

The influence of lattice defects on the crystal structure of hydrothermal BaTiO₃ powders

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Fine powders of Barium titanate (BaTiO₃) were hydrothermally prepared and heat treated at various temperatures from 400 °C to 1200 °C for 1 hour. The as-prepared and heat-treated powders were characterized by thermogravimetric analysis (TGA), Raman spectroscopy, and X-ray diffractometry (XRD). All these powders were identified as tetragonal phase by Raman spectroscopy. The XRD results show that the tetragonality or *c/a* ratio in heat-treated BaTiO₃ powders increases with heat treatment temperature. This suggests that lattice water and lattice vacancies suppress the phase transition from cubic to tetragonal in hydrothermal BaTiO₃ powders, but do not prevent it completely.

Key words: Crystal structure, Lattice defects, Hydrothermal, Barium titanate, powder.

Introduction

BaTiO₃ is an important material in the electronics industry due to its high dielectric constant and ferroelectric properties. Conventional synthesis of BaTiO₃ involves calcinations of barium carbonate and titanium dioxide mixture at high temperatures (> 1000 °C) [1]. Hydrothermal synthesis makes it possible to prepare crystalline nanometer-sized BaTiO₃ powders at a moderate temperature (< 374 °C) and pressure without the need of calcination [2-5].

While it is well known that the tetragonal phase is the only thermodynamically stable phase for BaTiO₃ at room temperature, the crystal structure of hydrothermally prepared BaTiO₃ has been discussed over 20 years. Many workers believe that it is in a metastable cubic phase at room temperature because no peak splitting was found in the XRD patterns of hydrothermal BaTiO₃ powders [6-11]. They proposed two models, a critical size model and a lattice defects model, to explain the XRD results. The critical size model is described as follows [7, 10, 11]: a substantial crystal distortion is involved in the cubic-to-tetragonal phase transition when BaTiO₃ is cooled through 130 °C, the Curie temperature for BaTiO₃. While this transformation can be easily completed in large particles, it is impossible for the particles below a “critical-size” due to the high strains which result from the phase transformation in fine powders. Like the critical size model, the lattice defects model [6, 8, 9] also

suggests that the high strains in powders suppress the cubic-to-tetragonal transformation. But according to the lattice defects model, the strains are introduced by a high concentration of lattice defects such as lattice water, and barium vacancies in the hydrothermal BaTiO₃ powders.

Clark *et al.* [12] suggested that hydrothermal BaTiO₃ is a tetragonal phase. They argued that XRD is unable to resolve the subtle distortion of the tetragonal phase due to peak overlap, and Raman spectroscopy is a more sensitive technique to probe this small tetragonal distortion. They observed Raman peaks characteristic of tetragonal symmetry at 305 cm⁻¹ in hydrothermal BaTiO₃ powders of size 20-40 nm, while XRD revealed only cubic phase in the same powders [12]. Our own previous results [13] also showed by Raman spectroscopy that a tetragonal-to-cubic transition occurs with a decrease of the Ba/Sr ratio in hydrothermal barium strontium titanate (BST) powders. By contrast, by XRD, no tetragonal phase was found in any hydrothermal BST powders [13]. All these results suggest hydrothermal BaTiO₃ is a tetragonal phase even though no peak splitting was found in the XRD patterns.

The effects of lattice water and other lattice defects on the crystal structure of hydrothermal BaTiO₃ powders have not been fully understood. Clark *et al.* [12] hydrothermally synthesized and then heat treated the hydrothermal BaTiO₃ powders. They found as-prepared and all heat-treated powders were in the tetragonal phase by Raman spectroscopy, and no significant change in the Raman spectra of heat-treated powders. Peak splitting in XRD was observed only when the heat treatment temperature reached 1100 °C. They believed it was lattice vacancies, not lattice water, which was crucial

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for the crystal structure of hydrothermal BaTiO₃ powders, because significant migration of lattice vacancies needs a temperature of at least 1000 °C, while the elimination of lattice water is complete at 600 °C [12]. By contrast, Hennings and Schreinemacher [4] found that peak splitting showed up in the XRD pattern of BaTiO₃ powders heat treated at 200 °C; and complete tetragonal distortion, $(c-a)/a \approx 1\%$, of the perovskite unit cell was obtained at 600 °C [4]. This result indicates water at the surface and in the lattice of hydrothermal powders plays a major role in the crystal structure. Clearly, more work needs to be done to understand the effect of lattice water and lattice vacancies on the crystal structure of hydrothermal BaTiO₃ powders.

