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Hydrothermal Synthesis of Tetragonal Barium Titanate

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Hydrothermal synthesis of $BaTiO_3$ at 240 °C in the presence of chloride ions leads to the formation of the tetragonal polymorph upon cooling through the Curie temperature. In the absence of Cl^-, the metastable cubic structure is formed. Though the exact role of Cl^- is not clear, it appears that it leads to formation of larger (~1 μm) crystals as compared to smaller crystals (~0.2 μm) in its absence. Combination of diffraction and calorimetry provides unambiguous support for the presence of the tetragonal form.

Introduction

Compounds in the $BaO-TiO_2$ system play an important role in the electronics ceramic industry.[1] $BaTiO_3$, a member of this system, finds extensive use as thermistors, multilayer capacitors, and electrooptic devices.[1,2] Considerable research has focused on the synthesis of this material, including traditional ceramic processing which involves mixing of oxides or salts followed by calcination.[3] More recently, the focus has turned to low-temperature synthesis methods which have the potential to make high-purity, homogeneous ultrafine powders.[4] Among these methods are use of reactants such as titanium and barium alkoxides[5] as well as double alkoxides,[6] oxalates,[7] citrates,[8] as well as processes involvingj sol-gel[9] and hydrothermal chemistry.[10] Of considerable interest is the generation of crystalline, tetragonal $BaTiO_3$ directly at low temperature (<250 °C) both from a fundamental crystallization point of view and for technologies involving the formation of thin films.

The hydrothermal synthesis method has the most potential in this regard.[11] Typically, this reaction involves the reaction of $Ba(OH)_2$ and a titanium source, such as titanium alkoxide, titanium oxide, or titanium oxide gels. The reaction has to be carried out in a strongly alkaline solution (~0.1 M OH^- or above), and crystalline $BaTiO_3$ has been reported to from at temperatures between 85 and 250 °C within hours. However, in all these syntheses, the crystalline product recovered is cubic, though the tetragonal form is the thermodynamically stable form at room temperature.[12] It is of interest as to why the stable tetragonal form is not synthesized under the hydrothermal condition. Also, the physical and chemical changes that occur upon heating the as-synthesized metastable cubic form to temperatures in excess of 1000 °C in order to stabilize the tetragonal form upon cooling is of interest.[4] It has been reported by Christensen that the tetragonal form can be directly synthesized by the hydrothermal method at temperatures between 450 and 600 °C, with the process being favored at the higher temperatures. This communication was brief, and the percentage of the tetragonal from and its characteristics were not discussed.[13] There has been one other report on the hydrothermal process for $BaTiO_3$ synthesis at these high temperatures.[11] Literature reports indicate that there could exist a possible correlation between the lack of stabilization of the thermodynamically tetragonal stable form at room temperature for the hydrothermally synthesized samples and the grain size of these particles. The difference between the cubic and tetragonal form arises from the inequality in the *a* and *c* axes in the latter polymorph. To accommodate the dimensionality change in the *c* direction as the sample is cooled below the Curie point, the crystal has to distort. In a single crystal or polycrystal with grain sizes exceeding tens of microns, this distortion can readily be accommodated by twinning.[14] However, in crystals with small grains, such twinning is not possible and the internal strains are then sufficiently large to force the crystal to remain in the cubic state. Thus, synthesis procedures that result in small-grained particles will be resistant to the conversion from the cubic to the tetragonal form. This appears to be borne out by experiments.[11,13] None of the material hydrothermally synthesized at temperatures of 250 °C or less is recovered as the tetragonal form until a high-temperature treatment (~1000 °C) is done.[12] These particles all have fine submicron grain sizes. The method reported by Christensen at temperatures of 500 °C have sizes of 500–1000 μm and turned tetragonal on cooling through the Curie temperature.[13]

In this study, we have examined the possibility of directly synthesizing crystals of $BaTiO_3$ that are in the tetragonal form using hydrothermal methods. The strategy has been to examine the composition and temperature conditions in which larger crystals of $BaTiO_3$ can form. Examination of the influence of various alkali-metal cations, alkylammonium ions, and anions at temperatures below 250 °C has shown that Cl^- can lead to formation of crystals of $BaTiO_3$ that are in the stable tetragonal form at room temperature.

