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Influence of Solvents on the Microstructure and Dielectric Properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ Thin Films Prepared by a Diol-Based Sol–Gel Process

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$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST, $x = 0.5$) thin films were prepared on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates using a diol-based sol–gel method. Two different solvents were employed, ethylene glycol and propylene glycol (1,2-propanediol). The influence of the solvent on the sol structure, microstructure development, and dielectric properties of BST thin films is analyzed and discussed. It is observed that films prepared with ethylene glycol show higher values of the dielectric permittivity ($\sim 40\%$ higher) and lower values of dielectric losses when compared with films prepared from propylene glycol precursors. The dielectric permittivity is 459 and 302 at 1 kHz for films prepared with ethylene glycol and 1,2-propanediol, respectively, and annealed at 800 °C. IR studies revealed that the stabilization of a titanium precursor with propylene glycol is incomplete. During the phase-formation process, a higher content of a second phase is formed for the propylene glycol-delivered films. However, microstructure analyses revealed smaller grain size and surface roughness and higher density for films prepared with ethylene glycol. These differences are attributed to the relative high boiling point and latent heat of vaporization and to the linear molecular structure of ethylene glycol. Ethylene glycol as a solvent allows for the preparation of BST thin films with improved dielectric properties.

I. Introduction

Ferroelectric thin films have been extensively studied because of the significant technological and scientific interest in their practical applications. Barium strontium titanate, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST), studied because it combines a high dielectric constant, low dielectric losses, low-leakage current density, and a composition dependent on the Curie temperature, is one of the promising ferroelectric materials. In the past decade, BST compounds have attracted much attention for their potential device applications, such as its use as the dielectric material for dynamic random access memories (DRAM),¹ uncooled infrared detectors,² gas detection devices,³ and tunable microwave applications.⁴

BST thin films have been prepared by chemical and physical deposition methods. Dielectric constants on the order of 150–600⁵ have been reported for films prepared by chemical methods, whereas values ranging from 300 to 800 were reported for films prepared by physical methods.⁶ The

observed discrepancies are related to the processing and processing variables.⁷ Moreover, the results obtained so far have shown that thin BST layers usually exhibit dielectric constants that are lower than those of the bulk.⁸ The origin of the differences has been attributed to three phenomena: an intrinsic size effect that results in a drop in permittivity with decreasing crystal dimension, a reduction in polarizability due to nonstoichiometry, and changes in polarizability caused by the biaxial strain arising from the thermal expansion mismatch with the substrate.⁹ Also, fine grain microstructure, high stresses, the presence of oxygen vacancies, the formation of interfacial layers, and the oxidation of the bottom electrode or Si are believed to be factors that can contribute to the degradation of the electrical properties of films on Si-platinized substrates compared with that of the bulk materials.¹⁰ Hence, the improvement and optimization of the processing conditions of thin films are still a key aspect from the technological point of view.

Chemical solution deposition (CSD) and particularly sol–gel processing offers some advantages in terms of low-temperature preparation, compositional homogeneity, the possibility of covering a large substrate area, cost-effectiveness, and processing simplicity when compared with the other

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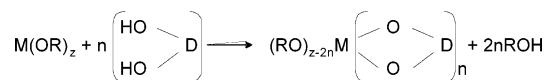
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methodologies, namely, physical deposition methods. In the sol–gel technique, the influence of the processing conditions on the chemistry of the precursors and subsequently on the properties of the obtained films is well-known,¹¹ although not fully established. Within this methodology, solvents play a key role. In the sol–gel synthesis of BST films, 2-methoxyethanol (MOE) and acetic acid are the most commonly used solvents and stabilizers. However, to avoid the use of the teratogenic MOE solvent, which represents a significant safety concern, and to inhibit its use on a manufacturing-plant scale, researchers have undertaken modifications of the process that include the employment of diols as substitutes for the former.¹² Other alternatives based on propionic acid and 1-butanol, which yield excellent films and are also not teratogenic, have been reported as well.¹³

