Solvothermal Preparation and Characterization of Barium Titanate Nanocubes

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A simple low-temperature solvothermal scheme has been developed to produce pure, well-controlled characteristics in terms of size, morphology, and monodispersity of barium titanate ($BaTiO_3$) nanocubes. Characterizations of products were performed by XRD, TEM, HRTEM, EDS, and their sizes were 40–50 nm. The formation process of the $BaTiO_3$ nanocubes was also discussed.

Single-crystalline nanostructures, such as nanocubes, nanotubes, nanorods, nanobelts, and nanowires, have stimulated intensive interest because of their unique applications in mesoscopic physics and the fabrication of nanoscale devices.[1] Recently, there have been a large number of reports about the preparation of nanocube materials including metals,[2] metal oxides,[3] and sulfides.[4] However, only a few attempts were made to prepare complex oxides with perovskite structure such as barium titanate ($BaTiO_3$)[5] and lead titanate ($PbTiO_3$).[6] Barium titanate ($BaTiO_3$), because of its high dielectric constant and low loss characteristics, has been widely used as a key material in various applications such as multilayer capacitors, infrared detectors, thermistors, transducers, electro-optic devices, etc,[7] and the rapid development in multilayered ceramic capacitors MLCCs[7] requires the size of $BaTiO_3$ particles to be lowered down to tens of nanometers for reduction of capacitor dimension. Conventional synthesis of barium titanate is by the solid-state reaction. Solid mixtures of barium carbonate and titanium dioxide are prepared at high temperature (1100 °C) or by calcination of chemically derived intermediates. The powders thus produced are often low in purity and are composed of large and nonuniform particles. To resolve the problems arising from the conventional ceramic techniques and to produce homogeneous and stoichiometric $BaTiO_3$, wet-chemical synthetic methods, such as the hydrothermal/solvothermal method,[8] the sol–gel method,[9] the oxalate route,[10] microwave heating,[11] coprecipitation,[12] a microemulsion process,[13] and a polymeric precursor method[14] have been developed. In this paper, we used a simple low-temperature solvothermal method to prepare single-crystalline $BaTiO_3$ nanocubes. This may provide a new approach to the investigations on shape-controlling of the inorganic materials.

Typical synthesis procedure: 0.005 mol of tetrabutyl titanate ($Ti(OC_4H_9)_4$) dissolved in 20 mL of *n*-butanol, and 0.006 mol of $Ba(OH)_2\cdot 8H_2O$ was added into the solution. The mixture was transferred to a Teflon-lined stainless steel autoclave (ca. inner volume of 33 mL) and heated at 180 °C for 24 h under autogenous pressure. The resulting $BaTiO_3$ powders were filtered, washed with 0.1 M formic acid and deionized water three times, respectively, and finally dried at 80 °C for 12 h in an oven.

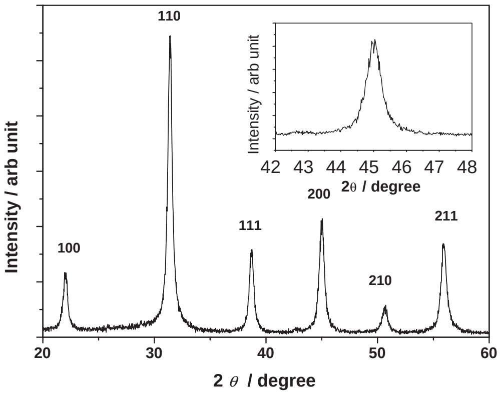
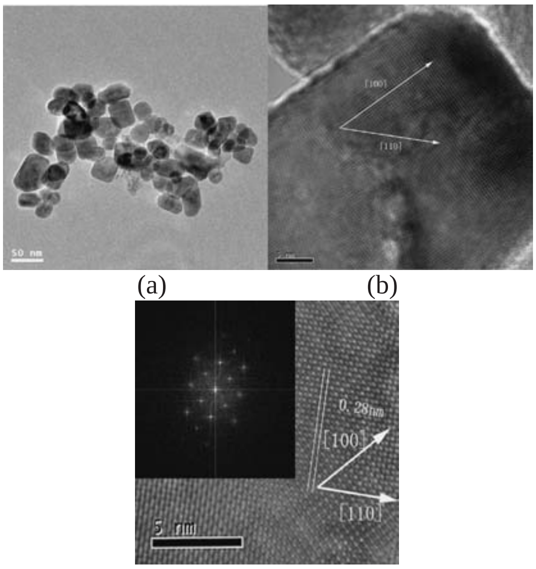


Figure 1. XRD pattern of $BaTiO_3$ nanocubes obtained from the solvothermal route. Inset is the local fine XRD pattern scanned at around $2\theta \approx 45°$.

