2590 *Chem. Mater.* **2000,** *12,* 2590−2596

Porous Behavior and Dielectric Properties of Barium Strontium Titanate Synthesized by Sol−Gel Method in the Presence of Triethanolamine

Pramod K. Sharma,* V. V. Varadan, and V. K. Varadan

CEEAMD, 212 Earth and Engineering Science Bldg., The Pennsylvania State University,
University Park, Pennsylvania 16802

Received January 18, 2000. Revised Manuscript Received June 9, 2000

This investigation presents a novel method of preparation of barium strontium titanate (BST) from [Ba(2,4-pentadionate)-Sr(2,4-pentadionate)-Ti(OC_3H_7)$_4$-TEA-i-PrOH-water] system. Triethanolamine (TEA) was used as an additive, which prevents the precipitation of oxides from the alcoholic titanium isopropoxide solution in the presence of excess water. An increasing molar ratio of water from 4.5 to 6.5 did not show any precipitation in the precursor sols in the presence of triethanolamine. Thermal behavior of the xerogel was studied by thermal gravimetric analysis (TGA). X-ray diffraction (XRD) indicated that the pure BST phase was crystallized at 900 °C. Triethanolamine was observed to influence the porous behavior of the final powders. Pore diameter of the powder calcined at 900 °C, was increased from 0.013 μm to 0.080 μm when the molar ratio of triethanolamine increased from zero to four. Therefore, a porous powder of BST was obtained at a higher molar ratio of triethanolamine. Porous behavior was also studied with respect to water and heat treatment, and explained with the help of density measurements and scanning electron microscopy (SEM). A low dielectric constant was obtained for the highly porous BST as compared with the high value for dense material.

I. Introduction

Barium titanate ($BaTiO_3$) and its related compounds have been extensively used in the preparation of high dielectric capacitors, PTC resistors, transducers, and ferroelectric memories.[1] Nevertheless, this material is not used in its true chemical form, but rather combined with special additives to modify and improve its electrical properties. Sr^{2+} is one of the common additives to $BaTiO_3$ for varying its Curie temperature (T_c) and Co^{2+} for decreasing the high-electric field losses without affecting the ferroelectric constants.[2,3] It is to be noted that addition of strontium lowers the Curie temperature below normal ambient operating temperatures. As a result, barium strontium titanate BST ceramics are now being investigated with regard to various electronic applications. BST ceramics exhibit a number of attributes that make them useful for the fabrication of microwave phase shifters.[3] Recently, it has been found that this material has tremendous applications to tunable filters, oscillators, and phase shifting elements for directional phased-array antennas.[4−7]

$Ba_{1-x}Sr_xTiO_3$ powders can be prepared by various methods such as coprecipitation, oxalate, hydrothermal, and sol−gel method. These are the low-temperature methods of synthesizing the BST (<1000 °C). Traditionally BST is prepared by a solid-state reaction, which involves ball milling of $BaCO_3$ or BaO and TiO_2. This mixture is calcined at higher temperatures around 1200 °C.[8] Traditional methods are not suitable for the preparation of ceramics used for high performance applications because the materials have very large particle size, nonhomogeneity, and high impurity content.

Among others, sol−gel provides an alternative to the conventional synthesis methods. The sol−gel materials are transformed to ceramics by heating at relatively low temperature and have better chemical and structural homogeneity than those obtained by conventional methods. A sol is a colloidal suspension (1−1000 nm) of particles in the dispersing liquid medium. In this suspension, the dispersion phase is so small that gravitational forces are negligible and interactions are dominating by short-range force, e.g., van der Waals attractions and surface charges. Colloidal particle suspensions exhibit Brownian motions. These types of colloids can be used to generate polymers or particles from which ceramics can be obtained. The final product obtained by the sol−gel route depends on several factors such as precursor, solvent, pH, catalyst, water amount, sol temperature, stirring time, and additive.[9]

---

* Corresponding author.

(1) Haertling, G. H. *J. Am. Ceram. Soc.* **1999**, *82*, 797.

(2) Coffeen, W. W. *Ceramic Capacitors-Past,Present and Future*; Cerm. Ind., published in three parts: Nov. 1974, Feb. 1975, and June 1975.

(3) Wul, B. M.; Goldman, I. M. *Dokl. Akad, Nauk SSSR* **1945**, *46*, 157.

(4) Selmi, F.; Komarneni, S.; Varadan, V. K.; Varadan, V. V. *Mater. Lett.* **1990**, *10*, 235.

(5) Herbert, J. M. *Trans. Brit. Ceram. Soc.* **1963**, *63*, 645.

(6) Ghodgaonkar, D. K.; Hughes, R.; Selmi, F.; Varadan, V. V.; Varadan, V. K. Antenna propagation International Symposium. *Proc. IEEE* **1992**, *6*, 273.

(7) Varadan, V. K.; Ghodgaonkar, D. K.; Varadan, V. V.; Kelly, J. F.; Glikerdas, P. *Microwave J.* **1992**, *1*, 116.

(8) Bauger, A.; Moutin, J. C.; Niepce, J. C. *J. Mater. Sci.* **1983**, *18*, 3041.

