Synthesis and Processing of Barium Titanate Ceramics from Alkoxide Solutions and Monolithic Gels

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We report the sol–gel processing of barium titanate ($BaTiO_3$) ceramics from methoxyethoxide precursors. The effects of heat treatment on phase and microstructure development for solution- and gel-derived ceramics are reported. Drying of monolithic alcogels yielded the low-temperature (T < 125 °C) crystallization of $BaTiO_3$. Crystallization was associated with gel syneresis. Nanocrystalline $BaTiO_3$ gels which crystallized before the removal of solvent were used as monolithic precursors for the powderless processing of fine-grain dielectrics. Lower levels of hydrolysis content for solution-derived ceramics led to higher crystallization temperatures for the perovskite phase. In these cases, $BaTiO_3$ crystallized via an intermediary oxycarbonate phase. The efficiency with which carbonaceous species were eliminated during calcination of powders derived from sols or gels was investigated by thermal analysis, infrared spectroscopy, and helium gas pycnometry. Dielectric properties were determined for dense ceramics derived from monolithic xerogels. Micrographs illustrate the development of structure for ceramics derived from the xerogel precursors.

Introduction

The chemical processing of electrical ceramics is of interest for the low-temperature synthesis and densification of insulators. Ferroelectric materials, which have high dielectric constant values (K) and useful electromechanical and optical properties, are under continuous evaluation.[1] Sol–gel processing routes are of interest for the synthesis of ceramic powders, fibers, monoliths, and thin layers.[2] Polymeric sol–gel processing differs from other chemical methods by the polycondensation of molecular species within the liquid phase, which often results in the crystallization of complex oxides at significantly reduced temperatures. This is in contrast to many of the other chemical methods of preparation, such as metalorganic decomposition (MOD) and oxalate or citrate salt decomposition methods. For $BaTiO_3$ synthesis these methods often can be viewed as modifications to the conventional mixed-oxide route, since intermediary oxides and/or carbonates form during heat treatment.[3,4]

Since the sol–gel route cannot be reduced to a simple solid-state reaction, a question arises about the pathways by which the crystalline material forms from the gel precursors, i.e., the gel-to-ceramic conversion. In this work, the crystallization of $BaTiO_3$ from methoxyethoxide precursors is reported. Of interest is the determination of the effect of hydrolysis content on the pathway to crystallization for the perovskite phase. Indeed, the benefits of sol–gel processing are fully realized in this ceramic-forming system only when the hydrolysis and condensation reactions are driven by sufficient amounts of water.

Barium titanate is traditionally synthesized by calcining a mixture of $BaCO_3$ and TiO_2 at temperatures on the order of 1100–1200 °C. High temperatures are required to accelerate the solid-state diffusion between carbonate and oxide powders. The solution routes mentioned above, other than polymeric sol–gel, are successful in lowering the crystallization temperature because of a high degree of mixing on a short-length scale, for similar carbonate and/or oxide precursors.[2] These routes are not entirely unique, since they can employ, at some stage in the preparation, a similar reaction pathway:

$$BaCO_3 + TiO_2 \rightleftharpoons BaTiO_3 + CO_2 \qquad (1)$$

Sol-gel processing with alkoxide precursors often allows for the formation of barium titanate by different routes. Rehspringer et al. described the direct crystallization of the perovskite at 725 °C from a sol–gel-derived monolithic Ba–Ti–O glassy precursor.[5] Similarly, $BaTiO_3$ was reported to crystallize at 750 °C during the thermally activated collapse of an amorphous gel structure in the barium cyclohexanebutyrate/titanium(IV) 2-ethylhexoxide system.[6] This gel-derived material was reported to be free of carbonates prior to crystallization, according to infrared (IR) spectroscopy results. Mosset et al. used large-angle X-ray scattering techniques to observe the evolution of structure for a barium acetate/tetraethoxytitanium(IV) gel during heat treatment.[7] They concluded that $BaTiO_3$ crystallizes at 650 °C from the monolithic gel, but in this case, through the normal carbonate/oxide reaction route! Campion et al. reported that $BaTiO_3$ crystallized at 400 °C from a Ba,Ti methoxyethoxide gel-derived mixture of amorphous oxide and

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[1] Hench, L. L., West, J. K., Eds. *Chemical Processing of Advanced Materials*; John Wiley and Sons: New York, 1992.

[2] Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: New York, 1990.

[3] Phule, P. P.; Risbud, S. H. *J. Mater. Sci.* **1990**, *25*, 1169.

[4] Shaikh, A. S.; Vest, G. M. *J. Am. Ceram. Soc.* **1986**, *69*, 682.

[5] Rehspringer, J. L.; Poix, P.; Bernier, J. C. *J. Non-Cryst. Solids* **1986**, *82*, 286.

[6] Kirby, K. W. *Mater. Res. Bull.* **1988**, *23*, 881.

[7] Mosset, A.; Gautier-Luneau, I.; Galy, J.; Strehlow, P.; Schmidt, H. *J. Non-Cryst. Solids* **1988**, *100*, 339.

