Anisotropy in Morphology and Crystal Structure of BaTiO₃

Nanoblocks

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Single crystalline {100} dominant BaTiO₃ nanoblocks were synthesized by the hydrothermal method using aqueous sources of Ba and Ti, and organic additives. BaTiO₃ nanoblocks with neat surface and standard corner angle show two kinds of morphology, cubic and cuboid shapes. Based on TEM images of BaTiO₃ nanoblocks, the percentage of nanocuboids improved from 24.3% to 51.8%, as the average size of nanoblocks varied from ~ 15 nm to ~ 25 nm. The asymmetric morphology of BaTiO₃ nanocuboids reveals an anisotropic growth pattern. One straightforward method was employed to discuss the crystal phase of BaTiO₃ nanocuboids by using the HR-TEM images and the corresponding FFT patterns. The d spacing of {100} crystal planes show diverse values. The ratios of d spacing of (100) crystal plane and the perpendicular (001) plane are larger than one. The short edge direction in BaTiO₃ nanocuboids coincides with their [001] crystal orientation. According to the enlarged FFT filtered HR-TEM images, the shape and oriented array of the unit cells in nanocuboids played a crucial role on the formation of anisotropy in morphology. Co-considering the DSC result, the findings indicate the existence possibility of tetragonal phase in BaTiO₃ nanocuboids with less than 30 nm size.

Keywords: BaTiO₃ nanoblocks, nanocuboid, tetragonal phase, anisotropy,

1. Introduction

Anisotropy of BaTiO₃ nanomaterials has attracted much attention [1-3] owing to its vital role in tuning the shape and properties. The morphology of BaTiO₃ nanomaterials is key factor to decide the ultimate performance of perovskite-based nanoelectronics [3-7]. In this regard, it is desirable to analyze the anisotropy in morphology of BaTiO₃ nanomaterials and achieve their tailor-synthesis. Over the past decade, the anisotropic properties of one-dimensional or two-dimensional BaTiO₃ nanomaterials with diversified morphologies have been investigated systematically [7-13]. However, few of reports focused on the anisotropy in the morphology of BaTiO₃ nanoblocks with cuboid shape. Compared with one or two dimensional nanomaterials, BaTiO₃ nanocuboids can provide a larger interface and a close-packing ordered architecture, which are crucial for “bottom-up” nanotechnology applications. The surface of BaTiO₃ nanocuboids is dominated by six {100} crystal plans. Their aspect ratios (length edge/width edge) are more than one and indicate an anisotropic growth process. Due to the highly symmetric limitation, it is difficult to synthesize amount of BaTiO₃ nanocuboids. This has hindered the development of their investigation and applications. In this work, we synthesized batch of BaTiO₃ nanocuboids and studied their anisotropy.

Due to the miniaturization of multilayer ceramic capacitors (MLCCs), much effort was paid to study the tetragonal phase and cubic phase of BaTiO₃ nanocrystals [14-16]. Conventional BaTiO₃ nanocrystals with irregular shape always show the cubic phase in the range of several tens nanometer, which is known as the so-called “size-effect”. Moreover, the existence of impurities (lattice hydroxyl, carbonate, et.al) resulted in the decrease of the dielectric constant of BaTiO₃ nanocrystals [17]. Recently, some groups

explored the crystal phase of BaTiO₃ nanocrystals with different size [17-20]. The results indicate that the tetragonal phase disappears gradually, as the size of BaTiO₃ nanocrystals decreases from 140 nm to 30 nm. The disappeared tetragonal phase and ferroelectric property of BaTiO₃ nanocrystals are attributed to the surface relaxation and the expansion of lattice. Thus, how to realize the stable tetragonal phase of ultrafine BaTiO₃ nanocrystals is one of important research targets for industrial applications. The previous report pointed out the net structure strain could cause the rotation of the TiO₆ octahedral and change its bond length [21]. These structural deformation can result in the crystal phase transition of perovskite materials. The lattice strain can be induced in the anisotropic BaTiO₃ nanocuboids during the nucleation and growth process. Thus, BaTiO₃ nanocuboid is one of promising candidates to realize the tetragonal phase of perovskite materials in nano-scale.