The goal of this research is to study the water incorporation in BaTiO₃ powders under hydrothermal conditions and to gain more insight into the effect of lattice defects on the structure of hydrothermal powders.

Experimental Procedure

Hydrothermal BaTiO₃ powders were synthesized by reacting Ti(OH)₄ gel with a 1 M Ba(OH)₂ solution. The Ti(OH)₄ gel was prepared by dissolving TiCl₄ (Alfa Aesar, Ward Hill, MA, US) in ice-cold distilled water, and reacting it with 3% NH₄OH solution. The resulting gel was filtered and cleaned with distilled water. Then, the freshly prepared gel was suspended in a 1 M Ba(OH)₂ solution at 80 °C in an autoclave (Model 4744, Paar Instrument Company, Moline, IL, US). After that, the autoclave was sealed and placed in a forced-air convection oven at 200 °C for 24 hours in air. After cool down, the resultant powders were filtered, washed and dried at 100 °C for 24 hours in air. The heat treatment of hydrothermal powders was carried out in a furnace at various temperatures from 400 °C to 1200 °C for 1 hour in air.

The particle size and morphology were observed using a field emission scanning electron microscope (JSM 6335F, JEOL, Tokyo, Japan). Thermogravimetric analysis of the as-prepared powders was carried out using a TA Instrument TG-DTA simultaneous thermal analyzer (model TGA-2950) over the temperature range of 50 °C - 900 °C. The crystal structure of the as-prepared and heat-treated BaTiO₃ powders was determined by Raman spectroscopy and XRD. A laser of 514.5 nm wavelength was used to perform Raman spectroscopy (Ramanscope 2000, Renishaw, Gloucestershire, UK). Powder XRD was performed on a D5005 diffractometer (Bruker AXS, Madison, WI, US) using Cu K_α radiation over a 2θ range from 10° to 90°. The peak splitting at around 45° was used to identify the tetragonal phase. The lattice parameters of the tetragonal phase were obtained by Gaussian fitting of XRD data at 45° using "Peakfit" software.

Results and Discussion

Figure 1 shows an SEM micrograph of hydrothermal BaTiO₃ powder. The particles are spherical and uniform in size. The average particle size is around 140 nm.

Because hydrothermal synthesis of BaTiO₃ powders was carried out in an aqueous solution, water was inevitably incorporated into these hydrothermal powders. Figure 2 shows the TGA curves of hydrothermal and commercial BaTiO₃ powders. Below 600 °C, the weight loss is due to water evaporation. Notice that there is much more water in hydrothermal powders (1.40 wt%) than in commercial powders (0.22 wt%). The water in hydrothermal powders can be classified as: physical absorbed water and lattice water. The physical absorbed water is on the surface of the hydrothermal powders and can evaporate below 200 °C. On the other hand, the lattice water exists in the lattice structure and can be removed in the temperature range of 200-600 °C. Above 600 °C, the weight loss is attributed to the

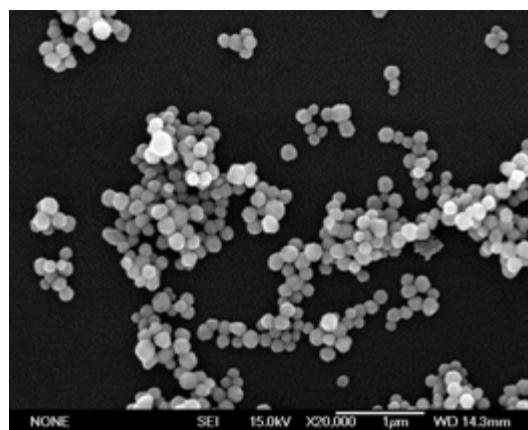


Fig. 1. SEM image of hydrothermal BaTiO₃ powders.