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barium carbonate.[8] This mixture was reported to derive from a barium titanyl oxycarbonate with the chemical formula $Ba_2Ti_2O_5CO_3$ at 300 °C. Kumar et al. reported the formation of an oxycarbonate with the same stoichiometry, as a microcrystalline intermediary phase en route to crystallization of $BaTiO_3$ (635–670 °C) via a citrate precursor method,[9] as did Gopalakrishnamurthy et al. for the decomposition synthesis of $BaTiO_3$ from barium titanyl oxalate tetrahydrate.[10]

Also, $BaTiO_3$ can be synthesized directly by low-temperature wet chemical methods. Kiss et al. used a method reported by Flaschen for the low-temperature (<100 °C) preparation of $BaTiO_3$ by hydrolysis of a titanium alkoxide ($Ti(OR)_4$) under highly basic conditions:[11,12]

$$Ti(OH)_6^{2-} + Ba^{2+} \rightarrow BaTiO_3 + H_2O \qquad (2)$$

Additionally, Mazdiyasni et al. reported the formation of $BaTiO_3$ by the hydrolysis of a barium isopropoxide–titanium tetra-*tert*-amyl-oxide solution.[13] The perovskite was reported to form directly by chemical reaction at low temperatures (<50 °C). Kutty and Padmini reported the low-temperature synthesis of a variety of ABO_3 perovskites, including $BaTiO_3$, through the direct reaction of a solution of the A-site cation hydroxide with an inorganic B-site gel comprised of hydrous oxide particles.[14] $BaTiO_3$ was formed by chemical reaction at temperatures less than 100 °C. Such a procedure is similar to that used during the hydrothermal processing of $BaTiO_3$ with finely divided TiO_3 particles and $Ba(OH)_2$. Chaput and Boilot also reviewed the low-temperature reaction pathways.[15]

Clearly, there is no single reaction pathway to describe the synthesis of sol–gel-derived materials. $BaTiO_3$ seems to crystallize from certain gels by carbonate/oxide reaction routes,[7] or, in other cases, by the collapse of an amorphous gel network.[6] Meanwhile, the perovskite phase has been shown to form by way of direct wet chemical reaction in some alkoxide and alkoxide/hydroxide systems.[12,13] In the present work, we focus on the crystallization of $BaTiO_3$ from both solution and monolithic gel precursors in the Ba,Ti methoxyethoxide system.

We also present here some results for compositional differences observed between the starting solutions and the gel network which subsequently forms with gelation and aging. A dialytic technique was used with a semipermeable membrane and a polymer dialysis solution for the separation of solvent and low molecular weight species from the gel network. The dialysis product was analyzed as a function of time. The method was adapted from the work of Miller and Zukoski, who concentrated and densified aqueous suspensions and colloidal gels derived from Al_2O_3 or nanosized ZrO_2 particles.[16]

Finally, in this paper we describe a method of preparation for fine grain $BaTiO_3$ ceramics from monolithic gel preforms. Previously, we have reported on the processing and properties of nanocrystalline $BaTiO_3$ in thin-layer form by the sol–gel route.[17,18] Properties were reported which are not normally observed for large-grain (>1 μm) ceramics and single crystals. Now we report a method for the preparation of monolithic bulk gels and their heat treatment which gives rise to ceramics with fine microstructures.

Experimental Section

Barium and titanium methoxyethoxides ($Ba(OCH_2CH_2OCH_3)_2$ and $Ti(OCH_2CH_2OCH_3)_4$) were synthesized and combined to prepare a 0.2 or a 0.4 M stock solution according to the work of Campion et al.[8] All manipulations were carried out under dry argon or under flowing dry nitrogen. The barium methoxyethoxide solution was prepared by the combination of excess 2-methoxyethanol (anhydrous $HOCH_2CH_2OCH_3$, Aldrich Chemical Co., 99+%) with barium metal (Alfa-Johnson Matthey 99.5%) at 0 °C with stirring. After 10 min the mixture was allowed to warm to room temperature for 10 min, before refluxing at 130 °C for 5 min. The resulting solution was clear and amber in color. Extended refluxing led to darker Ba methoxyethoxide solutions. A titanium solution was prepared by an exchange reaction of titanium(IV) isopropoxide ($Ti(OC_3H_7)_4$, Aldrich Chemical Co., 97%) with 2-methoxyethanol (2-MOE). These two reactants were combined at room temperature with stirring and refluxed for 1 h. Excess 2-MOE and the 2-propanol byproduct were removed by distillation to give a clear, viscous, light yellow solution.

