for system compositions coinciding with Nb₂O₄,92 and Nb₂O₄,96, new, single discrete phases exist, that these phases possess structures not unlike α Nb₂O₅. In the following, we will first present a brief review of the status of the systems Nb–O and Ta–O. Since it is not the present intent to consider suboxides in these systems in any detail, the remainder of this section will be devoted to a discussion of the single-phase composition region in the vicinity of the pentoxides. Further, as little work has been reported on the Ta₂O₅₋ₓ solid solution, the focus will be on Nb₂O₅₋ₓ about which considerable information is available.

In addition to the phases reported by Norin and Magneli (1960), about which more will be said subsequently, a number of other suboxides have been reported in the system Nb–O. Some of these are said to occur at atmospheric pressure, while others have been observed only at reduced pressure. Under an ambient oxygen composition and partial pressure, Terao (1963) identified the sequence:
Nb–O (solid solution), NbO₂ (tetragonal), NbO₆ (hexagonal),
γ Nb₂O₅ (monoclinic), and α Nb₂O₅ (monoclinic).

Under reduced pressure only, Terao found an NbO₂ (tetragonal) phase, as well as cubic NbO and a tetragonal NbO₂ phase.

Brauer (1941), much earlier, in his comprehensive study of niobium oxides, had, however, found only three suboxides over the entire pressure-composition range. These were NbO, NbO₂ and Nb₂O₅. The status of the system as described by Brauer was essentially confirmed by Elliott and Komjathy (1960) in a more recent investigation. They reported a maximum solubility of oxygen in niobium of 0.7 weight percent, congruent melting points of 1945°C for NbO and 1915°C for NbO₂. Eutectic reactions occur between the Nb–O solid solution and NbO at 915°C and between NbO and NbO₂ at 1810°C. The NbO₂ melts incongruently at 1510°C.

Unlike the observed behavior in the Nb–O system, Lagergren and Magneli (1952) were unable to form a suboxide of tantalum, either at atmospheric or reduced pressure. What had been discovered by them was that Ta₂O₅ underwent a polymorphic reversible phase transition. They found that the low-temperature form, β, was extremely resistant to reduction by hydrogen at 1250°C while the high-temperature, α, phase could be reduced in a vacuum furnace yielding a mixture of Ta and Ta₂O₅. Schönberg (1954) disputed these results claiming that reduction of the Ta₂O₅ resulted in the sequential generation of six phases. These were identified as α, a Ta–O solid solution containing up to 5 atom percent of oxygen in a body-centered lattice (this is in fair agreement with work reported by Brauer, 1941, in which he found a solubility of oxygen in Ta of <5 percent), β, having an upper composition limit coinciding with the stoichiometry Ta₄O₉, γ, with a probable composition TaO and possessing the NaCl structure, δ having the formula TaO₂ and the rutile structure and ε, lying within the TaO₂–Ta₂O₅ composition interval. Schönberg also disclaimed the existence of α Ta₂O₅ (termed δ by him). Wasilewski (1953) during this time period had reported a Ta₂O phase and others have reported several other ill-defined phases which need not be discussed here.

Most recently, Dubrovskaya et al. (1964) duplicated a number of previously reported experimental techniques for preparing tantalum suboxides. They demonstrated to their own satisfaction that tantalum suboxide phases were artifacts, that inadvertently, the reduction techniques led to the formation of tantalum carbides, nitrides, and oxycarbides. They found on the basis of their investigative work that the Ta–O system is of the simple eutectic variety, and that the only two phases observed over the entire composition interval are Ta and Ta₂O₅. This work is quite convincing and we tend to accept their findings.
Brauer (1940, 1941) found that Nb$_2$O$_5$ may exhibit deviations in stoichiometry between the limits Nb$_2$O$_5$ and Nb$_2$O$_{4.8}$ in the temperature interval 1350–1400°C. Greener et al. (1961) studied the nonstoichiometry of Nb$_2$O$_5$ under atmospheric and reduced pressure using a conductivity technique. In the temperature range 300–600°C, an exponential dependence of conductivity with temperature was found at atmospheric pressure. This dependency showed a slope of 1.65 eV. In isothermal experiments, in which $p_{O_2}$ was varied between $2 \times 10^{-3}$ atm and 1 atm, the conductivity showed dependency $\propto p_{O_2}^{-0.24}$. This was interpreted as indicating an oxygen vacancy defect structure involving singly charged anion vacancies. The $-1/4$ as well as $-1/6$ power dependencies on $p_{O_2}$ and implications of same may be inferred from the following.

