

# Chapter 9

## Lead Compounds

Julie M. Schoenung

**Abstract** Lead compounds include over forty naturally occurring minerals from which five lead oxides can be derived. The lead oxides, as well as some lead silicates, are used as raw materials in lead-containing glasses and crystalline electronic ceramics. The presence of lead in glass increases the refractive index, decreases the viscosity, increases the electrical resistivity, and increases the X-ray absorption capability of the glass. The lead in electronic ceramics increases the Curie temperature and modifies various electrical and optical properties. The refinement of metallic lead from minerals and recycled goods such as lead acid batteries and cathode ray tubes is a multistep process, supplemented by oxidation steps to produce lead oxides. Lead compounds are known to be toxic and are therefore highly regulated.

### 1 Introduction

Lead and lead compounds have been used in a multitude of products for centuries. Lead (metal) is occasionally used as a “pure” material, but this is relatively rare when compared with the extent of its use in alloys and in ceramic compounds and glasses.

Lead is the 82nd element in the periodic table. It is present in the IVA column below carbon, silicon, germanium, and tin, and in the sixth row between thallium and bismuth. It is metallic in its pure state and crystallizes into the face-centered-cubic crystal structure. Lead has a low bond energy, as is evidenced by its low melting point (327°C). Lead and its alloys exhibit low elastic moduli, yield strength, and tensile strength when compared with other metals, glasses, and technical ceramics (see Table 1). The fracture toughness is also low when compared with other metals. The lead atom is large (atomic radius = 0.175 nm) and exhibits two possible oxidation states: +2 and +4. Lead is one of the commonly used heaviest metals with an atomic weight of 207.2 amu and a density of bulk material 11.35 g cm<sup>-3</sup> at 20°C. These fundamental, chemical, and physical attributes define the foundation for the reason why lead is used in most of its applications. The most common and important applications of lead and lead compounds in ceramics and glasses are described in Sect. 2.

**Table 1** Selected mechanical properties of various materials [1]

Material	Elastic modulus (GPa)	Yield strength (MPa)	Tensile strength (MPa)	Fracture toughness (MPa m <sup>1/2</sup> )
Lead alloys	12.5–15.0	8–14	12–20	5–15
Aluminum alloys	68–82	30–500	58–550	22–35
Copper alloys	112–148	30–500	100–550	30–90
Iron alloys	165–217	170–1,155	345–2,240	12–280
Glasses	61–110	264–2,129 <sup>a</sup>	22–177	0.5–1.7
Technical ceramics	140–720	524–6,833 <sup>a</sup>	160–800	0.8–6.0
Leather	0.1–0.5	5–10	20–26	3–5
Polyethylene	0.6–0.9	18–29	21–45	1.4–1.7
Polypropylene	0.9–1.6	21–37	28–41	3.0–4.5
Polyvinylchloride	2.1–4.1	35–52	41–65	1.5–5.1

<sup>a</sup> Yield strength for glasses and ceramics is measured in compression; all other materials are measured in tension

Lead is found in a wide variety of naturally occurring minerals (see Table 2). These minerals range from rather simple substances, such as pure lead, PbTe, PbSe, and PbS, to complex hydroxides, such as  $\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{SO}_4)\text{OH}$  and  $\text{Pb}_{26}\text{Cu}_{24}\text{Ag}_{10}\text{Cl}_{62}(\text{OH})_{48}3\text{H}_2\text{O}$ . As shown in Table 3, these minerals represent a wide range of crystal systems, of which the most common are monoclinic, orthorhombic, and tetragonal. Low hardness values (typically between 2 and 3 Mohs with extreme values of 1.5 for pure lead and 5.5 for plattnerite) and high theoretical densities (typically greater than 5 and as high as 11.3 g cm<sup>-3</sup>) are characteristic of these lead-containing minerals.

As described in Sect. 3, these minerals can be refined to produce metallic lead, or they can be processed to produce lead oxides. Because of lead's two oxidation states, four lead oxide compositions are possible: PbO, PbO<sub>2</sub>, Pb<sub>2</sub>O<sub>3</sub>, and Pb<sub>3</sub>O<sub>4</sub>. The PbO composition can form into two different crystal structures: orthorhombic (called massicot) and tetragonal (called litharge). Thus, five possible lead-containing oxides are available for glass and ceramic fabrication. The JCPDS cards that describe the crystallographic characteristics for these oxides are as follows: 05-0561 for litharge (PbO), 38-1477 for massicot (PbO), 41-1492 for platnerite (PbO<sub>2</sub>), and 41-1494 for minium (Pb<sub>3</sub>O<sub>4</sub>). Litharge is the most commonly used oxide for glass and ceramic fabrication. Alternatively, lead silicates can also be used. These include (2PbO–SiO<sub>2</sub>), (PbO–SiO<sub>2</sub>), and (4PbO–SiO<sub>2</sub>). Selected physical, thermal, and mechanical properties of the lead oxides are listed in Table 4. It can be seen that for all of these oxides, the lead content is very high (85–93 wt%), the density is high (8.9–10.1 g cm<sup>-3</sup>), and the hardness values are low (2–2.5 Mohs). The melting point values show more variability, ranging from 290 to 888°C. Thermodynamic data for the lead oxides, lead silicates, and selected lead-containing minerals are presented in Table 5.

Many lead-containing products, including leaded glass, can be recycled and provide another source of material to supplement the naturally occurring minerals. The processing required to produce metallic lead and lead oxides are outlined in Sect. 3. Descriptions of the most important sources of lead and statistics on lead production and consumption are also presented.

The use of lead and lead compounds, although ubiquitous at present, is expected to decrease in the future because of health concerns. It is commonly known that lead is toxic to humans, especially children. As a consequence, legislative bodies have

