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Hydrothermal Synthesis and Dielectric Properties of Tetragonal $BaTiO_3$

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Hydrothermal synthesis of barium titanate ($BaTiO_3$) at 240 °C using different barium salts as starting reactants is examined. It is found that halide salts (I^-, Br^-, Cl^-) result in the highest tetragonal content, followed by acetate, nitrate, and hydroxide salts. The tetragonal content was quantified from differential scanning calorimetry by following the endothermic Curie transition around 130 °C and reached as high as 37−39% for the materials made with the barium halides. The particle sizes ranged from 0.15 to 0.37 μm, as estimated by scanning electron microscopy. Sintering and dielectric properties of the barium titanates synthesized from different barium sources were examined. $BaTiO_3$ made from the chloride salt sintered with high densities at 1250 °C with grain sizes of 1−5 μm and a room-temperature dielectric constant (1 kHz) of 2960.

Introduction

Barium titanate ($BaTiO_3$) is extensively used as the dielectric in ceramic capacitors.[1] There is considerable interest in evaluating new methods for its synthesis[2] as well as in examining its mechanical and electrical properties.[3] $BaTiO_3$ exists in various crystallographic modifications, with a tetragonal ferroelectric form with high dielectric constant at temperatures between 0 and 130 °C, above which the unit cell converts to a paraelectric cubic structure.[4,5] At room temperature, the dielectric constant for $BaTiO_3$ ceramics prepared from fine powders can be in the range 1500−6000, depending on the grain size.[6] Because of these high dielectric constants, tetragonal $BaTiO_3$ is used to manufacture multilayer capacitors in which layers of $BaTiO_3$ (5−25 μm) alternate with thin-film electrodes.[7] Attainment of lower firing temperatures without sacrificing high densities and dielectric constants is an important objective of research in this area.[1]

Conventional synthesis of $BaTiO_3$ involves heating $BaCO_3$ and TiO_2 at temperatures in the range 1000−1200 °C[8] and often results in introduction of impurities and polydispersity. Alternative methods of synthesis to produce finer and purer powders are being investigated.[2] In addition, adapting these methods for direct formation of thin films is also being actively pursued.[9] These synthesis methods include thermal decomposition of mixed Ba−Ti oxalates,[10] citrates,[11] and alkoxide salts.[12,13] The intimate atomic level contact between Ba and Ti maintained via the ligands results in the formation of $BaTiO_3$ at lower temperatures.[10b,14] Another method that has enjoyed considerable success is hydrothermal synthesis, in which $Ba(OH)_2$, TiO_2, or gels of Ba−Ti acetate are heated (80−150 °C) in an aqueous environment in the presence of hydroxide ion.[15] Electrochemical methods under hydrothermal conditions have also been employed.[16] These procedures result in submicron cubic and paraelectric $BaTiO_3$ at room temperature and need to be heated to temperatures above 1100 °C to obtain the ferroelectric tetragonal form at room temperature.[17] In some hydrothermal preparations, the transition to tetragonal form is reported to occur after heating to 800 °C.[17c] Heat treatment results in both densification and grain growth, factors that are often difficult to control, and necessitates the use of dopants.[18] Controlling grain growth is important, since

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optimum electrical performance is obtained with grain sizes around 1 μm at the highest sintered densities.[6,19] However, there have been reports of hydrothermal synthesis of submicron powders (0.1 μm) that will densify with small grain size and high dielectric constants without addition of dopants.[20] But, even with these samples, temperatures in excess of 1150 °C are required for sintering.

Though the stable crystalline polymorph of $BaTiO_3$ at room temperature is the tetragonal form, hydrothermal synthesis at ~90 °C leads to the formation of cubic material.[15c] Synthesis temperatures in the range of 600 °C will result in formation of large (submillimeter) tetragonal crystals of $BaTiO_3$.[15b] Temperatures of hydrothermal synthesis exceeding 200 °C lead to the first appearance of the tetragonal form.[15h] Kajiyoshi and coworkers have shown that the crystals formed on Ti substrates increased in size from 0.3 to 2 μm, as the hydrothermal synthesis temperature increased from 400 to 800 °C.[15e] Uchino et al. noted that particles with average sizes greater than 0.2 μm were tetragonal with Curie transition temperatures of 130 °C.[22] Arlt and coworkers noted that the dielectric constant of sintered samples decreased with grain sizes lower than 1 μm and proposed that this occurs because the ferroelectric structure changes to a pseudocubic form.[6b] The reasons for the existence of a limiting size in order to exhibit tetragonality is being debated and is related to strains that develop in the particle that prevent it from assuming the tetragonal form,[6,23] as well as the presence of OH impurities in the lattice leading to defects and resulting microstrains that keep the particles cubic.[17b,c]

A low-temperature procedure that directly results in the formation of powders of the tetragonal form would be of interest. Such materials can be pressure sintered (hot pressed),[21] thus avoiding the necessity of lengthy high-temperature sintering and uncontrolled grain growth and porosity development. In a previous study, we have shown that inclusion of Cl^- in the reactant composition for hydrothermal synthesis leads to formation of the tetragonal form of $BaTiO_3$ at synthesis temperatures as low as 240 °C.[15e] The advantage of working at these temperatures is that conventional Teflon-lined bombs can be used, which is important since highly caustic solutions are used in these syntheses. We present here a study on the influence of barium salts on the hydrothermal synthesis of $BaTiO_3$ as well as the thermal, microscopic, sintering, and electrical properties of these powders.