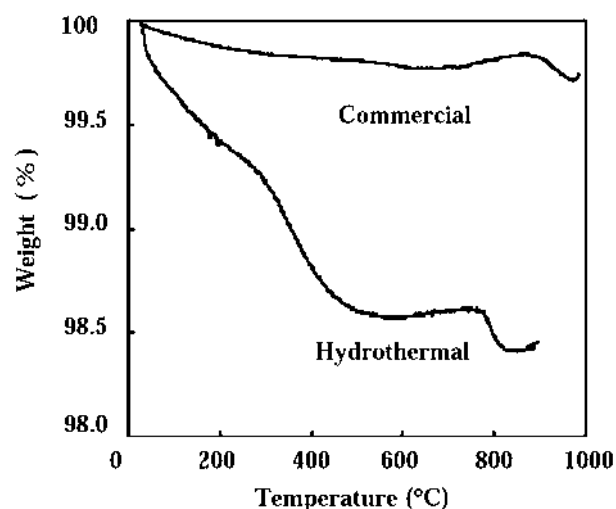


Fig. 2. TGA curves of hydrothermal and commercial BaTiO₃ powders.

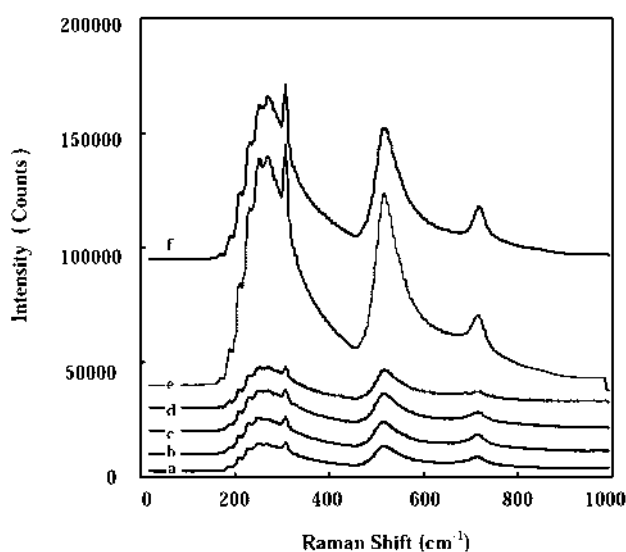


Fig. 3. Raman spectra of hydrothermal BaTiO₃ powders: a) as-prepared, and after heat treatment at b) 400 °C, c) 600 °C, d) 800 °C, e) 1000 °C, and f) 1200 °C for 1 hour.

disintegration of BaCO₃.

The lattice water or hydroxyl groups (OH⁻) exist in the lattice as point defects, occupying the sites of oxygen (O²⁻) in hydrothermal BaTiO₃ powders. To satisfy the electro-neutrality condition, barium vacancies (V_{Ba}^{''}) are also introduced into the powders. Thus, there is large quantity of lattice defects in hydrothermal powders. The lattice water and lattice vacancies can be removed by heat treatment at 200 °C - 600 °C, and 1000 °C - 1200 °C respectively [12].

The crystal structure of as-prepared and heat-treated powders was analyzed with Raman spectroscopy (Figure 3). The peak at 305 cm⁻¹, the characteristic peak of the tetragonal phase in BaTiO₃, is present in all powders, indicating the presence of the tetragonal phase. This is in agreement with Clark *et al.*'s result [12]. There is no significant change in the Raman spectra except that there is an intensity jump at 1000 °C. This might be related to the migration of lattice defects, because it is believed that 1000 °C is the lowest temperature for the multistage migration of lattice defects such as barium and oxygen vacancies [12, 14].

XRD was also used to determine the crystal structure of as-prepared and heat-treated BaTiO₃ powders. Figure 4 shows a selection of XRD patterns over a 2θ range 44°-46°. Notice that for the as-prepared powders and the powders annealed at 400 °C, 600 °C, the peaks at around 45° are asymmetric, indicating two peaks at this position. Clear peak splitting shows up in the powders annealed at 800 °C, 1000 °C, and 1200 °C. The software "Peakfit" was used to deconvolute the spectra at around 45° into two separate peaks and determine the positions of these two peaks. Figure 5 shows an example of experimental and deconvoluted peaks for BaTiO₃ powders heat treated at 800 °C. The two small