**Table 2** Various lead-containing minerals [2]

Mineral	Chemical name	Chemical formula
Altaite	Lead telluride	PbTe
Anglesite	Lead sulfate	PbSO <sub>4</sub>
Arsentsumebite	Lead copper arsenate sulfate hydroxide	Pb <sub>2</sub> Cu(AsO <sub>4</sub> )(SO <sub>4</sub> )OH
Baumhauerite	Lead arsenic sulfide	Pb <sub>3</sub> As <sub>4</sub> S <sub>9</sub>
Bayldonite	Hydrated copper lead arsenate hydroxide	Cu <sub>3</sub> Pb(AsO <sub>4</sub> ) <sub>2</sub> •H <sub>2</sub> O
Beudantite	Lead iron arsenate sulfate hydroxide	PbFe <sub>3</sub> AsO <sub>4</sub> SO <sub>4</sub> (OH) <sub>6</sub>
Bideauxite	Lead silver chloride fluoride hydroxide	Pb <sub>2</sub> AgCl <sub>3</sub> (F,OH) <sub>2</sub>
Bindheimite	Lead antimony oxide hydroxide	Pb <sub>2</sub> Sb <sub>2</sub> O(OH)
Boleite	Hydrated lead copper silver chloride hydroxide	Pb <sub>26</sub> Cu <sub>24</sub> Ag <sub>10</sub> Cl <sub>62</sub> (OH) <sub>48</sub> •3H <sub>2</sub> O
Boulangerite	Lead antimony sulfide	Pb <sub>5</sub> Sb <sub>4</sub> S <sub>11</sub>
Caledonite	Copper lead carbonate sulfate hydroxide	Cu <sub>2</sub> Pb <sub>5</sub> CO <sub>3</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub>
Cerussite	Lead carbonate	PbCO <sub>3</sub>
Clausthalite	Lead selenide	PbSe
Crocote	Lead chromate	PbCrO <sub>4</sub>
Cumengite	Lead copper chloride hydroxide	Pb <sub>21</sub> Cu <sub>20</sub> Cl <sub>42</sub> (OH) <sub>40</sub>
Diaboleite	Copper lead chloride hydroxide	CuPb <sub>2</sub> Cl <sub>2</sub> (OH) <sub>4</sub>
Dundasite	Hydrated lead aluminum carbonate hydroxide	Pb <sub>2</sub> Al <sub>4</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>8</sub> •3H <sub>2</sub> O
Fiedlerite	Lead chloride fluoride hydroxide	Pb <sub>2</sub> Cl <sub>4</sub> F(OH) <sub>2</sub>
Galena	Lead sulfide	PbS
Gratonite	Lead arsenic sulfide	Pb <sub>9</sub> As <sub>4</sub> S <sub>15</sub>
Hedyphanite	Lead calcium arsenate chloride	Pb <sub>2</sub> Ca <sub>2</sub> (AsO <sub>4</sub> ) <sub>3</sub> Cl
Jordanite	Lead arsenic antimony sulfide	Pb <sub>14</sub> (As,Sb) <sub>6</sub> S <sub>23</sub>
Laurionite	Lead chloride hydroxide	PbClOH
Leadhillite	Lead sulfate carbonate hydroxide	Pb <sub>2</sub> SO <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Massicot	Lead oxide	PbO
Meneghinite	Lead antimony sulfide	Pb <sub>13</sub> Sb <sub>7</sub> S <sub>23</sub>
Mimetite	Lead chloroarsenate	Pb <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> Cl
Minium	Lead oxide	Pb <sub>5</sub> O <sub>4</sub>
Native lead	Elemental lead	Pb
Neelite	Lead iron arsenate chloride	Pb <sub>2</sub> Fe(AsO <sub>4</sub> ) <sub>2</sub> Cl <sub>4</sub>
Phosgenite	Lead carbonate chloride	Pb <sub>2</sub> CO <sub>3</sub> Cl <sub>2</sub>
Plattnerite	Lead oxide	PbO <sub>2</sub>
Pseudoboleite	Hydrated lead copper chloride hydroxide	Pb <sub>2</sub> Cu <sub>4</sub> Cl <sub>10</sub> (OH) <sub>8</sub> •2H <sub>2</sub> O
Pyromorphite	Lead chlorophosphate	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl
Semseyite	Lead antimony sulfide	Pb <sub>5</sub> Sb <sub>3</sub> S <sub>21</sub>
Susannite	Lead sulfate carbonate hydroxide	Pb <sub>2</sub> SO <sub>4</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Vanadinite	Lead chlorovanadinate	Pb <sub>5</sub> (VO <sub>4</sub> ) <sub>3</sub> Cl
Wulfenite	Lead molybdate	PbMoO <sub>4</sub>

targeted the use of lead in numerous products, mandating labeling, recycling, and/or complete termination of use. The known health risks and existing legislative initiatives dealing with lead and lead compounds are summarized in Sect. 4.

**Table 3** Crystal structure, hardness, and density for various lead-containing minerals [2]

Mineral	Crystal system	Hardness (Mohs)	Density (g cm <sup>-3</sup> )
Altaite	Isometric	2.5–3	8.2–8.3
Anglesite	Orthorhombic	2.5–3.0	6.3+
Arsentsumebite	Monoclinic	3	6.4
Baumhauerite	Triclinic	3	5.3
Bayldonite	Monoclinic	4.5	5.5
Beudantite	Rhombohedrons, pseudocubic	4	4.3–4.5
Bideauxite	Isometric	3	6.3
Bindheimite	Isometric	4–4.5	7.3–7.5
Boleite	Tetragonal	3–3.5	5+
Boulangerite	Monoclinic	2.5	5.8–6.2
Caledonite	Orthorhombic	2.5–3	5.6–5.8
Cerussite	Orthorhombic	3.0–3.5	6.5+
Clausthalite	Isometric	2.5	8.1–8.3
Crocote	Monoclinic	2.5–3	6.0+
Cumengite	Tetragonal	2.5	4.6
Diaboleite	Tetragonal	2.5	5.4–5.5
Dundasite	Orthorhombic	2	3.5
Fiedlerite	Monoclinic	3.5	5.88
Galena	Cubic and octahedron	2.5+	7.5+
Gratonite	Trigonal	2.5	6.2
Hedyphane	Hexagonal	4.5	5.8–5.9
Jordanite	Monoclinic	3	5.5–6.4
Laurionite	Orthorhombic	3–3.5	6.1–6.2+
Leadhillite	Monoclinic	2.5–3	6.3–6.6
Massicot	Orthorhombic	2	9.6–9.7
Meneghinite	Orthorhombic	2.5	6.3–6.4
Mimetite	Hexagonal	3.5–4	7.1+
Minium	Tetragonal	2.5–3	8.9–9.2
Native lead	Isometric	1.5	11.3+
Nealite	Trigonal	4	5.88
Phosgenite	Tetragonal	2.0–3.0	6.0+
Plattnerite	Tetragonal	5–5.5	6.4+
Pseudoboleite	Tetragonal	2.5	4.9–5.0
Pyromorphite	Hexagonal	3.5–4	7.0+
Semseyite	Monoclinic	2.5	5.8–6.1
Susannite	Trigonal	2.5–3	6.5
Vanadinite	Hexagonal	3	6.6+
Wulfenite	Tetragonal	3	6.8

**Table 4** Selected physical, thermal, and mechanical properties of various lead oxides

Oxide	Formula weight (g mol <sup>-1</sup> )	Lead content (wt%)	Crystal system	Density (g cm <sup>-3</sup> )	Melting point (°C)	Hardness (Mohs)
PbO (massicot)	223.2	92.8	Orthorhombic	9.64	489	2
PbO (litharge)	223.2	92.8	Tetragonal	9.35	888	2
PbO <sub>2</sub>	239.2	86.6	Tetragonal	9.64	290	5.5
Pb <sub>2</sub> O <sub>3</sub>	462.4	89.6	Monoclinic	10.05	530 <sup>a</sup>	
Pb <sub>3</sub> O <sub>4</sub>	685.6	90.1	Tetragonal	8.92	830	2.5