Experimental Section

Materials. 99.999% pure reagents of $BaCl_2$, BaI_2, $BaBr_2$, $Ba(NO_3)_2$, and titanium(IV) isopropoxide were obtained from Alfa/Johnson Matthey, Inc. $Ba(C_2H_3O_2)_2$ (99.999%), BaF_2 (99.999%), $Ba(OH)_2$ (99%), and TiO_2 (anatase) were purchased from Aldrich Chemical Co. NaOH was acquired from J. T. Baker Inc. Commercial $BaTiO_3$ samples were obtained from TAM Ceramics and Transelco Division of Ferro Corp.

Synthesis. The cubic form of barium titanate was synthesized in a 125 mL capacity Teflon bottle at 95 °C. The synthesis procedure and reagent compositions were as follows: 0.05 mol of NaOH was initially dissolved in 50 mL of degassed nanopure water. After the solution had cooled to room temperature, 0.0125 mol of each $BaCl_2$ and anatase were added. Formation of barium carbonate was avoided by purging N_2 gas through the solution. The solution was shaken vigorously and kept in an oven at 95 °C. The system was shaken every six hours to promote complete reaction. After 48 h, the precipitate was washed with 100 mL of hot nanopure water and then dried at 95 °C for 1 h.

The tetragonal form of barium titanate was synthesized in a 23 mL capacity acid digestion bomb (Parr Instrument Co.) at 240 °C. The following synthesis procedure and reagent compositions were used: 0.005 mol of $BaCl_2$, 0.003 mol of hydrated titanium oxide, and 0.01 mol of NaOH in a 10 mL of degassed nanopure water. Hydrous titanium oxide was prepared by hydrolyzing titanium(IV) isopropoxide with 1 M hydrochloric acid followed by washing the precipitate with nanopure water. The mixture was purged with N_2 gas for ~5 min before the addition of NaOH. After the addition of the base, the bomb was immediately sealed and placed in an oven at 240 °C for 7 days. The samples were removed and extensively washed with water to remove any adsorbed ions. In the case of synthesis with $BaCl_2$, washing was done until no Cl^- was detected in the wash. X-ray fluorescence analysis of the recovered $BaTiO_3$ showed no traces of Cl^- ion. The same molar compositions, synthesis and washing procedure were followed when a barium source other than $BaCl_2$ was used. However, with the other ions, no tests for any adsorbed ions in the $BaTiO_3$ were done.

Sintering. The synthesized $BaTiO_3$ powders were diepressed under 130 MPa of pressure into discs with 7.06 mm in diameter and approximately 2 mm in thickness. The compacted dics were dried at 120 °C in an oven (Blue M) for 5 h before sintering. The sintering was investigated using a high-temperature Orton Dilatometer (Model 600D). Both the heating and cooling rates were 5 °C/min. Sintered pellets were made using a 1700 °C box furnace (Lindberg) at a variety of temperatures from 1250 to 1350 °C for 5 h. Densities of the sintered specimen were measured using Archimedes principle.

Characterization. Diffraction patterns were acquired from a Rigaku Geigerflex D/Max-3B powder diffractometer with nickel-filtered Cu Kα (1.5405 Å) source. Powder X-ray diffractions were taken in the continuous mode over two ranges of 2θ, 2–80° and 44–46°. The former was obtained at a scan speed of 2°/min with 0.050°/sampling step, and the latter was acquired at a scan speed of 0.5°/min with 0.010 sampling interval.

The calorimetric measurements were performed with a DSC 910S differential scanning calorimeter (TA Instruments). The thermal data was acquired and processed with TA Instruments 9900 computer/thermal analyzer. Sample weights of approximately 20 mg were used in crimped aluminum pans. DSC signals were measured against a crimped reference aluminum pan filled with 10 mg of alumina. The alumina content of the reference pan was used to adjust the baseline, and its weight was determined experimentally. Thermal scans were measured from 50 to 200 °C at a heating rate of 20 °C/min. Enthalpy values at the transition peak were calculated by integrating the area under the curves. The DSC temperature was calibrated against an indium reference sample through its melt (156.6 °C). All the samples were heated once to 200 °C before DSC analysis to eliminate any water content and to ensure reversibility.