10.1021/cm000041u CCC: $19.00

Table 1. Effect of Water, TEA, and Temperature on Density

molar ratio[a]					
Ba	Sr	water	TEA	*T* (°C)	density (G/cm$^{3)}$
0.65	0.35	1	1	900	3.6 (4.8 at 1200 °C)
0.65	0.35	2	1	900	3.1
0.65	0.35	3	1	900	
0.65	0.35	4	1	900	2.8 (4.1 at 1200 °C)
0.65	0.35	2	1	900	3.1
0.65	0.35	2	4	900	2.6 (3.8 at 1200 °C)
0.65	0.35	2	1	1000	3.9
0.65	0.35	2	1	1200	4.3
0.65	0.35	2	1	1300	4.6

[a] Molar ratio with respect to ($Ti(O-C_3H_7)_4$). Total volume of reactant solution using solvent was 250 mL.

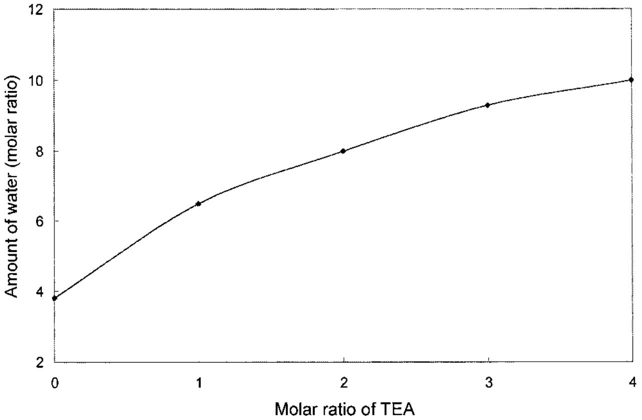

Figure 1. Effect of molar ratio of TEA on the addition of water to the sol.

Sol−gel process involves two primary processes, hydrolysis and condensation.[10] Therefore, the amount of water used during the initial processing is extremely important. A linear polymeric network is formed at the lower water concentration and a branched polymeric network is obtained at high concentration of water. Physical properties such as density, surface area, and porous behavior depend on the amount of water used during processing.[10] On the other hand, some chemicals named "additives", e.g., glycol, ethanolamines, glycerol, etc., were found to suppress the precipitation of oxides from the alcoholic solution of the metal alkoxide.[11,12] It has been found that sometimes excess water is required for a complete hydrolysis. However this excess water leads to precipitation of oxides in the solution. Therefore, larger amounts of water can be added to the sol in the presence of these additives so as to control the degree of hydrolysis of the alkoxides and subsequent polymerization reaction without any precipitation.

The goal of this study is to synthesize BST powder with low dielectric constant and low loss tangent. This paper presents an alternative sol−gel route to synthesize BST using [2,4-pentadionate precursors of Ba and Sr salt-$Ti(O\text{-}i\text{-}Pr)_4$-$H_2O$-triethanolamine-i-PrOH] system. We shall then illustrate how to control the pore size and density of the resulting BST powder by adjusting the concentration of water and triethanolamine (abridged to TEA), which are the major sol−gel synthesis parameters. The influence of water and TEA on the dielectric properties of the final powder was also studied in terms of the physical properties of the BST.

II. Experimental Section

Titanium tetraisopropoxide (1 mol) and triethanolamine (TEA), were mixed in the appropriate molar ratio (refer Table 1) with methoxyethanol solvent (100 mL) and refluxed for 1 h at 90 °C. Separate solutions of Ba and Sr were prepared by dissolving 2,4-pentadionate salts of Ba and Sr, in 100 mL of methoxyethanol. The composition of reactants are taken in molar ratio with respect to titanium tetraisopropoxide and given in the Table 1. Mild heating was required for a complete dissolution of the salts. The metal−salt solution was then transferred to the titania sol slowly. The solution was refluxed for another 6 h. The sol was then hydrolyzed by a particular molar ratio of water. It is important to note that direct addition of water leads to precipitation in the sol. Therefore, a mixture of water/solvent has to be prepared and then added to the sol drop by drop. Excess methoxyethanol was used to maintain the total volume of the reactant solution (250 mL). The resultant sol was refluxed for another 2 h for hydrolysis to complete. This sol was then kept in an oven at 90 °C for six to 7 days to obtain the xerogel.

The xerogel was studied by thermal gravimetric analysis (Delta series TGA7). X-ray diffraction was used for phase identification with a Scintag diffractometer (DMC 105) with Cu Kα radiation for 2θ from 25 to 70°. Pore size determination was made by using Micromeritics mercury porosimeter (II 9220). The density of the powder was measured by a Micromeritrics densimeter (ACCU PYC 1330). A Hitachi scanning electron microscope (3500N) was used to investigate the morphology of the materials.

For electrical measurements, each powder was pressed into a pellet under a load of 2.5 tons and was subsequently sintered at temperatures of 900, 1200, and 1300 °C for 0.5 h in air. Poly(vinyl alcohol) (3 wt % with respect to weight of the powder) was used as a binder. Ag paste was painted on both sides of the pellets, and they were dried at 90 °C for 24 h to form ohmic contact electrodes. Permittivity values at 1 kHz and 1 MHz were measured at room temperature with an impedance analyzer (HP 4192A).

III. Result

Figure 1 shows the effect of TEA on the amount of water that can be added to the sol without allowing precipitation to occur. Comparison of the various solutions resulted in the observation that the TEA stabilized the solution to precipitation. The amount of water increased significantly with increasing molar ratio of TEA.

The XRD patterns of the as-prepared and heat-treated powders (at the molar ratio of TEA and water equal to 1 and 2 respectively) are shown in Figure 2. It can be seen in Figure 2a that the as-prepared powder was amorphous. The amorphous nature of the xerogel existed at temperatures $<$ 400 °C. Peaks of $BaCO_3$ appeared when the powder was calcined at 400 °C. Upon heating to 500 °C, the crystallization of the BST powder along with the secondary phase i.e. $BaCO_3$ (at $2\theta \approx 34.7°$ and 44.7°) was evident. According to the XRD pattern (refer to Figure 2c), peaks due to the secondary phase disappeared at higher temperature.

