Hydrothermal preparation of nanometer ZnO powders

WEN-JUN LI, ER-WEI SHI, YAN-QING ZHENG, ZHI-WEN YIN
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China

Zinc oxide powder is an important material for applications such as sensors, varistors, pigments, electrography, medical materials, etc. [1]. Various methods adopted for the preparation of zinc oxide crystallites include the sol-gel method [2], evaporative decomposition of solution (EDS) [3], wet chemical synthesis [4] and gas-phase reaction [5], etc. The hydrothermal synthesis is an ideal method which is widely used to synthesize the oxide powders with high quality. However, it is difficult to synthesize nanometer ZnO powders by the traditional hydrothermal route. In 1999, our groups first reported the hydrothermal discharging-gas method [6] which was used to synthesize the acicular ZnO particles. The letter describes our successful attempt in the preparation of nanometer ZnO powders using $Zn(CH_3COO)_2$ solution as precursor by the hydrothermal discharging-gas method.

The reaction vessel adopted in the experiments is a silver-lined tube-type stainless steel autoclaves with 30 mm inner diameter and about 215 ml capacity. In the upper part of the autoclave are located the discharge valve for discharging gas and a gas manometer. The $Zn(CH_3COO)_2$ solution with the concentration ranges of 0.5–1.5 mol/l is used as precursor. The percentage of fill is 70% in the experiment. The reaction temperature ranges from 160 °C–250 °C, and no temperature gradient is applied. After the temperature of autoclave is elevated to a desired value and remains stable for 1 h in a furnace with a constant temperature-controlling device, the discharge valve is immediately opened to complete reaction. Meanwhile, the power is cut off to make the autoclave cool to room temperature. After the preparation process is completed, the obtained solid products are washed out with water into a glass beaker, then each is filtered. The as-dried products are studied by X-ray diffractometer, and electron microscope. The results are shown in Table I.

From Table I, it can be seen that the crystallite size of ZnO powders, which are prepared using 1 mol/l $Zn(CH_3COO)_2$ solution as precursor at different temperatures is greatly different; when reaction temperature rises from 160 °C to 250 °C, the crystallite sizes of ZnO powders decrease from 3500 nm to 70 nm. Fig. 1 shows the TEM micrograph of the product prepared using 1 mol/l $Zn(CH_3COO)_2$ solution as precursor at 250 °C. In Fig. 1, it can be seen that the crystallite size of ZnO powder is 70 nm, the morphology is prismatic form. The XRD pattern is shown in Fig. 2.

In order to discover the formation mechanism of ZnO powders by hydrothermal discharging-gas method, the experiments are carried out using $Zn(CH_3COO)_2$ solution as precursor without discharging-gas condition. It is concluded that when the discharge valve is not opened, no powders are precipitated in the reaction vessel. It suggests that only when the discharge valve is opened does the hydrolysis of CH_3COO^- ion occur. The reaction processes are shown as follows:

$$CH_3COOH(l) = CH_3COOH(g) \quad (1)$$

$$CH_3COO^- + H_2O = CH_3COOH(l) + OH^- \quad (2)$$

So, the nucleation rate of ZnO crystallite is possibly affected by the hydrolysis rate of CH_3COO^- ion when the discharge valve is opened. The crystallite size is related to the nucleation rate in crystalline procedure. The bigger the nucleation rate is, the smaller the crystallite size is. So, in order to disclose the factors affecting the crystallite size, the nucleation mechanism of ZnO powders under hydrothermal conditions must be first studied.

The formation mechanism of crystals in solution mainly contains the formation of growth units and the incorporation of growth units into crystal lattice. The problem is to clarify what the growth unit is for a given location and then how growth units are linked together. From the analysis of IR spectra, [7, 8] Raman spectra [9, 10] and low angle diffraction of X-ray [11–13] of the solution structure, it can be found that there exist the complexes whose ligands are OH^- ion in the supersaturation solution. Moreover, according to the calculation equation of the stability energy of complexes with OH^- ligand [14], it is obtained that the cation existing in the

TABLE I The experimental results of ZnO powders synthesized by the hydrothermal discharging-gas method

