Synthesis of Tetragonal BaTiO₃ by Microwave Heating and Conventional Heating

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Hydrothermal synthesis of barium titanate was done by both microwave heating and conventional heating. The synthesis process was evaluated by examining samples at different processing times by X-ray diffraction. For samples produced by both heating methods, the metastable cubic phase crystallized first and gradually transformed to a tetragonal phase. Microwave synthesis showed advantages of shortened crystallization time, increased *c*/*a* ratio, and upon sintering led to a larger degree of increased *c*/*a* ratio. Elemental analysis showed a smaller Ti/Ba ratio and larger relative amount of Cl⁻ ion in the microwave-treated sample than those in a conventionally treated sample. Sintering at 850 °C for both samples resulted in the samples exhibiting a clear transition temperature of around 125 °C as measured by DSC.

I. Introduction

Barium titanate is of interest due to its high dielectric constant and ferroelectric properties at temperatures below 130 °C where it assumes a tetragonal phase.[1,2] BaTiO₃ finds a wide range of applications in electronic and electrooptic devices.[1,2] The ferroelectric and dielectric properties of BaTiO₃ strongly depend on the grain size and the density of the particles.[3–8] Traditionally, this material is prepared by heating mixtures of BaCO₃ and TiO₂ at a temperature between 1000 and 1200 °C accompanied by the introduction of impurities.[2,9] This procedure leads to powders that are coarse and inhomogeneous in size. Another problem concerned with this synthesis is the high cost required by high-temperature sintering.

In the past decades, considerable research has focused on new synthesis routes using low temperatures and corresponding mechanistic studies. These syntheses include the decomposition of complex double salts such as oxalates and citrates of barium and titanium between 600 and 800 °C with the crystals forming during the combustion of the chelating agents.[10–15] A high sintering temperature around 1300 °C is required to ac-

complish the transformation from the cubic phase to the tetragonal phase and to achieve high density. The second class of synthesis is the evaporative decomposition of organometallic precursors through an atomizer burner with fine-grained powders deposited directly.[16,17] Sintering is also needed to obtain the tetragonal phase. The third method deals with the simultaneous hydrolysis of barium and titanium alkoxides in neutral or basic solution and with further coprecipitation of barium and titanium.[18–24] The cubic phase is obtained after aging at 80–150 °C.[22–24] A problem with this procedure is that Ti–O–Ti cross-linking forms rapidly, which may result in the phase segregation of TiO₂ and BaTiO₃.[6] Sintering at high temperature is again required to transform the cubic phase to the tetragonal phase and to obtain high density. A modification of the third method is aging of TiO₂ gels in the presence of Ba(OH)₂ or of the mixture of TiO₂ gels and inorganic barium salts in strongly basic solutions.[25–27] The TiO₂ phase (amorphous, rutile, or anatase) and temperature are among

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those factors affecting the crystallite size and the final phase of the resultant perovskite.[28,29]

Of all these methods, hydrothermal treatment is of particular interest because the tetragonal phase can be synthesized directly from the hydrothermal reaction of hydrated TiO_2 gels and barium chloride in a fairly strong alkali hydroxide solution at 240 °C (pH greater than 13)[27] without going through a sintering stage. The proposed mechanism[6,30] for this reaction is that a metastable cubic phase forms first from the direct contact of titanium and barium in strongly basic solutions. Base is believed to act as a necessary solvent to assist in dissolving the titania gel, forming the $Ti(OH)_6^{2-}$ species and making it possible for barium and titanium contact via oxygen. In a neutral or acidic solution, the perovskite structure cannot be obtained. $BaTiO_3$ first appears as a relatively small crystallite in which the high strain makes the metastable cubic phase possible. When the crystals grow larger and the strain inside is gradually released or when the metastable cubic phase materials are sintered at high temperature with a different mechanism, the tetragonal phase perovskite is obtained.

Recently, the method of microwave heating is finding wider and wider applications in material synthesis because the heating is due to the interaction between microwaves and materials.[31,32] Microwave radiation couples with and is absorbed by the material and the electromagnetic energy is converted to thermal energy. Heat is generated from inside the material, in contrast with conventional heating methods where heat is transferred from outside to inside. This internal heat allows a reduction of processing time and energy cost and makes new material syntheses possible. Microwave heating is suitable for dielectric materials which includes many ceramic materials since the degree of absorption of microwaves by a material is related to the dielectric constant and the dielectric loss factor of the material.[31]

Barium titanate is a fairly good dielectric material when it adopts a tetragonal phase.[1,2] Synthesis of barium titanate by microwave heating is the subject of this research. Specific goals are to determine if the tetragonal phase can be obtained in a microwave oven; to determine whether any differences in the samples exist during and after processing by these two heating methods, and to determine any differences in properties of these differently prepared materials.

II. Experimental Section

Synthesis of BaTiO₃. The synthesis procedure follows the treatment of Dutta et al.[30] for making tetragonal $BaTiO_3$ with the following modifications. In these experiments, the reagent compositions are the same; i.e., 0.005 mol of $BaCl_2 \cdot 2H_2O$, 0.003 mol of titanium oxide, 0.005 mol of NaOH, and 10 mL of

distilled deionized water (DDW). Hydrated titanium oxide was prepared in the same way.[30] A volume of 10 mL of DDW was used to transfer the hydrated titanium oxide from a centrifugation tube to a plastic bottle, where N_2 was bubbled through to drive off any CO_2 in the water. Ten minutes later, $BaCl_2 \cdot 2H_2O$ was added and the bottle was covered and shaken vigorously to make the reagents mix uniformly. N_2 was bubbled again through the mixture to prevent the formation of $BaCO_3$. Ten minutes later, NaOH solid was added to the mixture, and N_2 continued to pass through for another 10 min. The mixture was then transferred to an autoclave where it was immediately sealed and placed in the microwave furnace or conventional oven. The aging temperature was 170 °C instead of 240 °C, which is the same as previously reported,[30] since the maximum operating temperature for the autoclaves in our microwave oven is 170 °C. After certain periods of time, samples were taken out and washed completely with distilled deionized water. They were then dried at 85 °C overnight.