SEM micrographs of as-prepared, 900 °C, and 1200 °C fired BST samples are shown in Figure 3a−c. Either free primary particles (<100 nm) or clusters (as a whole $<$ 1 μm) composed of several primary particles of size

---

(9) Brinker, C. J.; Scherer, G. W. *Sol−gel science: The physics and chemistry of sol−gel processing*; Academic Press: Boston 1990.

(10) Mehrotra, R. C. *Struct. Bond.* **1992**, *77*, 153.

(11) Takahashi, Y.; Matsuoka, Y. J. *Mater. Sci.* **1988**, *23*, 2259.

(12) Takahashi, Y.; Niwa, K.; Matsuki , M.; Kobayashi, K. *J. Am. Ceram. Soc.* **1987**, *95*, 942.

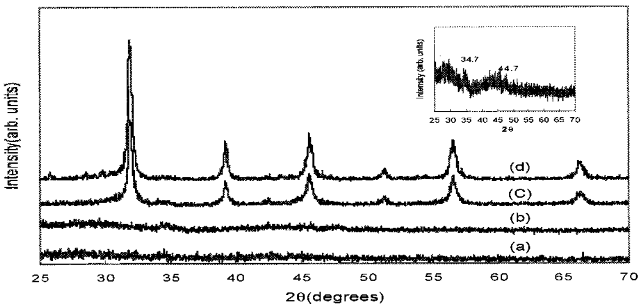

Figure 2. Xray diffraction of the powder derived with 1 molar ratio of TEA and 2 molar ratio water (a) as prepared, (b) 400 °C, (and inset) (c) 500 °C, and (d) 900 °C.

between 0.1 and 0.5 μm, were observed in the micrograph (refer to Figure 3a). These primary particles grow individually when the powder was heated at higher temperatures as shown in Figure 3b,c. The size of the particle increased when the as-prepared powder was calcined at 900 °C. Pores were also seen in the matrix at this temperature. Figure 3c is a micrograph of the sample fired at 1200 °C. Two effects were seen due to heat treatment: (A) The particle size increased to ≈600−800 nm as compared to the sample fired at 900 °C, and (B) the pores, which were observed in the sample fired at 900 °C (refer micrograph of Figure 3b) reduced in size when heated at 1200 °C.

Figure 4 shows the graphical representation of the pore size distribution (PSD) of different powders used in this investigation under different molar ratios of water. The PSD at one molar ratio of TEA and two molar ratio of water, was a monomodal curve as shown in Figure 4. The PSD has changed to bimodal at 3−4 molar ratio of water. It is interesting to note that the peaks of the distribution curve appeared at different values of pore size. This figure also illustrates that the powder with 1 molar ratio of water, contained a large percentage of fine pores as compared to other samples at [H_2O] > 1 molar ratio. The peaks in the pore size distribution curves shifted from 0.019 to 0.072 μm when the molar ratio of water was increased from 1 to 6.

Addition of TEA, results in similar behavior but the PSD is observed to be monomodal for all molar ratios unlike PSD of the powders derived at different molar ratios of water. Again macro- and mesopore were observed in all samples and shown in the Figure 5. The figure also showed that the pore size increased from 0.013 to 0.080 μm when molar ratio of TEA was increased from 0 to 4. A comparison is shown in Figure 6 for the pores generated by TEA and water.

The density of the powder produced with lower molar ratio of water and TEA was found to be higher than the one derived with higher molar ratio as shown in Table 1. Density of the powder was increased with increasing temperature from 900 to 1200 °C.

It can be assumed that the accumulation of organic in the xerogel increased with increasing molar ratio of TEA. This organic in the pores of the matrix evaporated during the heat treatment. It could be supported by our TG analysis of the powder. Two weight losses were observed in the temperature range 300−500 °C and 500−650 °C, in the TG curve (refer to Figure 7). No weight loss was observed beyond the temperature of 700 °C.

