Chemistry Letters Vol.34, No.7 (2005)

Solvothermal Synthesis of Single-crystalline $BaTiO_3$ Nanocubes in a Mixed Solution

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(Received April 5, 2005; CL-050452)

The preparation of single-crystalline cubic perovskite $BaTiO_3$ nanocubes with edge length of 40–90 nm via a solvothermal method without surfactant was reported, and the formation mechanism of the $BaTiO_3$ nanocubes was discussed.

Inorganic materials with uniform shape and size are of fundamental interest and technological importance because of their unique size- and shape-dependent properties. Besides a lot of reports about the synthesis of 1-dimensional (1-D) and 2-D nanomaterials,[1] the 0-D nanomaterials, such as quantum dot,[2] nanosphere,[3] and nanocube,[4] related to their specific physical and chemical properties. Recently, there have been great breakthroughs in the synthesis of nanocube materials including metals,[4–6] metal oxides,[7] halides,[8] and chalcogenides.[9] However, only a few attempts were made to prepare ternary complex oxides with cubic shape.[10] Barium titanium trioxide ($BaTiO_3$) is the most important ferroelectric materials, which is a good candidate for a variety of applications, such as piezoelectric actuators, multiplayer ceramic capacitors (MLC) and positive temperature coefficient resistors (PTCR), because of its excellent dielectric, ferroelectric and piezoelectric properties. Besides the solid-state synthesis, many wet chemical methods, such as sol–gel method,[11] hydrothermal (solvothermal) method,[12] and sol-precipitation process,[13] are developed to prepare ultrafine $BaTiO_3$. Although remarkable advancements have been achieved in the synthesis of size-controlled $BaTiO_3$, there were only a few literatures about the synthesis of shape-controlled $BaTiO_3$[1d,1e,14,15] in addition to the synthesis of $BaTiO_3$ particle with approximately spherical shape.[11] Herein, we report a solvothermal method without surfactant to prepare single-crystalline $BaTiO_3$ nanocubes. This facile approach to $BaTiO_3$ nanocubes may provide a possibility for detailed experimental investigations on shape-dependent properties of the materials.

In a typical synthesis, 9.1 mmol of titanium tetrachloride ($TiCl_4$) was dropped slowly into 20 mL of absolute ethanol to form a clear yellowish solution A. 14.6 mmol of barium hydroxide ($Ba(OH)_2{\cdot}8H_2O$) (Ba/Ti mol ratio is 1.6) was dissolved into 20 mL of ethylene glycol monomethyl ether ($HO(CH_2)OCH_3$) to form solution B. The solution A was added dropwise into the solution B and then white slurry appeared. After being stirred for 10 min, 40 mL of distilled water was dropped into the formed white slurry, and the white slurry became clear solution immediately. Then, 125 mmol of NaOH was added into the abovementioned solution and it again became white slurry. At last, the white slurry was stirred for 10 min and transferred into a 100-mL Teflon-lined autoclave for a solvothermal process at 240 °C for 24 h. After the solvothermal process completed, the gained precipitation was filtrated, washed with distilled water, and then dried in an oven at 110 °C for 12 h.

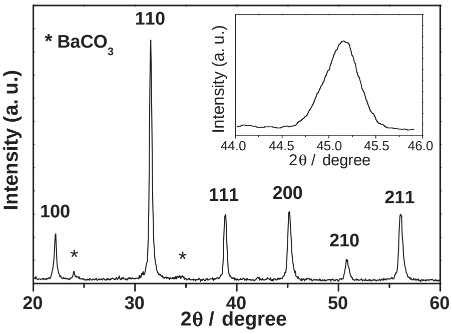

Figure 1. Power X-ray diffractogram of $BaTiO_3$ nanocubes with cubic crystallographic assignments. The inset shows 200 diffraction peak of the sample, illustrating an approximative symmetrical single peak.

The phase purity of the as-prepared products was evidenced using a D/max2500 X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). Diffraction peaks in Figure 1 can be indexed to a perovskite-structured, cubic phase $BaTiO_3$ with calculated cell constant of $a = 4.006$ Å which is numerically close to the reported values of the bulk materials (JCPDS File No. 31-174). The absence of splitting for 002/200 peak (see Figure 1 inset) indicates that the cubic phase is stable at room temperature. The reason for the broadness of the reflections is probably that the grain sizes of the sample are on a nanometer scale. There are no other impurities but orthorhombic $BaCO_3$ (JCPDS File No. 5-378) as a by-product, which is labeled with asterisk mark in Figure 1. The undesired impurities $BaCO_3$ can be reduced by carrying out the experiment under inert atmosphere or by washing the product with dilute acetic acid.