In this work, high quality BaTiO₃ nanoblocks were synthesized by hydrothermal method using aqueous sources and organic additives. The high-resolution transmission electron microscopy (HR-TEM) images and the corresponding fast Fourier transform (FFT) patterns were employed to study the anisotropy in morphology and the subtle difference in the lattice constants of BaTiO₃ nanocuboids. The examination of individual BaTiO₃ nanoblocks with regular cuboid shape and atomically flat surfaces provided a detailed glimpse of the crystalline structures at small accessible length scale.

2. Experimental

2.1. Material synthesis

Single crystalline {100} dominant BaTiO₃ nanoblocks were synthesized by the hydrothermal method using aqueous sources of Ba and Ti compound, which has been published previously [2, 22]. In a brief description, Ba(OH)₂·8H₂O and TALH

(Bis(ammonium lactate) titanium dihydroxide) were added into the distilled water and acted as the source materials. NaOH was used to control the pH value of the precursor solution. The concentration of NaOH is 1.2M. Oleic acid and tert-butylamine acted as the surfactant and additives to control the shape of BT nanoblocks. The molar ratio of Ba, Ti, oleic acid and tert-butylamine is 1: 1: 8: 6. The solution was filled into an auto sealed autoclave and heated at 220°C for 72h under mechanical stirring. After cooled at room temperature, white powders were washed by ethanol for several times and collected by a centrifugation process. After drying, the precipitation was dispersed into mesitylene. The surface of BaTiO₃ nanoblocks was covered by oleic acid moleculars. Owing to the role of the fatty molecular, the nanoblocks can disperse in mesitylene solution and form a suspension.

2.2. Structural characterization

X-ray diffractometry (XRD, Rigaku RINT-2100V) was employed to confirm the crystal property of BaTiO₃ nanoblocks. The morphology of the prepared BaTiO₃ nanoblocks was investigated by using a transmission electron microscopy (TEM; Model JEM-2010F, with an accelerating voltage of 200 kV). Differential scanning calorimetry (DSC; STA 7000) measurement on the BaTiO₃ nanocubes was carried out under pure nitrogen environment.

3. Results and discussion

3. 1. Anisotropy in morphology of BaTiO₃ nanoblocks

Fig. 1 shows the TEM images of BaTiO₃ nanoblocks with different average size. It can be observed that the nanoblocks possess two kinds of morphologies: cubic shape and cuboid shape. The values of nanocuboids/total nanoblocks were obtained by taking a statistics of about 250 particles, which were selected randomly from TEM images. A

nanoblock with an edge length of less than 20 nm was distinguished to belong to the group of the ~ 25 nm. As the average size of BaTiO₃ nanoblocks varied from ~ 15 nm to ~ 25 nm increased, the values increased from about 24.3 % to 51.8 %. This result manifests the amount of BaTiO₃ nanocuboid increased gradually. Based on the analysis of TEM images, the size-dependent values of cuboid / total nanoblocks were attributed to the anisotropy growth of BaTiO₃ nanoblocks. The aspect ratios of these nanoblocks were measured and displayed in Fig. 1 (c) and (d). The average values of ~ 25 nm group and ~ 15 nm group were ~ 1.23 and ~ 1.07, respectively. The result indicates that the aspect ratio of BaTiO₃ nanocuboids also shows a size-dependence property. In addition, since the nanocuboids existed in the final product, the self-assembly of nanoblocks with orderly arrangement might be achieved by precisely tuning the evaporation rate of solvents [23].

HR-TEM images can provide valuable information regarding the anisotropy in morphology and the crystal phases of the BaTiO₃ nanoblocks. Fig. 2 displays the HRTEM images of four randomly-selected BaTiO₃ nanoblocks with clear cuboid shape. The lengths of the long edge (L_L) direction and the short edge (L_S) direction in mono-dispersed BaTiO₃ nanocuboids were measured and shown in the Fig. 2. The values of L_L / L_S are larger than one and display the anisotropy in morphology of BaTiO₃ nanocuboids. According to the Gibbs-Curie-Wulff theory, the crystal growth rate along a certain crystallographic orientation is proportional to the surface energy [24]. The morphology of nanocrystals is determined by the facet with the minimum surface energy. To tailor the final shape of nanocrystals, the affinity of surfactants is employed to modulate the growth rates of different crystal directions [25]. Recently, the anisotropy of nano-sized transition metal oxide was studied and the fatty acid was used