The microstructure and morphology of the powder and the sintered samples were investigated using Hitachi S-4000 scanning electron microscope equipped with a field emission gun. The sintered samples were polished with 1 μm diamond paste followed by vibratory polishing. The samples were ultrasonically cleaned in acetone and thermally etched at 1200 °C for 1 h. A gold layer was then sputter coated on the samples. The average particle sizes are the mean values

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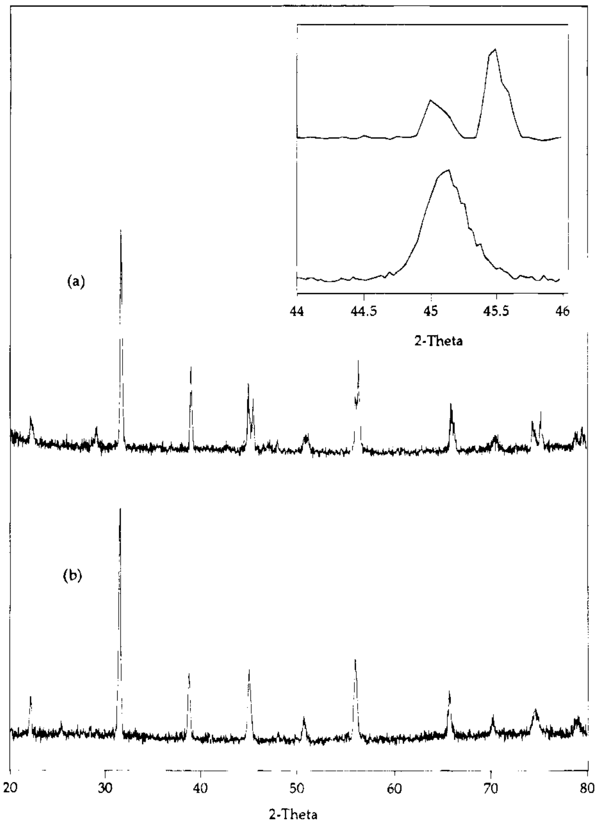

Figure 1. XRD powder pattern of $BaTiO_3$ powders: (a) tetragonal form; (b) metastable cubic form. Inset shows clearly the splitting of the (200 + 020) and (002) reflections for the tetragonal form.

calculated from diagonals of about 50 particles. The average grain sizes were determined by the interception method.

The dielectric behavior was investigated using a computer-interfaced impedance analyzer (HP 4192A). The sintered samples were surface ground using no. 600 grind papers. Thickness and diameter of the samples were measured by a micrometer. Electrodes were made by putting on silver paste at 700 °C for 1 h. These samples were placed between two silver thin plates connected to the impedance analyzer by silver wires. The dielectric constants and dielectric losses were measured at a frequency of 1 kHz. The sample temperatures were controlled by a temperature controller (Orton Model 29).

Results

Quantification of the Tetragonal Content of $BaTiO_3$. Since the goal of this program is to synthesize tetragonal form of $BaTiO_3$, it is important to establish the analytical methodology necessary to quantitate the amount of tetragonal form. Typically, the presence of the tetragonal form is inferred from the powder diffraction pattern which exhibits two reflections due to (200) + (020) and (002) around a 2θ of 45°.[24] In the cubic form, only a single reflection is present in this region. Figure 1 shows the diffraction pattern of a sintered, tetragonal $BaTiO_3$ (~1300 °C) sample and a cubic $BaTiO_3$ hydrothermally prepared at 95 °C. The inset shows the clear difference between the tetragonal form and the metastable cubic form. A calibration method for estimating the phase composition using the aforementioned diffraction intensities for reflections around 45° has been published.[24] We have found it difficult to use the diffraction data for quantification, especially at low contents, because of complications due to band-broadening effects. Anomalous effects in the intensity due to varying crystallographic textures is also possible.[25] Another way of distinguishing the two polymorphic forms is to measure the dielectric constant, but this procedure involves sintering which leads to grain size growth, and also the nature of powders and porosity play an important part.[26] This led us to examine alternate methods which can be used on the powders without any prior treatment. Tetragonal $BaTiO_3$ converts to the cubic form at the Curie transition temperature typically between 120 and 130 °C. This transition has been observed by thermoanalytical techniques.[17a,b,27] It has been shown that this phase transition is associated with a change in the specific heat, indicative of a second-order transition.[27a] However, there is also a volume change associated with the transformation of the tetragonal to the cubic form, which would indicate a first-order phase transition, suggesting that this may be an example of a hybrid transition. Figure 2a shows the change in enthalpy (ΔH) as measured by differential scanning calorimetry of a sintered tetragonal $BaTiO_3$ sample. A transition is clearly evident around 125–135 °C. Kay has noted from crystallographic observations that the transition from tetragonal to cubic is not sharp and is spread out around a temperature interval of 8 °C, and this is reflected in the width of the DSC curve.[28] The tetragonal to cubic transformation is characterized by a ΔH of 0.9 J/g. Blattner et al.[27a] obtained a value of 0.84 J/g by integration of the specific heat curve, whereas Vivekandan et al. reported 0.73 J/g[17] from a DSC measurement. The transition temperature for the tetragonal form in Figure 2a is observed at 128 °C, whereas the cubic form in Figure 2b shows no transition. The possibility of correlating the ΔH of this transition with amount of tetragonality in the

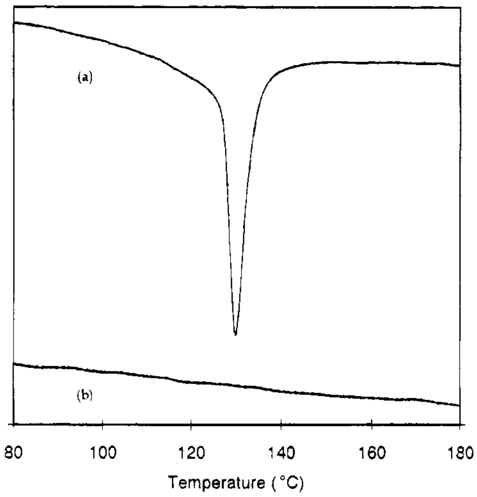

Figure 2. DSC traces for (a) tetragonal and (b) metastable cubic form. Alumina was used as reference in both cases.