<sup>a</sup>Decomposition temperature

**Table 5** Thermodynamic properties of various lead-containing minerals, lead silicates, and lead oxides [3]

Chemical formula	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J (mol K) <sup>-1</sup> )	$C_p$ (J (mol K) <sup>-1</sup> )
PbTe	-70.7	-69.5	110.0	50.5
PbS	-100.4	-98.7	91.2	49.5
PbSe	-102.9	-101.7	102.5	50.2
PbCO <sub>3</sub>	-699.1	-625.5	131.0	87.4
PbSO <sub>4</sub>	-920.0	-813.0	148.5	103.2
PbCrO <sub>4</sub>	-930.9			
PbMoO <sub>4</sub>	-1,051.9	-951.4	166.1	119.7
PbSiO <sub>3</sub>	-1,145.7	-1,062.1	109.6	90.0
Pb <sub>2</sub> SiO <sub>4</sub>	-1,363.1	-1,252.6	186.6	137.2
PbO (Massicot)	-217.3	-187.9	68.7	45.8
PbO (Litharge)	-219.0	-188.9	66.5	45.8
PbO <sub>2</sub>	-277.4	-217.3	68.6	64.6
Pb <sub>3</sub> O <sub>4</sub>	-718.4	-601.2	211.3	146.9

$\Delta_f H^\circ$  standard molar enthalpy (heat) of formation at 298.15 K in kJ mol<sup>-1</sup>;  $\Delta_f G^\circ$  standard molar Gibbs free energy of formation at 298.15 K in kJ mol<sup>-1</sup>;  $S^\circ$  standard molar entropy at 298.15 K in J (mol K)<sup>-1</sup>;  $C_p$  molar heat capacity at constant pressure at 298.15 K in J (mol K)<sup>-1</sup>

## 2 Applications

Lead is one of the most widely used substances in the world, with applications as a pure metal, as an alloying element in other metals, as an additive in organic substances, and as an additive or primary material component in ceramics and glasses. Lead, in metallic form is used in numerous applications, including lead-acid batteries, lead sheet and pipe, sheathing for electrical cable, radiation shielding, and lead shot and weights. As an alloying element, lead is used extensively in lead–tin solders for electronic packaging and other applications. Lead is also an alloying element in bronzes, steels, and aluminum alloys. As an additive in organic substances, lead is used in pigments, paints, polymers, and gasoline. The focus of the remainder of this section, however, is the use of lead in making ceramics and glasses.

The applications for lead and lead compounds, mostly oxides, as used in ceramic and glass applications can be categorized as follows:

### Glasses

1. Leaded glass (“crystal”) for household products
2. Glazes and enamels for ceramic whitewares
3. High-index optical and ophthalmic glass
4. Radiation shielding glass
5. High electrical resistance glass for lamps and display technologies
6. Glass solders and sealants for glass-to-glass joining and hermetic glass-to-metal sealing

### Electronic ceramics

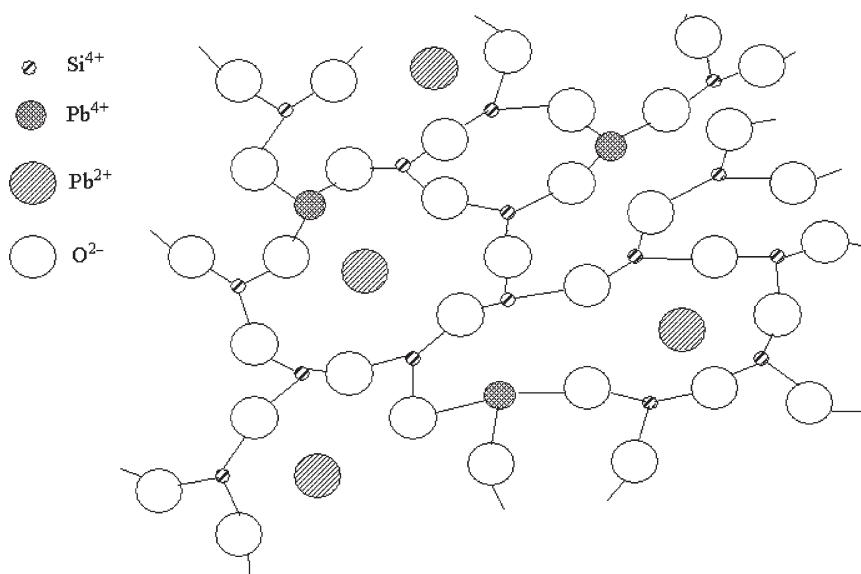
1. Capacitor dielectrics
2. Piezoelectrics
3. Electrooptic devices

The primary reasons for adding lead to glass are to increase the refractive index of the glass, to decrease the viscosity of the glass, to increase the electrical resistivity of the glass, and to increase the X-ray absorption capability of the glass used for radiation shielding. The primary reason for using lead-based electronic ceramics is to modify the dielectric and piezoelectric properties, such as Curie point and piezoelectric coupling factor.

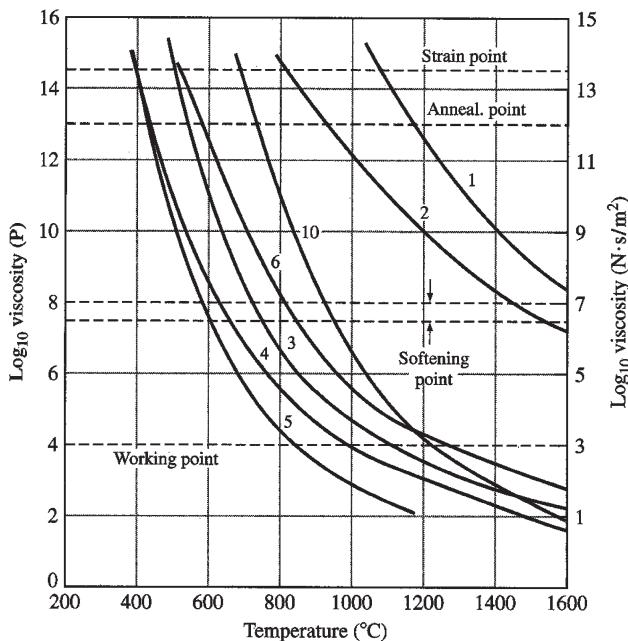
There are numerous glass products that contain lead. Because lead has two oxidation states (+2 and +4), the lead in glass can act as either a network former by replacing the silicon atom, or a network modifier by causing the formation of nonbridging oxygen atoms [4, 5], as shown in Fig. 1. The presence of lead breaks up the Si–O network and significantly reduces the viscosity of the glass (see Fig. 2). The working point of a high-lead glass, for instance, is reduced to approximately 850°C, compared to ~1,100°C for soda lime glass and >1,600°C for fused silica.