as surfactant [26, 27]. In our case, barium ions are denser of the (100) facets and the oleic acid molecules bind preferentially the Ba ions. [2, 22]. Based on the FFT pattern (inset of Fig. 2), the surfaces of nanoblocks are dominated by {100} crystal planes. If all of these {100} crystal planes possess the equal growth rate, nanoblocks with symmetrical cubic morphology will be synthesized. However, the existence of nanocuboids indicates the difference in the growth speed of the six {100} facet. The corresponding inverse FFT images of Fig. 2 (e) and (f) provide the detailed information for the lattices of BaTiO₃ nanocuboids. The number of stacking lattices in different directions can be calculated or counted one by one easily. Due to the weak scattering for electron beam, oxygen atoms are difficult to be detected by HR-TEM observation. As exhibited in the filtered images, the difference in the number of stacking lattices in different directions (L_L and L_S) indicates an anisotropic growth pattern of nanocuboids [25, 27]. Moreover, the difference is enlarged with the increase of the size of nanocuboids. As mentioned above, the results of Fig. 1 (c) and (d) manifest the size-dependent property of the aspect ratio of nanoblocks. The observation in HR-TEM course confirms this property of BaTiO₃ nanocuboids in atomic scale.

3. 2. Crystal Structure of BaTiO₃ nanocuboids

The crystal phases of mono-dispersed BaTiO₃ nanocuboids were analyzed in detail by using HR-TEM and the corresponding FFT patterns. One kind of straightforward method was employed to discuss the crystalline structure of single BaTiO₃ nanocuboids. The values of d spacing of different crystal faces in BaTiO₃ nanocuboids were calculated by using the corresponding reciprocal lattice spots in the FFT patterns. Diverse values of the d spacing of different crystal planes are displayed in Fig. 3. In the same BaTiO₃ nanocuboids, the values of the d spacing in L_S direction are larger than

those in L_L direction. The ratios of d spacing of (100) crystal plane and the perpendicular (001) plane are in a range of 1.014~1.018. The results are coincident with those of previous reports, which focus on the tetragonal phase of BaTiO_3 [28-30]. As well known, the DSC technique is low sensitive for small amount of tetragonality in nanomaterials. In previous reports, Begg et al. pointed out that the DSC peak disappeared when the BaTiO_3 possessed a tetragonality c/a less than 1.0061 [30]. Combined with the DSC result (Fig. 6), the FFT results can indicate the presence of an amount of the tetragonality in BaTiO_3 nanocuboids. To confirm the calculating results of FFT pattern, the FFT filtered HR-TEM images were utilized to directly measure the d spacing of {100} crystal faces. The corresponding inverse FFT images (Fig. 3 (c), (d) and (g), (h)) provide the detailed information of the lattices of BaTiO_3 nanocuboids. The lattice fringes in different directions can be observed easily. Ten layers of the crystal lattices in different directions were selected to decrease the measurement error. As displayed in the enlarged images of Fig. 3, the measured values of d spacing are corresponding with those of the FFT pattern.

As for tetragonal BaTiO_3 , there is an average relative displacement along the c -axis of titanium (Ti) cation from its centrosymmetric position (as shown in Fig. 4 (a)). This displacement brings the creation of a polarization of $26\mu\text{C}/\text{cm}^2$ along the $\langle 001 \rangle$ direction [17, 20, 31, 32], and induces residual strain in BaTiO_3 [33]. Xia, et.al mentioned that the internal strain in the lattice was related with the anisotropic growth of nanocrystals [34]. In our case, co-considering the value of lattice constant in different direction of nanocuboids and the result of DSC, the displacements of Ti cations occurred in BaTiO_3 nanocuboids. The Ti cations were displaced in the [001] direction in the tetragonal phase. The enlarged FFT filtered image of Fig. 3 (d) and (h) shows a

