



ELSEVIER

August 2002

Materials Letters 55 (2002) 281–284

**MATERIALS  
LETTERS**

www.elsevier.com/locate/matlet

# Hydrothermal synthesis and optical property of nano-sized $\text{CoAl}_2\text{O}_4$ pigment

Zhizhan Chen\*, Erwei Shi, Wenjun Li, Yanqing Zheng, Weizhuo Zhong

*Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China*

Received 20 April 2001; received in revised form 23 October 2001; accepted 25 October 2001

## Abstract

Nano-sized  $\text{CoAl}_2\text{O}_4$  was synthesized by hydrothermal method. The powder was characterized by XRD, DTA–TG, TEM, BET, IR, XPS, and UV–Vis techniques. The particle size was ca. 70 nm, and the particle size distribution was narrow. The BET surface area was  $29.22 \text{ m}^2 \text{ g}^{-1}$ . It was thermally stable. The maximum absorption was  $\sim 600 \text{ nm}$ . © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:*  $\text{CoAl}_2\text{O}_4$ ; Hydrothermal method; Optical property

## 1. Introduction

$\text{CoAl}_2\text{O}_4$  is a double oxide with a normal spinel-type structure. It is well known as Thenard's blue for its impressive optical property and widely used in the ceramics, glass, paint industry, and color TV tubes as contrast-enhancing luminescent pigment [1].

$\text{CoAl}_2\text{O}_4$  pigment is usually synthesized at high temperature at solid state from a mixture of the two oxide components [2,3]. However, the reaction involves processing temperatures  $>1000 \text{ }^\circ\text{C}$  for extended time periods, which influences the pigment tonalities. Recently, various solution chemical synthesis techniques [4–15] have been utilized to prepare the pigment. Among them, the sol–gel process has big advantages for coating; hydrothermal synthesis can prepare powders without calcination. Various oxides and complex oxides with narrow particle size distribution,

single phase, and controlled particle morphology have been synthesized by hydrothermal technique. However, little attention has been paid to preparing spinel oxides. No literature precedence, to our knowledge, is available on the synthesis of  $\text{CoAl}_2\text{O}_4$  by this method. In this letter, the hydrothermal method is introduced to synthesize  $\text{CoAl}_2\text{O}_4$ . The results illustrate the effectiveness of the technique in producing the nano-sized and narrow size distribution pigments.

## 2. Experimental

An appropriate amount of analytic grade  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  with the molar ratio of  $\text{Zn}^{2+}/\text{Al}^{3+} = 1:2$  was dissolved in the distilled water and then titrated dropwise by 3 M NaOH till the pH was 8.5 under fast magnetic stirring at  $25 \text{ }^\circ\text{C}$ . The concentrations of  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  were 0.15 and 0.3 mol  $\text{dm}^{-3}$ , respectively. Sixty milliliters of feedstock was charged into an 80-ml teflon-lined autoclave and

\* Corresponding author.

treated hydrothermally for 24–48 h at 210–245 °C. After the autoclave was cooled naturally, a dark blue precipitate was collected. The sample was filtered off, washed with distilled water, and then dried at 120 °C for 12 h.

Products were characterized by X-ray diffraction (RAX-10, Japan), thermal analysis (STA 429, Netzsch, Germany), transmission electron microscopy (JEM-2010, JEOL, Japan), X-ray photoelectron spectroscopy (VG Scientific), infrared spectroscopy (1600 Series, Perkin Elmer). The surface area was measured by N<sub>2</sub> adsorption (ASAP2000, Miromeritics). Optical property was studied by ultraviolet and visible spectrophotometer (Lambda 20, Perkin Elmer).

### 3. Results and discussion

Fig. 1 shows the typical XRD patterns of the precursor treated at various temperatures. When the

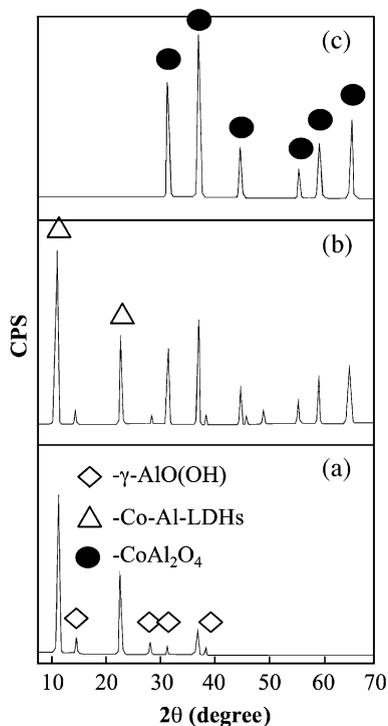


Fig. 1. XRD patterns of the powders synthesized hydrothermally at different temperatures (a) 215, (b) 230 and (c) 245 °C for 24 h using 0.15 mol dm<sup>-3</sup> CoCl<sub>2</sub> and 0.3 mol dm<sup>-3</sup> AlCl<sub>3</sub> as starting materials.