If stoichiometric Nb$_2$O$_5$ loses oxygen, the equilibrium may be depicted by Eq. 1

$$\text{Nb}_2\text{O}_5 (\text{solid}) \rightleftharpoons \text{Nb}_2\text{O}_{5-x} (\text{solid}) + X \frac{1}{2} \text{O}_2 \quad (1)$$

In theory, the generated oxygen vacancies may contain the two electrons originally coupled to an anions site, or may lose one or both of these electrons to the lattice. In either of these latter two alternatives, vacancies would be functioning as donors, imparting n-type conductivity to the pentoxide.

The several equilibria involving liberated oxygen O$_2$, oxygen ions in the lattice (O), vacancies containing two (O$^2$), one (O$^1$), and no (O$^0$), electrons are given by Eqs. 2–4

$$\text{O}^2 \rightleftharpoons \text{O}^2 + \frac{1}{2} \text{O}_2 \uparrow \quad (2)$$

$$\text{O}^2 \rightleftharpoons \text{O}^1 + e^- \quad (3)$$

$$\text{O}^1 \rightleftharpoons \text{O}^0 + e^- \quad (4)$$

If we assume that a vacancy site, once formed, becomes singly or doubly ionized, then conservation of the total vacancy concentration formed, i.e., [O$^2$], in terms of the concentration of singly and doubly ionized vacancies is given by Eq. 5

$$[\text{O}^2] = [\text{O}^1] + [\text{O}^0] \quad (5)$$

We may define two boundary cases. In the first, we assume that all generated vacancies are singly ionized. Consequently, Eq. 5 reduces to $[\text{O}^2] = [\text{O}^1]$ and it follows that $[\text{O}^1] = [e^-]$. Equation 4 becomes irrelevant.

In the second case we assume that all vacancies are doubly ionized. Now Eq. 5 reduces to $[\text{O}^2] = [\text{O}^0]$ and $[\text{O}^0] = 1/2 [e^-]$. Further, Eqs. 3 and 4 may be combined to give Eq. 6

$$\text{O}^2 \rightleftharpoons \text{O}^0 + 2e^- \quad (6)$$
Case 1. The pertinent equilibria for Eqs. 2 and 3, after introducing the equivalencies cited, are given by Eqs. 7 and 8, respectively.

\[ K_1 = p_{O_2}^{1/2} [O^1] \]  

(7) 
since the term \([O^2] >> [O^2]\) and may be considered constant.

\[ K_2 = \frac{[O^1]^2}{[O^1]} \]  

(8)

Solving Eqs. 7 and 8 for \([O^1]\) we obtain

\[ K_1 K_2 p_{O_2}^{-1/4} = [O^1] \]  

(9)

The argument presented is the basis for Greener et al.'s conclusions concerning the vacancy state in defect Nb\(_2\)O\(_5\).

Case 2. The pertinent equilibria are given by Eqs. 2 and 6. The equilibrium constants for these processes, taking account again of the equivalencies we have suggested are given by Eqs. 10 and 11

\[ K_1 = p_{O_2}^{1/2} [O^0] \]  

(10)

\[ K_2 = \frac{4 [O^0] [O^0]^2}{[O^0]} \]  

(11)

Solving Eqs. 10 and 11 for \([O^0]\) we obtain

\[ \left( \frac{K_1 K_2}{4} \right)^{1/3} p_{O_2}^{-1/6} = [O^0] \]  

(12)

Using oxidized Nb powder, Kofstad and Anderson (1961) conducted weight changes versus \(p_{O_2}\) experiments. The partial pressures of oxygen were developed in the equilibrium

\[ CO_2 = CO + \frac{1}{2} O_2 \]  

(13)

The pentoxide, present as the \(\alpha\) phase when Nb powder is oxidized above 800°C (Kofstad and Kjollesdal, 1961) was found to show a linear weight change dependency on \(p_{O_2}^{-1/6}\) in the temperature interval 927–1410°C, and in the pressure interval \(10^{-7}–10^{-18}\) atm \(p_{O_2}\). In accordance with Eq. 12, the \(p_{O_2}^{-1/6}\) oxygen partial pressure dependency implies that the vacancies in Nb\(_2\)O\(_5\) are doubly ionized oxygen vacancies. For Nb\(_2\)O\(_{5-x}\), Kofstad and Anderson found a maximum value of \(X = 0.1\) at \(10^{-11}\) atm. For the reaction shown in Eq. 1, the formation of 1/2 mole of \(O_2\) (1 mole of \(O^2\) vacancies) has a partial molar enthalpy of formation \(\Delta H^0 = -103\) kcal/mole \(O_2/2\). This value was found to be independent of \(X\) for \(X > 4 \times 10^{-3}\).
The partial molar entropy of formation, $\Delta S^\circ$, was found to be 15 esu. Explicitly, the magnitude of $X$ as a function of $p_{O_2}$ is given by Eq. 14