series of parallel straight lattice fringes, which indicates the oriented array of unit cells with displaced Ti cations. Based on the Ostwald ripening theory, the lattice structure of nanocrystals is close to perfection as much as possible to decrease the total Gibbs free energy. If the array of unit cell is random, owing to the difference in lattice spacing between a-axis and c-axis, some defects (edge dislocation, stacking dislocation, etc) will be formed in BaTiO₃ nanocuboids and induce the increased total free energy. Moreover, the polarization of unit cells can result in the formation of the dipoles, which will promote their ordered array. Thus, the direction of unit cell array is oriented in the nanoblocks (marked in Fig. 4 (b)). The displacement of Ti⁴⁺ cations causes the lattice stretch of unit cell in [001] orientation (as shown by Fig. 4(a)). When unit cells with rectangular shape array in order and constitute one nanocuboid, the long side of nanocuboid might be easily recognized as be parallel with the [001] crystal direction. However, it is interesting that the stretch direction of unit cells is perpendicular to the L_L direction of nanocuboids. And the L_s direction is coincident with the [001] crystal orientation. Observing precisely the filtered images of Fig. 3, the number of stacking layers in the L_s direction is obviously smaller than that in the L_L direction. The difference in the number of stacking lattice in [100] orientation and the perpendicular [001] orientation results in the formation of nanocuboids. It is considered that the disparity of the number of stacking layers is associated with the shape and ordered arrangement of unit cells. As unit cells with the displaced Ti⁴⁺ cations array orderly in BaTiO₃ nanocuboids, the cubic symmetric structures transform into the distorted ferroelectric structures. This distortion of crystalline structures will introduce the lattice strain into the inner section of nanocuboids. As for tetragonal BaTiO₃ nanocuboids, the strain exists in [001] crystal direction. The relationship between the strain and

polarization of BaTiO₃ has been calculated from first-principles [35]. If the polarization is larger than 20 μ C/cm², the strain reaches about 3.5E-3%. Based on the calculated elastic constants of the tetragonal phase, the stress is $\sim$ 0.5 GPa. The strain can influence the growth rate of stacking lattice in [001] crystal orientation. Thus, the nanoblocks will tend to select the other growth directions during ripening process. The stacking rate of lattice layers in [001] orientation is smaller than that in the other crystal orientations. Due to the role of oleic acid, only {100} crystal faces are protected and the L_L and L_s sides are formed after growing process. After nanocuboids are produced, their L_L sides are perpendicular with [001] direction. As displayed Fig. 1(b), 2 and 3, the values of L_L of BaTiO₃ nanocuboids are not less than $\sim$ 24 nm, and those of L_s vary from $\sim$ 15 nm to $\sim$ 23 nm. This result indicates that the BaTiO₃ nanocuboids prefer to grow along [100] orientation to obtain small lattice strain and low strain energy. Furthermore, it is conjectured that the strain confined the length of L_s no larger than 23 nm for 72 hours hydrothermal process. The anisotropy in shape of nanocuboids is able to be observed as the values of L_L increased about 24 nm. Owing to the role of strain, the growth rate on L_s direction is unstable and not uniform for different samples. Then, the length of L_s varies in a wide range. According to above discussion, the anisotropy in morphology and the tetragonal crystal phase of BaTiO₃ nanocuboids are related with the shape and ordered array of unit cell.

Fig. 5 displays two-dimensional unit cells and one nanoblock with pseudo-cuboid shape. Because the density of barium ions on the {100} facets is higher than on the other crystal facets, the {100} facets are protected by the adsorption of oleic acid [2, 22]. The surface in the complete section of nanoblock is composed by {100} crystal planes. Step and terrace structures are clearly observed in the incomplete section of the

nanoblock, marked by red arrows in Fig. 5 (b), and the height of the each step is identical to one or two unit cells. It can be considered that the nanoblock is in the growing process. As displayed in Fig. 5 (c), the formation of nanoblocks is associated with the array of unit cells.

3. 3. DSC measurement of BaTiO₃ nanoblocks

As one thermo-analytical technique, the DSC measurement can be used to test the crystal phase transition of nanocrystals. The scan rate in the thermal analysis process is 2°C/min. In this study, the DSC measurement was carried out to confirm the phase transition of BaTiO₃ nanoblocks and shown in Fig. 6. The testing temperature range is from 273K to 423K. To eliminate the influence of the capping organic materials on the surface of samples, the nanoblocks pre-treated at 500°C for 30 min under oxygen gas ambience before DSC measurement. It should be noted that the pre-treatment had no effect on the shape of nanoblocks. The morphology of BaTiO₃ nanoblocks with and without the pre-treatment at 500°C for 30 min under oxygen gas ambience was observed by FE-SEM and displayed in Fig S1. The cubic or cuboid shape of BT nanoblocks could be retained after heat treatments. The Fig. 6 shows a broad exothermic peak starting from ~75.3°C, which corresponds to a phase transition from tetragonal phase to cubic phase. The DDSC graph is used to show the differential of DSC value, and a sharp peak is in the graph. Previous reports has proved that the nanocubes with 10 ~15 nm size possess ferroelectric properties at room temperature [2, 18]. It is well known that the ferroelectric to paraelectric transition is almost corresponding to the phase transition temperature of BaTiO₃ materials. The findings in DSC graph indicate that the ferroelectric transition of nanoblocks is distributed over a wide range of temperatures [29, 36], and belongs to a diffused phase transition [37]. Thus, the synthesized BaTiO₃

nanoblocks are behaving as “ferroelectric relaxor” materials. In addition, the previous study illustrated that the phase-transition temperature of perovskite BaTiO_3 is size-dependent [38].