The morphology of the as-synthesized $BaTiO_3$ nanocubes was examined with field emission scanning electron microscopy (FESEM, JEOL-JSM-6301F) and transmission electron microscopy (TEM, Hitachi-600-2). Typical FESEM and TEM images of $BaTiO_3$ nanocubes are shown in Figures 2A and 2B, respectively, from which smooth $BaTiO_3$ nanocubes can be found with edge length of 40–90 nm and more than 80% of the as-obtained $BaTiO_3$ particles are of cubic shape from 300 observed particles, although there are also some near-spherical and irregular shape particles in the as-prepared powder. The chemical composition of the as-prepared nanocubes was analyzed by energy-dispersive X-ray spectroscopy (EDS). The result indicates that the Ba/Ti atomic ratio is 1.0165 and excess of Ba is due to the existence of $BaCO_3$.

Figures 3A and 3B show TEM micrograph of two single $BaTiO_3$ nanocubes with rectangle and square shape, respectively. The analysis of $BaTiO_3$ nanocubes shows the absence of domain boundaries within each nanoparticle, suggesting all nano-

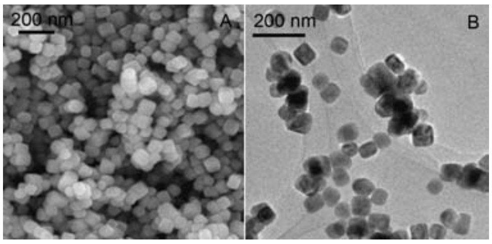

Figure 2. FESEM image (A) and low magnification TEM image (B) of $BaTiO_3$ nanocubes.

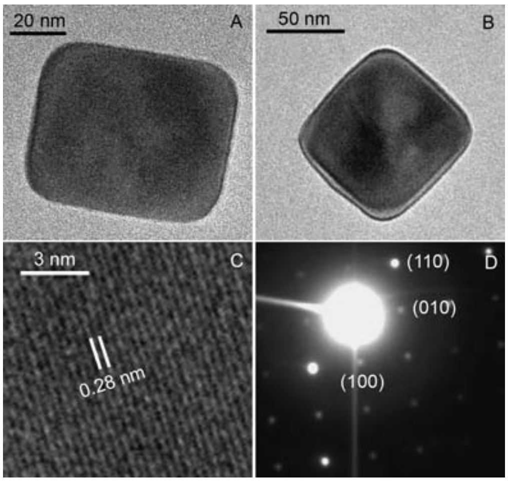

Figure 3. (A) and (B) TEM image of an individual $BaTiO_3$ nanocube with rectangle and square plane, respectively. (C) A high-resolution TEM image of the nanocube. (D) Selected area electron diffraction (SAED) pattern obtained from an individual particle.

particles consist of single crystal. Figure 3C shows a high-resolution TEM (HRTEM, JEOL-JEM-2010) image of a single $BaTiO_3$ nanocube, in which clear lattice fringes suggest its single-crystalline structure. The spacing of the fringes was measured to be about 0.28 nm, which corresponds well with the spacing of {110} planes at 0.2844 nm. These fringes make an angle of 45° with the edge of the nanocube. The selected area electron diffraction (SAED) pattern recorded on the nanocube of Figure 3C is shown in Figure 3D, which reveals its single-crystalline nature. Numerous SAED pattern analyses demonstrate that the as-synthesized $BaTiO_3$ nanocubes are all of single crystals. Further studies indicated that the higher reaction temperature ($=240\,°C$) and higher Ba/Ti molar ratio in reactant ($=1.6$) are necessary to obtain $BaTiO_3$ particles with cubic shape. On the other hand, different source materials, such as $BaCl_2$ and TiO_2, have not obvious influence on the particle shape but result in different particle size.

The growth of $BaTiO_3$ particles under our experimental condition is possibly subjected to dissolution–crystallization mechanism.[16–18] In hydrothermal preparation of $BaTiO_3$, the morphology of a few particles was found to be cubic in our previous experiment and other literatures.[16] Because of the equilibrium between crystallographic habit growth and preferential dissolution of high-energy faceted edges, for the fully-grown barium titanate particles the dominant morphology is spherical and only a few particles still retain cubic. Under our synthesis conditions, the equilibrium breaks and more spherical nuclei develop into cubic particles. In addition, the particle growth after nucleation in hydrothermal synthesis is often reported via either solute addition reaction or aggregation.[16] However, HRTEM analysis does not reveal any evidence of the presence of defect structures such as stacking faults or grain boundaries, suggesting that the particles grow by solute addition reaction to form single crystal under our experimental conditions.

In summary, the present study shows that single-crystalline $BaTiO_3$ nanocubes with cubic perovskite structure can be synthesized by the solvothermal method in a mixed solution. This approach to nanocube $BaTiO_3$ synthesis provides a reaction environment that under the appropriate conditions eliminates particle growth by aggregation after nucleation and retains crystallographic habit growth, which causes the spherical nuclei to develop into single-crystalline cubic particles. This method has the potential to be applied to the synthesis of other perovskite oxides.

The financial support from the National Key Nature Science Foundation of China (No. 20133040) was gratefully acknowledged.

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