Mixed metal alkoxide solutions were hydrolyzed to different extents by addition of water in 2-MOE. The sealed solutions were allowed to age and gel (in some cases) before thermal processing. Drying was carried out in air between 25 and 150 °C. Some of the dried products were lightly ground with a mortar and pestle to give powders for characterization and further heat treatment. The drying of alcogels at temperatures above 50 °C gave transport monolithic xerogels which were sintered between 800 and 1300 °C to form dense ceramics with various microstructures. The heating rate was 15 °C/min, and the specimens were kept at temperature for different periods of time. Scanning electron microscopy (SEM) was carried out on fracture surfaces to determine grain size and shape. Electrical measurements were made on gel-derived ceramic monoliths.

Some wet gels were dialyzed with a 10 wt % solution of poly(acrylic acid) (Aldrich Chemical Co., M_w 450 000) in 2-MOE using a regenerated cellulose semipermeable dialysis membrane with a 12 000–14 000 molecular weight cutoff (Spectrum, Inc.). The hydrolyzed alkoxide solution was syringed into the dialysis tubing before sealing each end. After gelation, the sealed tube and the enclosed gel were placed in the polymer solution for the extraction of solvent and any low molecular weight species. The dialysis product was characterized by inductively coupled plasma emission (ICPE) spectroscopy.

Differential thermal analysis (DTA) was carried out on a Innovative Thermal Systems DTA equipped with a DuPont test cell. Thermogravimetric analysis (TGA) was obtained on a TA Instruments 2950 TGA. Powder densities were determined by a Quantachrome helium gas micropycnometer. A Perkin-Elmer Fourier transform infrared spectrometer (FTIR) was used for transmission infrared spectroscopy. X-ray diffraction (XRD) data were obtained with a Rigaku D-max IIIA diffractometer (Cu Kα). An Hitachi S-800 high-resolution SEM was used for the study of microstructures. Dielectric

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(8) Campion, J.-F.; Payne, D. A.; Chae, H. K.; Xu, Z. *Ceram. Trans.* **1991**, *22*, 477.

(9) S. Kumar, S.; Messing, G. L.; White, W. B. *J. Am. Ceram. Soc.* **1993**, *76*, 617.

(10) Gopalakrishnamurthy, H. S.; Rao, M. S.; Kutty, T. R. N. *J. Inorg. Chem.* **1975**, *37*, 891.

(11) Kiss, K.; Magder, J.; Vukasovich, M. S.; Lockhart, R. J. *J. Am. Ceram. Soc.* **1966**, *49*, 291.

(12) Flaschen, S. S. *J. Am. Chem. Soc.* **1955**, *77*, 6194.

(13) Mazdiyasni, K. S.; Dollof, R. T.; Smith II, J. S. *J. Am. Ceram. Soc.* **1969**, *52*, 523.

(14) Kutty, T. R. N.; Padmini, P. *Mater. Res. Bull.* **1992**, *27*, 945.

(15) Chaput, F.; Boilot, J.-P. *J. Am. Ceram. Soc.* **1990**, *73*, 942.

(16) Miller, K. T.; Zukoski, C. F. *J. Am. Ceram. Soc.* **1994**, *77*, 2473.

(17) Z. Xu, Z.; Chae, H. K.; Frey, M. H.; Payne, D. A. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 339.

(18) Frey, M. H.; Payne, D. A. *Appl. Phys. Lett.* **1993**, *63*, 2753.

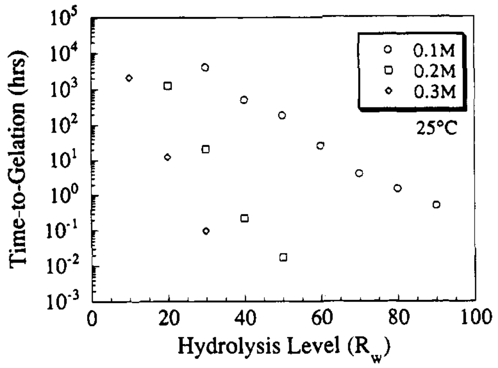

Figure 1. Time-to-gelation as a function of hydrolysis content and alkoxide concentration.

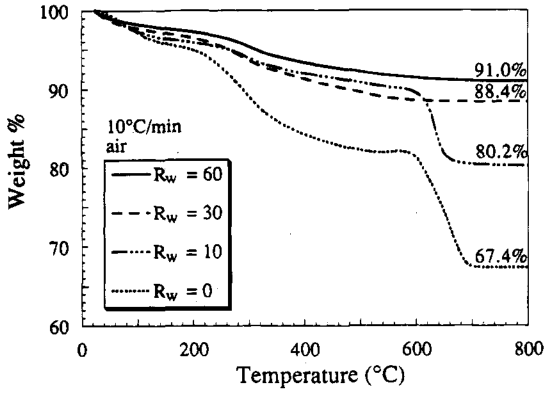

Figure 2. Thermogravimetric analysis of powders obtained from dried alkoxide solutions and gels which were aged for 2 days before drying at 150 °C.

properties were measured on a Hewlett-Packard 4284A LCR meter, and polarization reversal characteristics were determined on a modified Sawyer-Tower circuit.