Experimental Section

The following procedure was adapted from the work of Christensen.[13] The reactions were carried out in a 23-mL Teflon-lined stainless steel autoclave (Parr Instrument Co.) without any agitation. A typical procedure was the dissolution of 0.01

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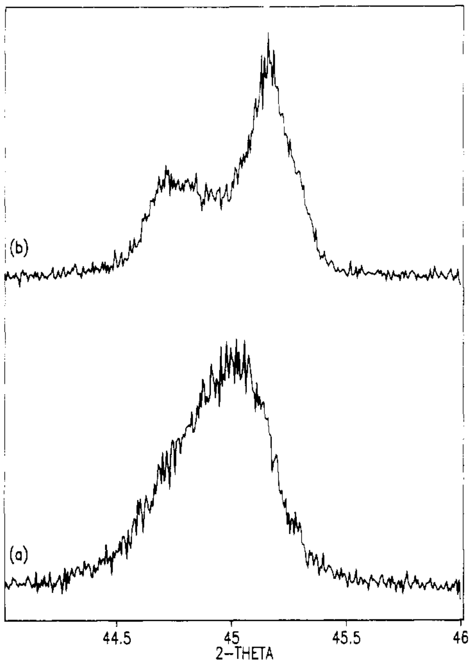

Figure 1. X-ray diffraction patterns of $BaTiO_3$ synthesized hydrothermally from (a) $Ba(OH)_2$ and (b) $BaCl_2$.

mol of NaOH in 10 mL of degassed, deionized (Nanopure) water, followed by addition of 0.0025 mol of $BaCl_2$ (Aldrich) (or $Ba(OH)_2$) and TiO_2 (Anatase, Aldrich). After heating at 240 °C for various time periods, the product was recovered by filtration and washed extensively with water. No unreacted TiO_2 or $BaCO_3$ was evidenced in the reaction production by X-ray diffraction.

Diffraction patterns were obtained using a Rigaku D/Max 2B powder diffractometer using Ni-filtered Cu Kα radiation. Calorimetry measurements were taken with a Perkin-Elmer 7 Series thermal analysis system, using 35-mg pellets in a crimped Al pan at a heating rate of 20 °C/min and an uncontrolled cooling rate. Single-point BET surface area measurements were conducted on a Micromeritics Pulse Chemisorb 2700 after samples were dried at 400 °C for 1 h. Micrographs were taken with the JOEL JSM-820 scanning electron microscope. X-ray fluorescence measurements for Cl analysis were done with a Kevex 0700 instrument.

Results

The role of the halide ion Cl^- on the hydrothermal synthesis was examined by comparison of the following reactant compositions: $0.25Ba(OH)_2$:1NaOH:$0.25TiO_2$:$55.5H_2O$ and $0.25BaCl_2$:1NaOH:$0.25TiO_2$:$55.5H_2O$. Figure 1 compares the powder diffraction pattern in the 40–50° 2θ region, at room temperature for $BaTiO_3$ generated from barium hydroxide and barium chloride compositions by heating at 240 °C for 7 days. This region of the diffraction pattern is characteristic of the tetragonal versus cubic form of $BaTiO_3$. There is a splitting of the (200) reflection in the tetragonal form, with the lower angle shoulder indexed at (002).[12a] In the cubic form this peak remains unsplit. On the basis of this correlation, it is apparent from Figure 1 that the $BaTiO_3$ formed from $BaCl_2$ is in the tetragonal form as compared to the cubic form formed from $Ba(OH)_2$. This is further substantiated by the differential scanning calorimetry data shown in Figures 2 and 3. The $BaTiO_3$ made with $BaCl_2$ clearly shows an endothermic transition on heating and an exotherm on cooling, at 127 and 123 °C, respectively. This corresponds to the tetragonal to cubic transition (Currie point). The change in enthalpy corresponding to this transition is 413 mJ/g. For a commercial sample of $BaTiO_3$ synthesized by the conventional mixing and firing approach, we found the ΔH to be 643 mJ/g, indicating that the hydrothermal synthesis is not resulting in complete formation of the tetragonal polymorph. The $BaTiO_3$ made from $Ba(OH)_2$, on the other hand, shows no transition in the DSC, as is to be expected for the cubic form. These data clearly establish that the presence of the Cl^- under hydrothermal synthesis conditions at 240 °C results in $BaTiO_3$ that undergoes conversion to the tetragonal form upon cooling through the Curie point, whereas in its absence, the metastable cubic form is obtained at room temperature. Scanning electron micrographs of the $BaTiO_3$ made using the two different compositions are shown in Figure 4. In the presence of Cl^-, the crystals are of ~1-μm dimensions, considerably larger than the ~0.2-μm material made with $Ba(OH)_2$. The stabilization of the tetragonal form in the larger crystals is consistent with the current understanding of the relationship between lattice structure and grain size.[14]