$$K = 4 \left( \frac{X}{5} \right)^2 p_{O_2}^{1/2}$$  \hspace{1cm} (14)$$

While the data of Greener et al. and Kofstad and Anderson both support the contention that defect Nb$_2$O$_5$ is a metal excess semiconductor, they do not corroborate one another’s conclusion on the state of ionization of the oxygen vacancies. The conclusions each draws are, however, not necessarily in disagreement since each studied a different pressure range. It is not improbable that, within the limits of experimental uncertainty, one or the other mechanism predominates in a given pressure interval. The apparent disagreement led Blumen thai et al. (1965) to a reinvestigation of defect $\alpha$ Nb$_2$O$_5$ using several techniques including electrochemical cell measurements. These workers developed $O_2$ partial pressures via the use of $H_2/H_2O$ mixtures. Experiments were conducted between 900–1200°C. At 1000°C with $p_{O_2}$ lying within the range of experimental uncertainty $3.8 \times 10^{-18}–2.1 \times 10^{-18}$ atm, the vapor phase was found to be in invariant equilibrium with NbO$_2$ and Nb$_2$O$_3$. From this, it was concluded that there are no other stable oxides in the composition interval between NbO$_2$ and Nb$_2$O$_3$. Further, they found that at 889, 990, and 1090°C, $X$ had values of 0.113, 0.143, and 0.159, respectively. These data are in marked disagreement with the conclusions arrived at by Norin and Magneli (1960) and instigated isopiestic experiments designed to generate compositions claimed by the latter to be discrete phases. Mixtures having composition corresponding to Nb$_2$O$_3$ and Nb$_2$O$_4$.87 4 were equilibrated at 1100°C. This enabled synthesis of materials whose nominal compositions were Nb$_2$O$_4$.94 and Nb$_2$O$_4$.90 which approximate those studied by Norin and Magneli. Each of these compositions were found to be single-phase solid solutions of Nb$_2$O$_3$.

A $p_{O_2}^{-1/6}$ weight change dependency was found for pressure intervals $p_{O_2} > 10^{-11}$ atm. At lower oxygen overpressures disproportionately larger weight changes were detected. However, the authors could provide no explanation for the low-pressure behavior. Two possibilities do, however, appear plausible. For example, if in the low-pressure range, the equilibrium system is three phase, i.e., NbO$_2$–Nb$_2$O$_3$–O$_2$ or if NbO$_2$ exhibits a degree of molecular volatility, the excess weight loss would occur. Indeed, from some of the data presented by Lavrent’ev et al. (1961) it appears that Blumenthal et al.’s excess losses are coincident with the onset of invariant equilibrium. If this is correct, then Kofstad and Anderson have improperly defined the three-phase boundary since their linear dependency is shown to extend past it.

For the reaction involving the loss of 1 mole of O$_2$ from Nb$_2$O$_5$ (2 moles of vacancies being formed in the process), Blumenthal found $\Delta H^\circ = -164$
kcal/mole which is in poor agreement with the value of $-206$ kcal/mole given by Kofstad and Anderson (1961). It is in excellent agreement, however, with the value calculated by Kubaschewski (1956) from the data of Grube and Flad (1945), $\Delta H^\circ = -165$ kcal/mole.

Finally, Chen and Swalin (1966) investigated $\text{Nb}_2\text{O}_5$ stoichiometry using conductivity measurements of single crystals. In the range $10^{-6} - 1$ atm they found the dependency

$$\sigma = \sigma_0 p_o^{-1/n}$$

Above $800^\circ$C, $n = 4$ which agrees well with Greener et al.’s results, again over a similar pressure range to that used by the latter. The diffusion constant for oxygen vacancies in $\text{Nb}_2\text{O}_5$ was found to be

$$D = 4.7 \times 10^{-3} \exp \left( -\frac{1.2}{kT} \right) \text{cm}^2/\text{sec}$$

Above $800^\circ$C, the slope of the conductivity curve versus log$1/T$ was found to be 1.4 eV, while below this temperature, where the data exhibit considerable scatter, the value is 0.4 eV. The authors offer no explanation for the discrepancy between weight change and conductivity measurements. They do, however, discount the possibility that a different process predominates in each pressure range, since they would not expect the processes to show an abrupt transition.