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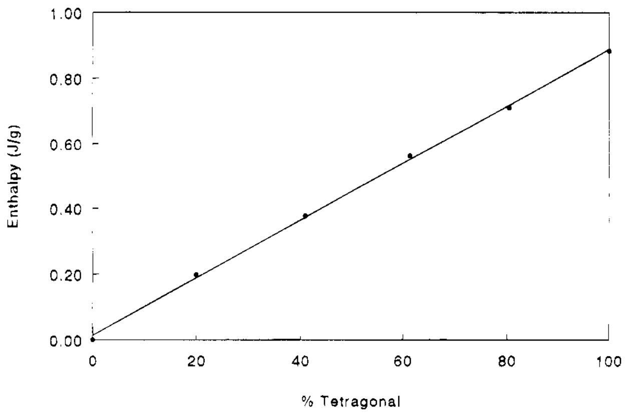

Figure 3. DSC calibration of the ΔH values for the tetragonal-to-cubic transformation versus tetragonal content.

Table 1. Tetragonal Content and Average Hydrothermal Particle Size of $BaTiO_3$ Prepared from Various Barium Salts

sample	% tetragonal	av particle size (μm)
$BaTiO_3$ (I^-)	39	0.4 ± 0.2
$BaTiO_3$ (Br^-)	38	0.3 ± 0.1
$BaTiO_3$ (Cl^-)	37	0.2 ± 0.1
$BaTiO_3$ (acetate)	23	0.2 ± 0.1
$BaTiO_3$ (NO_3^-)	8	0.2 ± 0.04
$BaTiO_3$ (OH^-)	~0	0.2 ± 0.04
commercial (Ferro)	27	0.5 ± 0.1
commercial (TAM)	14	0.5 ± 0.2

sample has been discussed.[17b] We determined that a problem in determining ΔH accurately is the sloping baseline of the DSC transition, making it difficult to estimate the area under the transition. This was alleviated by using alumina as a reference, Figure 2a being obtained in this manner. A calibration curve was then constructed by measuring ΔH for samples with known amounts of tetragonal and metastable cubic form prepared by physical mixing and is shown in Figure 3. We can readily get reproducibilities within a range of 10% and more typically, within 5%. The calibration shown in Figure 3 is used henceforth to quantitatively determine the tetragonal content of $BaTiO_3$ examined in this study. It has been noted in the literature that the Curie transition shifts from 130 °C to lower temperatures as particle sizes drop below 0.2 μm.[22] We find no evidence of any DSC transition for the metastable cubic form at temperatures between 50 and 150 °C.

Hydrothermal Synthesis of $BaTiO_3$. In an earlier study,[15f] we reported that in the presence of Cl^-, tetragonal $BaTiO_3$ was formed from a reactant composition containing Ba^{2+}, anatase, H_2O, Na^+, and OH^- under hydrothermal conditions at synthesis temperature of 240 °C. We have extended these studies by examining the role of other anions, Ba/Ti ratio, the Ti source, and OH^- concentration. It has been reported that the rate of $BaTiO_3$ formation is enhanced by using more reactive forms of TiO_2.[29] We examined the reactivity of both anatase and hydrous titanium oxide in stabilizing the tetragonal form. Using $BaCl_2$ as the barium source and a week of synthesis time at 240 °C, we found that the maximum tetragonal $BaTiO_3$ yields (~37%) were obtained with freshly generated hydrous titanium oxide (by hydrolysis of $Ti(OR)_4$) as the titanium source, Ba/Ti = 1.6 and [NaOH] = 1 M. Keeping this composition fixed, we varied the anions by substituting appropriate barium salts.

Table 1 shows the yields of the tetragonal form for $BaTiO_3$ with the various barium salts after 1 week of heating at 240 °C, along with the average particle size as estimated from the scanning electron micrographs. X-ray diffraction shows that $BaTiO_3$ is the only phase being formed, except in the case of F^-, where BaF_2 was also found. This arises from the limited solubility of BaF_2 (0.12 g/100 mL),[33] and since it was not possible to separate the BaF_2 from $BaTiO_3$, no further measurements are included on this sample. It is clear from Table 1 that the amount of tetragonal content varies in the order $I^- \sim Br^- \sim Cl^- >$ acetate $> NO_3^- > OH^-$. The correlation between the tetragonal content and particle size is not pronounced, though, samples of the largest particle sizes resulted in higher tetragonal content. Figure 4 shows the SEM pictures for $BaTiO_3$ using I^-, Cl^-, and NO_3^- as barium sources. ($BaTiO_3(X^-)$ represents the barium titanate obtained using the X^- salt of barium). Upon sintering these samples at 1300 °C for 5 h, the ΔH of all these samples were in the range 0.9–1 J/g, indicating 100% tetragonal content with the Curie transition around 125–128 °C, except for the $BaTiO_3(OH^-)$ sample. It exhibited a Curie transition at ~100 °C. X-ray fluorescence analysis indicated the presence of Sr, which must be incorporated from the $Ba(OH)_2$ source. It is well-known that incorporation of Sr^{2+} into the $BaTiO_3$ leads to a lowering of the transition temperature.[30] Also, in Table 1 we have included two commercial samples, which show the tetragonal content is between 14–28% as obtained from the vendors. After sintering of these samples, the tetragonality reached values >90%.