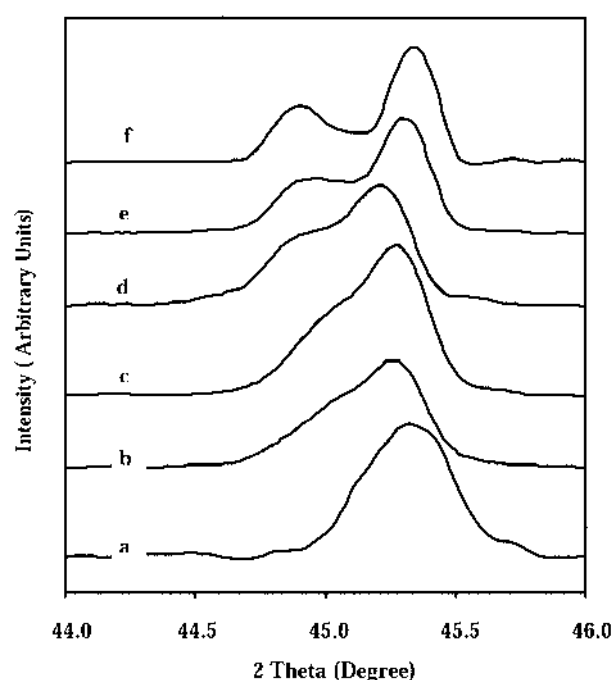


Fig. 4. XRD over the 2θ range of 44°-46° of hydrothermal BaTiO₃ powders: a) as-prepared, and after heat treatment at b) 400 °C, c) 600 °C, d) 800 °C, e) 1000 °C, and f) 1200 °C for 1 hour.

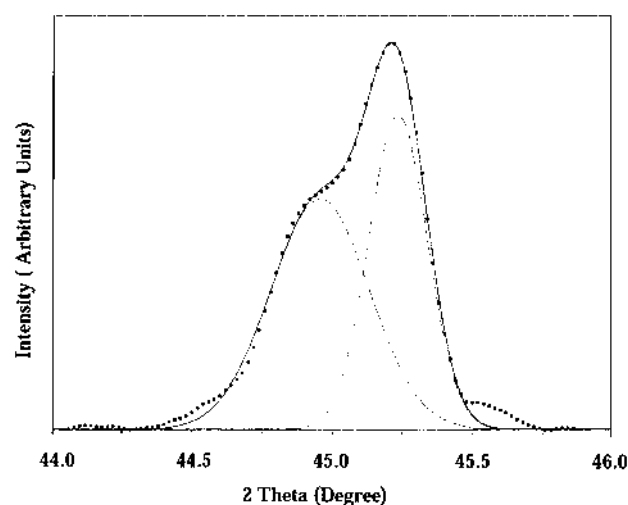


Fig. 5. Experimental and deconvoluted XRD patterns of hydrothermal BaTiO₃ powder after heat treatment at 800 °C for 1 hour. The two small peaks were obtained with best fit of Gaussian distributions, representing the peaks of (002) and (200). Notice that the calculated result, dashed line, fits very well with the experimental result.

separate peaks of (002) and (200) were obtained by best fit to Gaussian distributions. The magnitude of peak splitting, taken as the 2θ distance between the two peaks, was found to increase with temperature (Figure 6). Figure 7 shows the calculated lattice parameters *c*, *a*, and *c/a* ratio of annealed BaTiO₃ as a function of heat treatment temperatures. The *c/a* ratio increases with temperature, and the complete tetragonal distortion to *c/a* ≅ 1.01, of the BaTiO₃ perovskite unit cell is

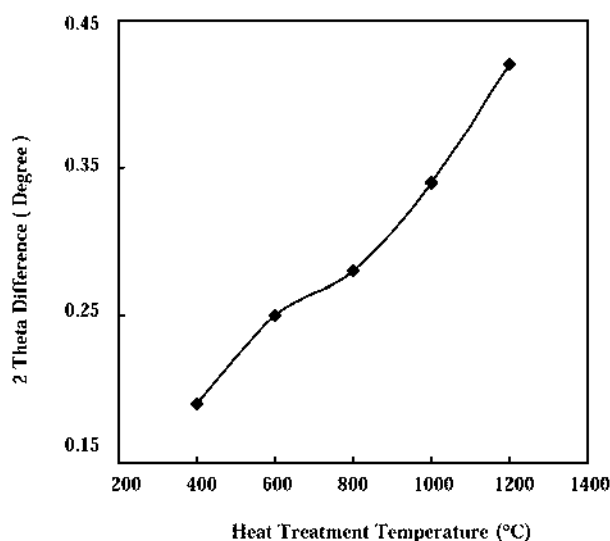


Fig. 6. Magnitude of peak splitting as a function of heat treatment temperature. The peak splitting is taken as the 2θ difference between peaks (002) and (200) at around 45° in the XRD patterns of heat-treated hydrothermal BaTiO₃ powders.