A model 10 microwave furnace from Microwave Materials Technologies, Inc. with both temperature and power control programs was used to synthesize barium titanate. A thermocouple connected to the controller of the microwave system was inserted directly in the sample to measure the sample temperature. The maximum output power is 1300 W, and the frequency of the electromagnetic field is 2.45 GHz. The heating rate was controlled by adjusting the output power automatically through an interface connected to the microwave furnace. Teflon-made autoclaves from CEM Inc, Matthews, NC, were used, and the thermocouple was inserted in the supernatant of the reaction mixture without touching the solid deposited at the bottom.

The same procedure was also performed in a conventional oven in order to make the comparison between microwave heating and conventional heating more effective and more comparable; synthesis conditions were kept as similar as possible. The temperature of the oven was set to 170 °C beforehand. It was estimated that it took about 25−30 min for the autoclaves to reach 170 °C in a conventional oven. Thus in the microwave oven, a 5 °C/min heating ramp was chosen to ensure that the autoclave in the microwave oven could reach 170 °C after 25−30 min, as is the case for conventional heating.

Characterization Methods. Powder X-ray diffraction data were collected on a Scintag 2000 PDS model with Cu Kα X-ray radiation at a 1.5406 Å wavelength. Step scans were used with a 0.03° step size. The X-ray beam voltage was 45 kV, and the beam current was 40 mA. The scanning range was from 15° to 60° 2θ. Peak deconvolution and the Scherrer equation were used to identify peak splittings and crystallite sizes.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with TA instruments Model 2950 and Model 2920, respectively. Samples were dried at 170 °C for 2 h to remove water attached to or absorbed on barium titanate just before the DSC analysis was done. Both TGA and DSC were done in N_2 atmospheres. Samples were equilibrated at 20 °C, and then heated to 900 °C in the TGA experiment and 500 °C in the DSC experiment, with the same heating rate (10 °C/min).

Chemical analyses of cation compositions were done by atomic absorption spectroscopy (AAS). Barium titanate samples were dissolved in dilute $HNO_3-H_2O_2$ solution for barium and titanium analysis without further treatment. Chemical analysis of Cl^- was done by absorbance spectroscopy of a colored material, which formed in the presence of chloride ion, and the absorbance was directly proportional to the concentration of chloride ion in the solution.

Diffuse reflectance infrared spectrometry was performed by a Nicolet Magna-IR Model 750. The mid-IR range was selected using a mercury−cadmium-telluride detector (MCT). Resolution of the instrument is up to 0.125 cm^{-1}. Before the experiments were done, samples were heated at 170 °C for 2 h to remove any adsorbed or attached water.

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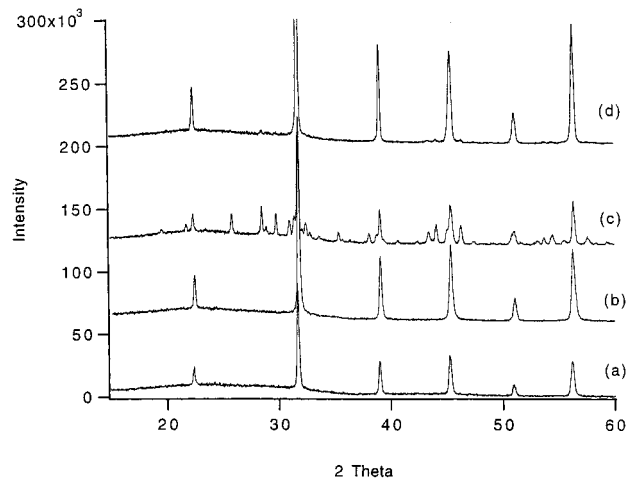(32) Wan, J. K. S. *Res. Chem. Intermediates* **1993**, *19*, 147−158.

Figure 1. Powder X-ray diffraction patterns of BaTiO$_3$ synthesized by microwave heating: (a) aging for 1 min, (b) aging for 20 min, (c) sample (a) sintered at 850 °C for 4 h, (d) sample (b) sintered at 850 °C for 4 h.
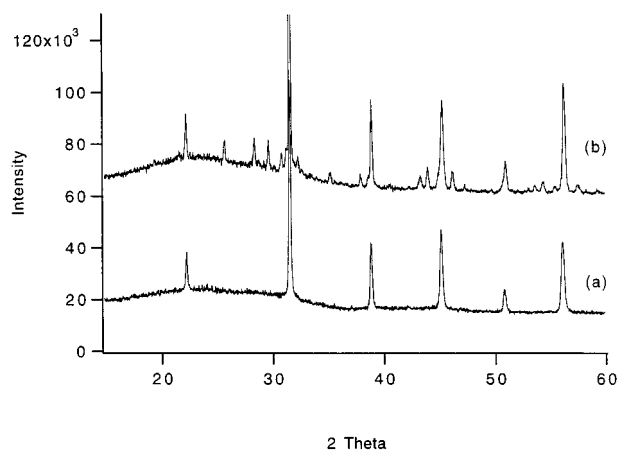

Figure 2. Powder X-ray diffraction patterns of BaTiO$_3$ synthesized by conventional heating: (a) aging for 1 h, (b) sample (a) sintered at 850 °C for 4 h.

Figure 3. Powder X-ray diffraction patterns of BaTiO$_3$ showing the transformation from cubic phase to tetragonal phase: (a) aging for 5 h, (b) aging for 4 days, (c) aging for 7 days, (d) sample (c) sintered at 850 °C for 4 h.

Table 1. Lattice Parameter Ratios versus Aging Time of the Microwave-Heated Samples As Determined by X-ray Diffraction

aging time	10 min	5 h	10 h	1 day	2 days	4 days	7 days
c/a ratio	cubic	cubic	1.0043	1.0051	1.0056	1.0063	1.0071
intensity ratio[a]	n/a[b]	n/a[b]	3.47	2.85	2.09	0.86	0.43

[a] The relative intensity ratio of the peaks corresponding to (002) and (200 + 020) reflections. [b] In cubic system there is no splitting of the 46° peak.