It has been reported in the literature that hydrothermal powders prepared at 100 °C need to be heated beyond 1150 °C to form the tetragonal structure.[17] In the case of the $BaTiO_3(Cl^-)$ sample, which is 37% tetragonal as synthesized, the tetragonal content continuously increased upon heating the powder, as shown in Figure 5. Thus for the sample heated to 900 °C, a tetragonal content of 60% was obtained.

Properties of the Hydrothermally Synthesized Sintered Powders. In examining the characteristics of the powders, we have focused on the $BaTiO_3$ samples synthesized using the chloride, acetate, and nitrate salts. The dilatometric curves are compared in Figure 6. Shrinkage begins around 900 °C for all samples which is lower than conventionally prepared $BaTiO_3$ (from $BaCO_3 + TiO_2$), presumably due to the finer particle sizes. Similar effects have been observed for small crystallites of $BaTiO_3$ derived from alkoxide-derived powders.[31a] The $BaTiO_3(NO_3^-)$ sample appears to densify in a two-step process. This is indicative of development of voids beyond 1200 °C, which are then difficult to eliminate;[31] in addition, the nitrate and acetate sample also show slight dedensification behavior

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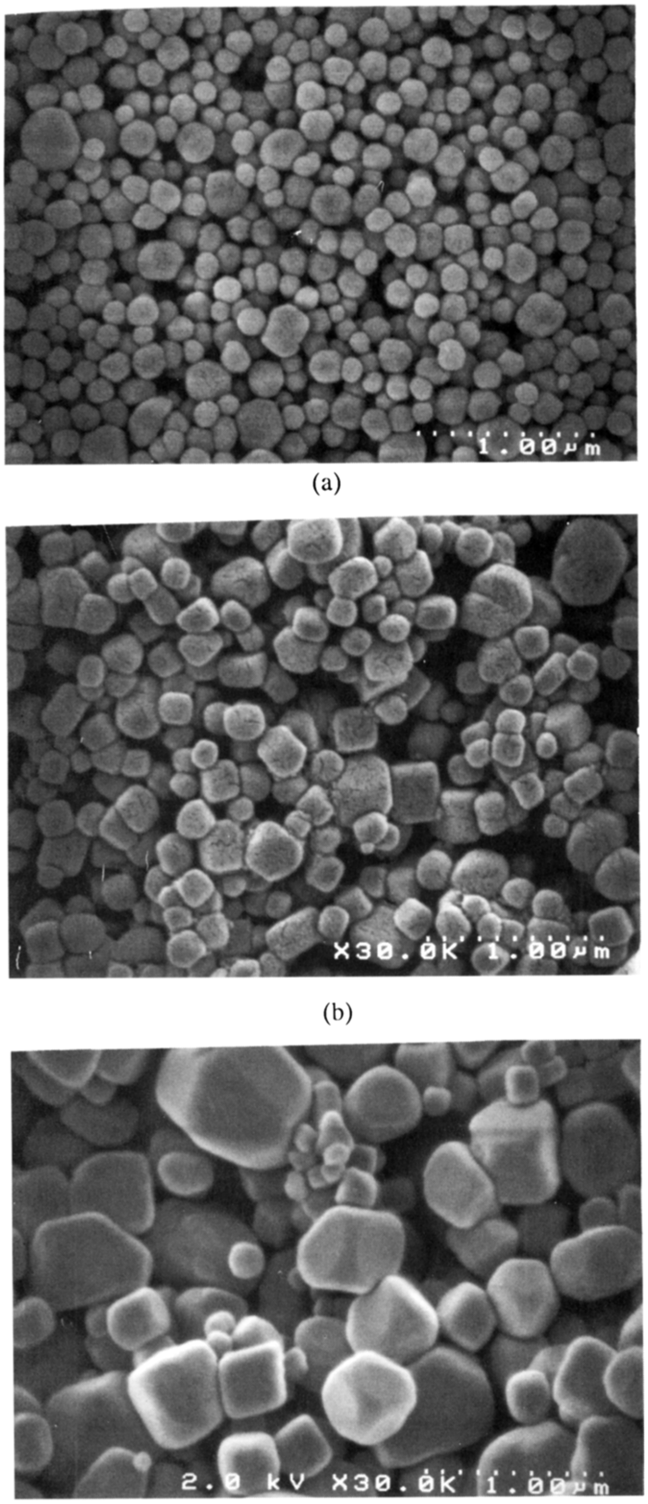


(a)

(b)

(c)

Figure 4. SEM micrographs of $BaTiO_3$ made with different barium salts: (a) nitrate; (b) chloride; (c) iodide.

at temperatures above 1400 °C. In densification studies of ZrO_2 powders, strong dedensification effects were noted at high temperatures.[31b] To a lesser degree, densification of $BaTiO_3$ mixed with $BaCO_3$ also show similar effects.[31a] Gases evolving from trapped nitrate or acetate could result in dedensification,[31b] though the samples were extensively washed to remove adsorbed species. Similar washing with the chloride sample resulted in complete removal of the chloride as determined by X-ray fluorescence. The cause of this slight dedensification in the acetate and nitrate sample is unclear.