Sample no.	$Zn(CH_3COO)_2$ (mol/l)	Temperature (°C)	Phase	Morphology	Crystallite size (nm)
1	1.5	200	ZnO	Prismatic form	15 and 900
2	1	200	ZnO	Isometric form	450
3	0.5	200	ZnO	Prismatic form	4500
4	1	160	ZnO, $Zn(CH_3COO)_2$	Prismatic form	3500
5	1	250	ZnO	Prismatic form	70

0261–8028

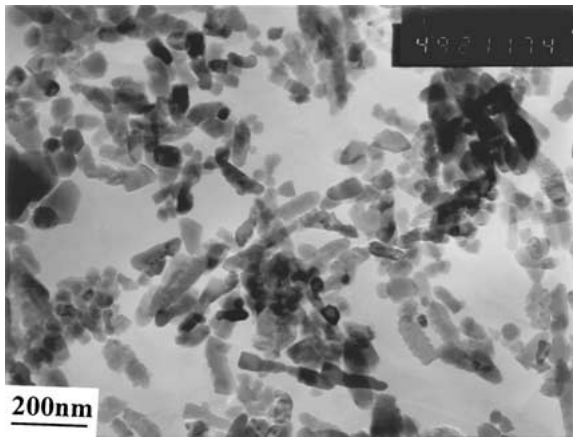

Figure 1 TEM micrograph of powders prepared by hydrothermal discharging-gas method using 1 mol/l $Zn(CH_3COO)_2$ solution as precursor at 250 °C.

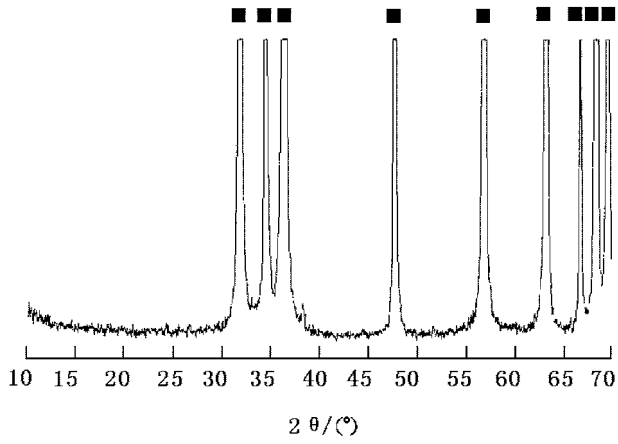

Figure 2 XRD pattern of powders prepared by hydrothermal discharging-gas method using 1 mol/l $Zn(CH_3COO)_2$ solution as precursor at 250 °C.

form of a given complex is more stable than a single cation. So, we introduce a hypothesis that the growth unit is the complex formed by the attraction of cation and OH^- ions, whose coordination numbers is equal to that of the cation in the crystal to be formed. In the ZnO crystal, the coordination number of Zn^{2+} ion is four. According to above hypothesis, the growth unit of ZnO crystal is the complex $Zn(OH)_4^{2-}$. Thus, the formation mechanism of ZnO crystallite under hydrothermal condition is represented as follows:

1. The formation of growth unit $Zn(OH)_4^{2-}$.

$$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-} \tag{3}$$

2. The incorporation of growth unit into crystal lattice by the oxolation reaction.

$$\begin{aligned} Zn(OH)_4^{2-} + Zn(OH)_4^{2-} &= Zn_2O(OH)_6^{4-} + H_2O \\ Zn_xO_y(OH)_z^{(z+2y-2x)-} + Zn(OH)_4^{2-} & \\ = Zn_{x+1}O_{y+1}(OH)_{z+2}^{(z+2y-2x+2)-} + H_2O & \end{aligned} \tag{4}$$

In the beginning of the nucleation, the growth unit $Zn(OH)_4^{2-}$ is first formed in solution due to the attraction of Zn^{2+} and OH^-, as shown in Equation 3. Then, under supersaturation condition, the clusters $Zn_{x+1}O_{y+1}(OH)_{z+2}^{(z+2y-2x+2)-}$ are formed by the oxolation reaction as shown in Equation 4. When the size of the clusters $Zn_{x+1}O_{y+1}(OH)_{z+2}^{(z+2y-2x+2)-}$ reaches the size of the so-called "critical nucleus", ZnO powders are precipitated.