Table 2. Lattice Parameter Ratios versus Aging Time of the Conventionally Heated Samples As Determined by X-ray Diffraction

aging time	1 h	5 h	10 h	1 day	2 days	4 days	7 days
c/a ratio	cubic	cubic	cubic[c]	1.0037	1.0046	1.0055	1.0063
intensity ratio[a]	n/a[b]	n/a[b]	n/a[b]	5.11	4.04	2.29	0.89

[a] The relative intensity ratio of the peaks corresponding to (002) and (200 + 020) reflections. [b] In cubic system there is no splitting of 46° peak. [c] The peak around 46° does not split but becomes broader.

III. Results

Hydrothermal Synthesis of BaTiO$_3$ by Both Microwave Heating and Conventional Heating. Perovskite BaTiO$_3$ was produced at 170 °C by both heating methods. In the microwave oven, cubic barium titanate crystal was formed after only 1 min. After 25 min of microwave treatment, almost all precursors were reacted. This was confirmed by heating the samples to 850 °C for 4 h and checking the X-ray diffraction patterns again. Before the sintering process only cubic perovskite BaTiO$_3$ was detected for both the 1 min sample and the 25 min sample. After sintering at 850 °C, still only cubic BaTiO$_3$ was detected in the X-ray diffraction pattern for the 25 min sample. For the 1 min sample the initially amorphous material or unreacted TiO$_2$ gel crystallized as a BaTi$_2$O$_4$ phase and coexisted with the already existing BaTiO$_3$, which could easily be detected in the X-ray diffraction studies. This result is shown in Figure 1. In a conventional oven, the first cubic BaTiO$_3$ appeared after about 1 h aging at 170 °C, and the total reagents were reacted after 4 h aging as shown in Figure 2.

Only after all reagents were reacted and a relatively pure cubic phase formed was BaTiO$_3$ gradually (10 h microwave vs 24 h conventional) transformed to the
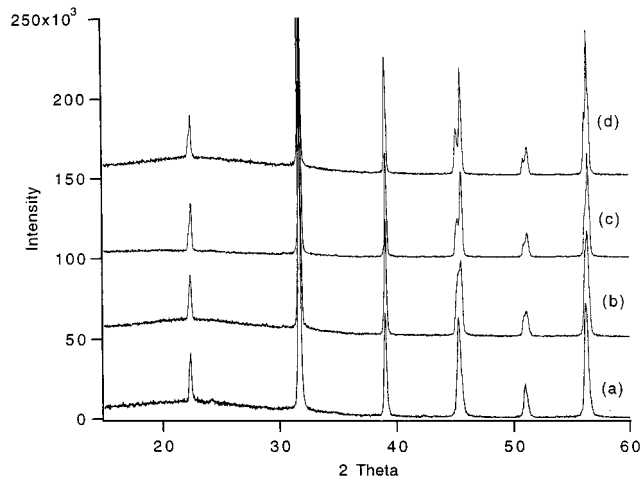
tetragonal phase as detected by X-ray diffraction. The tetragonal phase was best identified by the splitting of the peak with 2θ around 45−46° into two peaks, which correspond to the (002) and the (200 + 020) reflections, respectively,[27,33] as shown in Figure 3. The longer the aging time, the larger the splitting of the two peaks, with the longest aging time in our experiments of 7 days. The c/a ratios versus time for microwave heating and conventional heating are listed in Tables 1 and 2.

The resultant BaTiO$_3$ powders were further heated at higher temperatures (500 and 850 °C) for 2 or 4 h. Before the powders were heated, they were dried at 170 °C for 2 h to desorb any physisorbed or chemisorbed water. Characterization by X-ray diffraction was applied to the powders and was compared to the corresponding materials before the sintering process. For the sample having a cubic phase, no matter whether it was a microwave-heated sample or a conventionally heated sample, sintering at 850 °C for 4 h did not transform it to a tetragonal phase. For samples with the tetragonal phase, even if the splitting around 45−46° of 2θ was not considerable, the sintering process fostered the

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Table 3. Lattice Parameter Ratios for Samples before and after Sintering at 850 °C for 4 h[a]

	1		2		3		4	
	before	after	before	after	before	after	before	after
c/a ratio	1.0071	1.0089	1.0063	1.0071	1.0063	1.0081	1.0055	1.0061
change[b]	0.0018		0.0008		0.0014		0.0006	

[a] Samples: (1) microwave-heated sample with 7 day aging; (2) conventionally heated sample with 7 day aging; (3) microwave-heated sample with 4 day aging; (4) conventionally heated sample with 4 day aging. [b] Difference in the c/a ratio ($c/a_{after} - c/a_{before}$).
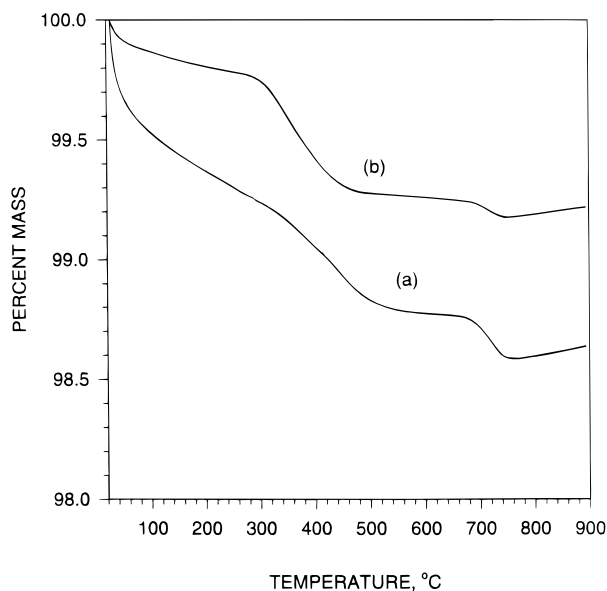

Figure 4. TGA of $BaTiO_3$ powders in a nitrogen atmosphere with 7 day aging: (a) microwave-synthesized sample, (b) conventionally synthesized sample.

splitting for both the microwave heated samples and the conventionally heated samples. This means that the c/a ratio for both samples was larger after sintering than before. However, the change of the degree of splitting for the microwave-treated sample was higher than that for a conventionally treated sample with the same aging time. The c/a ratios and other comparative data are listed in Table 3.