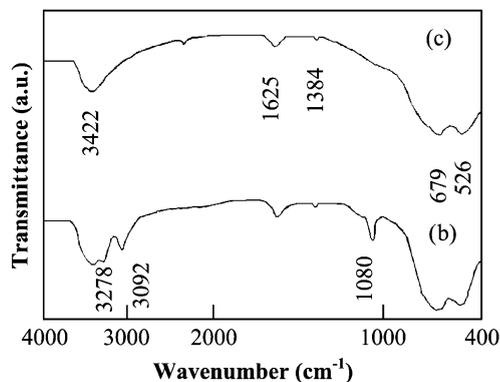


Fig. 2. IR spectra of the precursors treated at different temperatures, (b) 230, and (c) 245 °C for 24 h. Spectra were obtained using the usual KBr technique.

temperature was lower than 210 °C, the crystalline phase was Co<sub>1-x</sub>Al<sub>x</sub> layered double hydroxide (hereafter denoted as Co–Al-LDHs) [16]. When the precursor was treated at 215 °C, the amorphous Al(OH)<sub>3</sub> started to crystallize to form γ-AlO(OH). It was at this temperature that CoAl<sub>2</sub>O<sub>4</sub> phase was formed. The yield of CoAl<sub>2</sub>O<sub>4</sub> increased with the increasing treatment temperature. As evident from XRD, the pure phase CoAl<sub>2</sub>O<sub>4</sub> was prepared only when the temperature was 245 °C. Highly alkaline conditions (i.e., for the precursors precipitated at pH values more than 10) did not promote the formation of pure pigment. Experiments using the other base reagent such as NH<sub>3</sub>·H<sub>2</sub>O produced results significantly different from those described for NaOH. For the NH<sub>3</sub>·H<sub>2</sub>O system, regardless of the pH values of the solution (pH < 14) for precipitating the precursor materials, Co–Al-LDHs was the only phase produced by hydrothermal treatment. It was believed that NH<sub>3</sub>·H<sub>2</sub>O stabilized the intermediate Co–Al-LDHs structure. Therefore, the choice of base reagent was important to obtain the desired phase under the synthesis conditions.

The IR spectra of the solid phase powders synthesized at 230 and 245 °C were shown in Fig. 2. The band at ca. 3422 cm<sup>-1</sup>, which was a strong absorption band, is attributed to the OH stretching mode, [δ(OH)]. The band around 1625–1636 cm<sup>-1</sup> was assigned to the free water molecules, [δ(H<sub>2</sub>O)]. The ν<sub>3</sub> mode of the CO<sub>3</sub><sup>2-</sup> anion appeared around 1384 cm<sup>-1</sup> [17]. The bands around 526–542 and 679–693

$\text{cm}^{-1}$  arose from the  $\text{CoO}_4$  and  $\text{AlO}_6$  vibrations [9]. The vibration modes mentioned above were same for both of the two samples. However, the  $230^\circ\text{C}$  treated sample had other bands around  $3278$  and  $3092\text{ cm}^{-1}$ , which were due to the hydrogen bond between  $\text{H}_2\text{O}$  molecules and the  $\text{CO}_3^{2-}$  anions in the interlamellar layer, and  $1080\text{ cm}^{-1}$  band which corresponded to  $\nu_1$  mode of the  $\text{CO}_3^{2-}$  [18,19]. The IR differences between these two samples along with the XRD results confirmed that the  $230^\circ\text{C}$  treated samples contained Co–Al-LDHs. It was reasonably concluded that the Co–Al-LDHs might change into  $\text{CoAl}_2\text{O}_4$  topotactically when the temperature increased.

The DTA–TG curves were shown in Fig. 3. Two endothermic peaks, A and B, whose bottom were at ca.  $505$  and  $1015^\circ\text{C}$ , respectively, were the dehydration of  $\gamma\text{-AlO}(\text{OH})$  to  $\gamma\text{-Al}_2\text{O}_3$  and phase transformation of  $\gamma\text{-Al}_2\text{O}_3$  to  $\theta\text{-Al}_2\text{O}_3$ , the exothermic peak C, whose top was at ca.  $1322^\circ\text{C}$ , corresponded to the phase transition from  $\theta\text{-Al}_2\text{O}_3$  to  $\alpha\text{-Al}_2\text{O}_3$ . It suggested that there exists a little amount of  $\gamma\text{-AlO}(\text{OH})$  in spite of no detection from XRD [20,21]. The total weight loss was ca.  $2\text{ wt.}\%$ . The lack of any other noticeable exothermic effects concerning the formation of  $\text{CoAl}_2\text{O}_4$  suggested that no re-crystallization of the dispersed  $\text{CoAl}_2\text{O}_4$  occurs at temperatures up to  $1400^\circ\text{C}$ . It was thermally stable.

