CONF-900466--66

THE EFFECTS OF HYDROLYSIS AND ADDITIVE CONDITIONS ON THE GEL-TO-CERAMIC CONVERSION OF SOL-GEL DERIVED $PbTiO_3$

ROBERT W. SCHWARTZ,* C. D. E. LAKEMAN, AND D. A. PAYNE
Department of Materials Science and Engineering, and
Materials Research Laboratory
University of Illinois at Urbana-Champaign
105 S. Goodwin Ave., Urbana, IL 61801

SAND--89-3088C

DE90 012999

ABSTRACT

Lead titanate was prepared by sol-gel processing of metal alkoxide solutions. The effects of hydrolysis level (i.e., moles H_2O/mole $PbTiO_3$) and acid and base additives (HNO_3 or NH_4OH) on desiccated gel properties and the gel-to-ceramic conversion process were studied. The properties of the gels were characterized at three stages of the processing cycle: (i) the desiccated gel state; (ii) the amorphous state, following organic pyrolysis; and (iii) the crystalline state. Differences in the physical and structural properties of the desiccated gels, induced through manipulation of the hydrolysis conditions, persisted in the amorphous state, i.e., following organic pyrolysis. Minor differences remained after crystallization. The variation in material properties with low temperature processing (i.e., the gel-to-glass transformation) is considered from the standpoint of the effects of hydrolysis and additive conditions on gel network structure and consolidation behavior. The densification and crystallization behavior of the gels were also characterized. Through proper control of hydrolysis conditions, relatively dense ceramics were obtained at temperatures as low as 700°C.

INTRODUCTION

In recent years, sol-gel processing has generated considerable interest. While most of this interest has focused on the processing of amorphous materials in the silica system, an increasing trend has been to fabricate electronic ceramic materials [1]. Although in the latter case the goal is to prepare crystalline materials, in general, a similar processing route is followed: (i) precursor solutions are hydrolyzed with controlled amounts of water to form gels (or coatings); (ii) the gels are dried and heat treated for removal of residual organic species, to yield a "pure" amorphous material; and (iii) higher heat-treatment temperatures are used to promote densification and induce crystallization into the desired structure. The transformations associated the the first two processing steps, i.e, the sol-to-gel and the gel-to-glass transformations, have been studied extensively for the silica system [2-4], and effects of hydrolysis and catalysis conditions have been noted.

In a previous study, we determined that through control of the hydrolysis conditions, differences in the physical, structural, and microstructural properties of desiccated lead titanate ($PbTiO_3$) gels could be induced [5]. The focus of the present investigation was to characterize the transformation behavior (gel-to-glass and glass-to-ceramic) of the desiccated gels, and to determine if the property differences induced in the desiccated gels persisted into the pure amorphous state and into the crystalline perovskite state. If the differences induced in the desiccated gels persist in the amorphous state, both the densification and crystallization behavior of the material may be affected [4,6,7].

Lead titanate was selected for investigation since the ABO_3 family of perovskite materials are widely used for their electrical, ferroelectric, and electrooptic properties [8]. Numerous thin film applications based on PZT ($PbZrO_3$ - $PbTiO_3$) and PLZT (La modified PZT), most notably, radiation hard non-volatile memories [9] and optical storage devices [10], are currently under development. The preparation of PZT and PLZT monoliths by sol-gel processing is also of interest, since current processing methods require elevated temperatures [11].

---

* Present Address: Sandia National Laboratories, Albuquerque, NM 87185

EXPERIMENTAL

A method developed by Budd et al. was followed for the synthesis of the Pb-Ti precursor solution [1]. Lead acetate tri-hydrate ($Pb(OOCCH_3)_2 \cdot 3H_2O$) was dehydrated by three successive distillations in HPLC grade 2-methoxyethanol ($CH_3OCH_2CH_2OH$). In a separate reaction vessel, titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) was refluxed for 30 minutes in 2-methoxyethanol, and the by-product of the reaction, isopropanol, was removed by distillation. This resulted in an alkoxide exchange between the original isopropoxy groups of the titanium precursor and the methoxyethoxy groups of the solvent, yielding titanium methoxyethoxide ($Ti(OCH_2CH_2OCH_3)_4$). The lead and titanium solutions were then reacted (130°C, 60 min.) and concentrated by vacuum distillation, to form a 1 molar Pb-Ti mixed metal alkoxide solution. The reactions were characterized by ^1H and ^{13}C NMR [12].