During aging at 170 °C or after sintering at 850 °C the crystallites did not show any big difference in size. The average crystallite sizes for both microwave and conventionally treated samples were in the range of 4300–4700 Å as calculated by using the Scherrer equation. When hydrated barium chloride was used as a precursor, the particle size was 2000 ± 1000 Å [30] with aging at 240 °C rather than at 170 °C in our experiments.

Thermal Analysis. One of our goals in this study is to determine whether there are any differences in the final products of the microwave and thermally produced materials. The 7 day samples without sintering were chosen for TGA analysis. The same samples as well as their corresponding sintered counterparts were chosen for DSC analysis. Both analyses were performed in a N_2 atmosphere. The results are shown in Figures 4 and 5.

During the TGA analysis the samples were heated all the way to 900 °C at a heating rate of 10 °C/min. The total weight loss of the microwave-heated sample was 1.5%, while the total weight loss for the conventionally heated sample was 0.8%. From 25 to about 300 °C, the weight loss of the microwave-synthesized sample was almost 3 times that of the conventionally heated

Table 4. Elemental Analysis of $BaTiO_3$ Samples with 4 day Aging: (a) Microwave-Synthesized Sample, (b) Conventionally Synthesized Sample

	sample elemental amount (ug/g)			mole ratio based on Ba		
	Ba	Ti	Cl	Ba	Ti	Cl
a	506836	205420	3274	1	1.16	0.025
b	495854	254677	1281	1	1.47	0.010

sample. From 300 to 460 °C, both samples lost almost the same weight. From 460 to 760 °C the weight loss for the microwave-synthesized sample was twice that of the conventionally treated sample. Microwave-synthesized sample showed an almost continuous weight loss from 25 to about 460 °C, while the conventionally synthesized sample showed two different weight loss rates in this temperature range with the largest rate from 300 to 460 °C.

DSC was applied to the above as-synthesized samples as well as after they were sintered at 850 °C. Before they were sintered at 850 °C, no transition peak was observed for both of them if the heating ramp was 10 °C/min. If a 2 °C/min ramp was used, a very small peak was detected for the microwave-synthesized sample at 123 °C while still no peak was observed for the conventionally synthesized sample. After the as-synthesized samples were sintered at 850 °C for 4 h, both microwave-heated samples and conventionally heated samples showed a clear transition peak around 125 °C, which is 3 °C lower than the typical transition temperature for $BaTiO_3$ perovskite material prepared from high-temperature solid reactions. After the samples were cooled in the DSC chamber after an initial run, DSC analyses were done again on the used samples. The DSC data showed the exact same transition temperature as the first run which means that the transition is reversible. A 2–3 °C difference between the transition temperatures of the microwave heated sample and the conventionally heated sample was always observed with the microwave heated sample always having the lower temperature.

Elemental Analysis. The samples prepared in 4 days by both microwave and conventional heating were chosen, and the amounts of both cations and anions were analyzed. These results are shown in Table 4. In both samples, titanium was in an excess amount, while the mole ratio of Ti/Ba was larger for the conventionally heated sample. The chloride amount was smaller for this same sample. In the process of anion analysis, nitric acid was added to the samples, and the samples were then placed on a hot plate. The conventionally heated sample was dissolved in 2 h, while the microwave-heated sample did not dissolve but became a gel.

