Synthesis and Size Control of Tetragonal Barium Titanate Nanopowders by Facile Solvothermal Method

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A facile synthetic strategy was implemented to obtain nanosized barium titanate (BaTiO3) powders with tetragonal structure. The nanopowders were synthesized using solvothermal process employing diethanolamine and triethanolamine to suppress the particle growth and the as-prepared nanopowders were characterized using X-ray diffraction, scanning electron microscopy, and high-resolution dispersive Raman spectroscopy. It was found that the particle size can be easily tuned by adjusting the experimental parameters while retaining the tetragonality. The average diameters of the particles prepared with and without the organic amines were found to be 80 and 100 nm, respectively. All the synthesized BaTiO3 nanopowders exhibit a narrow size distribution with a uniform morphology. Rietveld refinement of the XRD patterns and Raman spectra revealed that the synthesized BaTiO3 nanopowders have tetragonal asymmetry dominant structures. A slight decrease in the tetragonality of the prepared powders with decrease in particle size is attributed to the presence of cubic shell layer and inner defects. The tetragonal-dominant structure was confirmed by normalizing the peak area of the Raman spectra.

I. Introduction

Barium titanate (BaTiO3) has been utilized extensively in various electroceramic areas, including thermistors,1 electroluminescence,2 electro-optical devices,3–5 and multilayer ceramic capacitors (MLCC)6,7 due to its ferroelectric response and high dielectric constant.8,9 As technological advances demand more complex portable devices with various functions, the fabrication of thinner dielectric layers of MLCCs becomes a more significant issue as these devices become more miniaturized. This requires reduction in BaTiO3 particle size to nanoscale dimensions. As the sizes of BaTiO3 particles decrease below 100 nm, the formidable challenge related to the fabrication of miniaturized MLCCs lies in the gradual decline in the dielectricity of the layers.10 It is well known that BaTiO3 exists in several polymorphic phases, such as tetragonal and cubic structures with ferroelectric and paraelectric features, respectively. In tetragonal BaTiO3, a structural deformation due to the displacement of the Ti atom from the octahedron center causes the ferroelectric stabilization of tetragonal BaTiO3.11 However, nanosized BaTiO3 reduces the spontaneous polarization of Ti atoms at the surface region, resulting in a cubic shell layer. Consequently, the main challenges lie in the synthesis of highly dielectric BaTiO3 nanopowders with decrease in particle size. Moreover, various defects can exist inside the particles, such as oxygen vacancies12 and lattice impurities.13,14 Therefore, to downsize the dielectric layers in MLCCs further, thinner cubic shell layers and a method that reduces the number of defects inside the BaTiO3 nanopowders should be considered to acquire the highest possible dielectricity.

Another issue pertaining to BaTiO3 nanopowders involves controlling the particle size distribution. Conventional solid-state synthesis can yield larger quantities, but it is difficult to achieve a narrow particle size distribution when the particle sizes are less than 100 nm. Particle dispersity affects the fabrication of MLCCs when using tape-casting and sintering processes. Nonuniform particle sizes can lead to vacancies inside BaTiO3 dielectric layers and abnormal grain growth after tape-casting and sintering. In this regard, various soft chemistry techniques have been explored to prepare BaTiO3 nanoparticles, such as spraying15 and electrophoretic deposition,16,17 as well as the catecholate,18 sol–gel,19–21 pyrolysis,22 hydrothermal synthesis using gel powders,23 and supercritical hydrothermal reaction methods.24 Although uniform BaTiO3 nanopowders are obtained using these methods, synthetic procedures are generally complex and expensive. Also, these nanopowders exhibit cubic structure instead of required tetragonal structure, which makes them unsuitable for miniaturized MLCC applications. Hence, a facile and cost-effective method is highly recommended to fabricate fine tetragonal BaTiO3 nanopowders to meet current demands.