Gels were prepared by combining equal volumes of the 1 molar precursor solution with a solution of water, additive and 2-methoxyethanol. Water additions (i.e., R, the molar ratio of water to mixed metal alkoxide) were varied from 2.0 to 4.0, in 0.5 molar steps. Both acidic (0.1 M HNO_3) and basic (0.1 M NH_4OH) hydrolysis conditions were studied. Gelation times ranging from 12 seconds to 22 hours were observed for hydrolysis under these conditions.

After gelation, the gels were aged for 30 minutes, and were then dried at 140°C for 48 hours. Drying was essentially complete within the first 6 hours. Phase separation was observed for both acidic and basic gels. The approximate weight loss during drying was ~80%, and was primarily attributed to evaporation of the phase separated solvent.

After drying, the gels were lightly crushed in a mortar and pestle to yield powders suitable for characterization of the physical properties. The powders were then subjected to a variety of heat treatments. Previous experiments had shown that, for the hydrolysis and drying conditions of interest, decomposition was complete by 350°C, with crystallization occurring at temperatures above 400°C [6,7]. Therefore, to prepare the pure amorphous $PbTiO_3$ required for evaluation of physical, structural, and microstructural properties, the gel-derived powders were heated at 10°C/min. to 400°C, and quenched. Skeletal densities of the amorphous materials were calculated from He pycnometry measurements, by assuming no inaccessible porosity. Heat treatments at 410°C for time periods from 30 minutes to 10 hours were carried out to determine the variation in physical properties during the crystallization process. The surface areas and pore characteristics of the gel-derived powders at the three process stages were determined by N_2 adsorption analysis.

Finally, the effects of hydrolysis and additive conditions on fired ceramic microstructure were also investigated. Small pieces of (fractured) gel monoliths, heat treated at 700°C for 60 minutes (ramp rate: 10°C/min.) were studied by SEM, and the average grain sizes were determined.

RESULTS AND DISCUSSION

In a previous study [5], we determined that the surface areas and pore volumes of desiccated $PbTiO_3$ gels increased with increasing R. We also found that, for comparable water additions, basic gels had higher surface areas and pore volumes than acidic gels. The observed variations in physical properties were attributed to differences in the level of condensation resulting from hydrolysis. For example, as reported for the silica system [2], hydrolysis under basic conditions (and/or with large water additions) was believed to lead to more highly condensed (crosslinked) structures, which were less capable of consolidation during drying. Therefore, the corresponding desiccated gels were characterized by larger pore volumes and greater surface areas.

In the present study, we characterized the variations in the physical properties associated with conversion of the desiccated gels to pure amorphous $PbTiO_3$ (i.e., the gel-to-glass transformation resulting from heat treatment at 400°C). Results are given in Figure 1. For each of the hydrolysis conditions studied, surface area (Figure 1a) decreased with heat treatment. Interestingly, differences in the surface areas of the amorphous materials, induced through manipulation of the hydrolysis conditions, were still present following organic pyrolysis. Unlike the desiccated gels, however, the heat