Refinement revealed that the cell constant was  $8.130\text{ \AA}$ , which was more than the literature value [22]. Transmission electron micrograph of the powders indicated uniform and nonaggregated particles, as seen in Fig. 4. The particles had octahedral morphologies. Each particle was distinguishable from another. Particle size distribution in TEM photograph was

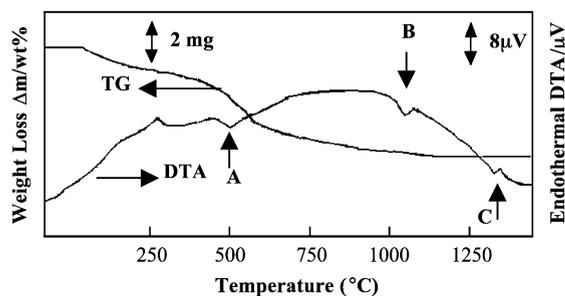


Fig. 3. DTA–TG curves of  $\text{CoAl}_2\text{O}_4$  pigment synthesized at  $245^\circ\text{C}$  for 24 h. Heating rate of  $10^\circ\text{C}/\text{min}$  in the air atmosphere.

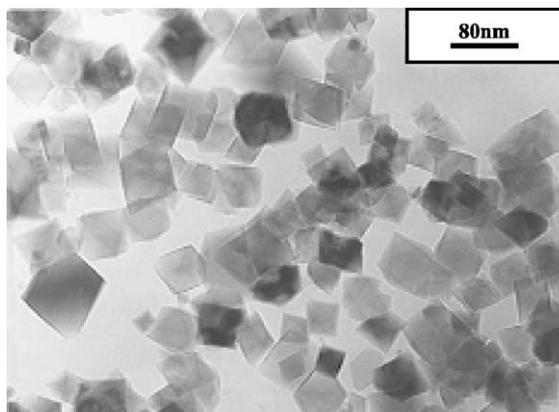


Fig. 4. TEM micrograph of  $\text{CoAl}_2\text{O}_4$  powders synthesized at  $245^\circ\text{C}$  for 24 h.

fairly narrow. Particle size from TEM observation was  $65\text{--}75\text{ nm}$ . The crystallite size of the powders, calculated from Scherrer's equation, using the broadening of the X-ray diffraction line (311) was ca.  $70\text{ nm}$ . The result was in agreement with the TEM observation. The specific surface area measured by the BET method was  $29.22\text{ m}^2\text{ g}^{-1}$ . The value indicated that the average particle diameters was  $50\text{ nm}$  based on the assumptions that all the particles had the same diameter and the same theoretical density based on the lattice parameter. Particle diameter was smaller than the particle size from TEM and XRD. This difference originated from the  $\gamma\text{-AlO}(\text{OH})$  impure phase in the pigment as illustrated in the

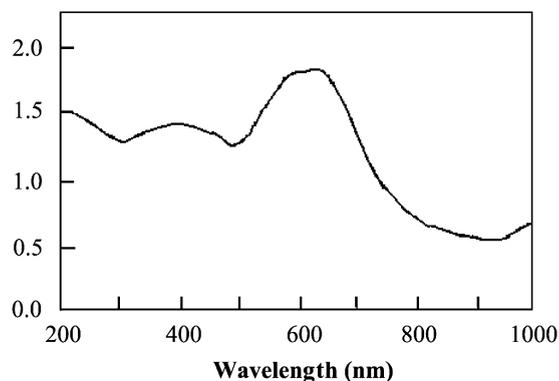


Fig. 5. UV–Vis spectrum of  $\text{CoAl}_2\text{O}_4$  pigment synthesized at  $245^\circ\text{C}$  for 24 h.

DTA–TG curves.[5] The effects of the precursor concentration, hydrothermal treatment time and temperature on the particle size were slight.

XPS data provided information on the chemical state of the elements in the near-surface region. The  $\text{Co}2p_{3/2}$  binding energy was 784.80 and 785.50 eV, respectively, and their peak shapes were similar for the hydrothermally obtained and fired samples at 1000 °C for 2 h. The relatively narrow peak width, the  $2p_{3/2}$  to  $2p_{1/2}$  separation of 15.5 eV, and the very flat weak satellite structure found on the high binding energy side of the  $2p_{3/2}$  and  $2p_{1/2}$  transitions indicated that few  $\text{Co}^{2+}$  cations occupied octahedral sites in the  $\text{CoAl}_2\text{O}_4$  spinel lattice [23]. Therefore, the pigment had normal spinel structure for both obtained and fired samples.  $\text{Co}^{2+}$  was in tetrahedral site. The molar ratios of Co/Al of the prepared and fired samples were 1:2.08 and 1:1.78, respectively. The information from XPS was mainly from the surface area. The cobalt fraction in the surface was increased when the sample was fired at high temperature.