Leaded glass, which is used in houseware applications such as decorative glassware and vases, is commonly (and erroneously) referred to as “crystal” because it exhibits a higher index of refraction than other glasses. Representative values of the index of refraction for various glasses are listed in Table 6. This property results in the glass appearing shinier, brighter, and more colorful than a typical glassware (soda lime silica) glass. Leaded glass for these applications typically use PbO as a raw material, with content ranging from 18 to 38 wt% PbO [10]; a representative value is 24.4 wt% PbO [11].

Glazes for ceramic bodies and porcelain enamels for metallic substrates are coatings that are applied to these surfaces with a variety of purposes: chemical inertness, zero permeability to liquids and gases, cleanability, smoothness and resistance to abrasion and scratching, mechanical strength, and decorative and aesthetic considerations [12].



**Fig. 1** Lead in glass, acting as either a network former or network modifier [6]



**Fig. 2** Viscosity versus temperature characteristics for various glass compositions [7]. 1, Fused silica; 2, 96% silica; 3, soda lime (plate glass); 4, lead silicate (electrical); 5, high-lead; 6, borosilicate (low expansion); 10. aluminosilicate

**Table 6** Refractive indices of various glasses [8,9]

Glass composition	Average refractive index
Silica glass, $\text{SiO}_2$	1.458
Vycor glass (96% $\text{SiO}_2$ )	1.458
Soda lime silica glass	1.51–1.52
Borosilicate glass (Pyrex™)	1.47
Dense flint optical glasses	1.6–1.7
Lead silicate glasses	2.126

These coatings are applied to numerous products including china, vases, sinks, toilets, and washing machines. Lead, in the form of litharge ( $\text{PbO}$ ), is often added to glazes, but not usually to enamels, because it reduces the viscosity of the glass, which in turn provides a smoother, more corrosion-resistant surface. The higher index of refraction that results is desirable for these applications. Lead-containing glazes typically have a composition between 16 and 35wt%  $\text{PbO}$  [13–15].

Optical glass includes a wide variety of applications. Of these, lead oxide is most often incorporated into optical flints, although it might also be added to optical crown glass, ophthalmic glass (crown or flint), and optical filter glass [16]. For example, products in which the presence of lead is valued include Cerenkov counters, magneto-optical switches and shutters, and the cores of fiberoptic faceplates [17]. One of the reasons why lead is added to optical glass is it creates a high index of refraction, which can facilitate total internal reflection. The lead content of optic glasses varies considerably:

6–65 wt% PbO in optical flint glass, 4 wt% PbO in optical crown glass, and 6–51 wt% in ophthalmic glass [4,16].

Radiation shielding glass is used in television and computer monitors that contain cathode ray tubes (CRTs) because CRTs generate X-rays [1]. Exposure of the viewer to these X-rays is undesirable and limited by US Federal Standard Public Law 90–602 (Radiation Control for Health and Safety Act, 1968). X-ray absorption by a given material is dependent upon the wavelength of the radiation and the density, thickness, and atomic number of the material. Because a lead-free glass might exhibit a linear absorption coefficient as low as  $8.0\text{cm}^{-1}$  [18], lead is often added to CRT glass to provide the required X-ray shielding. The primary glass components of the CRT include the panel (or faceplate), the funnel, and the neck. Representative lead compositions and linear absorption coefficients, for the corresponding glass components, are shown in Table 7.

As a result of the large ionic size of the  $\text{Pb}^{2+}$  ion (0.132 nm), the electrical resistivity of leaded glass is orders of magnitude higher than that of lead-free, soda lime glass (direct-current (DC) resistivity at  $250^\circ\text{C}$ :  $10^{8.5}$  and  $10^{6.5}$  ohm-cm, respectively [19]) [20,21]. This characteristic of leaded glass is a primary reason why it is used for the stem and exhaust tube in many light fixtures: incandescent, fluorescent, and high-pressure mercury fixtures, as well as for hermetic seals in electronic devices. A typical composition for leaded glass in lamps is 20–22 wt% PbO [19,22].

As discussed earlier, the presence of lead in glass results in a significant change in its viscosity characteristics (see Fig. 2). Although this is true for all of the lead-containing glasses discussed earlier, it is of particular significance for the applications of glass solders (for joining glass to glass) and sealants (for joining glass to metal), which are almost always made from high-lead glasses. For instance, leaded glass is used to join the panel of a CRT to the funnel, to seal electronic packages, to bond the recording head, and to seal the panel on a flat panel display. Compositions for these high-lead glasses range from 56–77 wt% PbO, with the higher values being more common [4,18,23].

Typical PbO content for the lead-containing glass products described earlier are summarized in Table 8.

Crystalline, lead-containing ceramics generally fall within the category of materials called PZTs/PLZTs, which are lead-(lanthanum) zirconate titanates. These materials

**Table 7** PbO content and linear absorption coefficient requirements in CRT components for color monitors [18]

Component	PbO content (wt%)	Linear absorption coefficient ( $\text{cm}^{-1}$ )
Panel	2.2	28.0
Funnel	23.0	62.0
Neck	28.0	90.0

**Table 8** Summary of lead oxide content in various glass products

Product	PbO content (wt%)
Leaded glass (“crystal”) for household products	18–38
Glazes and enamels for ceramic whitewares	16–35
High-index optical and ophthalmic glass	4–65
Radiation shielding glass	2–28
High electrical resistance glass	20–22
Glass solders and sealants	56–77

are ferroelectrics, with the perovskite ( $\text{CaTiO}_3$ ) crystal structure and unusual dielectric properties [24,25]. They are used in capacitor dielectrics, piezoelectrics, and electrooptic devices [26–28]. For capacitor applications, important properties include dielectric constant, capacitance deviation, and maximum dissipation factor. Lead-based compositions for capacitor dielectrics include lead titanate, lead magnesium niobate, lead zinc niobate, and lead iron niobate–lead iron tungstate. For piezoelectric applications such as sensors and actuators, important properties include electromechanical coupling factors, piezoelectric constants, permittivity, loss tangent, elastic constants, density, mechanical quality factor, and Curie temperature. Lead-based compositions for piezoelectrics generally fall into the PZT category [ $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ], although proprietary compositions generally include dopants such as Mg, Nb, Co, Ni, Mo, W, Mn, Sb, and Sn. For electrooptic applications, important properties include optical transmittance and haze; linear electrooptic effect coefficient ( $r_e$ ), second-order (or quadratic) electrooptic effect coefficient ( $R$ ), and half-wave voltage; dielectric constant, ferroelectric hysteresis loop characteristics, and piezoelectric coupling constants; and microstructure, grain size, and porosity. The general composition for electrooptic devices is PLZT:  $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ . The compositions for all three of these product applications represent a lead content on the order of 55–70 wt%.