From Equation 4, it can be seen that the formation rate of ZnO nucleus is proportional to the concentration of the growth unit $Zn(OH)_4^{2-}$ in solution. From Equation 3, it can be seen that the formation rate of the growth unit is proportional to the concentration of Zn^{2+} and OH^- ions. So, the formation rate of ZnO nucleus is proportional to the concentration of Zn^{2+} and OH^- ions. From above analysis concerning the formation mechanism of the ZnO crystallite by hydrothermal gas-discharging method, it can be found that compared with that of OH^- ion, the concentration of Zn^{2+} ion is large during nucleation. So, the nucleation rate of ZnO crystallite depends mainly on the concentration of OH^- ion. From Equation 2, it can be obtained that the concentration of OH^- ion is controlled by the hydrolysis rate of CH_3COO^-. So, the nucleation rate of ZnO crystallite is determined by the hydrolysis rate of CH_3COO^-. From Equations 1 and 2, it can be obtained that when temperatures rise, the rates of hydrolysis of CH_3COO^- increase due to the increase of the vaporization rate of CH_3COOH gas, which lead to the decrease of the size of the ZnO crystallite.

Moreover, it can also seen from Table I that the size of the ZnO crystallite prepared by hydrothermal discharging-gas method using the different concentrations of $Zn(CH_3COO)_2$ solution as precursors at 200 °C is also different greatly. When the concentration of $Zn(CH_3COO)_2$ solution is 0.5 mol/l, the crystallite size is 4.5 μm; When the concentration of $Zn(CH_3COO)_2$ solution is 1mol/l, the crystallite size is 450 nm; When the concentration of $Zn(CH_3COO)_2$ solution is 1.5 mol/l, the obtained particles have two kinds of sizes: 15 nm and 900 nm. The TEM micrograph is shown in Fig. 3a–c respectively.

It shows that the bigger the concentration of precursor is, the smaller the crystallite size of powders is. According to Equation 2, the hydrolysis rate of CH_3COO^- is proportional to the concentration of $Zn(CH_3COO)_2$ solution. So, increasing the concentration of $Zn(CH_3COO)_2$ solution, the ZnO crystallite size decreases due to the increase of the hydrolysis rate of CH_3COO^-. However, the crystallites with the size of 15 nm do not exist stablely in solution due to the large surface energy. A part of ZnO crystallites agglomerate to form the larger crystallites as shown in Fig. 3c.

To sum up, the size of the ZnO crystallite prepared using $Zn(CH_3COO)_2$ solution as precursor by hydrothermal discharging-gas method is mainly related to the hydrolysis rate of CH_3COO^- during nucleation, which can be controlled by the reaction temperature and the concentration of $Zn(CH_3COO)_2$ solution. The higher the reaction temperature is, the smaller the particle size of powder is; the bigger the concentration of precursor is, the smaller the particle size of powder is.