The UV–Vis spectrum was recorded as shown in Fig. 5. The minimum absorption was around 500 nm, and the maximum absorption was ca. 600 nm. The results were consistent with Meyer et al.'s [9] but different from Merikhi et al.'s [7]. Meyer et al. [9] produced nano-scaled  $\text{CoAl}_2\text{O}_4$  using microemulsion mediated sol–gel method. The particle size was about 100 nm after the precursor was sintered. Merikhi et al. [7] synthesized sub-micrometer  $\text{CoAl}_2\text{O}_4$  pigment using the polyol method and the particle size was 50–200 nm. Compared to Merikhi et al.'s [7] result, both of them had the same maximum absorption, but the minimum absorption of the hydrothermally obtained pigment was found towards longer wavelength. The phenomenon might be an effect of the different crystallite sizes.

In conclusion, nano-sized  $\text{CoAl}_2\text{O}_4$  pigment was successfully synthesized through hydrothermal route. It was thermally stable, and had maximum absorption around 600 nm. It can be used as high-grade pigment in color TV tubes.

## Acknowledgements

This project was supported by the National Nature Science Foundation of China with Grant No. 59832080.

## References

- [1] G. Buxbaum, *Industrial Inorganic Pigments*, 1st edn., VCH, Weinheim, Germany, 1993, p. 85.
- [2] J.M. Fernández Colinas, C. Otero Areán, *J. Solid State Chem.* 109 (1994) 43.
- [3] P.H. Bolt, F.H.P.M. Habraken, J.W. Geust, *J. Solid State Chem.* 135 (1998) 59.
- [4] T.Y. Tseng, J.C. Lin, *J. Mater. Sci. Lett.* 8 (1989) 261.
- [5] C. Otero Areán, M. Peñ arroya Mentrut, E. Escalona Platero, F.X. Llabrés i Xamena, J.B. Parra, *Mater. Lett.* 39 (1999) 22.
- [6] W.-S. Cho, M. Kakihana, *J. Alloys Compd.* 287 (1999) 87.
- [7] J. Merikhi, H.-O. Jungk, C. Feldmann, *J. Mater. Chem.* 10 (2000) 1311.
- [8] L.K. Kurihara, S.L. Suib, *Chem. Mater.* 5 (1993) 609.
- [9] F. Meyer, R. Hempelmann, S. Mathur, M. Veith, *J. Mater. Chem.* 9 (1999) 1755.
- [10] A. Rabenau, *Angew. Chem., Int. Ed. Engl.* 24 (1985) 1026.
- [11] W.J. Dawson, *Ceram. Bull.* 10 (1988) 1673.
- [12] S. Sō miya, K. Hishinuma, T. Akiba, *Bull. Mater. Sci.* 6 (1995) 811.
- [13] T.R.N. Kutty, R. Balachandran, *Mater. Res. Bull.* 19 (1984) 1479.
- [14] M.M. Lencka, R.E. Riman, *Chem. Mater.* 5 (1993) 61.
- [15] S. Chemlal, A. Larbot, M. Persin, et al., *Mater. Res. Bull.* 35 (2000) 2515.
- [16] J.T. Klopogge, R.L. Frost, *Appl. Catal., A: General* 184 (1999) 61.
- [17] R.A. Nyquist, R.O. Kagel, *Infrared Spectra of Inorganic Compounds (3800–45  $\text{cm}^{-1}$ )*, Academic Press, New York, 1971.
- [18] F. Kooli, K. Kosuge, A. Tsunashima, *J. Mater. Sci.* 30 (1995) 4591.
- [19] P. Jeevanandam, Yu. Kolytypin, A. Gedanken, Y. Mastai, *J. Mater. Chem.* 10 (2000) 511.
- [20] K. Yamakata, K. Hirota, O. Yamaguchi, *J. Am. Ceram. Soc.* 8 (1994) 2207.
- [21] T. Tsukada, H. Segawa, A. Yasumori, K. Okada, *J. Mater. Chem.* 9 (1999) 549.
- [22] JCPDS International Centre for Diffraction Data 10–458.
- [23] J.-G. Kim, D.L. Pugmire, D. Battaglia, M.A. Langell, *Appl. Surf. Sci.* 165 (2000) 70.