Results and Discussion

(1) Gelation and Thermogravimateric Analysis. The Ba,Ti methoxyethoxide system is characterized by its relative insensitivity to moisture, which is unusual in sol–gel processing and alkoxide synthesis. High levels of hydrolysis content are required to promote gelation in reasonable amounts of time. Figure 1 gives the time-to-gelation as a function of hydrolysis content and alkoxide concentration, where R_w is defined as the molar ratio of water to mixed metal alkoxide. The point of gelation was followed as viscosity increased to the point of rigidity for the gels and was found to be consistent throughout the experiments. The lack of sensitivity to moisture is in contrast to the behavior observed for the methoxyethanol-based Pb acetate/Ti methoxyethoxide precursor system commonly used in the preparation of $PbTiO_3$ ceramics, where hydrolysis with $R_w = 2$ is sufficient to cause gelation in less than 24 h. This distinct difference in gelation behavior is under continued investigation.

Figure 2 illustrates the TGA characteristics of powders obtained from dried (150 °C) 0.1 M solutions (R_w = 0, 10, 30) and a dried 0.1 M gel (R_w = 60). Figure 3 gives the respective powder densities for the calcined powders. A distinct weight loss occurred in the TGA analysis between 600–700 °C for powders prepared with low values of R_w. This second-stage weight loss was absent for powders prepared with higher levels of hydrolysis content. All the data indicate that increasing amounts of water decrease the formation of lower density carbonaceous species in dried powders through the release of organics in the form of alcohol during the initial drying stage. Weight loss was complete by 800 °C under all conditions, and the powders were virtually free of carbonates as determined by FTIR.

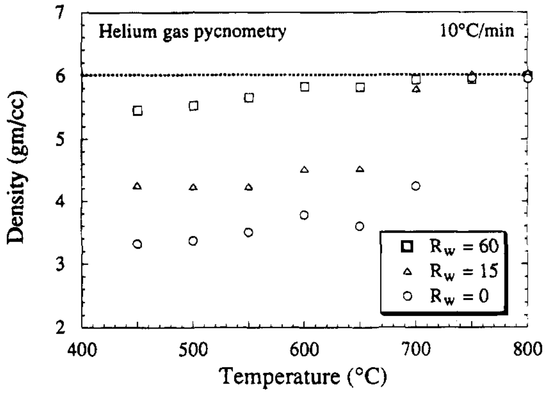

Figure 3. Powder density after heating to various temperatures at 10 °C/min (theoretical density of $BaTiO_3$ is 6.02 gm/cc).

(2) Crystallization Pathways. DTA revealed clear exotherms at about 590 and 740 °C for powders prepared with the lower levels of hydrolysis content (R_w < 30). A broad exotherm near 300 °C was observed for all powders, irrespective of the hydrolysis content and aging conditions. The low-temperature exotherm was attributed to oxidation of residual organic species. The sharper exotherms at about 590 and 740 °C (for low levels of hydrolysis content) were attributed to the formation of an intermediary phase (to be discussed later) and the perovskite phase, respectively. Figure 4 gives XRD data as a function of heat treatment for solution- and gel-derived powders which were first dried at 150 °C. $BaTiO_3$ started to crystallize via an intermediary phase at 740 °C for low levels of hydrolysis content, as well as for the unhydrolyzed alkoxide (i.e., MOD). XRD data for the dried, unhydrolyzed solution, heated to 600 °C (Figure 4a) is similar to that reported by Kumar et al. for an oxycarbonate phase formed by the citrate decomposition method.[9] In the present work, the intermediate formed from alkoxide precursors with little or no hydrolysis content at temperatures below 600 °C in air. For larger values of hydrolysis content (e.g., R_w = 60), $BaTiO_3$ (cubic) crystallized on drying (150 °C) and was the only crystalline phase observed on heat treatment. Thus, intermediate oxycarbonate phase formation is associated with low levels of hydrolysis content.

FTIR data in Figure 5 indicate absorption bands at 1350 and 1585 cm^{-1} for all of the as-dried powders, as well as bands attributed to residual methoxyethoxy ligands.[20] Bands near 1350 and 1585 cm^{-1} were assigned to carbonate species by Campion et al.[8] Peaks in this vicinity have also been observed in the sol–gel processing of acetate-containing systems and have been attributed to symmetric and asymmetric stretching

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(19) Schwartz, R. W.; Lakeman, C. D. E.; Payne, D. A. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 335.

(20) Lakeman, C. D. E. M.S. Thesis, University of Illinois at Urbana–Champaign, 1991.