### 3 Processing

Historically, in the United States, the consumption of lead in glasses and ceramics has been approximately 30,000–50,000 metric tons per year, which represents 2–3% of the total U.S. annual lead consumption [29]. If storage battery usage is not included in the annual total, as this product category represents over 86% of U.S. lead consumption annually, then glasses and ceramics represent 13–22% of the remaining demand for lead in the United States.

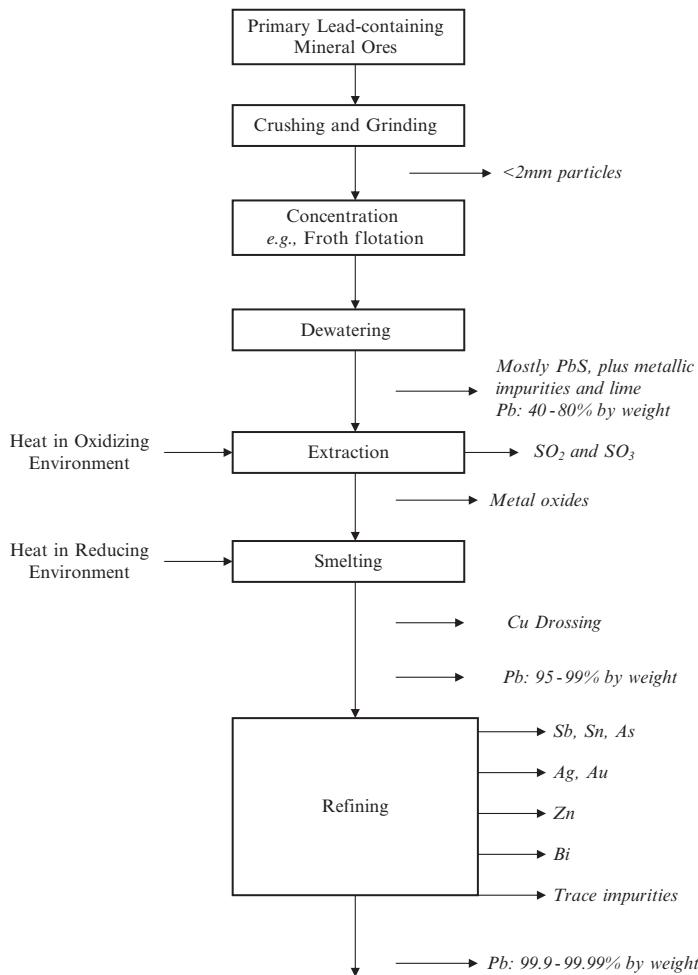
Litharge and the other lead oxides that are used in the production of glasses and ceramics are obtained primarily through the oxidation of refined (purified) metallic lead. Because metallic lead does not occur naturally in large quantities, it must be extracted from either primary sources (mineral ores) or secondary sources (recycled materials such as lead-acid batteries and cathode ray tubes). The processing required to refine metallic lead can be broken down into three major steps, as seen in Fig. 3:

1. Mining and concentrating
2. Extraction or smelting
3. Refining

The refining step is then followed by an oxidation step in order to produce lead oxide. Because these processes are discussed in detail in several other sources [1,30–32], the description provided below is intentionally brief.

For primary sources of lead, namely mineral ores, the process of mining and concentrating, indeed, begins at a mine. For secondary sources, this stage of the process is replaced by separation and sorting steps to remove the components in the batteries and CRTs that do not contain lead. The remaining process steps are fundamentally the same.

Considering the primary sources of lead, although there are over forty different minerals that contain lead (see Table 2), the three most common minerals from which



**Fig. 3** Process flow diagram for the concentration, extraction, and refining of lead

pure lead is derived are galena ( $\text{PbS}$ ), anglesite ( $\text{PbSO}_4$ ), and cerussite ( $\text{PbCO}_3$ ) with lead concentrations (by weight) of 87%, 68%, and 77.5%, respectively. Galena is easily recognized in the field because of its characteristic cubic shape, metallic luster, and high density. Anglesite and cerussite result from the natural weathering of galena. These three minerals exhibit the rock salt ( $\text{NaCl}$ ), barite ( $\text{BaSO}_4$ ), and aragonite ( $\text{CaCO}_3$ ) crystal structures, respectively. The JCPDS cards that describe the crystallographic characteristics for these minerals are as follows: 05–0592 for galena ( $\text{PbS}$ ), 36–1461 for anglesite ( $\text{PbSO}_4$ ), and 47–1734 for cerussite ( $\text{PbCO}_3$ ).

After being mined, these lead-containing minerals proceed through a concentration process that increases the lead concentration and removes waste (non-galena) rock, which is called gangue. The concentration process generally begins with crushing and grinding steps that ultimately result in particles  $<2\text{ mm}$  in size, followed by the actual concentration step, which is sometimes referred to as “beneficiation.” The most common

method used is froth flotation in which particles are separated on the basis of specific gravity. Additives, such as conditioners, are used to facilitate the separation process. Dewatering is then required, and the product remaining is primarily PbS. The concentration of lead in this product is generally between 40 and 80 wt%. Other substances contained in the material at this point include iron (Fe), zinc (Zn), copper (Cu), antimony (Sb), arsenic (As), silver (Ag), gold (Au), bismuth (Bi), and lime (CaO).

The extraction, or smelting, stage requires multiple steps. First, the lead concentrate is heated to remove the sulfur (as SO<sub>2</sub> and SO<sub>3</sub>) and to agglomerate the fine particles. This step leads to sintering and oxidation of the material, thus forming oxides of lead, zinc, iron, and silicon. Other substances such as lime, metallic lead, and residual sulfur might also be present. The next step is the actual smelting, in which the material is heated in a reducing environment so that the oxides are converted into molten metals that can be refined and separated. Various contaminants are also removed through combustion. The lead at this point is called bullion and has a concentration between 95 and 99% lead by weight. Prior to actual refining, there is one more step, the copper drossing step, which is yet another heat treatment by which copper is removed.

The lead refining stage can be divided into five steps, each of which is designed to remove (and collect) selected impurities. The impurities removed during each step are as follows:

1. Antimony (Sb), tin (Sn), and arsenic (As)
2. Silver (Ag) and gold (Au)
3. Zinc (Zn)
4. Bismuth (Bi)
5. Trace impurities

After these steps, the lead concentration is now between 99.9 and 99.99 wt%.