**IV. THERMODYNAMIC DATA**

**A. Introduction**

A considerable amount of detailed work, in the form of bomb calorimetry and galvanic cell reaction studies, has been published on $\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$. Despite the meticulous nature of such investigations, a source of confusion exists, arising because of uncertainties concerning the polymorphic state of the samples employed. In other instances uncertainties exist, because while the same phases were presumably examined, the x-ray patterns of these phases were dissimilar.

**B. $\text{Nb}_2\text{O}_5$**

In 1953 Orr published data on the enthalpic change of $\alpha \text{Nb}_2\text{O}_5$ from room temperature to the melting point, given as $1512^\circ$C, and from the melting point to $1537^\circ$C. The calorimetrically determined heat of fusion was, $\Delta H_f = 24.59$ kcal/mole with $\Delta S_f = 13.77$ cal/mole degree.
In the interval $0-1512^\circ\text{C}$ ($298-1786^\circ\text{K}$): in °K,

$$H_T - H_{298} = 36.23 \, T + 2.77 \times 10^{-3} \, T^{-2} + 4.88 \times 10^{5} \, T^{-1} - 12,685$$

From the melting point to $1810^\circ\text{K}$: in °K,

$$H_T - H_{298} = 59.90 \, T - 17,672$$

The rather high melting point, $1512^\circ\text{C}$, compared to our value $1491^\circ\text{C}$ (Holtzberg et al., 1957), that of Mohanty et al. (1964), $1487^\circ\text{C}$, and $1485^\circ\text{C}$ determined by Roth and Waring (1962), indicates that the starting material may have been impure. For example, Ta, which is difficult to determine spectroscopically, was a common impurity in commercially vended oxide during that time period, and would tend to raise the apparent melting point of Nb$_2$O$_5$.

In the following year, King (1954) reported on the low temperature heat capacity of $\alpha$ Nb$_2$O$_5$ in the range $-220^\circ\text{C}-0^\circ\text{C}$ ($53-298^\circ\text{K}$) using the same material employed by Orr. The values for the molar heat capacity were found to vary smoothly from 5.127 cal/mole degree at 53.24°K to 31.57 cal/mole degree at 298.16°K. The entropy calculated from measured data in the interval studied, and extrapolated data down to 0°K, is $S_{298.16}^{o}$ ($\alpha$ Nb$_2$O$_5$) = 32.8 cal/mole degree.

The above represent the only published heat capacity data for $\alpha$ Nb$_2$O$_5$ and are somewhat suspect because of the high melting point reported for the samples employed.

Using 99.69 purity Nb metal, Humphrey (1954) determined the standard heat of formation of Nb$_2$O$_5$ from the elements. The product of combustion was found to be the $\alpha$ phase and $\Delta H_{298.16}^{o}$ ($\alpha$ Nb$_2$O$_5$) was determined as $-455.2 \pm 0.6$ kcal/mole. Assuming that the entropy of formation of Nb$_2$O$_5$ and Ta$_2$O$_5$ were the same, Humphrey calculated $\Delta F_{298.16}^{o}$ ($\alpha$ Nb$_2$O$_5$) = $-247.7 \pm 0.2$ kcal/mole. Employing similar techniques, Morozova et al. (1959) obtained $\Delta H_{298.16}^{o}$ = $-472.5$ kcal/mole starting with 98.5 percent pure Nb, while Kusenko and Gel’d (1960a) reported $\Delta H_{298.16}^{o}$ = $-458.6$ for 98.52 percent purity starting niobium. The latter repeated their work (1960b) and obtained a new value of $-445.1 \pm 0.5$ kcal/mole starting with 99.33 percent pure Nb. Huber et al. (1961) repeated this work and reported a value $\Delta H_{298.16}^{o}$ ($\beta$ Nb$_2$O$_5$) = $-454.4 \pm 1.6$ kcal/mole. They determined the specific heat of this $\beta$ phase as 1.996 cal/gm° at 25°C. Unfortunately, Huber et al. provide no reference to what they term the $\beta$ phase. However, they refer to Humphrey’s data and presumably they employed Goldschmidt’s (1958) nomenclature where the high temperature form of Nb$_2$O$_5$ is termed $\beta$.

Finally, Kornilov et al. (1964a) also reported on $\Delta H_{298.16}^{o}$ ($\alpha$ Nb$_2$O$_5$) giving a value of $-453.5 \pm 0.4$ kcal/mole.
If we ignore the data of Morozova and Getskina as well as the first work of Kusenko and Gel'd in which low purity Nb metal was employed, the average value for $\Delta H^\circ_{298.16}(\alpha \text{ Nb}_2\text{O}_5) = -454.6 \pm 0.7$ kcal/mole.