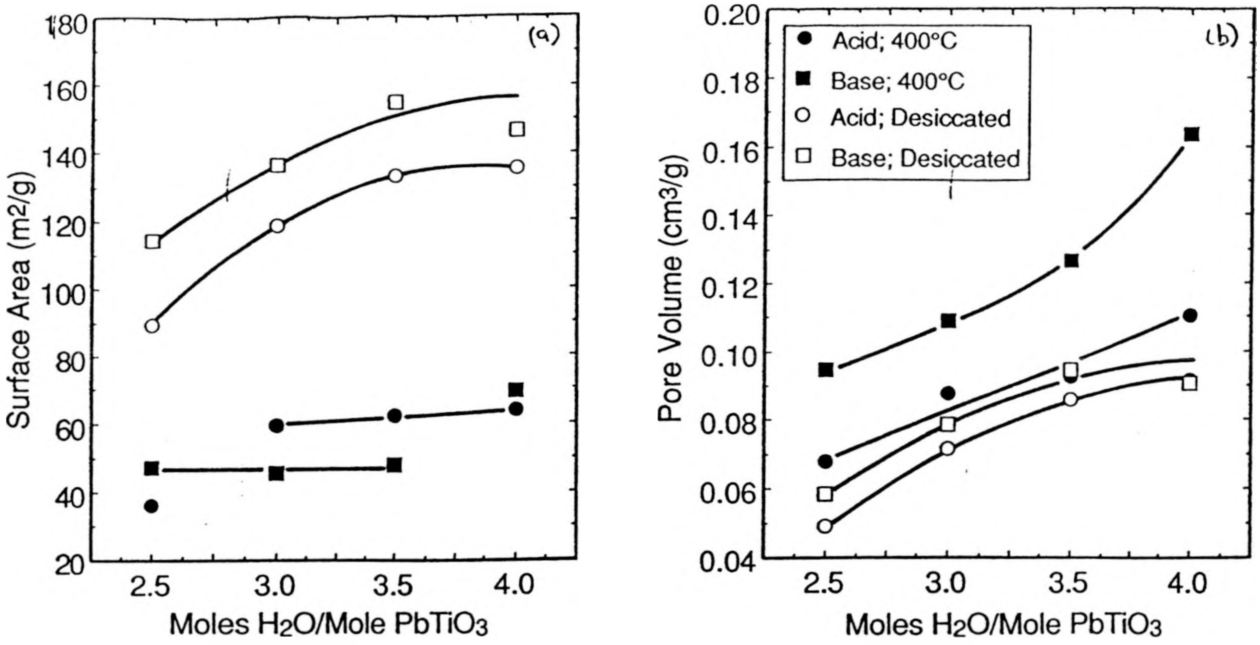

Figure 1. (a) Surface areas and (b) pore volumes of desiccated $PbTiO_3$ gels and pure amorphous $PbTiO_3$.

treated (pure amorphous $PbTiO_3$) gels prepared under acidic conditions were, in general, characterized by greater surface areas than basic gels prepared with comparable water additions. Acidic gels thus displayed a greater retention of their initial surface area upon heat treatment.

We also studied the variations in pore volume with heat treatment, and results are given in Figure 1b. As for the desiccated gels, the amorphous $PbTiO_3$ gels prepared under basic conditions with large water additions were characterized by the highest pore volumes. However, the pore volumes of the heat treated gels were substantially greater than the desiccated gels, i.e., pore volume increased with heat treatment. The gels prepared under basic conditions also displayed a greater increase in pore volume (with heat treatment) than did the acidic gels. The fact that the physical properties of the heat treated gels displayed different trends than the desiccated gels implies that the processes which occur during heat treatment, i.e.: (i) organic removal; (ii) continued condensation reactions (toward the equilibrium amorphous structure); and (iii) (macroscopic) consolidation of the gel; occur to different extents, depending on the initial hydrolysis conditions.

Other effects of hydrolysis conditions were also observed to persist in the heat treated (pure amorphous $PbTiO_3$) gels. Results are presented in Figure 2 for the effects of hydrolysis and additive conditions on structural free volume. In the present case, structural free volume (FV) was calculated from the skeletal density of the amorphous material, and the theoretical crystal density, according to:

$$FV = 1 - (\rho_a/\rho_c) \qquad (1)$$

Gels prepared under hydrolysis conditions leading to higher levels of condensation (base additive, high R) were characterized by lower free volumes, as expected. Since the free volumes of the basic gels were relatively independent of the amount of water used for hydrolysis, the amorphous materials prepared under basic conditions were evidently all highly crosslinked, irrespective of R. If the results for these materials are considered from the standpoint of traditional glasses, the materials would be characterized as having few non-bridging oxygen species.