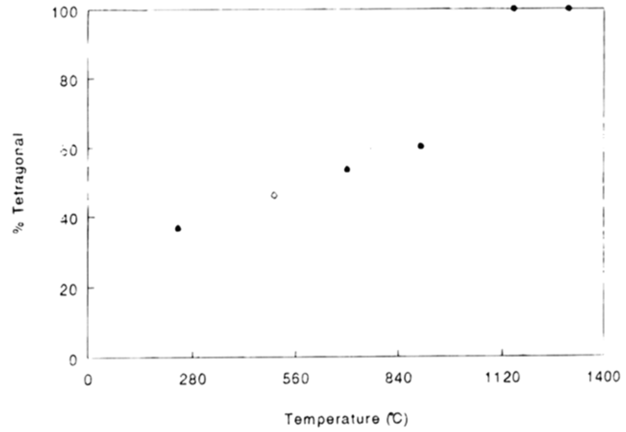


Figure 5. Growth in tetragonal content of $BaTiO_3(Cl^-)$ as a function of sintering temperature.

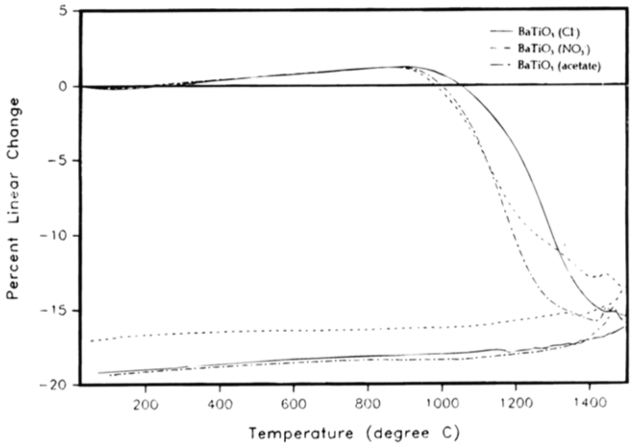


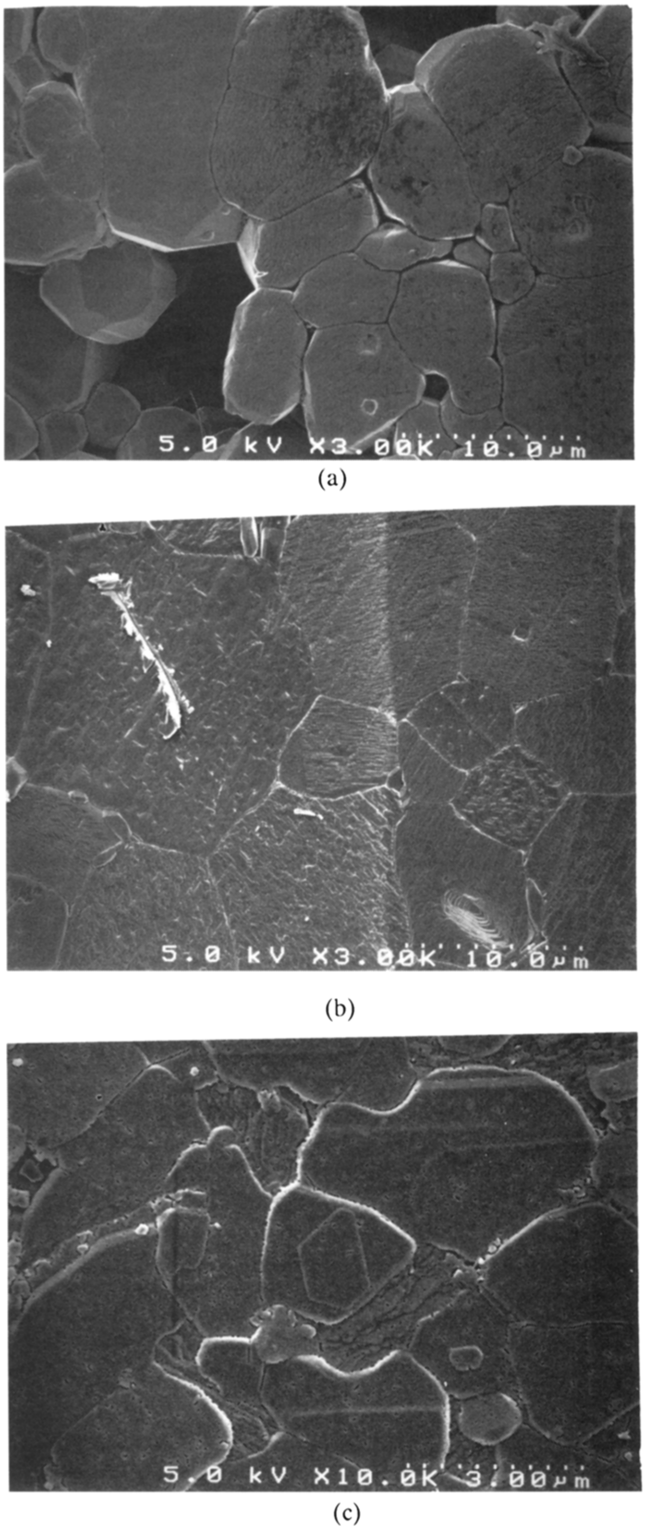
Figure 6. Dilatometric curves of $BaTiO_3$ synthesized from various barium salts.