Based on isothermal calorimetric studies of hydrated amorphous Nb$_2$O$_5$ prepared from the hydrolysis of NbCl$_5$, Shchukarev et al. (1960) reported a heat of hydration, $\Delta H^\circ_{298.16} = -4.7 \pm 0.27$ kcal/mole.

Gel'd and Lyubimov (1963) studied the self-diffusion of Nb in Nb$_2$O$_5$ in the range 900–1100°C using radio tracer techniques and found a value of 52–53 kcal/mole for the activation energy.

For the activation energy associated with oxidation of Nb to Nb$_2$O$_5$ Davignon (1966) found $\Delta H^\circ_a = 64.4$ kcal/mole, the process occurring at the metal oxide interface.

For the Nb$_2$O$_5$ phases amorphous, $\gamma$, and $\alpha$ we (Holtzberg et al., 1957) have determined the densities of powders pycnometrically at 25°C to be $\rho = 4.36$ gm/cm$^3$, $\gamma = 5.17$ gm/cm$^3$, $\alpha = 4.55$ gm/cm$^3$. Terao (1965) remeasured the $\alpha$ phase using powders and obtained 4.56 gm/cm$^3$ and Gatehouse and Wadsley (1964) calculated the density from single-crystal data and obtained 4.55 gm/cm$^3$. Terao, however, obtained a value of 5.81 gm/cm$^3$ for the $\gamma$ form. Moser (1965) had reported a value of $\gamma = 4.48$ gm/cm$^3$ also in marked disagreement with our value and that of Terao's. The discrepancies in the $\gamma$ data may be due to the difficulty in obtaining it in highly crystallized form, i.e., $\gamma$ exists in admixture with the $\delta$, poorly crystallized form of $\gamma$. As we saw in Sec. II, x-ray characterization of $\gamma$ also presents a problem.

C. Ta$_2$O$_5$

The earliest report on the specific heat of Ta$_2$O$_5$ was presented by Kelley (1940). His studies covered the range 53.4–294.2°C with $C_p$/mole being 5.872 and 32.10 cal/mole, respectively. He also calculated entropies at 298.1, using extrapolated values from 0–53.4°C and measured values above this. He obtained $S^\circ_{298.1} = 34.2 \pm 0.4$ cal/mole. A $\Delta F^\circ_{298.1}$ value was computed as $-453.7$ kcal/mole. Unfortunately, the Ta$_2$O$_5$ used by Kelley and a number of succeeding workers was a commercially purchased product whose state of polymorphism was uncharacterized.

In 1953 Orr reported on the high temperature enthalpy for Ta$_2$O$_5$, merely specifying that it was the same material employed by Kelley. For the temperature interval 298–1785°C the enthalpy change, referenced to 298°C is, in °K

$$\Delta H_T = \Delta H_{298} = 37.00 T + 3.28 \times 10^{-3} T^2 + 5.92 \times 10^3 T^{-1} - 13,309$$

Prior to 1954, a considerable number of papers dealing with the heat of
formation of $\text{Ta}_2\text{O}_5$ were published. The phase formed was generally questionable. These values are listed below:

- $-309.5$ kcal/mole (Muthman et al., 1907)
- $-498.3$ (Moose and Parr, 1924)
- $-480.5$ (Sieverts et al., 1930)
- $-486.0 \pm 0.5$ (Becker and Roth, 1933)
- $-499.9 \pm 1.0$ (Neumann et al., 1934)

In 1954 Humphrey, using 99.89 percent Ta as a starting material redetermined $\Delta H^{\circ}_{298} \text{Ta}_2\text{O}_5$ as $-488.8 \pm 0.5$ kcal/mole. The product of combustion was found to be the same variety of $\text{Ta}_2\text{O}_5$ as used by Orr (1953) and Kelley (1940) in their heat capacity measurements, but no further identification is provided. Unlike the case with Nb combustion where the $\alpha$ (high temperature) phase appears to be the product of the bomb calorimetric oxidation, this assumption for Ta cannot be made as we shall see shortly.

Humphrey also computed the free energy of formation, $\Delta F^{\circ}_{298} \text{(? Ta}_2\text{O}_5)$ to be $-456.5 \pm 0.6$ kcal/mole.