For the gels prepared under acidic hydrolysis conditions, structural free volume was observed to decrease with R. Thus, after heat treatment at 400°C, substantial structural differences existed in the amorphous $PbTiO_3$ prepared under acidic conditions. The acidic gels prepared with large water additions were characterized by more highly condensed structures than those prepared with low water additions. If the amorphous materials prepared under acidic, low water conditions are considered from

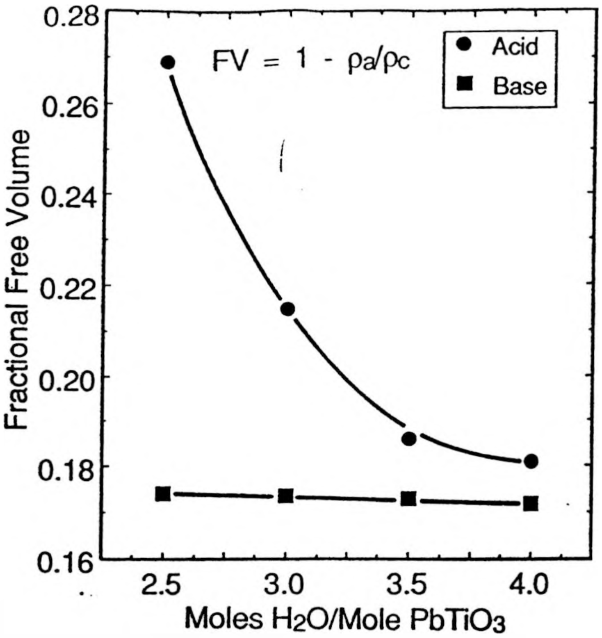

Figure 2. Free volume of amorphous $PbTiO_3$ prepared by heat treatment at 400°C.

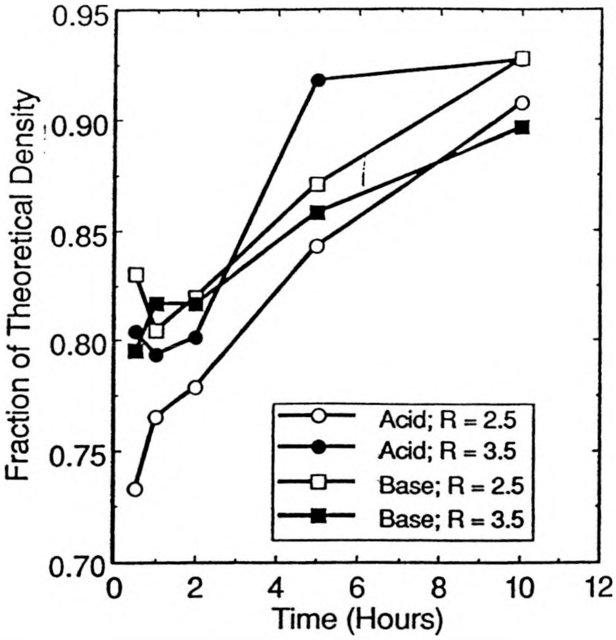

Figure 3. Effect of heat treatment time at 410°C on skeletal density of sol-gel derived $PbTiO_3$.

the standpoint of traditional glasses, they would be characterized as having a greater number of non-bridging oxygens; i.e., they have structures which are less condensed than materials prepared under basic conditions, or acidic, high water conditions. Structural differences of this nature are believed to be unstable, and with sufficient relaxation times in the vicinity of Tg, are expected to disappear [13].

Results for the variation in skeletal density as a function of heat treatment at temperatures near T_c, the crystallization temperature, were in agreement with these predictions, and are shown in Figure 3. While the skeletal densities of the amorphous materials (i.e., materials heated to 400°C and quenched) were quite different, with heat treatment at 410°C, the differences diminished. For the samples heat treated at 410°C for 10 hours, i.e., after the onset of crystallization, the skeletal densities reached ~90% of the theoretical crystal density (7.98 g/cm^3).