Fourier Transform Infrared (FTIR) Analysis. The samples prepared in 7 days by both microwave and conventional heating were chosen. The microwave sample prepared in 4 days was also chosen because it has the same c/a ratio as the 7-day conventional sample.
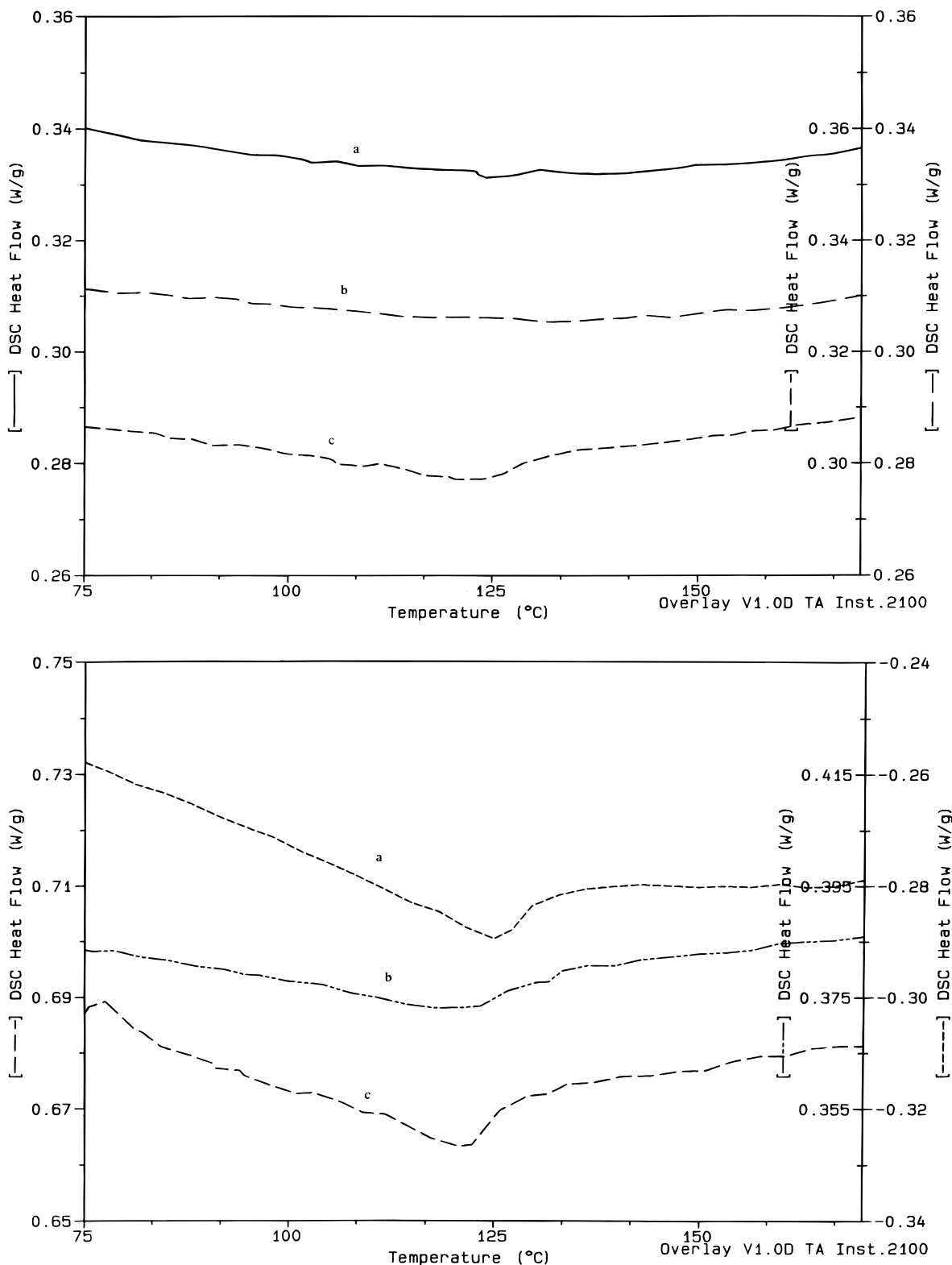
Figure 5. (A, top) DSC of BaTiO$_3$ powders without sintering: (a) conventionally synthesized sample with 7 day aging, (b) microwave-synthesized sample with 4 day aging, (c) microwave-synthesized sample with 7 day aging. (B, bottom) DSC of the corresponding sintered BaTiO$_3$ powders in Figure 5A: (a) conventionally synthesized sample with 7 day aging, (b) microwave-synthesized sample with 4 day aging, (c) microwave-synthesized sample with 7 day aging.

FTIR analyses were performed on the as-synthesized samples as well as the corresponding ones sintered at 850 °C for 4 h. Two ranges were studied, one between 400 to 700 cm^{-1}, which corresponds to the framework vibrations of BaTiO$_3$, and the other one between 3000 and 4000 cm^{-1}, which corresponds to the vibrations of surface functional groups. The results are shown in