Olette and Ancey-Moret (1963) determined the temperature dependency of $\Delta F^{\circ}$ and gave as the relationship, reduced by us to a molar dependency in °K

$$\Delta F^{\circ} = -480,000 + 96.65T$$

These authors make no mention of what phase was being studied. However, in 1968, Ignatowicz and Davies using a galvanic cell approach with the electrode system

$$\text{Ta, Ta}_2\text{O}_5|\text{ThO}_2 + 5\text{ percent CaO}|\text{Fe, FeO}$$

showed a temperature dependency

$$\Delta F^{\circ} = -480,100 + 97.65T \quad (1073-1373^\circ\text{K})$$

This is in excellent agreement with Olette and Ancey's result, particularly in view of the fact that two completely different methods were employed to evaluate the variation of the standard free energy of formation with temperature. Ignatowicz and Davies do not specify which Ta$_2$O$_5$ phase they worked with. However, they do mention that the pentoxide electrodes were fired at 1000°C. Based on what we know of the polymorphism of Ta$_2$O$_5$, we may deduce from this that the $\beta$ phase was involved in both pieces of work. If now, we use either Eq. 1 or 2 to determine $\Delta F^{\circ}_{298}$ we get approximately $\Delta F^{\circ}_{298} \simeq -451$ kcal/mole, in good agreement with Humphrey's value. Thus, we may assume that Humphrey was studying the $\beta$ phase and that indeed this is the same phase purchased commercially by Kelley and worked on by Orr.
The matter is not, however, closed for Huber et al. (1963) redetermined, \( \Delta H_{298}^{\circ} \), the heat of formation of Ta$_2$O$_5$. The value reported, $-487.7 \pm 0.9$ kcal/mole is in excellent agreement with that of Humphrey cited earlier. However, Huber et al., in referring to Humphrey’s paper, imply that the high-temperature phase was the end-product although, as we have noted, the latter, and the references quoted by him did not specify what phase was studied. Huber et al. also specify a specific heat for Ta$_2$O$_5$ as 1.276 cal/gm$^\circ$ (0.305 j/gm$^\circ$).

Kornilov et al. (1964b) again re-examined \( \Delta H_{298}^{\circ} \) of Ta$_2$O$_5$ and obtained a value of $-489.3 \pm 0.4$ kcal/mole. These authors were well aware of the absence in the previous work of specification of the state of the end-product and note that they obtained \( \alpha \) Ta$_2$O$_5$, referencing the work of Zaslavskii et al. (1955) who indeed used this nomenclature to describe the high-temperature form of Ta$_2$O$_5$. Kornilov et al. note specifically that the phase they obtained was different from that seen by Humphrey (1954). As noted, however, the latter gives no specific information on the x-ray pattern of his Ta$_2$O$_5$.

If we discount the implied, but not explicitly stated identification in Huber et al. (1963) (incorrectly referenced by Kornilov et al., i.e., correct journal and year, but incorrect authors), then we may conclude the following: The American workers were all dealing with \( \beta \) Ta$_2$O$_5$ while Kornilov and his co-workers were dealing with \( \alpha \) Ta$_2$O$_5$. The heats of formation for both phases are, however, the same within experimental limits, i.e., ca $-488.5$ kcal/mole.

The melting point of \( \alpha \) Ta$_2$O$_5$ we cite is ours (Reisman et al., 1956), $1872 \pm 10^\circ$C. Based also on our work, \( \beta \) Ta$_2$O$_5$ melts at $1785 \pm 30^\circ$C.

The density of Ta$_2$O$_5$ powders determined by the present authors (Reisman et al., 1956) is

- \( \beta \) Ta$_2$O$_5$, \( \rho = 8.18 \text{ gm/cm}^3 \)
- \( \alpha \) Ta$_2$O$_5$, \( \rho = 8.41 \text{ gm/cm}^3 \)

King et al. (1956) reported

- \( \beta \) Ta$_2$O$_5$, \( \rho = 8.41 \text{ gm/cm}^3 \)
- \( \alpha \) Ta$_2$O$_5$, \( \rho = 8.63 \text{ gm/cm}^3 \)

Zaslavskii et al. (1955) calculated values of

- \( \beta \) Ta$_2$O$_5$, \( \rho = 8.30 \text{ gm/cm}^3 \)
- \( \alpha \) Ta$_2$O$_5$, \( \rho = 8.53 \text{ gm/cm}^3 \)

Moser (1965) determined the density of \( \alpha \) Ta$_2$O$_5$ as

- \( \alpha \) Ta$_2$O$_5$, \( \rho = 8.58 \text{ gm/cm}^3 \)
Lehovic (1964) cites a range for $\beta$ Ta$_2$O$_5$ of

$$\rho = 8.02-8.27 \text{ gm/cm}^3$$

while Westphal (1963) obtained

$$\beta \text{ Ta}_2\text{O}_5, \rho = 8.27 \text{ gm/cm}^3.$$

The cause for the large spread in data for $\alpha$ and $\beta$ Ta$_2$O$_5$ cannot be explained, particularly in view of the fact that the two forms can be prepared separately without much concern of admixture.