In a diol route, also called the dihydroxy alcohol route, the dihydroxy alcohol is used as the solvent to modify the metal alkoxides. In that reaction, diols act as bridging–chelating ligands,¹⁴ replacing the alkoxy ligands and forming further bridges with other alkoxide groups, because of their second OH[−] group, which originates in large oligomer/polymer species, as is represented in Scheme 1:

Scheme 1. Chemical Reaction of Alkoxide with Diols



^a (D = dihydroxy alcohol)¹⁴

Such reactions are desirable for keeping heterometallic units during hydrolysis reactions, overcoming the poor solubility of polymeric metal alkoxides, and achieving a high homogeneity at a molecular level in multicomponent systems, which is crucial for attaining the required compositional stoichiometry of the final material.¹⁵ In the case of titanate-based systems, diol solvents form complexes with titanium precursors and their derivatives lead to the formation of long and repeated organic polymeric chains that prevent the hydrolysis and condensation of titanium species. As a consequence, the obtained solutions become sufficiently stable to allow for their being handled in air.¹⁶ Also, diol solvents present and originate the desired rheological properties (viscosity, surface tension) required for a good spin- or dip-coating processing of the solution on the substrate. For the synthesis of PZT thick films (3 μm) by sol–gel, the solvent nature (diols, such as propylene glycol, ethylene glycol, and 1,3-propanediol) was reported to influence the film quality. In this work, Lee et al.¹⁷ observed that PZT films derived from 1,3-propanediol showed a preferred (100) orientation, that the presence of second phases was avoided, and that the final properties were improved. Glycols were

also reported as being very effective as drying agents for the preparation of uniform and dense films,¹⁶ improving the cracking behavior of gel BST films.¹⁸ This is particularly significant because film uniformity and density have a major influence on the final dielectric properties of the film. However, the electrical properties of 400 nm BST films prepared with ethylene glycol reported by Giridharan et al.¹⁸ are poor, despite the improved film microstructure. On the other hand, the use of propylene glycol as a solvent for the preparation of BST films has not been reported yet, to the best of the authors' knowledge.

In the present study, the role of the diol solvents on the structure and dielectric properties of Ba_{0.5}Sr_{0.5}TiO₃ thin films prepared by sol–gel is investigated. Systematic studies on the structure of the gels, microstructure, and dielectric properties of BST films prepared with two diols, ethylene glycol and 1,2-propanediol (or propylene glycol), are conducted. The influence of the solvent on the final dielectric response is reported and discussed on the basis of the chemical features of each of the solvents.

II. Experimental Section

A precursor solution with a concentration of 0.2 M was prepared from barium acetate (Ba(CH₃COO)₂, >99.9%, Merck), strontium acetate hemihydrate (C₄H₆O₄Sr, 98%, ABCR GmbH&Co.KG) and tetra-*n*-butyl orthotitanate (C₁₆H₃₆O₄Ti, >98%, Merck). Ethylene glycol (C₂H₆O₂, >99.5%, Merck) and propylene glycol (C₃H₈O₂, >99.5%, Riedel-de Haën) were employed as solvents. Tetra-*n*-butyl orthotitanate was stabilized by the addition of the diol solvents in a 1:1 molar ratio of titanium:diol with heating for 1 h. Barium acetate and strontium acetate were first dissolved into heated glacial acetic acid (C₂H₄O₂, >99.8%, Merck) in a 1:1 M²⁺:HAc molar ratio. The HAc:diol molar ratio was 1:5. This was followed by the addition of equimolar amounts of the tetra-*n*-butyl orthotitanate solution previously modified with the solvents under constant stirring at room temperature. Finally, ethanol (C₂H₆O, >99.8%, Riedel-de Haën) was used to dilute the solution.