Figures 6– 9. Before sintering, in the higher frequency range, all samples show a broad peak around 3540 cm^{-1} indicating that all have chemically absorbed water. After sintering, the shoulder between 3600 and 3700 cm^{-1} remained for all samples. Other peaks were observed in the range 3200–3540 cm^{-1}. All three samples had peaks around 3515 and 3450 cm^{-1}, the
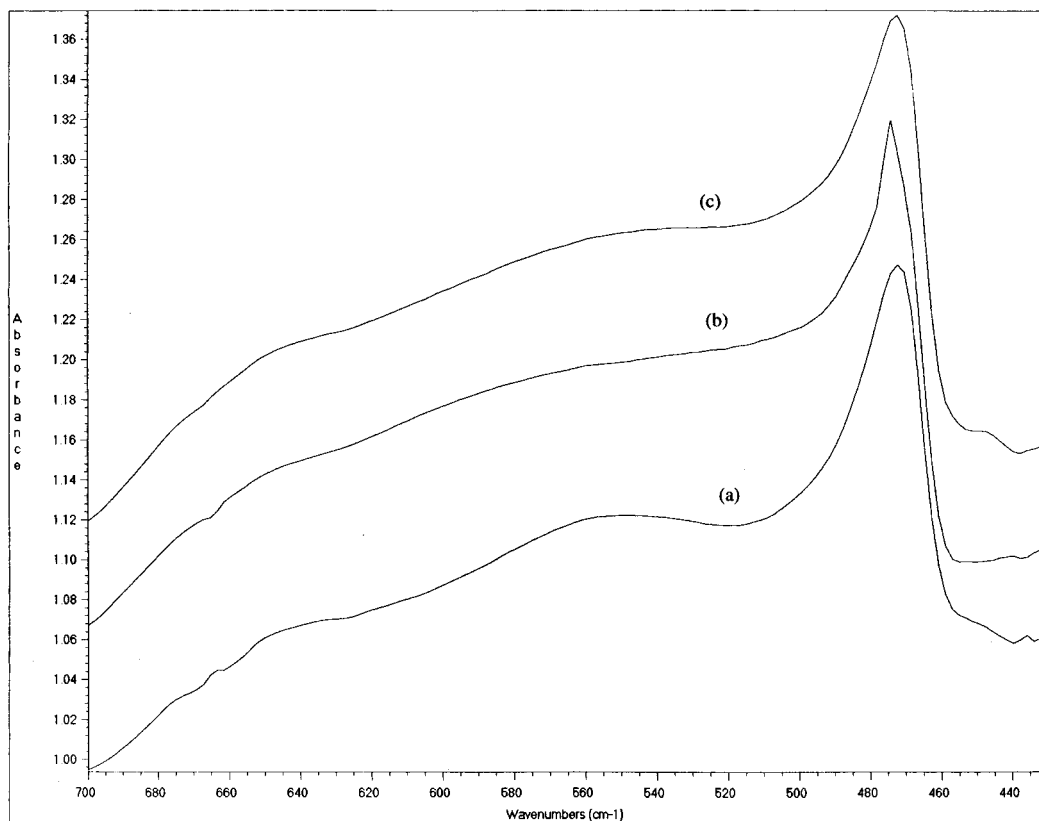
Figure 6. FTIR spectra of the BaTiO$_3$ framework range: (a) conventionally synthesized sample with 7 day aging, (b) microwave-synthesized sample with 4 day aging, (c) microwave-synthesized sample with 7 day aging.
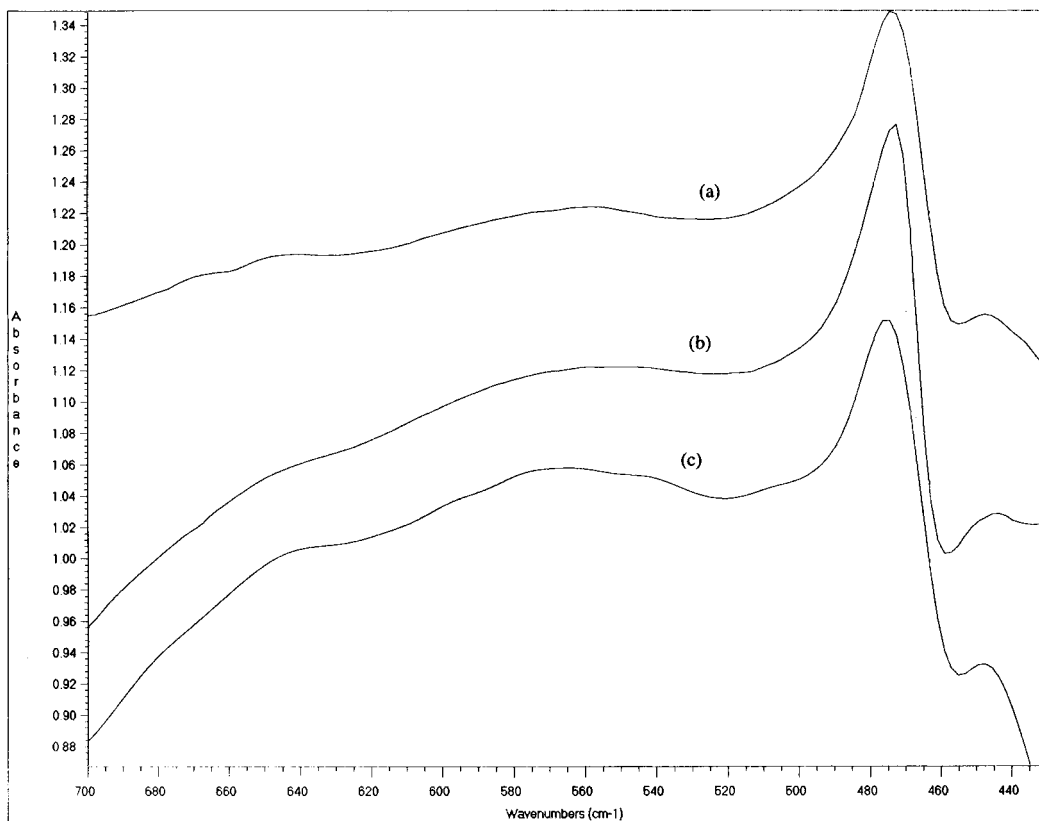

Figure 7. FTIR spectra of the corresponding sintered BaTiO$_3$ framework range: (a) conventionally synthesized sample with 7 day aging, (b) microwave-synthesized sample with 4 day aging, (c) microwave-synthesized sample with 7 day aging.

microwave samples also showed peaks around 3345 and 3480 cm^{-1}, and a shoulder around 3190 cm^{-1}. No corresponding peaks were observed for the convention-

ally synthesized samples. In the framework vibration range, broad peaks corresponding to BaTiO$_3$ as well as a sharp and high peak around 480 cm^{-1} corresponding
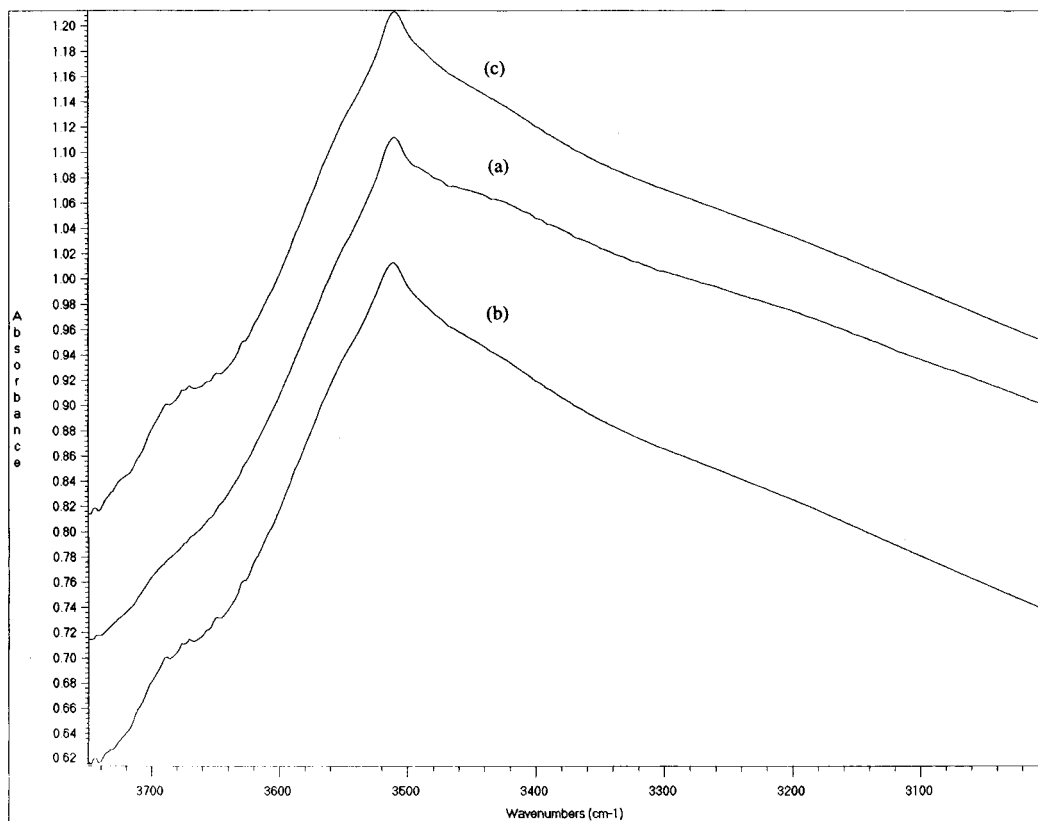
Figure 8. FTIR spectra of the BaTiO$_3$ functional group range: (a) conventionally synthesized sample with 7 day aging, (b) microwave-synthesized sample with 4 day aging, (c) microwave-synthesized sample with 7 day aging.