It should be noted that, although existing methods are well established, new methods for smelting and refining continue to be developed. For instance, “direct” smelters are available, which eliminate the need for sintering, and electrolytic refining can be used as a one-step method for simultaneously removing all impurities (except tin). Each method presents its own combination of product quality, process cost, and environmental management requirements.

Lead-containing glasses and ceramics do not use metallic lead as a raw material. Instead, lead oxides and lead silicates are used. Various processing techniques are used to produce the lead oxides from refined metallic lead. For instance, litharge (PbO) is the reaction product of lead and oxygen, and can thus be produced by heating lead in air or by blowing air into molten lead. Minium (lead tetroxide), which is more oxygen-rich than litharge, can be created by further oxidizing litharge in a controlled atmosphere at about 450°C. Lead silicates are made by mixing and heating litharge and sand (SiO<sub>2</sub>).

Primary and secondary sources of lead exist in the United States and throughout the world [29]. U.S. mine production of lead in concentrate is approximately 450,000–500,000 metric tons per year, which represents approximately 15% of the world production. Other countries with significant mine production of lead include Australia, Canada, China, Mexico, and Peru. Refining of secondary lead is dominated by the U.S. production, although other major sources include Canada, China, France, Germany, Italy, Peru, Spain, and the United Kingdom. In the United States, approximately 79% of the current lead refinery production is derived from secondary sources. Worldwide, secondary sources

account for approximately 45% of the total 6.4 million metric tons of lead refined each year. Current prices for metallic lead and for litharge ( $PbO$ ) are approximately \$0.95/kg and \$0.55/kg, respectively [33,34].

## 4 Health Effects and Legislation

Lead is ranked second on the CERCLA (Comprehensive Environmental Response, Compensation and Liability Act, 1980) Priority List of Hazardous Substances [35], indicating the national concern over lead with respect to its frequency of use, toxicity, and potential for human exposure. It is also one of the most highly regulated substances in the world. As a consequence, lead has been and will continue to be studied and monitored with respect to its human and ecological toxicity. At issue, primarily, is lead's human toxicity.

Lead can affect almost every organ and system in [the human] body. The most sensitive is the central nervous system, particularly in children. Lead also damages kidneys and the reproductive system [36].

The reader is referred to *Toxicological Profile for Lead* [37] for a comprehensive report on lead, including public health statement; health effects summary; chemical and physical information; production, import, use, and disposal information; description of the potential for human exposure; analytical methods used in monitoring health effects; regulations and advisories; a valuable glossary; and a comprehensive reference list. The US Center for Disease Control and US Environmental Protection Agency also maintain extensive databases on lead.

It is not readily apparent in most general audience publications whether lead compounds are also of concern (in addition to metallic lead), and whether they are regulated. An extensive review of the scientific literature, government regulations, and toxicology databases indicates, however, that within these circles, lead and lead compounds (inorganic) are grouped together and treated equally. At issue, actually, is the bioavailability of the lead, regardless of its source. Both lead and lead compounds are generally introduced into the body by either inhalation or ingestion. Inhalation is a greater concern because inhaled lead is almost entirely absorbed by the body, while only a fraction of ingested lead is absorbed [38]. The primary sink for inorganic lead is the blood. Within the body, lead is transported as if it were calcium, i.e., to soft tissues, teeth, and bones. Human exposure to inorganic lead and its compounds can result from various sources: occupational exposure, general exposure, environmental exposure (which affects general exposure), and hazardous waste disposal.

From the occupational exposure perspective, both the lead oxides used in ceramics and glasses and the lead-containing minerals from which lead is derived present risks, although appropriate precautions are generally taken to protect workers. Examples of occupational exposure warnings and carcinogen levels are presented in Table 9. In addition to these warnings about human exposure, inorganic lead and lead compounds also present a variety of dangers through chemical reactions either with other substances or upon heating [37,39].

From the human health (general exposure) perspective, elemental lead and inorganic lead compounds are identified as possible human carcinogens by the International Agency for Research on Cancer (IARC); they are also listed in the Hazardous

**Table 9** Carcinogen levels and occupational exposure warnings for lead and various lead compounds [39]

Substance	CAS No. <sup>a</sup>	Carcinogen level <sup>b</sup>	Warnings <sup>c</sup>	Reference
Lead	7439-92-1	A3	Dust, women	ICSC 0052
PbO	1317-36-8	A3	Dust, women	ICSC 0288
PbO <sub>2</sub>	1309-60-0	A3	Women	ICSC 1001
Pb <sub>2</sub> O <sub>4</sub>	1314-41-6	A3	Women	ICSC 1002
PbCO <sub>3</sub>	598-63-0	A3	All contact	ICSC 0999
PbCrO <sub>4</sub>	7758-97-6	A2	All contact, dust, women, children	ICSC 0003

<sup>a</sup> CAS: Chemical Abstracts Services

<sup>b</sup>A3: Animal carcinogen; A2: Suspected human carcinogen

<sup>c</sup>Dust, prevent dispersion of dust; women, avoid exposure of (pregnant) women; all contact, avoid all contact; children, avoid exposure of adolescents and children

Substances Data Bank provided by the National Library of Medicine. The US Environmental Protection Agency has classified lead as a Group B2 (probable) carcinogen and as a Category I contaminant (which results in the Maximum Contaminant Level Goal (MCLG) for drinking water being set at a value of zero) [40]. In response to EPA's classification, the State of California now regulates lead and lead compounds through Proposition 65, which requires labeling of all products that contain cancer-causing agents. The US Federal Drug Administration (FDA) also monitors lead exposure, because fine dust can settle on food or lead can leach from lead-containing food containers. Lead and lead compounds are regulated with respect to air quality standards, drinking water standards, and blood levels. Examples of some of these standards are presented in Table 10.

From the environmental loading perspective, lead and lead compounds are regulated by EPCRA (the Emergency Planning and Community Right To Know Act, 1986) as a persistent, bioaccumulative, and toxic (PBT) chemical. As such the disposal and release of these substances are subject to Toxic Release Inventory (TRI) reporting. In 2001, the threshold reporting level for lead and lead compounds was lowered from 5,000 to 220 kg per year. Results from the 2002 TRI Report [42] indicate that in the United States over 440,000 tons of lead and lead compounds were disposed of or released into the environment. This represents more than 97% of all PBT chemical releases in that year. Lead and lead compounds are also regulated by RCRA (Resource Conservation and Recovery Act, 1976). Thus, products that contain lead or lead compounds must be treated as hazardous waste. Discards of lead from glass and ceramic products into the municipal solid waste stream have been increasing, primarily as the result of CRT disposal. The US EPA estimated that lead discards from TV glass increased from 10,000 tons in 1970 to over 52,000 tons in 1986; lead discards from light bulb glass increased from ~500 tons to almost 700 tons in the same period; and for other glass and ceramic applications combined, the increase was from 3,300 tons to almost 7,800 tons [43].