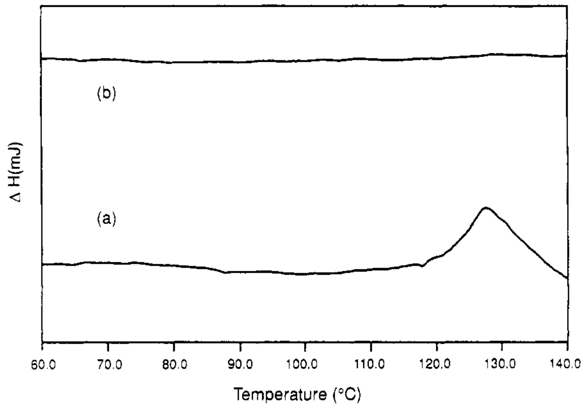

Figure 2. Differential scanning calorimetry traces of $BaTiO_3$ synthesized from (a) $BaCl_2$ and (b) $Ba(OH)_2$ during a heat cycle.

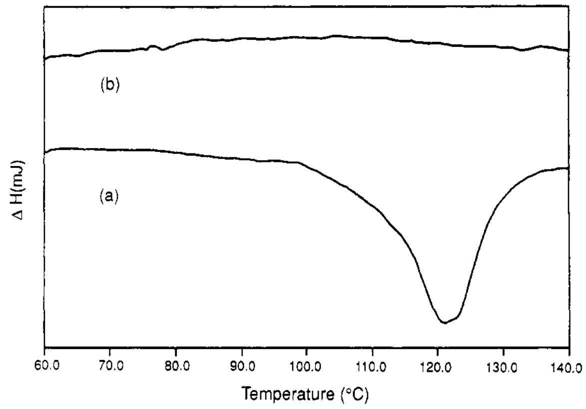

Figure 3. Differential scanning calorimetry traces of $BaTiO_3$ synthesized from (a) $BaCl_2$ and (b) $Ba(OH)_2$ during a cooling cycle.

The evolution of the crystalline form a function of time at 240 °C is shown in Figures 5 and 6. The data were collected at room temperature. The crystalline form at shorter periods of time (12 h) is primarily the metastable cubic form. This is also reflected in the ΔH values in the DSC for the transition from the tetragonal to cubic form at 127 °C. Samples heated for 12 and 30 h and 1 week had ΔH values of 276, 315, and 413 mJ/g, respectively. Clearly, increasing amounts of crystals are stabilized in the tetragonal form at ambient temperature as a function of heating time. The SEM pictures at these various time (Figure 5) show that the heating process results in growth of larger crystals. The surface area of the crystals are 20.7,