In this article, we report the preparation of BaTiO3 nanopowders via hydrothermal and solvothermal synthesis methods and describe their structural characteristics. To control the particle size, organic solvents of diethanolamine (DEA) and triethanolamine (TEA) were employed as part of a solvothermal process employing barium hydroxide monohydrate (Ba (OH)2·H2O (Ba-hydroxide), 98%, Aldrich, Milwaukee, WI) and titanium butoxide (Ti(OCH3)4·CH3)3 (Ti-butoxide), 97%, Aldrich) as starting materials. In a typical BaTiO3 nanopowder fabrication procedure, 17.018 g (50 mmol) of Ti-

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butoxide was mixed with 20 mL of high-purity ethanol, after which 7 mL of ammonium hydroxide solution (25% NH₃ in H₂O, Aldrich) was added to the solution mixture. A quantity of 14.204 g (75 mmol) of Ba-hydroxide was dissolved in 25 mL of preheated DI-water to prepare clear Ba-hydroxide solution in parallel. The aqueous Ba-hydroxide solution was then added to the solution mixture. To control the particle size, 5 mL of DEA ((C₇H₁₅)₂N(CH₂)₃), ≥98%, Aldrich) or TEA ((HOCH₂CH₂)₃N, ≥98%, Aldrich) was added to the solution mixture. The final suspension was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heat-treated at 200°C for 48 h. After the reaction, the resultant product was washed repeatedly using water and high-purity ethanol and then dried at 80°C for 24 h in an oven. Also, BaTiO₃ nanoparticles were prepared without organic amines as a control sample using similar procedure.

The structural characteristics and phase purity of the synthesized BaTiO₃ nanopowders were investigated using an X-ray diffractometer (XRD; Rigaku D/Max-RB (12 kW), Tokyo, Japan) with CuKα radiation (λ = 1.5418 Å) operating at 40 kV and 100 mA. The unit cell parameters were obtained via Rietveld refinement of the XRD data. The morphology of the nanopowders was observed using a field-emission scanning electron microscope (FE-SEM; Hitachi S-4800, Tokyo, Japan) and a field-emission transmission electron microscope (FE-TEM; Tecnal G² F30 S-Twin, Eindhoven, the Netherlands). The Raman spectra were recorded by a high-resolution dispersive Raman microscope (LabRAM HR UV/Vis/NIR, Horiba Jobin Yvon, Longjumeau, France) equipped with three laser sources (UV, Vis, and NIR), a confocal microscope, and a liquid-nitrogen-cooled charge-coupled device (CCD) multichannel detector (256 pixels × 1024 pixels). The measurements were performed using a 514.5 nm line of an argon ion laser at room temperature. A 50× objective lens was used, and the acquisition time for each Raman spectrum was approximately 10 min depending on the sample. The measured Raman shift was in the range 100–1000 cm⁻¹.

III. Results and Discussion

The as-synthesized BaTiO₃ nanopowders were characterized using XRD and SEM. Figure 1 shows the XRD pattern, a SEM image, and the particle size histogram of the hydrothermally synthesized nanopowders, in which organic amines were not added. The XRD pattern indicates that the synthesized material shows good agreement with the conventional tetragonal BaTiO₃ structure with the P4mm space group (JCPDS data No. 05-0626), with no impurity peak appearing in the diffractogram. Rietveld refinement gives lattice parameters a = 3.99454 Å and c = 4.02411 Å, which are very close to the reported values pertaining to this tetragonal structure (JCPDS data No. 05-0626). XRD pattern of as-synthesized BaTiO₃ powders show peak splitting at 45°. In general, the XRD patterns of the tetragonal BaTiO₃ show split peaks at 45° corresponding to the (hkI) Miller index (002) and (200), whereas cubic BaTiO₃ (JCPDS data No. 31-0174) has one single peak at 45° corresponding to (002). Therefore, we can conclude that the hydrothermally synthesized BaTiO₃ powders show a tetragonal- or tetragonal-dominant structure.

The SEM image confirms that the BaTiO₃ powders have a nonagglomerated shape with an average diameter of 106.69 nm. The particle-size distribution histogram of hydrothermally synthesized BaTiO₃ nanopowders revealed narrow size distribution ranges with the average particle dispersity (DSEM90/DSEM50) of 1.57. The structural and morphological characterizations converge in demonstrating that the hydrothermal synthesis process leads to the formation of the tetragonal BaTiO₃ phase with 100-nm grade nanopowders and a narrow size distribution.