The densities of the samples sintered at 1300 °C for 5 h were 5.23, 5.62, and 5.81 g/cm^3 for the nitrate-, acetate-, and chloride-derived samples, respectively. These account for 86.9, 93.4, and 96.5% of the theoretical densities. Figure 7 shows the SEM micrographs of these samples. The porosity is clearly greatest in the $BaTiO_3$ prepared from nitrate salt, though it had the smallest particle size. This is consistent with the dilatometric studies. The grain sizes of these sintered samples were in the range of 3−15 µm for the $BaTiO_3(NO_3^-)$, 3−21 µm for $BaTiO_3$ (acetate), and 1−5 µm for the $BaTiO_3(Cl^-)$. The dielectric constant and the loss as a function of temperature for all three materials is shown in Figure 8, and the electrical data are summarized in Table 2. The dielectric constant of the $BaTiO_3(Cl^-)$ was examined as a function of sintering temperature. The highest dielectric constant was observed for the sample sintered at 1250 °C for 5 h. A scanning electron micrograph of this sample is shown in Figure 9.

Discussion

The two issues that form the focus of this discussion are mechanism of synthesis of the tetragonal $BaTiO_3$ and the measured electrical properties of the various samples.

The mechanism of formation of $BaTiO_3$ from hydrothermal system has been discussed in the literature.[16,32]



(a)

(b)

(c)

Figure 7. SEM micrographs of $BaTiO_3$ samples after sintering at 1300 °C for 5 h, followed by polishing and etching. Samples were made with (a) nitrate, (b) acetate, and (c) chloride.

The relevant reactions are

$$TiO_2 + 2H_2O \rightleftharpoons Ti(OH)_4$$

$$Ba^{2+} + Ti(OH)_4 \rightleftharpoons BaTiO_3 + 2H^+ + H_2O$$

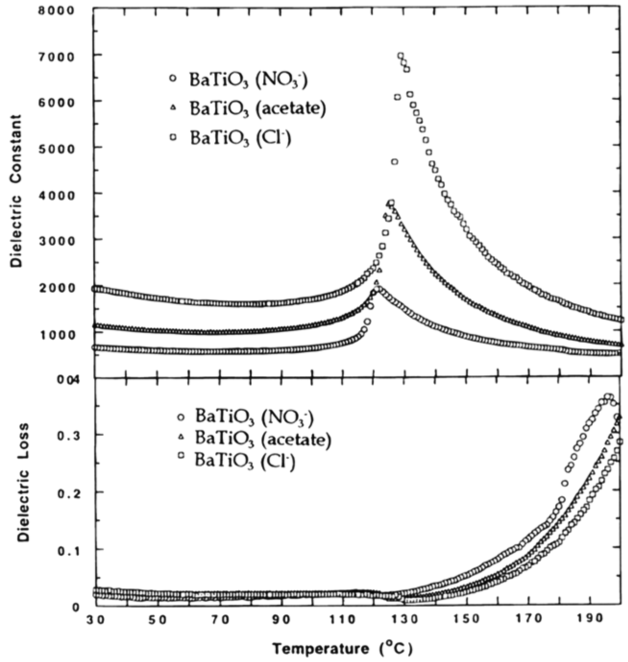


Figure 8. Dielectric constant and dielectric loss values as a function of temperature for $BaTiO_3$ synthesized from various salts.

Table 2. Properties of $BaTiO_3$ Sintered at 1300 °C for 5 h

sample	κ (30 °C)	tan δ (30 °C)	range of grain sizes (μm)	% theoretical density
$BaTiO_3(Cl^-)$	1938	0.0285	1–5	96.5
$BaTiO_3$(acetate)	1162	0.0288	3–21	93.4
$BaTiO_3(NO_3^-)$	677	0.0190	3–15	86.9

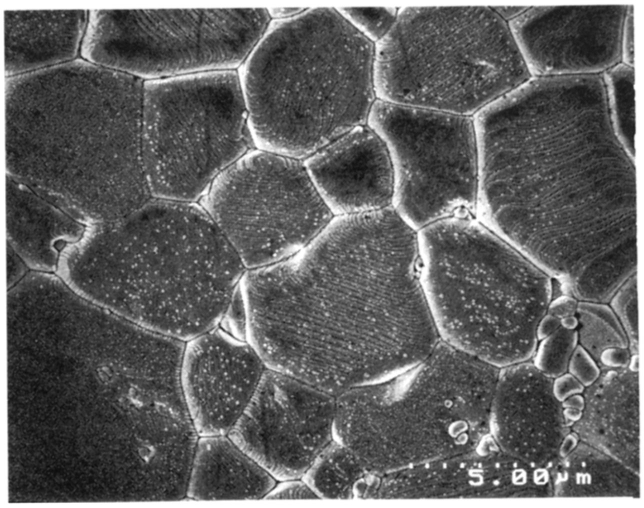


Figure 9. SEM micrograph of $BaTiO_3(Cl^-)$ sintered at 1250 °C for 5 h.