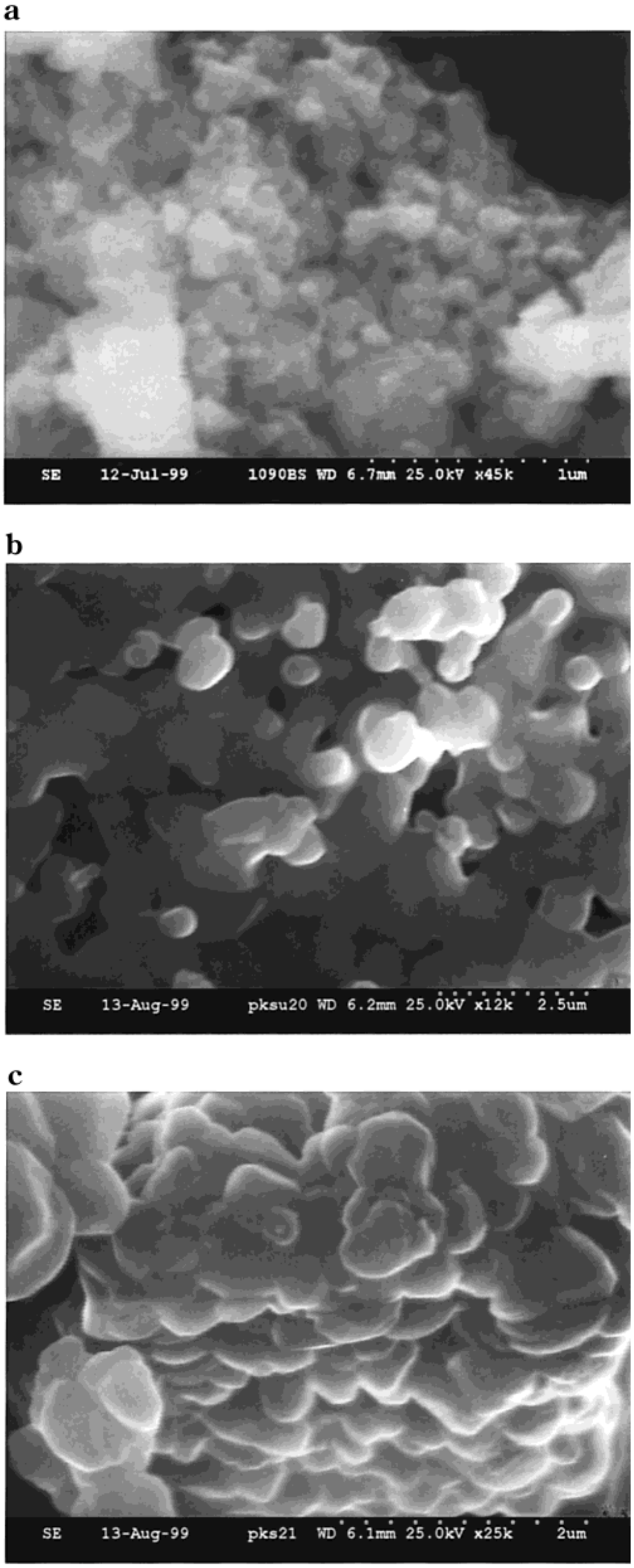

Figure 3. Scanning electron micrograph of the powder (a) as prepared, (b) 900 °C and (c) 1200 °C.

To study the effect of heat treatment on the xerogel (containing 1 and 2 molar ratio of TEA and water respectively), mercury porosimetry experiments were performed at every step of heat treatment. Figure 8 shows the effect of temperature on the pore size of the powders obtained in the presence of TEA. It can be seen in Figure 8 that the pore size increased when the

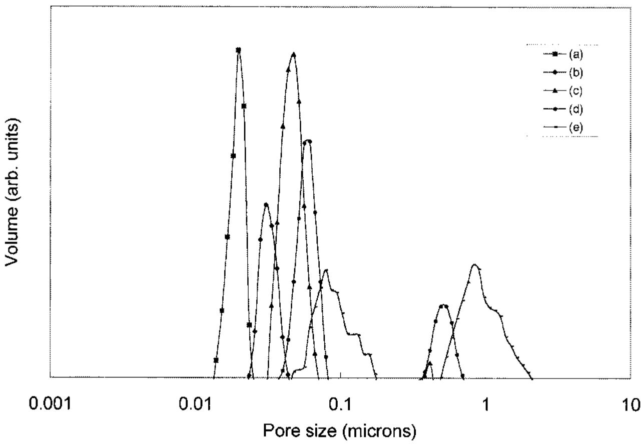

Figure 4. Pore size distribution of the powders calcined at 900 °C obtained from water (a) 1, (b) 2, (c) 3, (d) 4, and (e) 6 molar ratio.

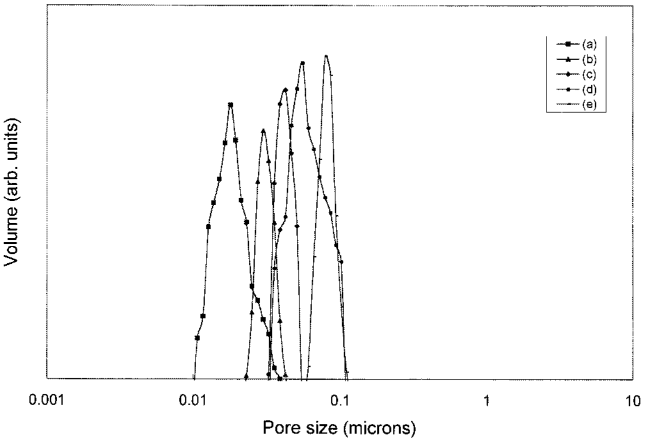

Figure 5. Pore size distibution of the powders calcined at 900 °C obtained from TEA (a) 0, (b) 1, (c) 2, (d) 3, and (e) 4 molar ratio.

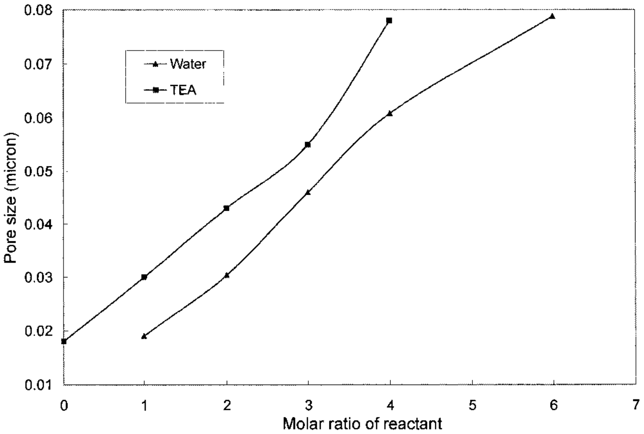

Figure 6. Effect of molar ratio of reactants on the pore size (determined by PSD peak of the powders derived with water and TEA).