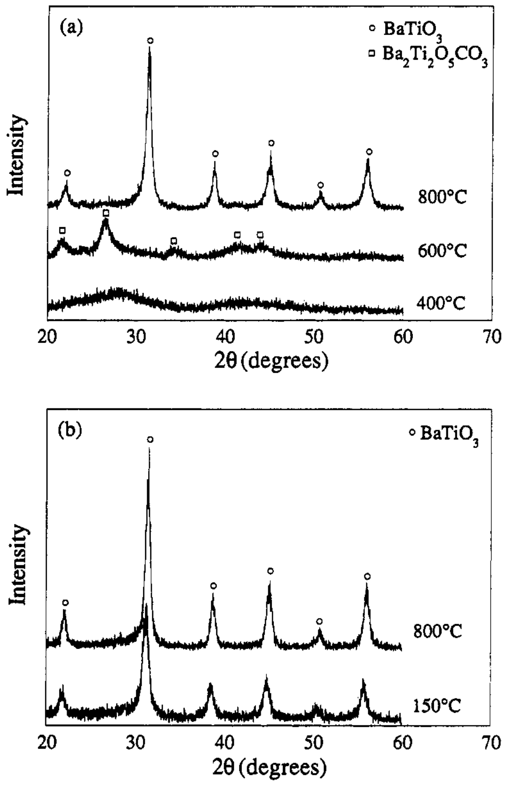

Figure 4. XRD data for crystalline phase development for a) a dried alkoxide solution, and b) a dried gel ($R_w = 60$), after heat treatment at various temperatures in air.

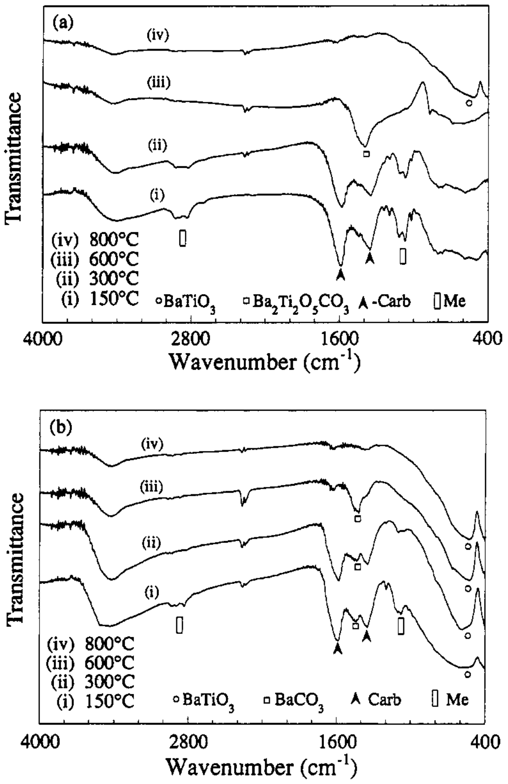

Figure 5. FTIR spectra for a) a powder obtained from a dried alkoxide solution, and b) a dried gel ($R_w = 60$), after heat treatment at various temperatures in air.

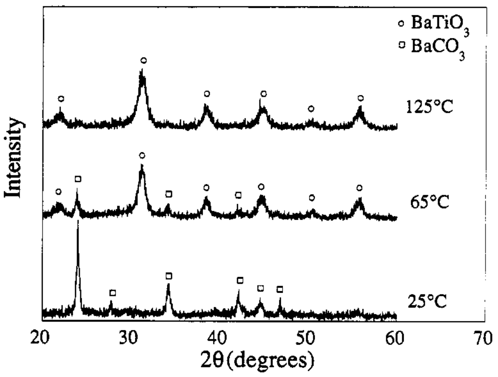

Figure 6. XRD data for gels dried in air at various temperatures.

modes of COO.[21,22] These bands, as well as those associated with the methoxyethoxy ligands, disappear after heat treatment at temperatures above 600 °C and clearly reveal the formation of a residual carbonate phase (i.e., $BaCO_3$) in calcined gels (1445 cm^{-1}, Figure 5biii). For powders derived from unhydrolyzed solutions which were dried and heated to 600 °C, a spectrum (Figue 5aiii) identical to that reported by Gopalakrishnamurthy et al. for $Ba_2Ti_2O_5CO_3$ was observed, in agreement with the XRD data discussed earlier (Figure 4a).[10] $BaTiO_3$ is clearly identified in the as-dried 150 °C xerogel (Figure 5bi) and only in powders derived from unhydrolyzed solutions when processed above 740 °C (Figure 5aiv). Thus, the hydrolysis content is important for the low-temperature crystallization of $BaTiO_3$.