In comparison, the BaTiO₃ nanopowders synthesized using the solvothermal process show differences both in terms of the particle size and tetragonality. The XRD patterns of the as-synthesized BaTiO₃ created by means of the DEA and TEA processes are shown in Fig. 2. Both patterns indicate a tetragonal BaTiO₃ structure with no impurity peak. However, evidence of peak splitting at 45° is not very distinct. This may be due to the peak broadening effect of nano-crystalline structures or to the cubic-dominant BaTiO₃ structure. The tetragonalties of the two samples as determined by Rietveld refinement were 1.0068 (DEA) and 1.0072 (TEA). These values are comparable to the tetragonality of nanopowders synthesized using a hydrothermal process. To compare the particle size, the morphologies of BaTiO₃ nanopowders created using the DEA and TEA processes were characterized by SEM. These results are presented in Fig. 3. The average sizes (DSEM50) of the two powders are 78.72 nm (DEA) and 84.78 nm (TEA). Micrograph images of the nanopowders revealed particle size reductions of 24.3% (DEA) and 18.5% (TEA) compared with a hydrothermally synthesized sample. Thus, organic amines serve to reduce the particle size of synthesized BaTiO₃ nanopowders while retaining their tetragonality.
The tetragonality values determined by Rietveld refinement of the XRD data are difficult to assign the crystal symmetry due to the peak broadening effect and low intensity. Therefore, an alternate analysis method is required to confirm the tetragonalities of BaTiO₃ nanopowders. Raman spectroscopy is capable of measuring the lattice vibrational spectra in an investigation of the tetragonal-cubic symmetry of BaTiO₃ samples. The Raman spectra of different BaTiO₃ particles (denoted by BTR1 to BTR7 based on tetragonality) are given in Fig. 4 and their corresponding size, lattice parameters, and tetragonality values are given in Table I. The Raman spectra of BTR1 to BTR6 samples, which have a tetragonal feature according to the XRD data, are consistent with the spectrum of tetragonal BaTiO₃ as reported elsewhere. It is known that tetragonal BaTiO₃ has Raman scattering bands of A₁(TO) at 250 cm⁻¹, B₁, E (TO + LO) at 307 cm⁻¹, [E(TO), A₁(LO)] at 520 cm⁻¹, and [E(LO), A₁(LO)] at 720 cm⁻¹. However, a mixture of the Raman scattering characteristics of both cubic and tetragonal asymmetry can be observed at around 180, 307, 520, and 720 cm⁻¹. In the present experiment, the scattering intensities at 250 and 307 cm⁻¹ gradually declined as the tetragonalities of the BaTiO₃ nanopowders decreased. It is interesting to note that there is a relationship between the peak intensity and the tetragonal features in the Raman scattering results. Figure 5 demonstrates the tetragonality of BaTiO₃ nanopowders as a function of the normalized area of peaks at 180, 250, 307, 520, and 720 cm⁻¹. The normalized peak areas are in very good agreement with the tetragonality determined from XRD data. These results indicate that Raman spectroscopy can serve as an alternate tool with which to evaluate nanosized BaTiO₃.

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To enhance our understanding of the roles of the organic solvents of DEA and TEA, the amount of DEA was varied.
in the experimental procedure. Table II presents a comparison of the particle size, distributions, and lattice parameters of various BaTiO₃ nanopowders synthesized using hydrothermal and solvothermal processes by varying the DEA content. The notation of the sample numbers indicates the different ratios of organic solvents and the addition of ethanol. When we added DEA of 2 (BT 4) or 10 mL (BT 5) to the solvothermal reaction, the average particle size decreased by 20%–30% compared with hydrothermally synthesized BaTiO₃ (BT 1). Although the volume ratio of organic amines was increased or decreased by 12.5% (BT 5) or 2.5% (BT 3), the particle size decreased in a similar manner by about 75 or 80 nm. Although the DEA process decreased the average particle size, the influence of the amount of DEA on the particle size was insignificant, whereas a reduction in the average size did not occur in BT 6 or 7 despite the addition of DEA. This phenomenon can be explained based on the kinetics of the reaction in relation to ethanol and DEA. During the solvothermal reaction, Ti-O bonds are broken via hydrolytic formation of hydrogen bonds with hydrated water of barium complexes (Ba²⁺ or BaOH⁺) in a solution. In the present study, ethanol is a solvent with weaker polarity than water; thus, the formation of Ti(OH)₄(4–x)⁺, which are soluble and react further with barium ions or complexes (Ba²⁺ or BaOH⁺) in a solution. In the present study, ethanol is a solvent with weaker polarity than water; thus, the formation of Ti(OH)₄(4–x)⁺, which can occur at a significantly faster rate. Simultaneously, DEA plays a role in the formation of hydrogen bonds with hydrated water of barium salts and exhibits a strong inclination to take Ba²⁺ or BaOH⁺ away from the hydroxide complexes. This process using DEA is advantageous, as more rapid formation of Ti(OH)₄(4–x)⁺ and the strong attraction with Ba²⁺ or BaOH⁺ can lead to an increase in the number of nucleation sites and can suppress the particle growth by means of the dissolution-precipitation reaction mechanism. This phenomenon requires both DEA and ethanol to suppress the growth reaction, otherwise a size reduction does not occur, as in the case of the BT 8 sample. Accordingly, with organic amines of DEA and TEA, smaller BaTiO₃ particles with a uniform size distribution can be synthesized than hydrothermally synthesized samples.