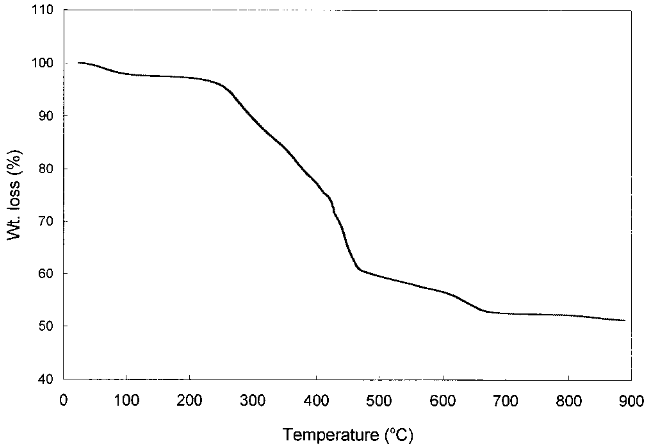

Figure 7. TGA of the powder derived with 1 molar ratio of TEA and 2 molar ratio of water.

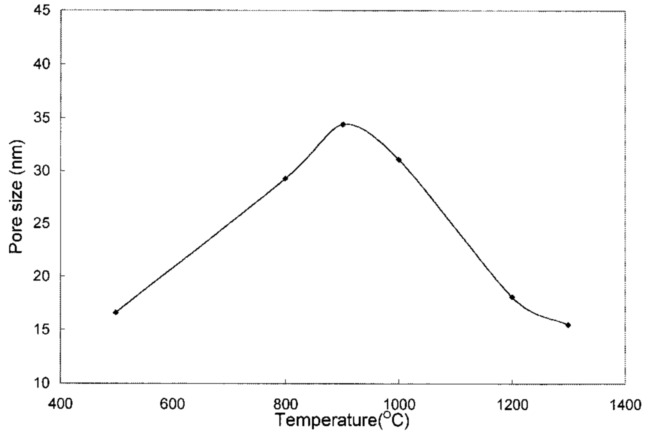

Figure 8. Effect of temperature on the pore size of powders derived with 1 molar ratio of TEA and 2 molar ratio of water.

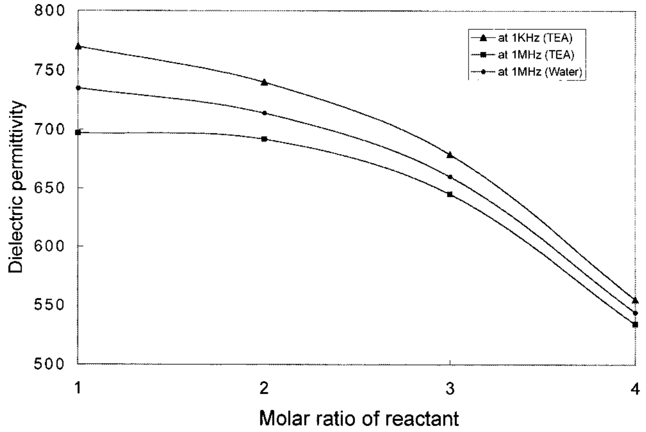

Figure 9. Variation in dielectric permittivity of the powders derived at different molar ratios of TEA (at 2 molar ratio of water) and water (at 1 molar ratio of TEA).

temperature was increased from 500 to 900 °C. However, pore size decreased when the temperature was increased further from 900 to 1200 °C and then remained constant with further increase in the temperature.

Figures 9 and 10 represent, respectively, the variation of dielectric constant and dielectric loss tangent, of the powders containing different molar ratios of TEA with 2 molar ratio of water, at 1 kHz and 1 MHz. These measurements were done at room temperature after calcining the samples at 1200 °C. Dielectric constant of $Ba_{1-x}Sr_xTiO_3$ at 1 kHz decreased with increasing molar ratio of TEA. When frequency increased from 1 kHz to 1 MHz, the dielectric constant decreased. The dielectric constant and dielectric loss tangent were also measured for the powder calcined at 900, 1200, and 1300 °C, as shown in Figures 11 and 12, respectively. The dielectric constant was 80 at 900 °C for the powder containing 1

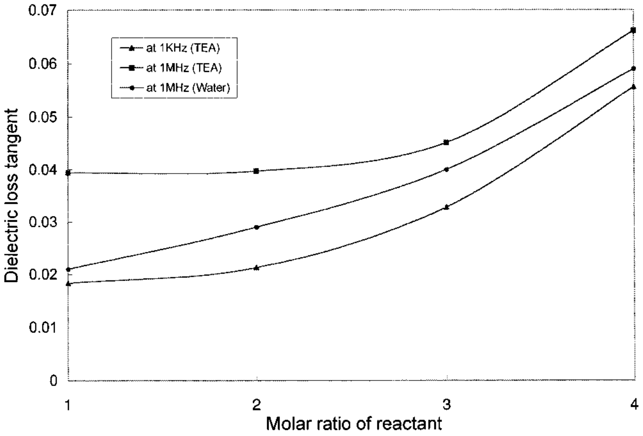

Figure 10. Variation in dielectric loss tangent of the powders derived at different molar ratios of TEA (at 2 molar ratio of water) and water (at 1 molar ratio of TEA).