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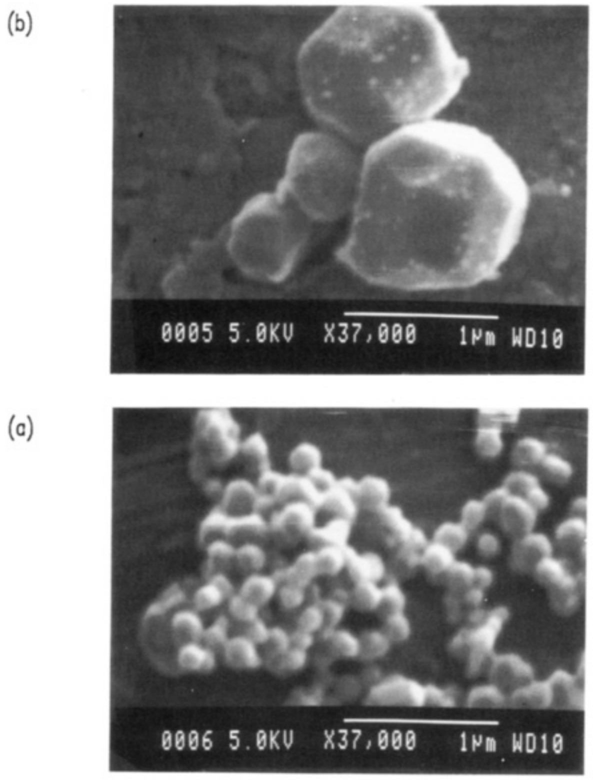

Figure 4. Comparison of SEM of $BaTiO_3$ synthesized with (a) $Ba(OH)_2$ and (b) $BaCl_2$.

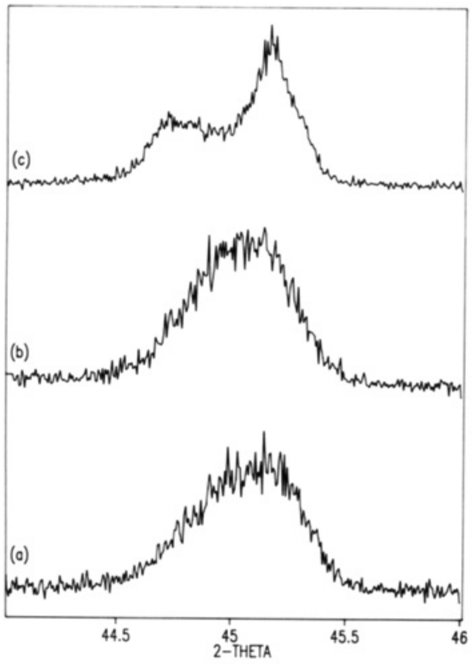

Figure 5. Powder diffraction of $BaTiO_3$ formed after heating the $BaCL_2$ composition at 250 °C for (a) 12 h, (b) 24 h, and (c) 1 week.

20.6, and 15.4 m^2/g after 12 and 30 h and 1 week of heating, respectively. It is also necessary for the temperature of reaction to exceed 200 °C. Figure 7 shows that for a sample heated to 160 °C for 1 week, only the metastable cubic form exists. No transition at ~120 °C corresponding to the tetragonal to cubic form is observed for this material in the DSC, indicating that the metastable cubic form is stabilized at room temperature.