Another area of investigation was to determine whether gel densification was complete prior to the onset of crystallization. Therefore, the effects of prolonged heat treatments at temperatures near T_c on the physical properties of amorphous $PbTiO_3$

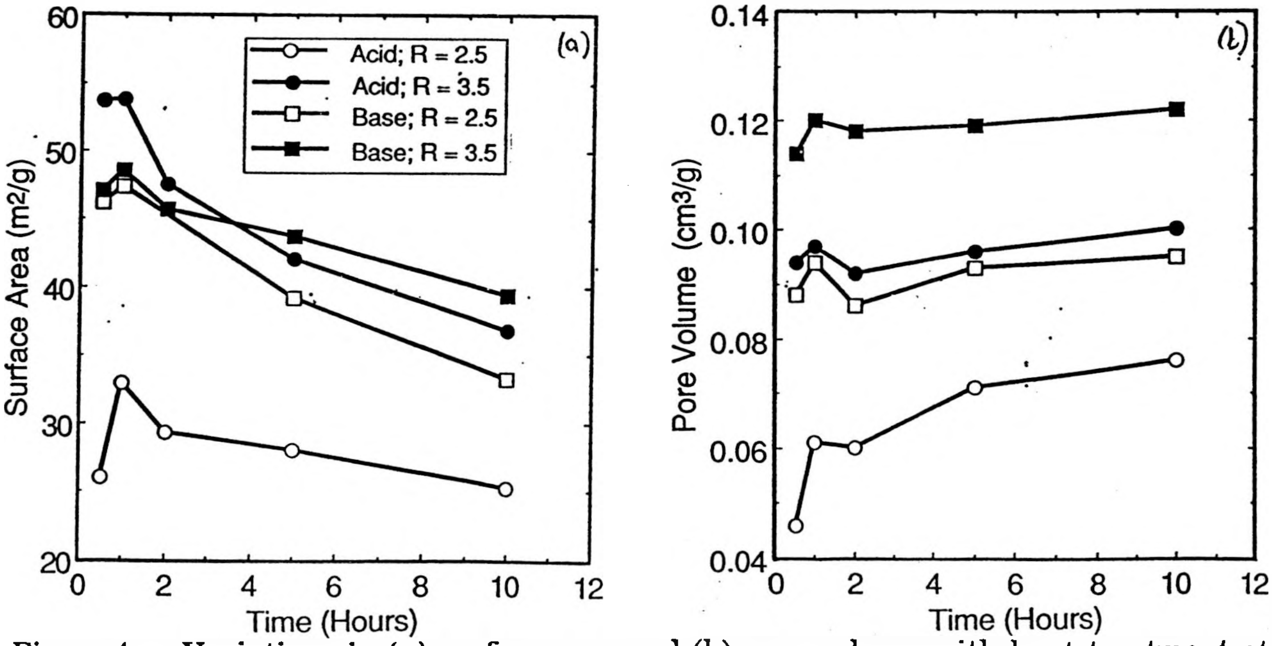

Figure 4. Variations in (a) surface area and (b) pore volume with heat treatment at 410°C.

gels were studied. Results are given in Figure 4 for the variations in surface areas and pore volumes associated with heat treatment at 410°C. While the materials were amorphous (to X-rays) for the shorter heat treatment times, all materials heat treated for 10 hours were at least partially crystallized. As can be seen in the figure, differences present in the desiccated gels still existed following the onset of crystallization. While the surface areas (Figure 4a) of the materials decreased slightly with prolonged heat treatment at 410°C, the surface areas still varied from approximately 25 to 40 m^2/g, depending on the initial hydrolysis conditions. The pore volumes of the partially crystallized materials (Figure 4b) were also dependent on the hydrolysis conditions. All of the materials retained significant pore volumes following the onset of crystallization, irrespective of the hydrolysis conditions. While materials at this stage of the processing cycle were thus relatively porous, slightly higher temperatures were apparently sufficient to promote densification (see below).

While considerable porosity was present in the amorphous $PbTiO_3$ prepared by heat treatment at 400°C followed by quenching (Figure 5a), gels heated to 450°C for 10 hours (Figure 5b) showed that not only crystallization, but also substantial densification, occurred. Thus, within this narrow temperature range, both structural rearrangement on an atomistic scale, i.e., crystallization, and rearrangement on the microstructural scale, i.e., densification, took place. The implication of this result is that since both crystallization and densification occur at low temperatures, low temperature fabrication of ceramic monoliths should be feasible, with the use of appropriate drying conditions.