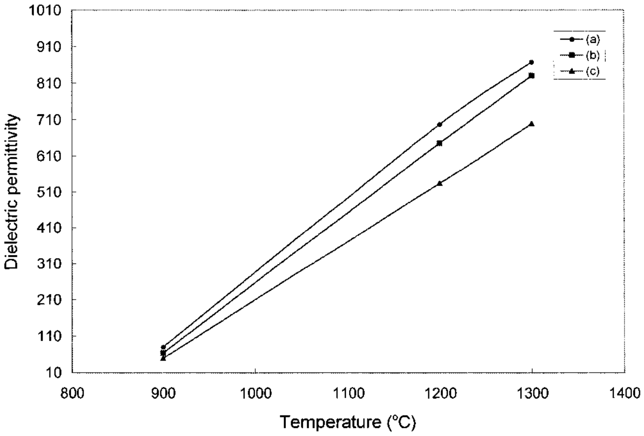

Figure 11. Variation of dielectric permittivity vs temperature at TEA (a) 1, (b) 3, and (c) 4 molar ratio at 1 MHz.

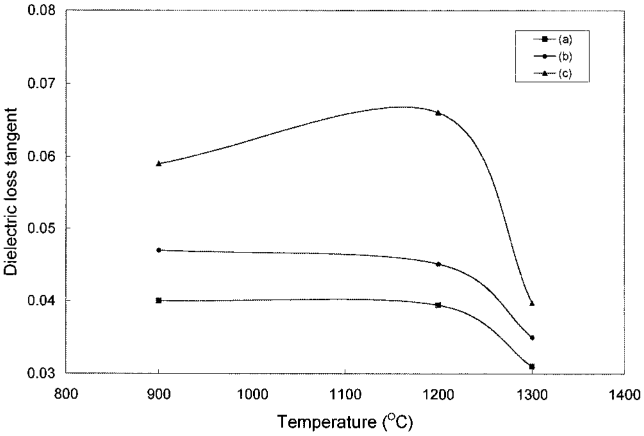

Figure 12. Variation of dielectric loss tangent vs temperature at TEA (a) 1, (b) 3, and (c) 4 molar ratio at 1 MHz.

molar ratio of TEA and increased constantly for further increase in temperature for similar molar ratio of TEA.

IV. Discussion

Water plays an important role in the formation of metal–oxide polymers by partial hydrolysis and subsequent hydrolyzed species in the sol–gel processing. It has been reported earlier that 4 mol of water are required for a complete hydrolysis of Ti(O-C_3H_7)$_4$.[13] Therefore, upon addition of excess of water (≥4 molar ratio) oxide precipitates quickly in the alcoholic solution which leads to a nonhomogeneity in the solution due to the shorter gelation time. But this solution can be stabilized by addition of TEA. It is observed that 6.5 molar ratio of water can be added to the sol solution without showing any oxide precipitation at molar ratio of TEA equal to 1 molar ratio as shown in Figure 1. Time of gelation is increased by addition of TEA in the sol. Hence this water content can be further increased with increasing molar ratio of TEA (refer to Figure 1). Two kinds of xerogels are studied which are prepared under different molar ratios of water and TEA.

The perovskite BST crystallizes at 500 °C as shown in Figure 2. The presence of $BaCO_3$ at the lower temperature is expected in the XRD studies of the samples (refer to Figure 2) since $BaCO_3$ is formed by the reaction of the crystal with atmospheric carbon dioxide during the conversion process. Presence of $BaCO_3$ is also reported by Takeuchi et al.[14] in the preparation of $BaTiO_3$. At higher temperature, the carbonate of Ba reacts with the remaining TiO_2 and forms $BaTiO_3$. Hence the peaks due to $BaCO_3$ disappear at higher temperature and a pure BST phase is obtained at 900 °C (refer to Figure 2d).

The primary particles attained a size of ≈0.5 μm at the temperature of 900 °C, were shown in Figure 3b. At this temperature, the micrograph shows that several pores distributed in the matrix compose the microstructure. This type of microstructure suggests that the clusters of particles readily sinter and densify if treated at higher temperature. These large pores can be easily eliminated either by treatment at higher temperatures or longer time. The SEM micrograph shown in Figure 3c supports the above interpretation due to the increase in size of the particles and reduction in pores with increasing temperature. This is consistent with several studies reported in the literature that the grain size increases with increasing temperature.[14,15] It is important to note that these pores did not completely disappear. Hence it can be assumed that this temperature is still lower for coalescence of finer pores. However, the particles arranged in the microstructure of Figure 3c at 1200 °C, clearly show that the large grain forming the densified matrix as compared with the microstructure of the sample fired at 900 °C. This argument can be explained with the help of porous behavior of the powder studied by mercury porosimetry and illustrated in the next section.

The pores can be categorized as micropores with width < 0.002 μm, mesopores with widths in the range of 0.002 to 0.050 μm, and macropores with width > 0.050 μm. Micropores can further be subdivided into supermicropores (from 0.0007 μm to 0.02 μm) and ultramicropores (<0.0007 μm).[16] Microprores and mesopores are two kinds of pores observed in this study due to the effect of water (refer to Figure 4). This nature of PSD with different molar ratios of water can be understood from the fact that the role of water is

---

(13) Aelion, R.; Loebel, A.; Eirich, F. *J. Am. Chem. Soc.* **1950**, *72*, 5750.

(14) Takeuchi, T.; Tabauch, M.; Aols, K.; Honjo, K.; Nakamura, O.; Suyama, Y.; Ohtori, N.; Nagasuwa, M. *J. Mater. Sci.* **1997**, *32*, 4053.

(15) Costa, M. E. V.; Mantas, P. Q. *J. Eur. Ceram. Soc.* **1999**, *19*, 1077.