3. 4. HR-TEM of BaTiO_3 nanocube

The crystal phases of one representative BaTiO_3 nanocube was analyzed in detail by using HR-TEM and the corresponding FFT patterns, as shown in Fig. 7. The edge morphology of nanocube also shows the step or terrace structure. All of steps start from the corner section and forward to the central portion of the edge of nanocubes, which forms a slight concave cubic shape (as in Fig. 7 (b)). The direction of four corners of nanocubes belongs to $\langle 110 \rangle$ crystal direction. This result shows that the growth rate on $\langle 110 \rangle$ direction is faster than that on $\langle 100 \rangle$ direction. Furthermore, the height of steps and the superimposed terraces indicate that the ordered arrangement of unit cells is related with the surface morphology and shape of the nanocubes. The values of d spacing of BaTiO_3 nanocube are calculated by using the FFT patterns and measured by the FFT filtered HR-TEM images. The ratio of d spacing is 1.001, which indicates the existence of cubic phase. Combining with above discussions, it is conjectured that the crystalline phases of BaTiO_3 nanoblocks possess both tetragonal and cubic phases.

4. Conclusion

The BaTiO_3 nanoblocks with different average size were synthesized by using hydrothermal method and showed both cubic and cuboid shapes. Anisotropy in morphology of single crystalline BaTiO_3 nanocuboids with neat surface and standard corner angle was investigated by precise analysis of TEM and HR-TEM images. The aspect ratios of L_L/L_S of mono-nanoblocks are counted by utilizing the TEM images. The 15 nm- and 25 nm-sized nanoblocks contain around 24.3% and 51.8% of

nanocuboids, respectively. Based on the precise analysis of the nanoblocks by using HR-TEM, the unique morphology of nanocuboids appeared an anisotropy growth pattern.

The lattice constant of BaTiO₃ nanoblocks was measured by using the HR-TEM images directly and calculated by using the corresponding FFT pattern. The ratios of d spacing of (100) crystal plane and the perpendicular (001) plane varied from ~1.014 to ~1.018. The existence of BaTiO₃ nanocuboid indicates the possibility of the existence of the tetragonal phase in the nano-scale range.

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Fig. 1 TEM images of BaTiO₃ nanoblocks with an average size of (a) 15 nm and (b) 25 nm; aspect ratio of (c) 15 nm nanoblocks and (d) 25 nm nanoblocks.

Fig. 2 (a), (b), (c) and (d) the HR-TEM images of four BaTiO₃ nanoblocks with diversified aspect ratios; (e) and (f) the corresponding FFT filtered images of (b) and (d), respectively.

Fig. 3 HR-TEM images and corresponding FFT patterns of BaTiO₃ nanocuboids with (a) a size of ~ 18 nm and (e) a size of ~ 28 nm; (b) and (f) the FFT pattern of (a) and (e); (c) and (g) the corresponding FFT filtered images of (a) and (e); (d) and (h) the partial enlarged images of (c) and (g), respectively.

Fig. 4 Illustration for (a) the cubic phase and tetragonal phase of BaTiO₃ nanocuboids, (b) the array of unit cells with the displaced Ti cations in BaTiO₃ nanocuboids.

Fig. 5 (a) TEM image and (b) HR-TEM image of BaTiO₃ nanoblocks with pseudo-cuboid shape; (c) HR-TEM image of the section in the square box of (a).

Fig. 6 DSC graphs of BaTiO₃ nanoblocks with an average size of 30 nm, which were pre-treated at 500°C for 30 min under oxygen gas ambience.

Fig. 7 (a) HR-TEM image of BaTiO₃ nanocubes with a size of ~ 23 nm; (b) Schematic diagram of BaTiO₃ nanocubes; (c) corresponding FFT filtered image of (a); (d) the partial enlarged images of (b), the length of the scale bar is 5 nm.

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

Figure 6

Figure 7

BaTiO₃ nanocuboid