Figure 9. FTIR spectra of the corresponding sintered BaTiO$_3$ functional group range: (a) conventionally synthesized sample with 7 day aging, (b) microwave-synthesized sample with 4 day aging, (c) microwave-synthesized sample with 7 day aging.
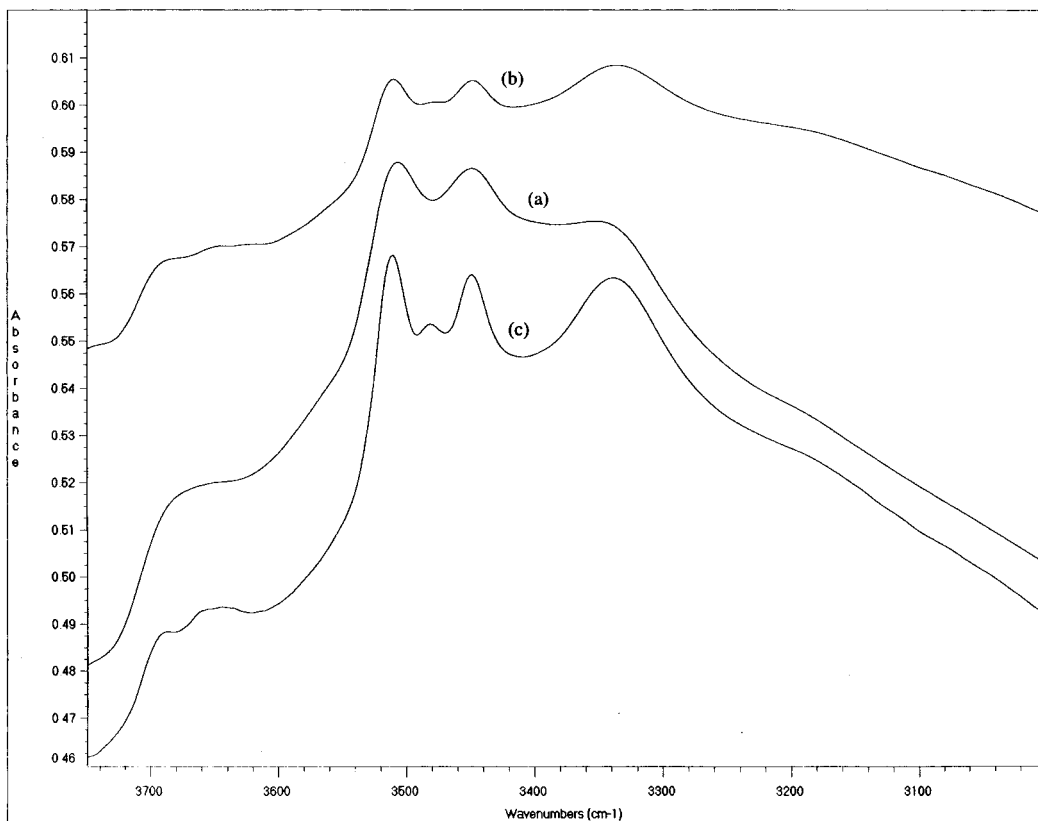
to TiO$_2$ framework vibrations showed up for all three samples before and after sintering. Peaks around 570 and 450 cm^{-1} are due to BaTiO$_3$ vibrations and have been assigned to surface modes. However, the differences in the framework vibration range between these samples were not significant.

IV. Discussion

Synthesis of BaTiO3 by Microwave Heating and Conventional Heating. Microwave heating can be used to prepare barium titanate. In the microwave synthesis, $BaTiO_3$ with a perovskite structure and a corresponding cubic phase can be formed in about 1 min, as shown in Figure 1. This was much faster than the conventional synthesis which took almost 1 h for the cubic phase to crystallize. A continuous transformation from the cubic phase to the tetragonal phase during the aging process was observed for both syntheses, as shown in Tables 1 and 2 of the continuous increase of the c/a ratio. In this reaction system basic solutions were used to dissolve the reagent (TiO_2 gel dissolved in solution). The Ti−O−Ti bonds were broken and are believed to lead to interaction of Ba and Ti via $Ti(OH)_6^{2-}$ groups. A metastable cubic phase crystallized from this solution.[4,27,33] This dissolution process is an endothermic process.

In the microwave synthesis, not only was heat transferred from the basic solution to the reaction mixture but TiO_2 itself produced heat due to its dielectric properties.[31] In the conventional synthesis, heat could only be transferred to the reaction mixture from external heat sources. This makes microwave heating treatment much more effective than conventional thermal treatment and also makes it possible to incorporate more water and ions in the materials produced via microwave synthesis. This is indicated in the results of elemental analysis as shown in Table 4. In the phase transformation process, for both synthesis methods, almost the same time was needed for the cubic phase to transform to the tetragonal phase which can be detected by X-ray diffraction. This implies that the transformation did not just depend on how the heat was produced and how efficient the heat transfer was. However, with the same aging periods starting from when the tetragonal phase was first observed by X-ray diffraction studies, microwave-treated samples had a larger splitting in the X-ray diffraction pattern.