The effect of drying temperature on $BaTiO_3$ formation was investigated further for hydrolyzed solutions. Gel coarsening and shrinkage (i.e., syneresis) was observed when higher temperatures were used for the drying of gels. When gels were heated in air at temperatures greater than 100 °C an initial 50% linear contraction of the wet gel was observed within 1 h, followed by progressive shrinkage and continuous drying over the next several hours. However, when gels were dried at lower temperatures (e.g., <50 °C) little syneresis was observed, and the drying rate was slower over several weeks. Drying at intermediate temperatures (e.g., 75 °C) was characterized by a certain degree of syneresis. Figure 6 gives XRD data for gels dried at various temperatures in air. The presence of crystalline $BaCO_3$ was observed in powders which were obtained by drying at low temperatures (e.g., 25 °C), whereas crystalline $BaTiO_3$ was formed in greater proportion when the drying temperature increased from 25 to 125 °C. XRD results were supported by FTIR measurements, and Figure 7 gives FTIR data obtained after drying at different temperatures. The IR spectrum of $BaTiO_3$ is characterized by a broad absorbtion band in the 525–575 cm^{-1} range, which is attributed to a TiO_6 octahedra stretching mode.[23] $BaCO_3$ absorbs broadly at 1445 cm^{-1} and sharply at 1064, 860, and 693 cm^{-1}.[24] Figure 6 indicates the presence of $BaCO_3$ for low drying temperatures, and its relative absence after drying at 150 °C. The increase in $BaTiO_3$ content with increasing drying temperature was coincident with syneresis of the gel. This may imply that thermally activated syneresis of the gel is driven by the low temperature crystallization of the perovskite (e.g., 150 °C). Syneresis is thought

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(21) Bilger, S.; Syskakis, E.; Naoumidis, A.; Nickel, H. *J. Am. Ceram. Soc.* **1992**, *75*, 964.

(22) Schwartz, R. W. Ph.D. Thesis, University of Illinois at Urbana-Champaign (1989).

(23) Last, J. T. *Phys. Rev.* **1957**, *105*, 1740.

(24) White, W. B. In *The Infrared Spectra of Minerals*; Farmer, V. C., Eds.; Mineralogical Society Monograph: London, 1974.

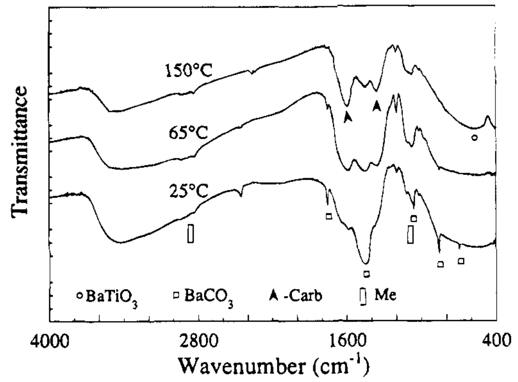

Figure 7. FTIR data for gels dried in air at various temperatures.

to result from polycondensation reactions that continue after gelation.[2] Thus, the perovskite is presumed to crystallize directly by condensation reactions on heating. This chemical reaction pathway is similar to that described by Mazdiyasni et al., where $BaTiO_3$ was reported to form by direct condensation between alkoxide precursors.[13] We propose that free barium species react with a predominately titanium-based gel network to form the perovskite structure.

The presence of $BaCO_3$ at low drying temperatures also suggests that a certain amount of the barium species was unattached to the gel network before drying and was free to react most probably with CO_2 in the atmosphere. We propose that $BaCO_3$ formed from the fully hydrolyzed barium species by the following reaction:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O \qquad (3)$$

That is, $BaCO_3$ formation is thought to result from the presence of free $Ba(OH)_2$ in solution and the exposure to air for gels dried at low temperatures and for long periods of time. The drying of any solution or gel in air at $T < 100$ °C resulted in the formation of a significant amount of $BaCO_3$. Presumably, carbonate formation could be avoided by drying in a controlled CO_2-free atmosphere. Drying in dry N_2 or argon is common. $Ba(OH)_2$ required for the formation of $BaCO_3$ results from hydrolysis with excess water or moisture in the atmosphere. Faster drying at higher temperatures ($T > 100$ °C) largely avoided the formation of carbonate. The perovskite phase developed by different pathways depending on the extent of hydrolysis (R_w) and the aging time for the higher drying temperatures ($T > 100$ °C). For example, for high R_w values ($R_w > 30$) and drying temperatures greater then 125 °C, $BaTiO_3$ crystallized directly in the aged gel. For lower R_w values and shorter aging times, $BaTiO_3$ crystallized from an intermediary oxycarbonate phase at temperatures greater than 740 °C. Thus, the water content and drying/aging temperature are important parameters for the low-temperature crystallization of $BaTiO_3$.

(3) Dialysis and Composition. The preservation of homogeneity and stoichiometry in electrical ceramics which are derived from solution precursors is of concern, since properties are dependent on composition and subsequent microstructure development on heat treatment. In sol–gel processing with mixed-metal alkoxide solutions, oxo alkoxides can form with different stoichiometries from the starting solutions.[25] Also, differential rates of hydrolysis and/or condensation reactions which occur between different species can lead to differences in composition between the gel network and the free species which remain in solution. This was observed in the dialysis experiments carried out on wet gels in the present work. After the gel was placed in the dialysis solution, an obvious shrinkage occurred over the course of a few days in the gel and in the flexible membrane—as solvent and low molecular weight species were extracted. ICPE analysis of a gel dialyzed after aging for three times the apparent time to gelation showed a clear 30% molar excess in titania content. We suggest the excess titania in the dialyzed material indicates that titania dominates the macromolecular network. Remarkably, undialyzed gels which crystallized during drying ($T > 100$ °C) showed less than 1% departure from perfect stoichiometry. These results suggest that barium species are not stable constituents of the gel network but can efficiently react either with the network at higher (>100 °C) temperatures to yield $BaTiO_3$ or with the atmosphere at lower temperatures to form $BaCO_3$. In the dialysis experiment, free barium species were extracted, whereas in the course of the higher temperature drying, they react to form stoichiometric $BaTiO_3$.