In the 1970s, a major concern was the documented evidence that the lead in lead-containing glazes used on whitewares used as food containers and for cooking could leach lead into food. The glass industry was responsive to these and related occupational concerns, established appropriate operating procedures and monitoring systems, as well as reduced the use of raw materials that were more soluble, such as lead carbonates [14,15,31,44]. Later, leaching of lead from leaded crystal, especially that used for wine decanters, became a concern [45]. This concern still exists, but is mitigated

**Table 10** Representative regulatory limits and guidelines for lead (in metallic lead and various inorganic lead compounds) in selected fates

Guideline/regulation	Organization	Limit	Units	Fate	G/R	Reference
Air content	US EPA	0.0015	mg m <sup>-3</sup>	Air	R	36
Permissible exposure limit (TWA)	US OSHA	0.0500	mg m <sup>-3</sup>	Air	R	41
Recommended exposure limit (TWA)	NIOSH	0.0500	mg m <sup>-3</sup>	Air	R	41
Threshold limit value (TWA)	ACGIH	0.0500	mg m <sup>-3</sup>	Air	G	39
Blood lead level of concern in children	US CDC	0.0100	mg dL <sup>-1</sup>	Blood	G	37
Blood lead level of concern	WHO	0.0200	mg dL <sup>-1</sup>	Blood	G	37
Blood lead level of concern	ACGIH	0.0300	mg dL <sup>-1</sup>	Blood	G	37
Blood lead level of concern	US OSHA	0.0400	mg dL <sup>-1</sup>	Blood	G	37
Blood lead level – medical treatment in children	US CDC	0.0450	mg dL <sup>-1</sup>	Blood	G	36
Blood lead level – medical removal	US OSHA	0.0500	mg dL <sup>-1</sup>	Blood	G	37
Leaching solution for cups and mugs	US FDA	0.0050	mg mL <sup>-1</sup>	Food	R	37
Leaching solution for pitchers	US FDA	0.0050	mg mL <sup>-1</sup>	Food	R	37
Leaching solution for ceramicware flatware	US FDA	0.0300	mg mL <sup>-1</sup>	Food	R	37
Maximum contaminant level	US EPA	0.0500	mg L <sup>-1</sup>	Landfill	R	37
Toxicity characteristic leaching protocol limit	US EPA	0.1500	mg L <sup>-1</sup>	Landfill	R	37
Drinking water action level	US EPA	0.0150	mg L <sup>-1</sup>	Water	R	37
Maximum contaminant level goals	US EPA	0.0000	mg L <sup>-1</sup>	Water	G	37
Drinking water guidelines	WHO	0.0500	mg L <sup>-1</sup>	Water	G	37

G/R: G = Guideline, R = Regulation; TWA: time weighted average; US EPA: US Environmental Protection Agency; US OSHA: US Department of Occupational Safety and Health Administration; NIOSH: National Institute for Occupational Safety and Health; ACGIH: American Conference of Governmental Industrial Hygienists; US CDC: US Center for Disease Control; WHO: World Health Organization; US FDA: US Food and Drug Administration

somewhat through educational programs such as those required by Proposition 65. At present, a major concern is the proliferation of electronic waste, which includes cathode ray tubes [38]. Recent studies document concern for leaching of lead from CRTs when exposed to simulated landfill conditions, i.e., using the Toxicity Characteristic Leaching Procedure (TCLP) test protocol established by the US EPA [46].

As a consequence of these and other documented concerns over lead poisoning, various new legislative issues have come into place that will further limit the future use of lead. In the European Union, for instance, the Reduction of Hazardous Substances (RoHS) Directive has forced the removal of lead from electronics, worldwide; in the United States, the States of California, Massachusetts, Maine, and Minnesota have banned the disposal of CRTs in landfills, forcing special handling and encouraging recycling; in Japan, lead-free products have been embraced and utilized as a marketing tool. These new laws and marketing pressures, plus the plethora of existing rules and regulations, are forcing industry to consider alternative materials that do not contain lead. Examples include lead-free glasses for lamp applications [43,47], for cathode ray tubes [43,48,49], and for glazes [43,49], as well as lead-free oxides to replace PZTs and PLZTs [43,50].

## 5 Summary

This chapter has provided an overview of lead and lead compounds, as used in glass and ceramic products. Some of the basic physical characteristics of (metallic) lead, lead-containing minerals such as galena ( $PbS$ ), and lead oxides have been provided. The lead oxide most important to glass and ceramic fabrication is litharge,  $PbO$ . Lead (oxide) is used in glasses for several reasons: to increase the refractive index of the glass, to decrease the viscosity of the glass, to increase the electrical resistivity of the glass, and to increase the X-ray absorption capability of the glass. For ceramic applications, which are primarily ferroelectric applications, the main reason to include lead (oxide) in the material is because it can significantly increase the Curie point. Leaded glasses have a wide range of chemical composition, from 2 to 77%  $PbO$  by weight, depending on the application; lead-containing ceramics typically contain 55–70 wt% Pb.

The lead oxides used in glasses and ceramics are derived from both primary lead-containing minerals and secondary recycled leaded glass. Several process steps are required to mine, concentrate, extract, smelt, and refine the lead, which is then oxidized to form lead oxide. Lead (and inorganic lead compounds such as lead oxides) is known to be toxic and probably carcinogenic to humans. As a result, these substances are highly regulated and the potential for lead exposure through water, land, and air is closely monitored. The legislative burden on lead users continues to increase, which has led to significant efforts to find lead-free alternatives for both glass and ceramic products.

**Acknowledgments** I would like to acknowledge the research assistance of Xiaoying Zhou and Tammy Tamayo, as well as Valerie Thomas and Dele Ogunseitan for their guidance on the health risks associated with lead.

## References

1. M.F. Ashby, *Materials Selection in Mechanical Design*, 3rd edn., Elsevier, San Francisco, 2005. ISBN 0-7506-6168-2.
2. Amethyst Galleries' Mineral Gallery, Amethyst Galleries, Inc., St. Augustine, FL, 2004.
3. *Standard Thermodynamic Properties of Chemical Substances*, CRC Press LLC, 2000.
4. G.W. McLellan and E.B. Shand, *Glass Engineering Handbook*, 3rd edn., McGraw-Hill, San Francisco, 1984.
5. Y.-M. Chiang, D.P. Birnie, III, and W.D. Kingery, *Physical Ceramics: Principles for Ceramic Science and Engineering*, Wiley, New York, 1997.
6. R.A. Flinn and P.K. Trojan, *Engineering Materials and Their Applications*, 4th edn., Wiley, New York, 1994.
7. W.F. Smith, *Foundations of Materials Science and Engineering*, 3rd edn., McGraw-Hill, San Francisco, 2004.
8. M. Barsoum, *Fundamentals of Ceramics*, McGraw-Hill, San Francisco, 1997.
9. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics*, 2nd edn., Wiley, New York, 1976.
10. M.J. Matthewson, Design properties for glass and glass fibers, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 741–745.
11. G.J. Fine, Consumer houseware applications, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1100–1103.