The effects of hydrolysis conditions on the microstructures of gels fired at 700°C (for 60 min.) were characterized by SEM. Results are shown in Figure 6 for fracture surfaces of an acid low water gel (Figure 6a) and a base high water gel (Figure 6b). Even at this stage of the processing cycle, minor effects of the initial hydrolysis conditions were present. For example, the gel (ceramic) prepared under acidic, low water

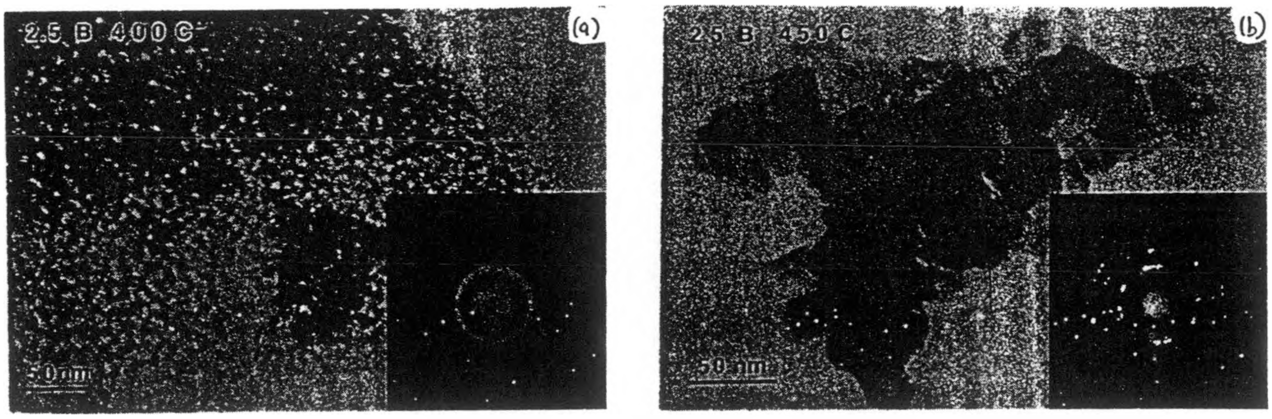

Figure 5. TEM photomicrographs of: (a) amorphous $PbTiO_3$ (400°C heat treatment; Hydrolysis Conditions: Base; R = 2.5); and (b) crystalline $PbTiO_3$ (Heat treatment: 450°C, 10 hours; same hydrolysis conditions).

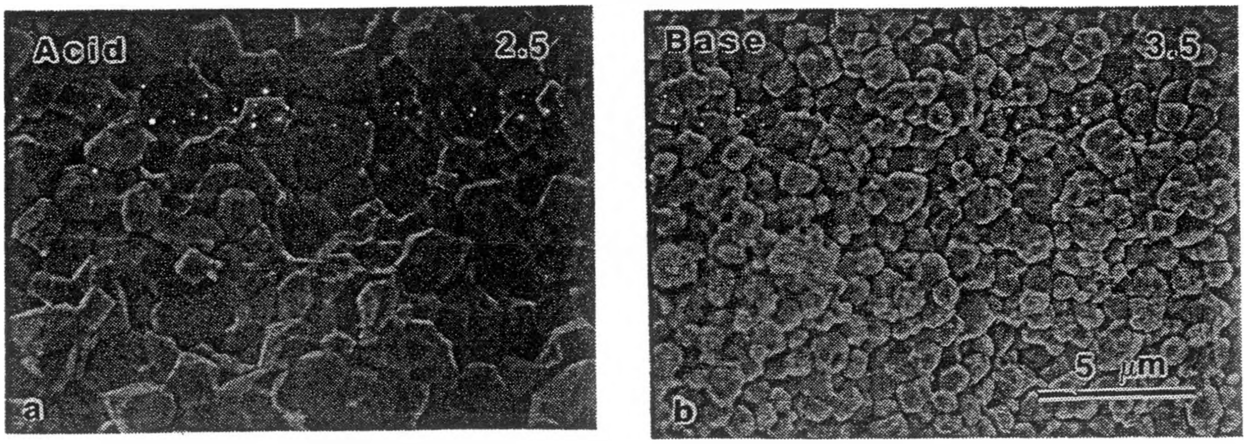

Figure 6. SEM fracturegraphs of fired $PbTiO_3$ microstructures: (a) acidic gel, R = 2.5; and (b) basic gel, R = 3.5. Heat treatment: 700°C, 60 min.