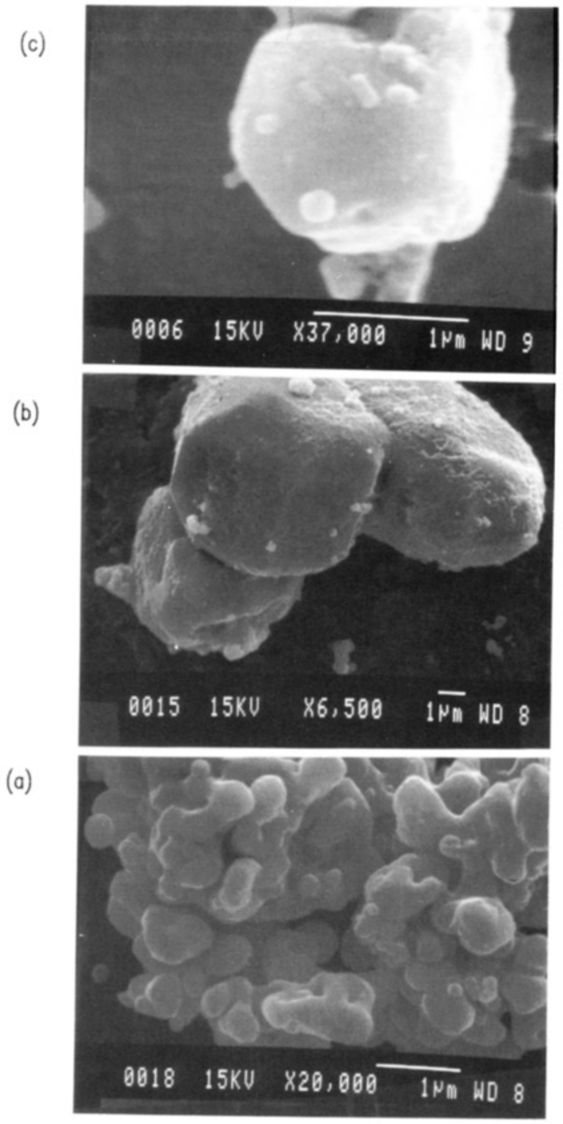

Figure 6. SEM of $BaTiO_3$ formed after heating the $BaCl_2$ composition at 250 °C for (a) 12 h, (b) 24 h, and (c) 1 week.

The necessity of the presence of Cl^- in forming the tetragonal structure is evidenced by the fact that addition of NaCl (twice the number of moles of Ba^{2+}) to the reactant composition with $Ba(OH)_2$ results in the tetragonal form. The SEM and XRD of this material is shown in Figure 8. The ΔH corresponding to the 120 °C transition is 411 mJ/g. Though peak splitting in the XRD of this material is not as pronounced as in the case of $BaCl_2$, the ΔH values corresponding to the tetragonal to cubic form are comparable.

Discussion

Hydrothermal synthesis of $BaTiO_3$ resulting in the stabilization of the tetragonal form at room temperature has only been reported for syntheses that are carried out above 450 °C.[11,13] Previous studies have shown that below 250 °C, the metastable cubic $BaTiO_3$ is observed at room temperature.[12] To stabilize tetragonal $BaTiO_3$, it is important that crystal sizes exceed 1 μm so as to accommodate the strains caused by the transformation from cubic to tetragonal structures.[14] This is consistent with the data presented above, which clearly illustrates that only with crystals of ~1-μm dimension, the tetragonal form is observed. The new finding in this study is that Cl^- mediated crystallization can bring about this process at temperatures below 250 °C.

The dynamic nature of the hydrothermal synthesis process has been recognized in the literature,[11] since the nature of crystals has been found to change with both time

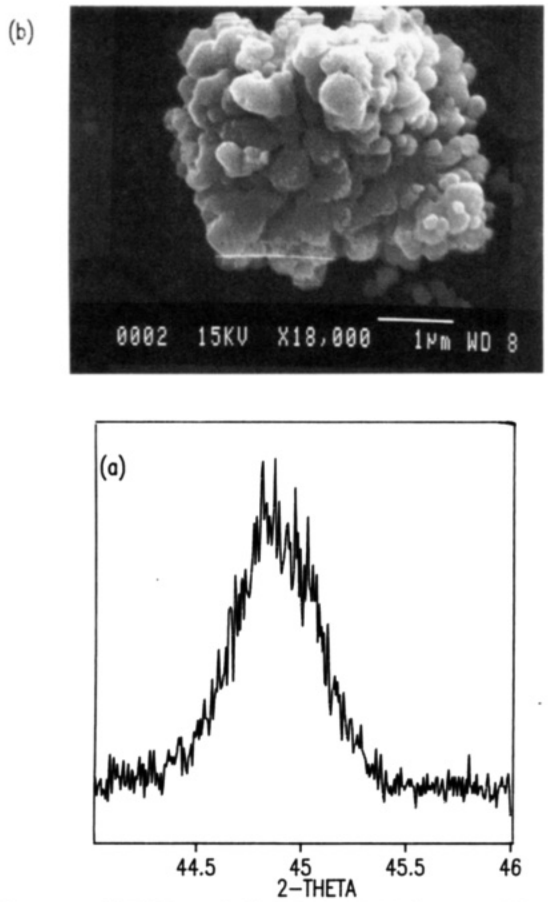

Figure 7. (a) XRD and (b) SEM of $BaTiO_3$ formed by heating the $BaCl_2$ composition for 1 week at 160 °C.