12. R.A. Eppler and L.D. Gill, Glazes and Enamels, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1061–1068.
13. R.A. Eppler, Glazes and Enamels, in *Advances in Ceramics*, Vol. 18: *Commercial Glasses*, D.C. Boyd and J.F. MacDowell, (eds.), American Ceramic Society, Westerville, OH, 1986, pp. 65–78.
14. J.E. Marquis, Lead in glazes – Benefits and Safety Precautions, *Am. Ceram. Soc. Bull.*, **50**(11), 921–923 (1971).
15. R.A. Eppler, Formulation of glazes for low Pb release, *Am. Ceram. Soc. Bull.*, **54**(5), 496–499 (1975).
16. E.W. Deeg, Optical glasses, in *Advances in Ceramics*, Vol. 18: *Commercial Glasses*, D.C. Boyd and J.F. MacDowell (eds.), American Ceramic Society, Westerville, OH, 1986, pp. 9–34.
17. E.W. Deeg, Ophthalmic and Optical Glasses, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1074–1081.
18. J.H. Connelly and D.J. Lopata, CRTs and TV picture tubes, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1038–1044.
19. J.R. Coaton and A.M. Marsden, *Lamps and Lighting*, 4th edn., Arnold/Wiley, London/New York, 1997.
20. N. Braithwaite and G. Weaver, *Electronic Materials: Inside Electronic Devices (Materials in Action Series)*, 2nd edn., The Open University, Boston, 2000.
21. N.P. Bansal and R.H. Doremus, *Handbook of Glass Properties*, Academic Press, San Diego, 1986.
22. P.R. Prud'homme van Reine, W.J. van den Hoek, and A.G. Jack, Lighting, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1032–1037.
23. R.R. Tummala and R.R. Shaw, Glasses in Microelectronics in the information-processing industry, in *Advances in Ceramics*, Vol. 18: *Commercial Glasses*, D.C. Boyd and J.F. MacDowell (eds.), American Ceramic Society, Westerville, OH, 1986, pp. 87–102.
24. L.L. Hench and J.K. West, *Principles of Electronic Ceramics*, Wiley, New York, 1990.
25. S.O. Kasop, *Principles of Electronic Materials and Devices*, 2nd edn., McGraw Hill, San Francisco, CA, 2002.
26. I. Burn, Ceramic capacitor dielectrics, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1112–1118.
27. K. Uchino, Piezoelectric ceramics, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1119–1123.
28. G.H. Haertling, Electrooptic ceramics and devices, in *Engineered Materials Handbook*, Vol. 4: *Ceramics and Glasses*, ASM International, 1991, pp. 1124–1130.
29. G.R. Smith, Lead, *Minerals Yearbook*, US Geological Survey, 2002.
30. M. King and V. Ramachandran, Lead, *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 1995.
31. Lead Processing, *Encyclopedia Britannica*, 2003.
32. *Emission Estimation Technique Manual for Lead Concentrating, Smelting and Refining*, National Pollutant Inventory, Environment Australia, 1999.
33. Current Metal and Scrap Prices, London Metal Exchange (LME), August 12, 2004.
34. P.N. Gabby and J.I. Martinez, Lead in April 2004, *Mineral Industry Surveys*, US Geological Survey, July 2004.
35. 2003 CERCLA Priority List of Hazardous Substances, Agency for Toxic Substances and Disease Registry, Atlanta, GA, May 2004.
36. Lead, CAS # 7439-92-1, Agency for Toxic Substances and Disease Registry ToxFAQs, ATSDR, Atlanta, GA, June 1999.
37. Toxicological Profile for Lead, US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA, July 1999.
38. J.M. Schoenung, O.A. Ogunseitan, J.-D. M. Saphores, and A.A. Shapiro, Adoption of Pb-free electronics: policy differences and knowledge gaps, *J. Ind. Ecol.*, **8**(4) (2004).
39. International Labour Organization, International Occupational Safety and Health Information Centre (CIS): Lead, ICSC 0052, 2002; Lead (II) Oxide, ICSC 0288, 2003; Lead Dioxide, ICSC 1001, 2002; Lead Tetroxide, ICSC 1002, 2002; Lead Carbonate, ICSC 0999, 2001; Lead Chromate, ICSC 0003, 2003, Geneva, Switzerland.
40. Maximum contaminant level goals and national primary drinking water regulations for lead and copper, *Fed. Regist.*, **56**(110) 26470 (1991).

41. NIOSH Pocket Guide to Chemical Hazards: Lead, National Institute for Occupational Safety and Health, Washington, D.C., 2004.
42. TRI Disposal or Other Releases, PBT Chemicals, 2002, US Environmental Protection Agency, April 2004.
43. *Preliminary Use and Substitutes Analysis of Lead and Cadmium in Municipal Solid Waste, EPA 530-R-92-010*, US Environmental Protection Agency, April 1992.
44. J.S. Nordyke, Lead products, *Am. Ceram. Soc. Bull.*, **65**(5) 737–738 (1986).
45. J.H. Graziano and C. Blum, Lead exposure from lead crystal, *The Lancet*, **337**, 141–142 (1991).
46. T.G. Townsend, S. Mussen, Y.-C. Jang, and I.-H Chung, Characterization of lead leachability from cathode ray tubes using the toxicity characteristic leaching procedure, Florida Center for Solid and Hazardous Waste Management, Report 99-5, Gainesville, FL, 1999.
47. B. Filmer, European Patent No. 0 603 993 A1, 1994.
48. P. Hedemalm, Some uses of lead and their possible substitutes, KEMI Report No. 3/94, The Swedish National Chemicals Inspectorate, PrintGraf, Stockholm, Sweden, Feb. 1994.
49. *Lead Review*, Nordic Council of Ministers, Copenhagen, Norway, January 2003.
50. I. Campbell, Lead and cadmium free glasses and frits, *Glass Technol.*, **39**(2) 38–41 (1998).
51. M. Ichiki, L. Zhang, M. Tanaka, and R. Maeda, Electrical properties of piezoelectric sodium-potassium niobate, *J. Eur. Ceram. Soc.*, **24** 1693–1697 (2004).