The high pH during synthesis is necessary to stabilize the $BaTiO_3$ versus TiO_2. In hydrothermal synthesis, $BaTiO_3$ is formed rapidly even at 85 °C, on the order of hours.[17] This form of $BaTiO_3$ has the metastable cubic structure and has dimensions of <0.1 μm. To make the tetragonal form, it is necessary to enhance the size of these crystals. The two factors that influence this are the time and temperature of synthesis. For example, in the case of synthesis of $BaTiO_3$ made from a hydrothermal treatment of Ba–Ti acetate gel, it was found that 5 nm nuclei grew to sizes of 200–300 nm over a time period of 10–15 h at 150 °C, and then extended heating did not increase this size.[15d] Hydrothermal synthesis at temperatures of 600 °C lead to crystals sizes of millimeters, as compared to submicron crystals at 95 °C.[15b,c] The growth of crystals occurs via the

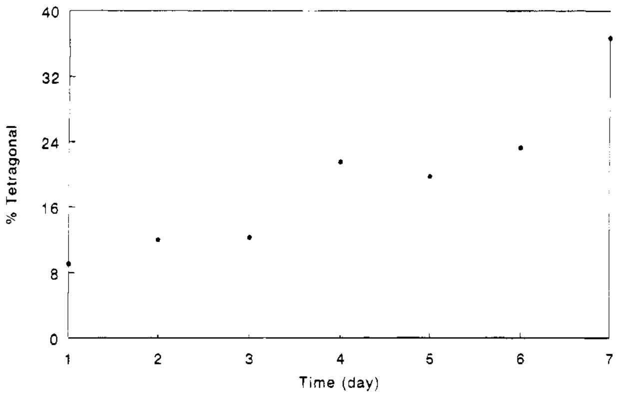


Figure 10. Change in tetragonal content for $BaTiO_3(Cl^-)$ as a function of time for hydrothermal synthesis at 240 °C.

reaction

$$BaTiO_3\ (\text{small, cubic}) + H_2O + 2H^+ \rightarrow Ba^{2+} + Ti(OH)_4 \rightarrow BaTiO_3\ (\text{large, tetragonal}) + H_2O + 2H^+$$

In this study, the experiments were done at temperatures of 240 °C for time span of 1 week. Figure 10 shows that the percent tetragonality increases during this time period, along with a slight average particle size increase from 0.21 to 0.23 μm, consistent with the dissolution–recrystallization mechanism. Also, the presence of anions in the reactant composition influences the particle size and tetragonal content of the product, in the following order: halides > acetate > NO_3^-. The anions perturb the dissolution–recrystallization process, though the exact mechanism is not clear. The solubility of the Ba salts (at 100 °C) follows the order $I^- > Br^- >$ acetate $\sim Cl^- > NO_3^-$,[33] reflecting closely the tetragonal content of the $BaTiO_3$ formed with these salts. A possibility is that the salts with increased solubilities promote the dissolution of $BaTiO_3$. The preferential regrowth of larger crystals arises from a phenomenon akin to Ostwald ripening.

The two factors associated with sintering are decrease of porosity and grain growth. In all of the $BaTiO_3$ samples sintered to 1300 °C, we have noted grain growth, but it was the least for the $BaTiO_3(Cl^-)$ sample (0.23 → 5 μm) and largest for the $BaTiO_3$(acetate) (0.19 → 21 μm) and $BaTiO_3(NO_3^-)$ (0.17 → 15 μm) sample. In addition, the $BaTiO_3(NO_3^-)$ sample did not sinter to a high density, though it had the finest particle size. It has been noted in the literature that very fine particles of $BaTiO_3$ may not sinter with high densities.[31a] The best electrical properties are obtained from the $BaTiO_3(Cl^-)$ sample since it not only densifies well but also maintains a smaller, more uniform grain size. Thus, higher densities are obtained when grain growth is inhibited.[34] Upon sintering the $BaTiO_3(Cl^-)$ sample at 1250 °C instead of 1300 °C, the grains were more uniform and the density was higher. This led to a room-temperature dielectric constant of 2960 as compared to 1938 for samples sintered at 1300 °C.

We find that the submicron, tetragonal (37%) $BaTiO_3(Cl^-)$ powders provide the combination of sinterability with limited grain growth resulting in better electrical properties. Such properties could arise from several factors. Having a significant fraction already in the tetragonal form, the sintering properties and grain growth of the powder could be different. We emphasize that heating the pseudocubic material to convert it to tetragonal form followed by milling will not result in the fine tetragonal powders that can be obtained by direct synthesis, as in this study. It will also be interesting to examine the aging features of tetragonal $BaTiO_3$ made hydrothermally, since the stresses and domain geometries are expected to be quite different from the conventional sintered samples. Efforts are underway to design improvement of the hydrothermal method in order to generate higher yields of tetragonal powders of $BaTiO_3$ under reasonable conditions of temperature and time.

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