Figure 1 shows a powder X-ray (Cu Kα) diffraction (XRD) pattern of prepared $BaTiO_3$ nanocubes by the solvothermal method. As shown in Figure 1, these patterns were assigned to cubic $BaTiO_3$ (JCPDS No. 31-174). The trace impurities, such as $BaCO_3$, BaO, can be removed by washing with dilute formic acid. Only one symmetric peak was observed around 45° (inserted XRD pattern), which further suggested that $BaTiO_3$ nanocubes prepared by the solvothermal method can be assigned to cubic *m*3*m* symmetry, not tetragonal polymorph. The reason maybe due to the effect of defects existed in $BaTiO_3$ crystalline grain and the size effect.[15]

Figure 2a shows the transmission electron microscopic image (TEM) of the products formed by the solvothermal method; the products mainly consist of uniform nanocubes with a mean edge length of 40–50 nm; Besides, a few of sphere and irregular nanoparticles were also observed. Energy dispersive X-ray spectroscopy (EDS) result of the products shows that the nanocubes are composed of Ba, Ti, and O with the atomic ratio close to 1:1:3. The higher magnification image (HRTEM) of the products in Figure 2b indicates that the nanocubes have good crystallinity. Figure 2c is the local enlarged image of Figure 2b. The inset shows the corresponding selected area diffraction (SAED) pattern, obtained by directing the incident electron beam perpendicular to one of the facets of the cube. The 2D lattice fringes of the HRTEM image were examined to be 0.28 nm, close to the (110) lattice spacing of the cubic $BaTiO_3$. These fringes make an angle of 45° with the edge of the nanocube, in other words, the (100) planes parallels to the edge of the nanocube (Figure 2b).

As some literatures reported, the growth of $BaTiO_3$ nanoparticles under hydrothermal/solvothermal conditions is probably attributed to dissolution–crystallization mechanism,[5a,16] and the crystallization process can be represented by the reactions as follows:



(a) (b)

(c)

Figure 2. (a) TEM image of $BaTiO_3$ nanocubes. (b) HRTEM image of an individual $BaTiO_3$ nanocube with rectangle plane, (c) The nanocube used for the HRTEM and SAED studies.

$$Ti(OC_4H_9)_4 + 4H_2O + 2OH^- \rightarrow Ti(OH)_6{}^{2-} + 4C_4H_9OH$$

$$Ba^{2+} + Ti(OH)_6{}^{2-} \rightarrow BaTi(OH)_6$$

$$BaTi(OH)_6 \rightarrow BaTiO_3 + 3H_2O$$

As we all know, it is an essential prerequisite to obtain $BaTiO_3$ that $BaTi(OH)_6$ condenses via dehydration. In order to control the dehydration of $BaTi(OH)_6$, *n*-butanol was used as the reactive medium. Tetrabutyl titanate can dissolve in *n*-butanol, and the lower solubility of $Ba(OH)_2 \cdot 8H_2O$ in *n*-butanol may insure the hydrolysis process of $Ti(OC_4H_9)_4$ is slower and more homogenous, moreover, *n*-butanol maybe play an important role in the dehydration process of $BaTi(OH)_6$ because *n*-butanol can formed an azeotrope with water (C_4H_9OH:$H_2O \approx 62:38$, at 92 °C). The azeotrope was boiled away merrily at reaction temperature, the dynamic equilibrium can continually extract water molecules of $BaTi(OH)_6$. In addition, lower alkalinity and amount of water are responsible for the lower solubility of $BaTiO_3$, thereby the overgrowth of $BaTiO_3$ crystals is avoided. In this work, excess barium source is necessary. Excess $Ba(OH)_2$ not only provide the required alkalinity, but the amount of water to hydrolyze $Ti(OC_4H_9)_4$ is ensured. In case the ratio of Ba/Ti is less than 1.2, $TiO_2 \cdot xH_2O$ often remained as the impurities. In hydrothermal preparation of $BaTiO_3$ nanoparticles, the morphology of the particles was found to be spherical in previous literatures.[17] Because of the equilibrium between crystallographic habit growth and preferential dissolution of high-energy faceted edges, the dominant morphology of prepared $BaTiO_3$ particles is spherical, and only a few particles still retain cubic. Under our synthetic conditions, this equilibrium breaks, and more spherical nuclei develop into cubic particles.[5b]

In summary, single-crystalline $BaTiO_3$ nanocubes have been prepared by a simple low-temperature solvothermal method using barium hydroxide and tetrabutyl titanate as starting materials. The nanocubes have uniform edge length and good monodispersity. Compared to hydrothermal method, *n*-butanol probably plays an important role in the preparation of uniform and monodisperse $BaTiO_3$ nanocubes.

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