The theoretical tetragonal asymmetry of BaTiO₃ is 1.011 (a = 3.992 Å, c = 4.036 Å), but in the present nanoparticles, the tetragonals are generally about 1.006 or 1.007. It is known that BaTiO₃ nanoparticles contain two general defects attributable to the reduction in the tetragonality of the nanopowders. The first defect is the presence of a cubic shell layer in BaTiO₃. In a bulk system, a cubic shell layer with a thickness of a few nanometers is essentially negligible, whereas in nano-sized particles, a few nanometers become a relatively critical value, decreasing the tetragonality of the nanopowders. In addition, hydrothermally synthesized BaTiO₃ contains some degree of internal pores due to the presence of OH⁻ groups in the BaTiO₃ nanopowders. These two defects can be presented as a model, as shown in Fig. 6(a). The presence of an outer shell and inner pores in our synthesized BaTiO₃ nanopowders were confirmed using scanning transmission electron microscopy (STEM), as shown in Fig. 6(b). Similarly, Zhu et al. has observed the outer shell of BaTiO₃ nanocrystals by HR-TEM. Therefore, the shell layer and inner pores inevitably influenced the tetragonality of the BaTiO₃ nanopowder.

Based on the BaTiO₃ model and on the HR-TEM observations by Zhu et al., if the cubic shell layer is assumed to have a thickness of 3 nm thick and if inner defects do not exist in the nanoparticles, the tetragonality as a function of the particle size is plotted as a solid line, as shown in Fig. 7. The calculated line was assumed that the nanoparticle pertain as spherical morphology. There is a drastic decrease in the tetragonality value, from 1.009 to 1.008, when the particle size is less than 80 nm. These values indicate that at an average particle size of 80 nm, the maximum attainable tetragonality of BaTiO₃ nanopowders is 1.0087. In a comparison with our synthesized results, all of the tetragonal asymmetry values of the synthesized BaTiO₃ nanopowders are presented in Fig. 7. The tetragonality values of BT 1 to 8 are plotted with the white circles, and the black circles represent those values of the reproduced BaTiO₃ nanopowders.

<p>| Table I. Average Particle Size, Lattice Parameter, and Tetragonality of BaTiO₃ Nanopowders for Raman Spectroscopy |</p>
<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Average particle size (nm)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Tetragonality (c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTR1</td>
<td>115.42</td>
<td>3.99375</td>
<td>4.02962</td>
<td>1.0090</td>
</tr>
<tr>
<td>BTR2</td>
<td>158.57</td>
<td>3.99009</td>
<td>4.02428</td>
<td>1.0086</td>
</tr>
<tr>
<td>BTR3</td>
<td>84.78</td>
<td>3.99435</td>
<td>4.02275</td>
<td>1.0072</td>
</tr>
<tr>
<td>BTR4</td>
<td>74.65</td>
<td>3.99260</td>
<td>4.01701</td>
<td>1.0061</td>
</tr>
<tr>
<td>BTR5</td>
<td>97.98</td>
<td>3.99849</td>
<td>4.02100</td>
<td>1.0056</td>
</tr>
<tr>
<td>BTR6</td>
<td>74.39</td>
<td>3.99721</td>
<td>4.01890</td>
<td>1.0054</td>
</tr>
<tr>
<td>BTR7</td>
<td>36.69</td>
<td>4.02867</td>
<td>4.03245</td>
<td>1.0009</td>
</tr>
</tbody>
</table>

Average particle sizes of BTRs were measured using SEM images (DSEM). Tetragonality (c/a) of BTRs were calculated by Rietveld refinement of X-ray diffraction data.