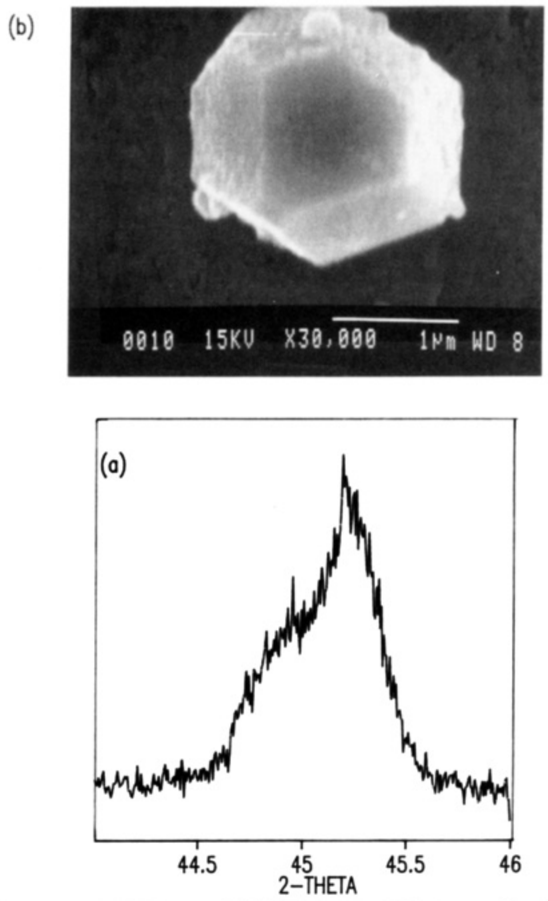

Figure 8. (a) XRD and (b) SEM of $BaTiO_3$ formed by heating the $Ba(OH)_2$ composition for 1 week at 240 °C in the presence of NaCl.

and temperature of synthesis. The OH^- must play a vital role in this process since in its absence $BaTiO_3$ is not formed. The mechanism of formation of $BaTiO_3$ from Ba^{2+} and Ti species is not well understood. Two proposed mechanisms involve a condensation reaction of $Ti(OH)_6^{2-}$ with Ba^{2+}[12b] and migration of Ba^{2+}[12a] into the TiO_2 structure with resulting breakage of TiOTi bands and incorporation of Ba^{2+}. In the latter mechanism, the role of OH^- could be to facilitate the hydrolysis of Ti–O–Ti bands. The dynamic nature of the interaction between TiO_2, Ba^{2+}, and OH^- leads to a crystallization mechanism involving nucleation, growth, and crystal dissolution. For the tetragonal form to be stabilized, it is clear from the various literature studies that the particle size has to be in the ~1-µm range in order to alleviate the lattice strain. Initial nucleation of $BaTiO_3$ leads to submicron crystals as shown in Figure 6. The role of the Cl^- seems to be to help the nucleation of larger crystals with the smaller crystals acting as seed nuclei. The exact mechanism by which the Cl^- bring about this change is unclear. X-ray fluorescence indicates that Cl^- is present as trace impurity (ppm) in the tetragonal $BaTiO_3$ and is probably not being incorporated into the perovskite structure. It is recognized that synthesis at higher temperatures (>450 °C) will lead to formation of larger crystals.[11,13] The presence of Cl^- is having the same effect at a lower temperature of synthesis. There are several possible roles that the Cl^- could be playing. It has been noted that in the presence of halide ions, the reactivity of TiO_2 gels is decreased.[12a] Even though the exact reason for this is unclear, it is possible that decreased reactivity could be due to adsorption of the Cl^- on the gel surface, thus impeding the diffusion of Ba^{2+}. If, as mentioned above, the tetragonal $BaTiO_3$ grows by a dissolution/recrystallization process and Cl^- retards the crystal growth process, then it may be able to stabilize the formation of larger crystals. This suggested role of Cl^- is speculative. However, the data shown in this paper clearly suggest that additives that do not directly enter into the chemical reaction in the hydrothermal synthesis process can stabilize the formation of the technologically important tetragonal $BaTiO_3$ crystals under milder conditions then have been reported previously.

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