Morphological characteristics of ZnO crystallites under hydrothermal conditions

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THE ZnO powder (micro-crystallites), an important functional material, has a wide application in the fields of ceramics, coatings and electronic devices. However, the powder, usually obtained by calcination of zinc oxalate, has a wide particle-size distribution and poor sintering activities, so various methods for its preparation have been developed. The hydrothermal method is widely used to prepare many superfine powders such as ZrO_2, $BaTiO_3$, PLZT, due to many advantages compared with other methods[1]. Recently, the powder of Ⅱ—Ⅵ compounds can also be prepared by this method[2]. Furthermore, crystallite shapes may be considered by virtue of the design and optimization of the hydrothermal conditions (temperature, precursor, mineralizer, etc) to obtain the required properties such as the required forms and attrition resistance, because the preparation process of oxide micro-crystallites under hydrothermal conditions is virtually a process of crystal growth. The formation of the observed habits of the crystallites under hydrothermal conditions may be discussed from crystal growth and crystal chemistry[3], and thus the control of the crystallite habit may be achieved based on these principles. Therefore, hydrothermal preparation of oxide superfine crystallites is of theoretical and practical importance.

1 Experimental

The stainless-steel vertical-tube autoclave with an inner diameter of 20 mm × 180 mm lined by a silver crucible with a volume of 30 mL was used as the reactive equipment. The hydrothermal reactive temperature range was 150—350℃, the practical pressure (fill 85%) measured at 300℃ was 40 MPa.

The newly-prepared hydroxide colloid $Zn(OH)_2$ obtained by adding the proper ammonia hydroxide to the chloride solutions (A. R.) was used as the starting material, and various mineralizers involving pure water, different concentrated potassium hydroxide solutions (0.5—6.0 mol/L KOH) were employed. The crystallites were naturally crystallized after the hydrothermal reactions (4—72 h), then washed and filtered. The obtained powder was dried at 120℃ for 24 h in the air for the X-ray diffraction (XRD) measurements, and TEM or SEM morphological analysis.

2 Results and discussion

2.1 Phase compositions of ZnO crystallites prepared under hydrothermal conditions

It was found that the XRD patterns of the obtained ZnO crystallites under various hydrothermal conditions show no difference to JCPDS No. 5-0664, which indicates that all have the wurtzite structure (hexagonal system, space group $P6_3mc$) although the hydrothermal conditions may strongly affect the phase composition of the materials (figure 1).

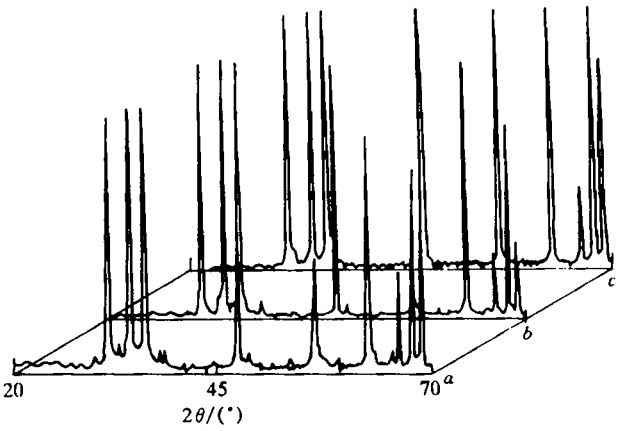

Fig. 1. XRD patterns of the products prepared under various hydrothermal conditions. (a) $Zn(OH)_2$ colloid (pure water, 300℃, 72 h); (b) $Zn(OH)_2$ colloid (4 mol/L KOH, 350℃, 4 h); (c) $Zn(OH)_2$ colloid (4 mol/L KOH, 350℃, 72 h).

2.2 The morphological characteristics of ZnO crystallites under hydrothermal conditions

It was found that the morphologies of ZnO crystallites obtained depend differently upon the hydrothermal conditions, particularly upon the solution basicity. We mainly examined the effects of the differently concentrated KOH (mineralizer) ranging from 0.5—6.0 mol/L while the total volume of the feedstock was kept the same on the crystallization habits of ZnO under centain hydrothermal conditions (150—350℃, 4—72 h). The results showed that the crystallites of ZnO obtainedfrom the hydrothermal condition without addition of KOH appear in elongated (fibrous) form, even after a high-temperature hydrothermal reaction (above 300℃), as shown in fig. 2 (a). The elongated forms are also observed on the crystallites obtained from the weak basic solutions, but at this time the aspect ratios (length/width) get small.

Under the hydrothermal conditions with an increasing concentration of KOH and a high reactive temperature, however, the habits of ZnO crystallites changed. It was found that the morphology of ZnO crystallites usually appeared in cone-shaped forms and represented a characteristic of polar crystals under a moderate-basicity hydrothermal condition (KOH 3—4 mol/L, temperature 250—350℃) whereas the habits of ZnO crystallites were observed in spherical shape and had the regular polyhedral faces under the hydrothermal condition having a strong basicity (above 4 mol/L) and a high reactive temperature (above 350℃), as shown in fig. 2(b), (c) respectively.

In brief, the morphology of ZnO crystallites usually tends to be a spherical shape under the hydrothermal conditions with a strong basicity of solution, a high reactive temperature and