The DSC data for the microwave heated samples showed a transition temperature in comparison to the corresponding conventional sample, which showed no transition. This might be due to the interaction of microwaves and the resultant tetragonal $BaTiO_3$ phase. In turn, microwave-treated samples may have some dielectric properties for interaction with the microwave field. From the results of elemental analyses for both syntheses, titanium was in an excess amount with the conventionally heated samples having relatively more titanium. This difference between the two samples may also be ascribed to the efficient heating during microwave synthesis. The excess amount of titanium did not react and was not observed by X-ray diffraction for those samples showing splitting in the X-ray diffraction patterns even after sintering at 850 °C for 4 h. The unreacted titanium might prevent the tetragonal phase of $BaTiO_3$ from showing the typical transition temperature for a microwave-treated sample or may prevent observation of a transition temperature for the conventionally heated sample. After the samples were sintered at 850 °C for 4 h, both samples showed a clear and reversible transition temperature. The transition temperatures of the microwave-treated and conventionally treated samples were 124 and 126 °C, respectively, in

comparison to the typical transition temperature of 128 °C. Samples with larger amounts of the impurity show a decrease of the transition temperature from the typical temperature.[2] The relative amount of chloride ion in samples can be used to account for the decrease of the transition temperature. However, the relative amount of unreacted TiO_2 may be just indicated by the intensity of the peak in the DSC data and may not be related to the transition temperature.

From the results of FTIR, in the framework vibration range, both microwave samples and conventional samples showed similar spectroscopy. The differences between them were not significant in terms of the peak positions and the relative intensities, and they do not totally match the standard tetragonal $BaTiO_3$ phase, although this may be due to both impurities (unreacted TiO_2), the small c/a ratio (1.008 vs the standard 1.011), the coexistence of both the tetragonal phase and the cubic phase and the measuring method (diffuse reflection method). In the range between 3000 and 4000 cm^{-1}, before the sintering process only a large peak around 3540 cm^{-1} was observed for all three samples, which suggests that a lot of adsorbed water was present. After the sintering process, however, differences were detected between microwave-synthesized samples and conventionally synthesized samples. Some peaks were the same in both microwave and thermally prepared samples; however, microwave samples showed two more peaks at 3345 and 3480 cm^{-1}. Peaks at these frequencies are probably due to functional groups such as OH groups, and these groups can be used to account for the differences between microwave-treated samples and conventionally treated samples. A more exact assignment of these transitions is needed to further understand differences between these materials.

Synthesis of $BaTiO_3$ at 170 °C. During the process of aging, when $BaTiO_3$ transformed from the cubic phase to the tetragonal phase, no obvious change of crystallite size was observed. There was also no substantial difference in crystallite sizes between microwave-heated samples and conventionally heated samples. The average crystallite size for both of them was around 4500−4700 Å by using the Scherrer equation on the XRD data. This observation is somewhat different from the observation reported by Dutta et al.[30] In their process, as $BaTiO_3$ changed from the cubic phase to the tetragonal phase, there was a continuous increase in the crystallite size which was explained as a strain release process and regarded as a reason for the tetragonal phase to increase stability.[30,33,34]

A 160 °C synthesis was studied with the result that only the cubic phase crystallized.[27] In our study here, a temperature of 170 °C was used which was a little higher than 160 °C, and the tetragonal phase was definitely detected by X-ray diffraction. This tetragonal phase did not behave like typical tetragonal $BaTiO_3$ in terms of its transition temperature and is defined as pseudotetragonal. On the basis of the anion analysis, Cl^- was inserted in the lattice of barium titanate and could be detected only after the lattice of barium titanate was broken down during dissolution.

The microwave-treated sample had more chloride than the conventionally treated sample. At 170 °C

(34) Naka, S.; Nakakita, F.; Suwa, Y.; Inagaki, M. *Bull. Chem. Soc. Jpn.* **1973**, *47*, 1168−1171.

during aging, Cl$^-$ might substitute for oxygen and insert in the lattice. Since Cl$^-$ ion is bigger than O^{2-} ion, strain in the lattice can be released on Cl$^-$ incorporation and thus generate the pseudotetragonal phase. When this pseudotetragonal BaTiO$_3$ was further heated to 850 °C for several hours, Cl$_2$ was released and the real tetragonal phase finally appeared, as detected by DSC, which showed not only that the transition temperature was the same as typical tetragonal BaTiO$_3$ but also that this transition was also totally reversible.

In previous studies, many low-temperature syntheses have been developed to prepare BaTiO$_3$. Most of them deal with making the cubic phase directly and then sintering the resultant powders at a temperature no less than 1300 °C in order to obtain the tetragonal phase.[10−24] By using hydrothermal methods, tetragonal BaTiO$_3$ could be crystallized at the lowest temperature of 240 °C,[27,30] and this product showed typical tetragonal character.[30] In our study, we observed a different growing process, which involves sintering of the resultant powder at a temperature lower than the typical sintering temperature to prepare the stabilized tetragonal phase. This process can be described as a transformation from a metastable cubic, to a pseudotetragonal, and finally to a tetragonal phase. Further mechanistic studies are under way in our laboratory to shed more light on these processes.

V. Conclusions

Tetragonal BaTiO$_3$ can be synthesized at 170 °C by both microwave heating and conventional heating followed by sintering at 850 °C for 2−4 h. A metastable cubic phase crystallizes much faster in microwave syntheses than in conventional syntheses. The *c/a* ratio is larger for microwave samples than for corresponding conventional samples. Sintering has a more significant effect on the splitting of the (002) and (200 + 020) peaks of X-ray diffraction patterns of microwave-heated samples than for conventionally heated samples. Both microwave and thermal samples that were sintered showed typical transition temperatures around 125 °C and phase transitions that were reversible for both samples.