On anodic films, Young (1958) had obtained a value of 7.93 gm/cm$^3$ while Klerer (1965) reported a value of 8.00 gm/cm$^3$. Since the nature of the anodic films is unknown, these data do not have much significance.

D. Dielectric Properties

A substantial amount of work has been done on the dielectric properties of anodic tantalum oxide films. Considerably less information is available on more definable material. King et al. (1956) gave a value of the dielectric constant for the $\beta$ phase, $\varepsilon = 23$ at 1 Kc while Pavlovic (1964) reported $\varepsilon = 21.7$ at 77°K and 24 at 292°K with no frequency dependence. On the $\alpha$ phase Pavlovic found varying results for $\varepsilon$ depending upon whether he used powder ceramics or plates cut from a boule, and depending in the latter instance on the direction measured. For example, at 77°K he determined the $\varepsilon$ of powders to be $\sim 65$ with no frequency dependence. For plates he found values as low as 30 and as high as 75, again being frequency independent at this temperature. The $\beta$ phase showed no variation of tan $\delta$ with temperature and the coefficient of temperature variation of dielectric constant obeyed the relation

$$\varepsilon^{-1} \left( \frac{\partial \varepsilon}{\partial T} \right) = 0.04 \times 10^{-3} (^\circ\text{C})^{-1}$$

Tan $\delta$ for the $\alpha$ phase showed marked temperature dependence above 200°K as did the dielectric constant. Pavlovic attributed this to Ta ion migration for which he determined an energy of activation of 0.64 eV. As similar temperature behavior is observed an anodic films, Pavlovic concluded that anodic Ta oxide was related to the $\alpha$ phase. This is not consistent, however, with the values of $\varepsilon$ reported for such films, i.e., Vermilyea (1958) found $\varepsilon = 27.6$ at 1 Kc and Klerer (1965) found 21.2 at 1 Kc.

Little work has been done on the dielectric properties of Nb$_2$O$_5$. Robinson and Roetschi (1968) did, however, report on the vapor transport derived B phase and give values of 50, 30, and 35 for the $a$, $b$, and $c$ axes, respectively. Data varied widely, however, with values as high as 10$^5$ being obtained on different crystals.
V. OXIDE-OXIDE INTERACTIONS

A. Introduction

During the past 15 years, the interactions of Nb$_2$O$_5$ and Ta$_2$O$_5$ with alkali, alkaline earth, and other oxides have been studied extensively. The former two series of interactions and the intermediate compounds and regions of variable composition formed in them are the basis of a formidable literature worthy of an independent survey lying outside the planned scope of the present work. The interest in these systems was occasioned by the opto-electronic properties exhibited by a number of the metaniobates and tantalates. In fact, work continues on such materials at an accelerated pace although the major emphasis has shifted from an interest in ferroelectric behavior to the more purely optical phenomena associated with electro-optic properties.

Other oxide interactions studied during this period of time have been primarily centered around Nb$_2$O$_5$ and include the systems Nb$_2$O$_5$–Ta$_2$O$_5$, –V$_2$O$_5$, –Al$_2$O$_3$ (Muller and Nicholson, 1962; Burdese and Bortera, 1963; Goldschmidt, 1960a), –Cr$_2$O$_3$ (Goldschmidt, 1960b), –TiO$_2$ (Roth et al., 1964; Roth and Coughanour, 1955), –WO$_3$ (Trunov et al., 1963), –MoO$_3$ (Trunov et al., 1963), –PbO (Waring and Roth, 1965), –ZnO (Pollard, 1961), and –ZrO$_2$ (Roth and Coughanour, 1955) among others. A brief survey of some of these systems has been presented by Felten (1965). An extension of his work at this time would involve a disproportionate amount of space and would again not be in keeping with the planned scope of the present work. Consequently, the following commentary will be restricted to a discussion of the state of knowledge for the interactions between Nb$_2$O$_5$ and either Ta$_2$O$_5$ or V$_2$O$_5$.