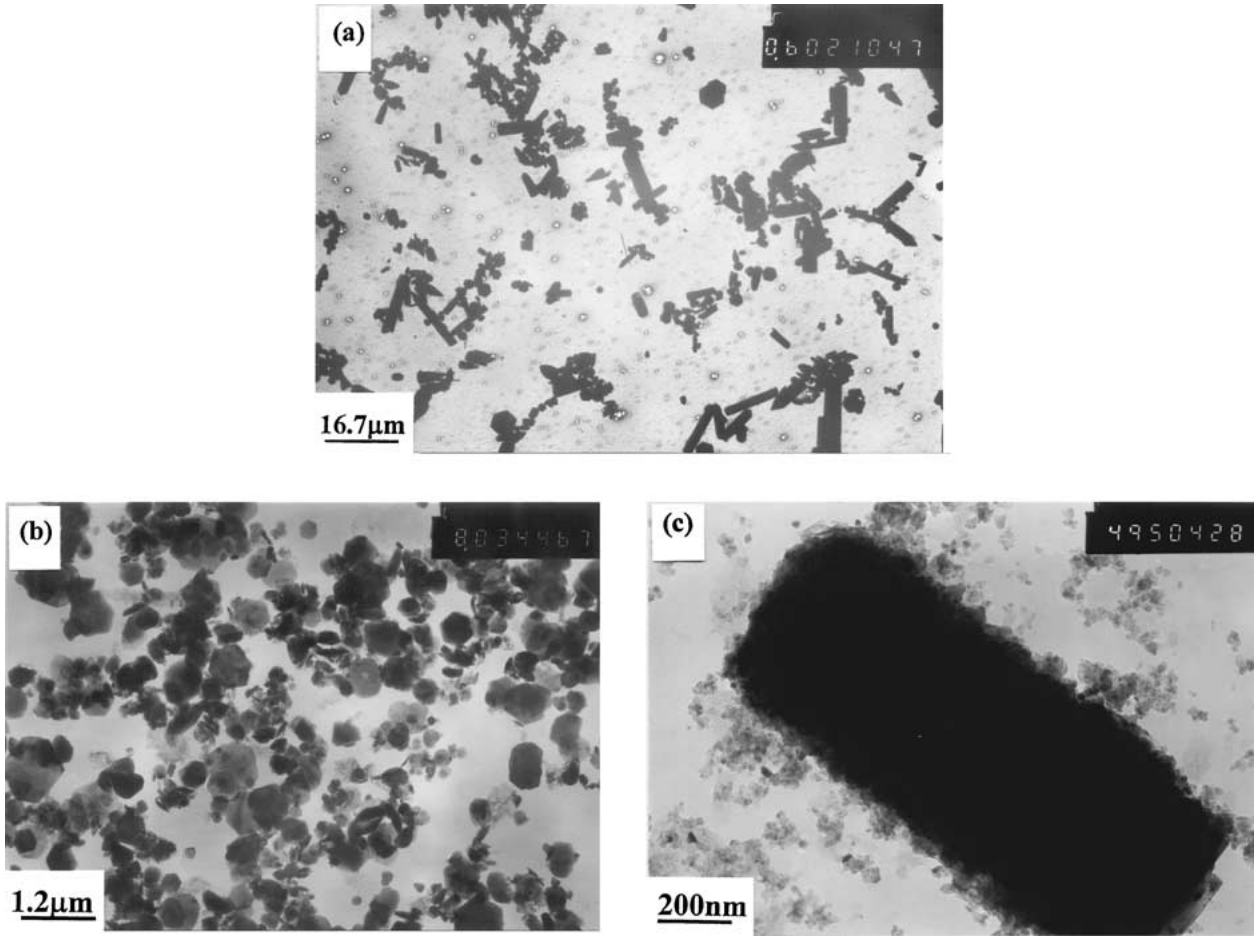

Figure 3 TEM micrograph of ZnO powder by hydrothermal discharging-gas method using $Zn(CH_3COO)_2$ solution with different concentration as precursor at 200 °C. (a) 0.5 mol/l, (b) 1 mol/l, (c) 1.5 mol/l.

References

1. S. HINGORANI and V. PILLAI, *Mat. Res. Bull.* **28** (1993) 1303.
2. R. J. LANF and W. D. BOND, *Am. Ceram. Soc. Bull.* **63** (1984) 278.
3. E. IVERS-TIFFEE and K. SEITZ, *ibid.* **66** (1987) 1384.
4. N. Y. LEE, M. S. KIM, I.-J. CHUNG and M.-H. OH, *J. Mater. Sci.* **26** (1991) 1126.
5. S. M. HAILE, D. W. JONHAGON and G. H. WISERM, *J. Amer. Ceram. Soc.* **72** (1989) 2004.
6. WEN-JUN LI, ER-WEI SHI, MING-YUAN TIAN *et al. J. Mater. Res.* **14**(4) (1999) 1532.
7. R. ROY, *Journal of Solid State Chemistry* **111** (1994) 11.
8. WEI-ZHUO ZHONG and DING-YUAN TANG, *J. Cryst. Growth* **161** (1996) 91.
9. WEI-ZHUO ZHONG and XI-LING YU, *Science in China (E)* **41**(4) (1998) 320.
10. Y. VRONKO, K. GORBACHEV and V. V. OSIKO, *ICCG-10 Poster* **B34** (1992) 57.
11. H. KOUTA, Y. KUWANO, K. ITO and F. MARUMO, *J. Crystal Growth* **114** (1991) 676.
12. P. ANDONOR, P. S. CHIEUX and Y. WASEDA, *J. Phys. Condens. Matter* **5** (1993) 4865.
13. *Idem.*, **48a** (1993) 955.
14. ZHI-XUN YAN, in "Complex Chemistry" (People Education Press, Beijing, People's Republic China, 1960) p .16.

Received 21 April 2000
and accepted 15 May 2001