<p>| Table II. Comparison of Average Particle Size, Particle Dispersity, and Lattice Parameter of BaTiO₃ Nanopowders Produced from Hydrothermal and Solvothermal Reactions |</p>
<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Amine</th>
<th>Amount of amine (mL)</th>
<th>Ethanol</th>
<th>Average particle size (nm)</th>
<th>Standard deviation (nm)</th>
<th>Particle dispersity (DSEM/DSEM)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Tetragonality (c/a)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT1</td>
<td>X</td>
<td>0</td>
<td>X</td>
<td>106.69</td>
<td>14.69</td>
<td>1.57</td>
<td>3.99454</td>
<td>4.02411</td>
<td>1.0074</td>
<td>Fig. 1</td>
</tr>
<tr>
<td>BT2</td>
<td>DEA</td>
<td>5</td>
<td>O</td>
<td>78.72</td>
<td>10.78</td>
<td>1.43</td>
<td>3.99129</td>
<td>4.01824</td>
<td>1.0068</td>
<td>Figs. 2(a) and 3(a)</td>
</tr>
<tr>
<td>BT3</td>
<td>TEA</td>
<td>5</td>
<td>O</td>
<td>84.78</td>
<td>11.07</td>
<td>1.42</td>
<td>3.99435</td>
<td>4.02275</td>
<td>1.0072</td>
<td>Figs. 2(b) and 3(b)</td>
</tr>
<tr>
<td>BT4</td>
<td>DEA</td>
<td>2</td>
<td>O</td>
<td>81.24</td>
<td>13.58</td>
<td>1.50</td>
<td>3.99792</td>
<td>4.02411</td>
<td>1.0066</td>
<td>–</td>
</tr>
<tr>
<td>BT5</td>
<td>DEA</td>
<td>10</td>
<td>O</td>
<td>76.76</td>
<td>17.69</td>
<td>1.75</td>
<td>4.00002</td>
<td>4.02439</td>
<td>1.0061</td>
<td>–</td>
</tr>
<tr>
<td>BT6</td>
<td>DEA</td>
<td>5</td>
<td>X</td>
<td>103.97</td>
<td>15.16</td>
<td>1.39</td>
<td>3.98999</td>
<td>4.02018</td>
<td>1.0076</td>
<td>–</td>
</tr>
<tr>
<td>BT7</td>
<td>DEA</td>
<td>10</td>
<td>X</td>
<td>103.72</td>
<td>15.55</td>
<td>1.41</td>
<td>3.98818</td>
<td>4.01920</td>
<td>1.0078</td>
<td>–</td>
</tr>
<tr>
<td>BT8</td>
<td>X</td>
<td>0</td>
<td></td>
<td>101.97</td>
<td>19.23</td>
<td>1.52</td>
<td>3.99333</td>
<td>4.01765</td>
<td>1.0061</td>
<td>–</td>
</tr>
</tbody>
</table>

X, not included; O, included; DEA, diethanolamine ([HN(CH₂CH₂OH)₂]; TEA, triethanolamine ([HOCH₂CH₂OH]₃N).

Average particle sizes of BTs were measured by SEM images (DSEM).

Tetragonality (c/a) of BTs were calculated by Rietveld refinement of X-ray diffraction data.
Tetragonal BaTiO₃ nanopowders of two different sizes were fabricated using facile and scalable hydrothermal and solvothermal methods. The average diameters of the BaTiO₃ particles obtained using hydrothermal and solvothermal reaction methods were around 100 and 80 nm, respectively, with a low particle dispersity ($D_{SEM90}/D_{SEM50}$) of approximately 1.5. The reduction in particle size can be attributed to the synergistic effect of organic amine and ethanol in increasing the number of nucleation sites and suppressing the particle growth via dissolution-precipitation mechanism. The tetragonality of the synthesized powders, as determined by Rietveld refinement of the XRD data and by high-resolution dispersive Raman spectra, decrease with the decrease in particle size. It was revealed that the reduced tetragonality features of BaTiO₃ nanopowders are caused by the presence of a cubic shell layer and inner pores, the effects of which become relatively critical in nanosized materials. Also, by measuring the normalized peak areas of the Raman spectra, we established a trend according to the tetragonality values of the BaTiO₃. These synthesized BaTiO₃ nanoparticles with tetragonal structure could be potentially used for the miniaturization of MLCC devices.

Acknowledgments

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