(4) Monolithic Xerogels as Ceramic Precursors. The electrical and structural properties of thin-layer electroceramics are well-known to differ from those exhibited by single crystals or large-grain ceramics. In the case of ferroelectric ceramics, a reduced value of K and a loss in reversible polarization (P) are reported.[18] These anomalies are often attributed to an ultrafine grain size effect. A reduction in crystallite size to the submicron regime certainly influences the room temperature crystalline and ferroelectric domain structures, and these effects are well documented and observed.[26] However, the evolution of electrical and structural properties of dense ferroelectric ceramics with grain sizes which continuously decrease to the nanoscale level have yet to be well characterized and reported. There is often an order of magnitude disparity in crystallite size between thin-layer microstructures and bulk ceramics for which grain size effects have been previously reported. This makes somewhat tenuous the proposed explanations for thin-layer properties in terms of a grain size effect. To process dense materials with nanocrystalline structures, we propose that the powderless processing route of polymerizable alkoxides with gel monoliths be developed.

Nanocrystalline materials were readily crystallized from polymeric gels in the present work. The attainment of high densities was more difficult, and high-field measurements are meaninfgul only on dense dielectrics. This may require an exploration of the various sol–gel precursor systems and processing possibilities. We now report here, for the first time (to our knowledge), microstructures for $BaTiO_3$ ceramics which were processed from xerogel precursors, together with dielectric and ferroelectric data.

Crystalline microstructures, as observed by high-resolution SEM, are given in Figure 8. After heat

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(25) Campion, J.-F.; Payne, D. A.; Chae, H. K.; Maurin, J. K.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 3244.

(26) Newnham, R. E.; Udayakumar, K. R.; Trolier-McKinstry, S. In ref 1.