(16) Pradhan, B. K.; Sandle, N. K. *Carbon* **1999**, *37*, 1323.

different during the sol processing. Brinker and coworker,[17] have observed that at lower molar ratio of water, essentially linear chains with only few cross-links resulted when tetraethoxysilane (TEOS) is hydrolyzed using a H_2O/TEOS ratio equal to 1. The studies of Strawbridge et al.[18] show that the H_2O/TEOS ratio of 2 is insufficient for complete hydrolysis. Therefore, molar ratio of the water less than 4 is expected to form linear chains. This linear chain can be assumed to influence the packing of chains during gelation and subsequent treatments, e.g., heat treatment.[18]

On the other hand molar ratio of water equal or higher than 4, may lead to a complete hydrolysis of the alkoxide. Aelion et al.[13] have found that the initial growth would still be expected via linear chain formation, but as the number of moles of water approaches to 4 molar ratio or higher molar ratio, the intermolecular reactions are more likely than intramolecular reactions. In this case, gelation occurs by the entanglement of the linear chain species.[13] Therefore, the powders derived with higher molar ratio of water have more interconnected pores between the particles or agglomerations. This is due to the fact that the PSD became broader and showed a bimodal behavior when molar ratio of the water increases to 3 molar ratio. The peak at the higher value of the pore size can be attributed to the agglomerations. The PSD of the powder with 4 molar ratio of water is observed to center at 0.5−1 μm. The study of Chen et al.[19] has shown a similar effect of water content on the pore diameter of the alumina−zirconia system. Their study clearly indicates that the pore diameter of the $Al_2O_3-ZrO_2$ system at 500 °C, increases with increasing water contents with respect to $Al(OC_4H_9)_3$.

Water content has also influenced the bulk density of the powder. It is supported by our density measurement. High value of density (≈3.6 g/cm^3) of the powder is obtained at 900 °C, which is derived at 1 molar ratio of water due to the finer pore size. This value of the density decreases to 2.8 g/cm^3 with increasing molar ratio of water due to the loose structure formed as a result of highly interconnected pores. It is consistent with the finding of Strawbridge et al.[18] that the density of silica oxide xerogels at 750 °C, is decreased from 1.8 to 1.70 g/cm^3 when molar ratio of water is increased from 2 to 10. Brinker et al.[20] have also stated that the gels prepared under the condition of slow hydrolysis exhibit extremely high bulk density due to fine pores in the structure.

Figure 5 shows that the pore size increased from 0.013 to 0.080 μm when molar ratio of the TEA is increased from 0 to 4. In fact TEA could be used as a drying control chemical additive to avoid crack formation. The additive prevents cracking, which takes place during the conversion of the wet gel to dry gel by increasing the pore size for a substantial evaporation of solvent. Hench et al.[21] and Wallace et al.[22] have already discussed the role of formamide in producing silica monoliths. They demonstrated that formamide increases pore diameter in the gel by reducing the capillary force exerted on the pore walls consisting of silica network. Later, Adachi et al.[23] and Ray et al.[24] also reported that the pore size of the monolithic gel can be increased by increasing the amount of *n*,*n*-dimethylformamide for the silica and zirconia system, respectively. Both studies are restricted to the temperature range of 60−150 °C. But the study reported in this paper indicates that the pores generated by TEA at the initial stage would also affect the final product obtained at a higher temperature.

Removal of carbonaceous species can also be observed in the TG curve (refer to Figure 7). Figure 7 shows that the weight loss in the temperature range 300−500 °C was accomplished due to the decomposition of carbonaceous matter. It is noticed that an additional 8% weight loss is observed in the powder containing 4 molar ratio of TEA for the same temperature range. Therefore, decomposition of these organics can be related to the formation of pores in the final powder. Powder with a low molar ratio of the TEA is found to have a finer pore size and hence a compact structure is obtained. This is in good agreement with our density measurement in which the highest density (≈3.1 g/cm^3) is observed in the powder, which contains 1 molar ratio of TEA. The pore sizes in the powder produced with TEA are found to be higher than the one obtained with water. The weight loss in the temperature range, 500−650 °C, is associated with formation of perovskite phase of BST.[25] This result is consistent with our XRD results.

The powder at 900 °C is observed to be highly porous. Heating at 1000 °C causes compaction in the powder and leads to finer pores of size < 0.035 μm. Pore size decreases with increasing temperature from 900 to 1200 °C as shown in Figure 8. This behavior can be explained with the help of density measurement. Density of the powder increases monotonically from 3.1 to 4.3 g/cm^3 in this temperature range. Therefore, it can be assumed that the coarser pore formed at 900 °C, may have a tendency to shrink with the temperature. This may be the initial stage of compaction of the material. It is consistent with our SEM study and illustrated in the previous section. Pore size remains unchanged when powder is heated above 1200 °C. This can be attributed to the fact that above this temperature the pores become finer and attain a size, which does not allow them to shrink anymore. Therefore, they do not add to the compaction process.

It has been observed that the highest value of dielectric constant ≈1014, decreases to the value ≈555, with increasing molar ratio of TEA from 0 to 4. Figure 9 reports a decrease in dielectric constant when frequency is increased from 1 kHz to 1 MHz. This trend of dielectric constant versus frequency is similar to that for $BaTiO_3$ reported by Kao et al.[26] However the value

---

(17) Brinker, C. J.; Keefer, K. D.; Assink, R. A.; Kay, B. D.; Ashley, C. S. *J. Non-Cryst. Solids* **1984**, *63*, 45.

(18) Strawbridge, I.; Craievich A. F.; James, P. F. *J. Non-Cryst. Solids* **1985**, *72*, 139.

