Preparation of BaZrO$_3$ cubes by composite-hydroxide-mediated approach at low temperature

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1. Introduction

Barium zirconate (BaZrO$_3$) is a widely investigated perovskite oxide of an advanced material such as a high-temperature proton conductor. Barium zirconate has been studied as a functional material for use in buffer layers in coated conductors and dielectrics in electric systems. It is necessary to control the homogeneity of the size and shape of these functional ceramics so that wet chemical reactions can take place without further calcination. In other words, the desired compounds must be synthesized at lower temperatures than those used with the solid-state reaction method. For nanoparticle preparation at low temperatures, solution-based chemical methods have been developed. M. Niederberger et al. reported a general soft-chemistry route to BaZrO$_3$ in which the primary particles of BaZrO$_3$ are not isolated but form a wormlike agglomerate with a diameter of 2–3 nm and a length of up to 50 nm. This agglomerate frequently assembles into a larger, ball-like structure. H. P. Kumar prepared BaZrO$_3$ nanoparticles through a single-step combustion process. The particle size of BaZrO$_3$ was in the range of 30–50 nm, with a mean size of 40 nm. A. Aimable et al. synthesized nanocrystalline BaZrO$_3$ using a hydrothermal process working continuously in supercritical conditions. A BaZrO$_3$ crystal around 100 nm in size was obtained. Morphology control is also very important for functional materials. Previous papers reported preparation cubes with various scales for many different inorganic compounds. High-temperature synthesis of cube-like BaZrO$_3$ particles using a sodium hydroxide (NaOH)–potassium hydroxide (KOH) salt mixture was reported by H. Zhou et al. In addition to that of BaZrO$_3$, nanocubes preparations of Ag, SrTiO$_3$, and BaTiO$_3$ were recently investigated. However, there have been no reports of the successful preparation of a BaZrO$_3$ nanocubes with sharp-edged corners because nanocubes preparation is very difficult. There are great possibilities for homogeneous BaZrO$_3$ nanocubes 10–20 nm in size. Therefore, we have studied the preparation of the BaZrO$_3$ nanocubes. This paper is a report of the preparation of small-scale BaZrO$_3$ cubes using zirconium dioxide (ZrO$_2$) as the starting material. ZrO$_2$ has three major crystalline structures: monoclinic, tetragonal, and cubic. The monoclinic phase becomes tetragonal at 1170°C and then cubic at 2370°C. Accordingly, monoclinic ZrO$_2$, which is stable at room temperature, was used as a starting material in this study. To make a BaZrO$_3$ cubes, it is necessary to dissolve ZrO$_2$ in a reaction medium and grow a crystal. However, ZrO$_2$ is difficult to dissolve in any solvent because of its stability. To solve this problem, we used the composite-hydroxide-mediated (CHM) approach. This method is based on chemical reactions of materials in eutectic hydroxide melted at around 200°C and ambient pressure in the absence of organic dispersants or capping reagents. In this method, the eutectic point at NaOH:KOH is equal to 51.5:48.5 as the molar ratio is about 165°C. Therefore, we tried to dissolve the ZrO$_2$ and prepare the BaZrO$_3$ cubes using mixed hydroxides with NaOH and KOH. In the present work, the preparation of a small-scale BaZrO$_3$ cubes was investigated using the CHM approach at a low temperature. We anticipated that BaZrO$_3$ cubes would be formed once ZrO$_2$ as the starting material was dissolved in the mixed hydroxides with NaOH and KOH at temperatures above 165°C.

2. Experimental procedure

BaZrO$_3$ was prepared by the CHM approach. As starting materials, 0.005 mol ZrO$_2$ (Kanto Chemical Co., Inc.; >99.9%) and 0.005 mol barium hydroxide (Bar(OH)$_2$, Ube Materials Industries Co., Ltd.; >99.9%) were used as starting materials and put into the Teflon reactor of a stainless-steel autoclave with 100 cm$^3$ of internal volume. A mixture of anhydrous hydroxides with 0.103 mol NaOH and 0.097 mol KOH (NaOH:KOH = 51.5:48.5 as the molar ratio) was added in the Teflon reactor. Then, the autoclave was sealed and heated in a dryer at 170–230°C for 18 h. After the reaction, the autoclave was cooled to room temperature. The product was collected by a centrifugal
separators. Hot distilled water was used to remove the hydroxides, and ethanol was used for the rinse. Finally, the product was dried in a dryer at 50°C overnight.

The crystallinity and phase purity of the prepared samples were analyzed by X-ray diffraction (XRD) using an Ultima IV (Rigaku Co., Japan) diffractometer with Cu Kα radiation (wavelength: 0.15418 nm) operating at 40 kV-30 mA in the 2θ range of 10–80° at room temperature. The morphology of the particles was examined by scanning electron microscopy (SEM; Model S-4500; Hitachi, Japan).