B. The System Nb$_2$O$_5$–Ta$_2$O$_5$

Three fairly detailed examinations of this system have been reported upon. The earliest was conducted by Schäfer et al. (1954) who on the basis of an x-ray approach postulated a continuous series of solid solutions. Key in their interpretation was the assumption that Nb$_2$O$_5$ possesses more than one stable polymorph, an assumption shown by the present authors and others to be untenable (see Sec. I on polymorphism in Nb$_2$O$_5$ and Ta$_2$O$_5$). Holtzberg and Reisman (1961) on the basis of differential thermal analysis, strip furnace, x-ray and quenching experiments proposed a completely different picture of the system. Key to their arguments was the contention that Nb$_2$O$_5$ is monomorphic under 1 atm pressure and Ta$_2$O$_5$ is dimorphic (Reisman et al., 1956a). The proposed phase diagram postulates the existence of an intermediate compound, 2Nb$_2$O$_5$–Ta$_2$O$_5$. The data were interpreted
as indicating that the 2:1 compound melts incongruently at an undetermined temperature and that it disproportionates between 1400 and 1450°C into $\beta$ Ta$_2$O$_5$ (ss) and $\alpha$ Nb$_2$O$_5$ (ss). An interesting feature of this study was the observation that Nb$_2$O$_5$ has a pronounced gettering action for both Al$_2$O$_3$ and SiO$_2$. During the extensive heat treatments required to equilibrate the (Nb, Ta)$_2$O$_5$ mixtures, SiO$_2$ and Al$_2$O$_3$ present in the furnace tube ambient atmosphere were readily absorbed by the pentoxides leading to the formation of artifact phases.

The system was subjected to a re-examination by Mohanty and co-workers (1962, 1964) whose results largely corroborated the equilibrium diagram proposed by us. The diagram proposed by Mohanty et al. shows some minor changes of that published by Holtzberg and Reisman (1961). Firstly, 2Nb$_2$O$_5$·Ta$_2$O$_5$ is shown exhibiting a slight solubility range for Ta$_2$O$_5$, to the extent of some 3 mole percent. Secondly, the lower temperature limit of stability of this compound is given at somewhere between 1350 and 1400°C. In addition, the opinion is expressed that the two phase region $\alpha$ Ta$_2$O$_5$ (ss) + $\beta$ Ta$_2$O$_5$ (ss) transition line is lower than that reported by us, although the precise delineation of temperatures could not be made because of nonreproducible temperature data. It is also contended that the $\alpha$ − $\beta$ Ta$_2$O$_5$ transition occurs at 1320 ± 10°C, in agreement with the value of Lagergren and Magneli (1952) and somewhat lower than the value of 1360°C reported by Holtzberg and Reisman (1961). Other data for this transformation have been presented in Sec. I. Finally, Mohanty et al. (1962) using single crystals indexed the 2:1 compound in the tetragonal system, whereas it had been assigned cubic symmetry by us on the basis of powder diffraction studies. The difference lies in the fact that a quadrupling of one of the lattice constants which could not be determined from the powder data is called for and the compound appears indeed to belong to the tetragonal system.

C. The System Nb$_2$O$_5$–V$_2$O$_5$

The only detailed study of this system reported to date is by Waring and Roth (1965) who propose the formation of three intermediate compounds V$_2$O$_5$·9Nb$_2$O$_5$, 2V$_2$O$_5$·23Nb$_2$O$_5$ and a very Nb$_2$O$_5$-rich compound, i.e., composition at ca 93–94 mole percent Nb$_2$O$_5$. All three compounds are reported as melting incongruently and a region of variable composition is believed to exist on the Nb$_2$O$_5$ side of the diagram. As with 2Nb$_2$O$_5$·Ta$_2$O$_5$, 2V$_2$O$_5$·23Nb$_2$O$_5$ only exhibits a limited range of temperature stability, decomposing into V$_2$O$_5$·9Nb$_2$O$_5$ + the undefined Nb$_2$O$_5$ rich phase at 1284°C. The authors contend that the system V$_2$O$_5$–Nb$_2$O$_5$ is not pseudobinary in nature on the basis of the argument that 2V$_2$O$_5$·23Nb$_2$O$_5$ has
the general formula $M_{50}O_{125}$ while the structural formula $V_2Nb_{20}O_{62}$, that is, $M_{50}O_{24}$, referring to $1/2$ the unit cell, has one less oxygen present. Considering the apparent isostructural nature of the stoichiometrically different $V_2O_5 \cdot 9Nb_2O_5$ and $2Nb_2O_5 \cdot Ta_2O_5$ phases claimed by Waring and Roth, the requirement that the 2:23 compound is oxygen deficient does not appear to be a valid or demonstrated constraint.

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