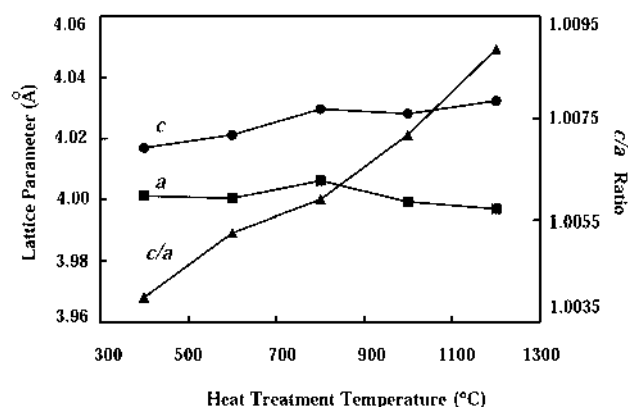


Fig. 7. Lattice parameters c , a , and the c/a ratio in heat-treated hydrothermal BaTiO₃ powders as a function of heat treatment temperature. The magnitude of tetragonality in heat-treated powders, indicating by the c/a ratio, increases with heat treatment temperature.

obtained at 1200 °C.

The Raman and XRD results suggest that hydrothermal BaTiO₃ powders are in the tetragonal phase, irrespective of the post-hydrothermal heat treatment; both lattice water and lattice vacancies affect the magnitude of the tetragonal distortion. Although the high concentration of lattice defects in hydrothermal BaTiO₃ powders, like lattice water and barium vacancies, do not completely prevent the cubic-to-tetragonal phase transformation as supposed by the “lattice defects” theory, the strains introduced by lattice defects make the unit cell distortion (c/a ratio) much smaller than that in the standard BaTiO₃. This is the reason that no peak splitting was observed in the XRD patterns of hydrothermal BaTiO₃ powders even though they are in tetragonal phase.

It is well known that the crystal structure of hydrothermal BaTiO₃ powders is affected by hydrothermal conditions like precursors, and temperature [15-18]. Dutta *et al.* [15, 16] examined the effect of different barium salts as precursors on the crystal structure of hydrothermal BaTiO₃, and they found that the halide salts (I-, Br-, Cl-) resulted in the highest tetragonal content, followed by acetate, nitrate, and hydroxide salts [15, 16]. Since barium acetate was used by Hennings and Schreinemacher [4] and barium hydroxide was used in this work as precursors, it is understandable that Hennings and Schreinemacher found the complete tetragonal distortion, $c/a \cong 1.01$, was obtained at an annealing temperature of 600 °C, while we found it at 1200 °C. Kajiyoshi *et al.* [17] and Bendale *et al.* [18] also found that the tetragonal phase in hydrothermal BaTiO₃ powders was easier to obtain when the temperature was at or above 200 °C [17, 18]. The hydrothermal temperature used by Clark *et al.* [12] was 85 °C, and in this work it was 200 °C. The difference in hydrothermal temperatures is the possible reason that clear peak splitting in the XRD patterns of annealed powders in this work showed up at a much lower temperature compared with Clark *et al.*'s results.

Summary

Nanometer-sized BaTiO₃ powders have been synthesized and heat-treated at temperatures from 400 °C to 1200 °C. In all cases, the BaTiO₃ powders were found by Raman spectroscopy to be in the tetragonal phase, while peak splitting was only found in the XRD patterns of heat-treated powders. Both lattice water and lattice vacancies suppress but can not prevent the cubic-to-tetragonal transformation. Removal of lattice defects facilitates the phase transformation and increases the magnitude of tetragonality in hydrothermal BaTiO₃ powders. Tetragonality in hydrothermal BaTiO₃ powders is also affected by the hydrothermal conditions.

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