(19) Chen, Y.-W.; Yen, J.-M.; Li, C. *J. Non-Cryst. Solids* **1995**, *185*, 49.

(20) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Ashley, C. S. *J. Non-Cryst. Solids* **1982**, *48*, 47.

(21) Hench, L. L.; Orcel, G. *J. Non-Cryst. Solids* **1986**, *82*, 1.

(22) Wallace, S.; Hench, L. L. *Mater. Res. Soc. Symp. Proc.* **1984**, *32*, 47.

(23) Adachi, T.; Sakka, S. *J. Non-Cryst. Solids* **1988**, *99*, 118.

(24) Ray, J.; Chatterjee, M.; Ganguli, D. *J. Mater. Sci. Lett.* **1992**, *11*, 968.

(25) Bao, D.; Wang, Z.; Ren, W.; Zhang, L.; Yao, X. *Ceram. Inter.* **1999**, *25*, 261.

(26) Kao, C.-F.; Yang, C.-L. *J. Eur. Ceram. Soc.* **1999**, *19*, 1365.

(≈1014) of dielectric constant at [TEA] = 0, is observed to be lower than the value reported by Syamaprasad et al.[27] (≈1064) at 1 kHz. In this study, the permittivity value is measured for the sample heated at 1200 °C as compared with the study of Syamaprasad et al.[27] which is heated at 1380 °C. Hence the lower value of dielectric constant in this study is due to the loose material which was not fully dense. On the other hand dielectric loss tangent increases with increasing concentration of TEA. High loss is observed with the powder derived with 4 molar ratio of TEA as shown in Figure 9. This material contains large number of pores and has a loose structure due to the low density (≈3.8 g/cm^3) in comparison with the material obtained at 1 molar ratio of TEA (≈4.3 g/cm^3). It is well-documented that the permittivity of $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ ceramic depends on the pores in the structure and density described by Costa et al.[15] and Hayashi et al.[28] respectively. Similar behavior of dielectric constant and dielectric loss tangent, is observed when the molar ratio of water is changed from 1 to 4 and measured at 1 MHz (refer to Figures 9 and 10). Thus, the results of dielectric measurement are consistent with the relationships of pore size and dense behavior of the materials. Varadan et al.[29] have shown that the dielectric constant of BST synthesized by the sol−gel method decreases from a value of 150 to 17 when the porosity is increased from 70% to 85%. The variation in the porosity of BST powder is achieved by ball milling of BST powder with graphite and then sintering at 1250 °C. Their study also states that dielectric loss tangent is porosity dependent. High loss is noticed for the powder, which has high porosity. In their study when porosity increases to 22%, dielectric loss tangent is found to reduced by 13% at 1 MHz. It has also been observed that the change in pore size is higher for any change of TEA than the powders obtained from different molar ratio of water (1−4) as shown in Figure 6. Therefore, the dielectric constant of the powders derived in the presence of TEA is lower than the powders obtained with the different molar ratios of water at the frequency of 1 MHz.

The effect of heat treatment on the dielectric constant is shown in Figure 11. This behavior can also be explained with the help of density and pore size. The lower value of dielectric constant at 900 °C can be due to the highly porous material, which is not well densified. The enhancement in the dielectric constant from 80 to 868 can be due to decrease in pore size, which leads to a densification with the temperature as shown in Figure 11. On the contrary, dielectric loss tangent decreases with increasing temperature (refer Figure 12). It is also supported by our density measurement, which showed that there was 43% enhancement in the density when temperature increased from 900 to 1300 °C. This trend of dielectric constant and loss is similar for others molar ratios of TEA. A similar kind of relation between the density and dielectric constant has been reported elsewhere.[29,30] Therefore, the goal of synthesizing BST with low dielectric constant and low loss tangent at high temperature was partially achieved. It is evident from Figures 11 and 12 that the materials with low dielectric constant had high loss tangent. Synthesizing improved the loss characteristics but increased the dielectric constant significantly. This is not surprising since porosity is decreasing with the temperature.

V. Conclusion

The amount of water, which is important for hydrolysis, can be enhanced in the presence of TEA, which itself acts as an additive. TEA inhibits oxide formation during the course of processing when a higher amount of water is added to the sol as shown in Figure 1. Water as well as TEA affect the physical properties of the final powder. Powders with large pore sizes can be achieved at the higher molar ratio of water and TEA, and hence highly porous material can be obtained at high molar ratio of water and TEA. However, the increase in pore size in the powder for a change of TEA is found to be higher than the powder for any change in water molar ratio. The change in physical properties in the powders, e.g., pore sizes and density, are observed to change the dielectric constant and loss. A low dielectric constant can be achieved for the porous powder; therefore, a different range of dielectric constant can be obtained by tailoring the pore size and compaction of the powder with the help of altering the molar ratios of water and TEA. This method offers an alternative scheme for the preparation of highly pure and homogenized BST.

CM000041U

---

(27) Syamaprasad, U.; Galgali, R. K.; Mohanty, B. C. *Mater. Lett.* **1988**, *7*, 197.

(28) Hayashi, T.; Shinozaki, H.; Sasaki, K. *J. Eur. Ceram. Soc.* **1999**, *19*, 1011.

(29) Varadan, V. K.; Selmi, F.; Varadan, V. V. U.S. Patent, 5,557,286, 1996.

(30) Stojanovic, B. D.; Pavlovic, V. B.; Pavlovic, V. P.; Djuric, S.; Marinkovic, B. A.; Ristic, M. M. *J. Eur. Ceram. Soc.* **1999**, *19*, 1061.