3. Results and discussion

The crystallization and morphology of a product are influenced by many experimental parameters such as the type and size of the starting materials; the reactant concentration, temperature, and time; the solvent; the pressure; and the pH of the solution for the liquid reaction process. In particular, the reaction temperature is one of the most important reaction parameters controlling the phase composition and morphology of the particles. Figure 1 shows the XRD patterns of products that were obtained by the CHM approach at various reaction temperatures from 170 to 230°C for 18 h. As shown in Fig. 1(a), the products were a mixture of BaZrO3 and ZrO2 at 170°C synthesis. The diffraction peaks of the BaZrO3 could be assigned to the cubic phase (JCPDS file 6-0399). In addition, ZrO2 remained even though BaZrO3 was formed. Accordingly, we conducted synthesis at a high temperature above 170°C. The products prepared at 200°C were mixtures of BaZrO3 and ZrO2 [Fig. 1(b)]. However, whereas the XRD peak intensities of the BaZrO3 were high compared with 170°C synthesis, the XRD peak intensities of the ZrO2 were decreased. That is, ZrO2 was dissolved in the medium and reacted with Ba(OH)2 at a reaction temperature of 200°C compared with 170°C. When the reaction temperature was increased to 230°C, BaZrO3 was dramatically obtained, although a small number of ZrO2 peaks remained [Fig. 1(c)]. Incidentally, XRD peaks of BaCO3 were observed at various temperatures. While we wanted to try the synthesis above 230°C, we did not do so because of the possibility that the Teflon vessel would melt and break. The XRD results showed that a mixture of anhydrous hydroxides with NaOH and KOH dissolved the ZrO2 and accelerated the reaction with Ba(OH)2. BaZrO3 then was formed at 230°C. SEM micrographs of products that were obtained by the CHM approach at various reaction temperatures from 170 to 230°C for 18 h are shown in Fig. 2. At the reaction temperature 170°C, there were no cubic particles, although microstructure powders were observed. The majority of the microstructure powders were non-reaction ZrO2. On the other hand, the morphology of the partial samples changed to the cubic shape at 200°C [Fig. 2(b)]. Judging from the XRD patterns shown in Fig. 1, the cubic-shaped particles were BaZrO3. Furthermore, the powders prepared at 230°C clearly had a cubic shape with a sharp-edged BaZrO3 corner [Fig. 2(c)]. The particles were 50–240 nm in size.

From the results shown in Fig. 1, some of the ZrO2 starting material remained after the CHM synthesis at 230°C for 18 h. We consider that the ZrO2 was not perfectly dissolved in the reaction medium. Accordingly, BaZrO3 was prepared at 230°C for 72 h. The XRD patterns, shown in Fig. 3, are of products obtained by the CHM approach at various reaction times at 230°C for 18 and 72 h. When the reaction temperature increased to 72 h, there was weak XRD peak of ZrO2. In other words, ZrO2 was almost dissolved in the reaction medium, and BaZrO3 was formed. Furthermore, SEM micrographs of products that were obtained by the CHM approach at 230°C for 72 h are shown in Fig. 4. BaZrO3 cubes with a sharp-edged corner were clearly observed. The following reactions are the formation mechanism of BaZrO3 in this study. Firstly, the anhydrous hydroxides were

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**Fig. 1.** XRD patterns of BaZrO3 at various temperatures. Temperature: (a) 170°C, (b) 200°C, (c) 230°C. ○: BaZrO3, □: ZrO2, ▲: BaCO3.

**Fig. 2.** SEM micrographs of BaZrO3 at various temperatures. Temperature: (a) 170°C, (b) 200°C, (c) 230°C.
melted above 165°C. Secondly, MOH, where M is described as either Na or K, reacted with ZrO₂, resulting in the formation of M₂ZrO₃ and H₂O. In addition, the hydroxide in the solvent dissociated into H₂O and O²⁻ ions.

\[
2\text{MOH} + \text{ZrO}_2 \rightarrow \text{M}_2\text{ZrO}_3 + \text{H}_2\text{O} \\
2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^{2-}
\]

Finally, indissoluble solid BaZrO₃ was generated by the reaction between M₂ZrO₃ and Ba(OH)₂.

\[
\text{M}_2\text{ZrO}_3 + \text{Ba(OH)}_2 \rightarrow \text{BaZrO}_3 \downarrow + 2\text{MOH}
\]

Incidentally, oxygen, including anhydroxydrides, is the source of the formation of the perovskite oxide in BaZrO₃.

4. Conclusions

In conclusion, in this research, we succeeded in preparing small-scale BaZrO₃ cubes synthesized by the CHM approach at a low temperature using ZrO₂ and Ba(OH)₂ as a starting material and a mixture of anhydrous hydroxides with NaOH and KOH as the reaction medium. The XRD measurement confirmed the perovskite BaZrO₃ particles and indicated that the lattice of the obtained BaZrO₃ could be assigned to the cubic structure. The SEM observation revealed that the BaZrO₃ particles had a cubic shape, a length of 50–240 nm, and sharp-edged corners. That is, small-scale BaZrO₃ cubes was shaped from ZrO₂ and Ba(OH)₂.

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References


Fig. 3. XRD patterns of BaZrO₃ at various times. (a) 18 h, (b) 72 h. ▲: BaZrO₃, △: ZrO₂, ■: BaCO₃.

Fig. 4. SEM micrograph of BaZrO₃ at 230°C for 72 h.