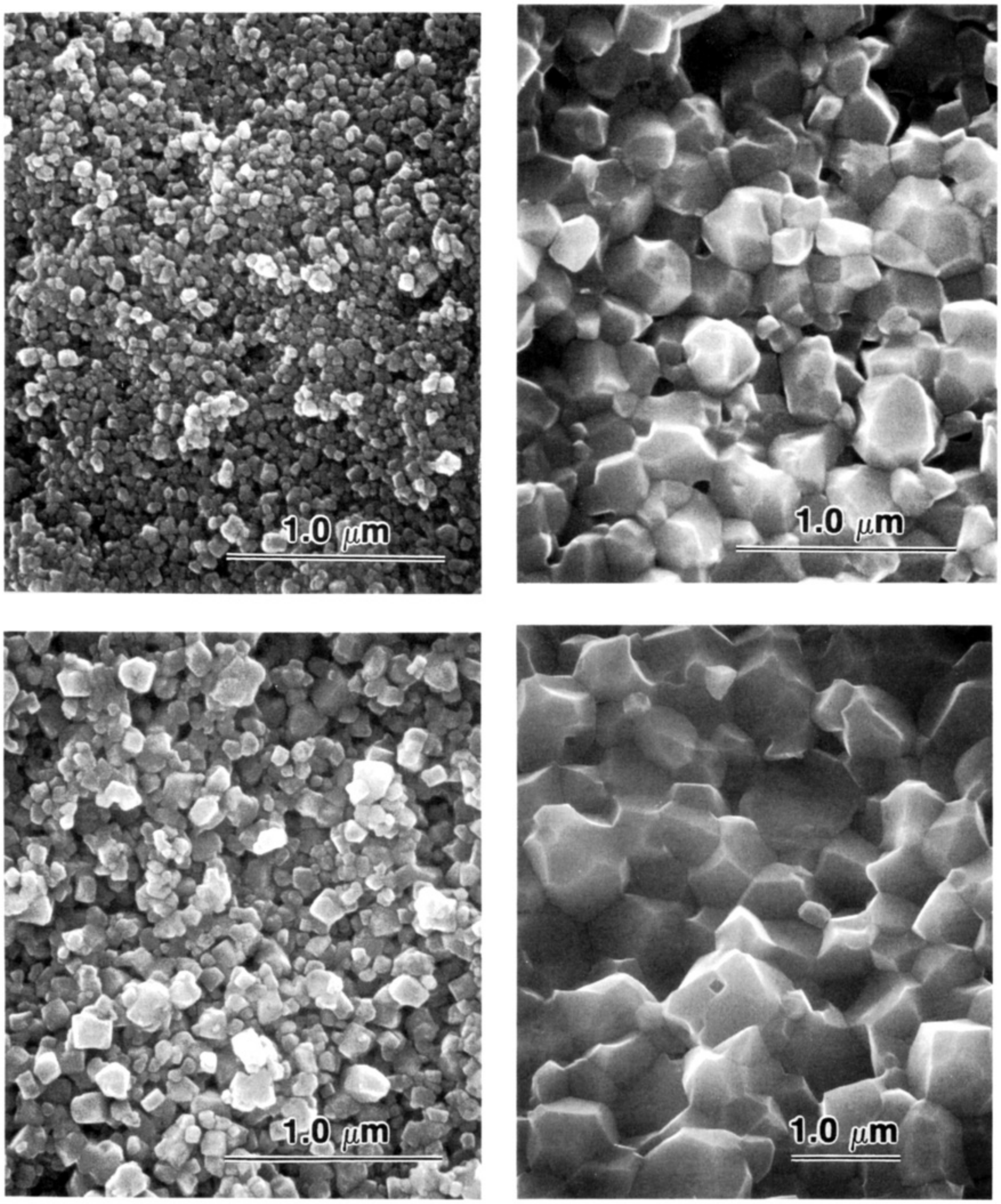

Figure 8. Scanning electron photomicrographs illustrating the microstructures of gel-derived ceramics heated to (a, top left) 800 °C, (b, bottom left) 975 °C, (c, top right) 1060 °C, and (d, bottom right) 1100 °C in air.

treatment at 800 °C, the microstructure was found to be comprised of 20–40 nm grains for ceramics prepared from hydrolyzed and aged gels dried at 125 °C. On further heat treatment, higher densities (>95%) were obtained by 1000 °C with a grain size of about 0.1 μm. Continuous grain growth and pore elimination gave rise to dense submicron microstructures. XRD revealed the global crystal structure to be of cubic symmetry (*Pm*3*m*) for the nanocrystalline material. The crystal structure gradually developed at room-temperature tetragonal distortion (*P*4*mm*) after heat treatment and grain growth at higher temperatures. This structural transformation has been associated with a grain size effect in ferroelectric ceramics.[26] The ferroelectric tetragonal phase for $BaTiO_3$ is stabilized at room temperature and atmospheric pressure only when the crystallite size has grown beyond a critical size.[26] Microstructural constraints in sintered ceramics often result in crystallite size effects which are not identical to those observed for free particles. The onset of ferroelectricity in dense $BaTiO_3$ with grain sizes progressively growing from the nanoscale to the microscale level is the subject of a continuing investigation.

Figure 9 gives dielectric data for a xerogel-derived $BaTiO_3$ ceramic monolith, with an average grain size of less than 5 μm, together with $P-E$ hysteresis loop characteristics. The room-temperature properties were determined as follows: $K' = 2630$, $\tan \delta = 2.2\%$, $P_r = 0.06$ C/m^2, and $E_c = 0.2$ MV/m. The properties are consistent with those reported for similar microstruc-

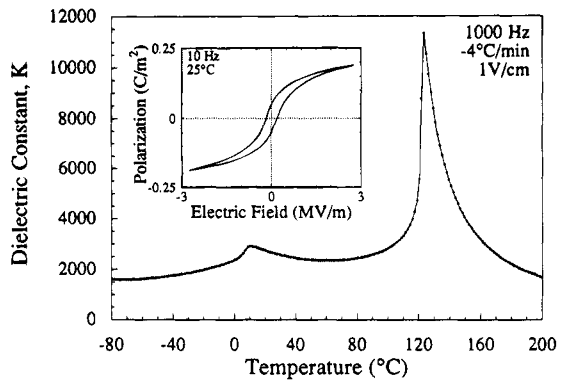

Figure 9. Dielectric and ferroelectric properties for monolithic gel-derived $BaTiO_3$ ceramic of <5 μm grain size.

tures obtained by conventional powder processing methods.[27] In the present case, they were prepared by a powderless processing method in which alkoxide solutions were hydrolyzed and condensed into a monolithic precursor to the ceramic form.

Conclusion

The crystallization of $BaTiO_3$ from alkoxide solutions and gels in the Ba,Ti methoxyethoxide system was realized by various pathways, depending on the hydrolysis content, aging conditions, and drying temperature. Solutions hydrolyzed with small additions of water crystallized at 740 °C by way of an intermediary oxycarbonate phase. Fully hydrolyzed gels crystallized on drying at 125 °C into cubic $BaTiO_3$. At lower drying temperatures, $BaCO_3$ formed by reaction of $Ba(OH)_2$ with ambient CO_2 for both solutions and gels. Consistent with this observation, dialysis experiments confirmed that the macromolecular gel network was titania-rich. Increasing additions of water allowed for the efficient release of carbonaceous species during hydrolysis and drying, as indicated by TGA and measurements of powder density. Monolithic gel precursors sintered to dense $BaTiO_3$ ceramics with fine microstructures. The insulating properties were consistent with those reported for polycrystalline ceramics prepared by conventional powder processing methods.

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(27) Arlt, G. *Ferroelectrics* **1990**, *104*, 217.