conditions had a larger grain size (~1.5 μm) and appeared less porous than the gel prepared under basic, high water conditions (grain size ~0.9 μm). Investigations of polished sections are required to determine if there is really a true difference in the porosity content of the two materials. The dense uniform microstructure of the ceramic prepared under acidic low water conditions (Figure 6a) indicates that the temperatures required to fabricate dense ceramics by sol-gel processing (i.e., 700°C) are considerably lower than those used in the processing of co-precipitated PLZT powders (i.e., ~1100°C) [11].

CONCLUSIONS

Variations in the surface areas and porosity characteristics of desiccated $PbTiO_3$ gels, induced through control of the hydrolysis conditions, were studied as a function of heat treatment, i.e., after the gel-to-glass and glass-to-ceramic transformations. Differences in the physical properties of the desiccated gels persisted into the pure amorphous state, following pyrolysis of residual organic constituents. Differences in the skeletal structures of the amorphous materials were also noted, but were observed to decrease with prolonged heat treatment at temperatures near Tc. The heat treated (amorphous) gels were relatively porous, and the onset of crystallization prior to complete densification was observed. Studies are currently in progress to determine if it is possible to completely densify the amorphous materials (at lower temperatures) prior to crystallization. Minor differences in crystalline ceramics prepared under the various hydrolysis conditions were also evident.

ACKNOWLEDGEMENTS

We acknowledge the support of the U.S. Department of Energy under contract DMR DE-AC02-76ER01198. The use of the facilities of the Center for Electron Microscopy, the Materials Research Laboratory, and the Center for Cement Composite Materials is gratefully acknowledged. We also thank D. J. Eichorst and L. F. Francis for helpful technical discussions.

REFERENCES

1. K. D. Budd, S. K. Dey, and D. A. Payne, in Better Ceramics Through Chemistry II, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. 73, Pittsburgh, PA 1986) pp. 711-716.
2. C. J. Brinker and G. W. Scherer, J. Non-Cryst. Sol., 70, 301 (1985).
3. C. J. Brinker and G. W. Scherer, in Ultrastructure Processing of Ceramics, Glasses and Composites, edited by L. L. Hench and D. R. Ulrich (John Wiley & Sons, Inc., New York, 1984), pp. 43-59.
4. C. J. Brinker et al., in Science of Ceramic Chemical Processing, edited by L. L. Hench and D. R. Ulrich (John Wiley & Sons, Inc., New York, 1986) pp. 37-51.
5. R. W. Schwartz, D. A. Payne, and A. J. Holland, Proc. Intl. Conf. Ceramic Powder Processing Science, Oct., 1988.
6. R. W. Schwartz and D. A. Payne, in Better Ceramics Through Chemistry III, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. 121, Pittsburgh, PA 1986) pp. 199-207.
7. R. W. Schwartz, PhD Thesis, University of Illinois, 1989.
8. B. Jaffe, W. R. Cook, and H. Jaffe, Piezoelectric Ceramics, (Academic Press, New York, 1971).
9. J. F. Scott and C. A. Araujo, Science, 246, 1400 (1989).
10. C. E. Land, M. A. Butler and S. J. Martin, IEEE IEDM Tech. Digest, 251 (1989).
11. G. H. Haertling in Ceramic Materials for Electronics, edited by R. C. Buchanan (Marcel Dekker, Inc., New York, 1986) pp. 139-225.
12. S. Ramamurthi, accepted for publication in J. Am. Ceram. Soc.
13. A. R. Cooper, in Better Ceramics Through Chemistry II, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. 73, Pittsburgh, PA 1986) pp. 421-430.