Thin films were prepared by spin-coating the above solution at 3000 rpm for 30 s on cleaned platinum-coated silicon substrates. The spin-coated films were heat-treated at 350 °C for 3–5 min for each deposited layer. This cycle was repeated in order to get films with a final thickness around 300 nm. The films were annealed for 1 h at different temperatures from 400 to 800 °C in an air atmosphere. The stability of the BST precursor sols was analyzed by measuring their rheological behavior using a cone and plate viscometer (Carri-med, CSL500). The structure of the precursor solutions was studied by infrared spectroscopy (FTIR, Mattson, 7000 spectrometer). The phase-evolution analysis was conducted by thermogravimetric (TG), differential thermal analysis (DTA), and X-ray diffraction (XRD, Rigaku, D/Max-B) analysis. For the TG analysis, we prepared dried powders by drying the precursor solution at 80 °C for 2 days. The morphology and thickness of the BST films were evaluated by scanning electron microscopy (SEM, Hitachi, S-4100) and atomic force microscopy (AFM, Digital-Instruments, Nanoscope III). For electrical characterization, gold electrodes (Ø ≈ 0.6 mm) were sputtered on the surface of the film using a shadow mask to form metal–insulator–metal (MIM) capacitors. The dielectric permittivity and loss factor were measured at different frequencies between 100 Hz and 1 MHz at room

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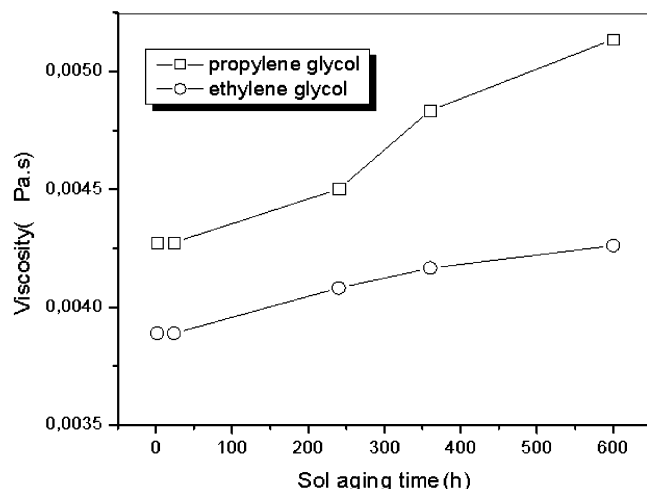


Figure 1. Viscosity vs sol aging time.

temperature. The capacitance–voltage (C–V) behavior was evaluated with a Hewlett-Packard LCR meter (HP 4284A) impedance/gain analyzer, using a small ac signal of 0.2 mV at 5 kHz. All the measurements were performed at room temperature.

III. Results

Figure 1 shows the variation of the sol viscosity with aging time for the precursor solution with ethylene glycol and propylene glycol solvents. The ethylene glycol precursor sol has a more stable behavior with time. After the solution was aged for 600 h, the viscosity variation was less than 10% for the ethylene glycol solution compared with 20% variation obtained for the propylene glycol precursor sol. The higher viscosity variation for this last precursor might be caused by the continuous condensation reactions and agglomeration of polymeric species from the fast hydrolysis rates.

Figure 2 shows the infrared spectra of fresh precursors prepared with the two diol solvents. Both spectra present similar features in the frequency range between 2000 and 500 cm^{-1} . The bands in the frequency range 1550–1400 cm^{-1} correspond to the asymmetric and symmetric COO stretching vibrations of the acetate ligands. The bands around 1714 and 1260 cm^{-1} might correspond to the formation of esters during the condensation reaction between the diol solvent and acetic acid in the preparation process. The bands between 800 and 500 cm^{-1} are mainly attributed to the formation of metal oxides (M–O: Ba–O, Sr–O, Ti–O). However some significant differences can be observed in these spectra. In the spectrum of the propylene glycol stabilized precursor, a shoulder band at 1137 cm^{-1} is observed that it is not present in the ethylene glycol one. This peak corresponds to Ti(–OR), indicating that the alkoxy groups of $\text{Ti}(\text{O}_i\text{Bu})_4$ are still present and are not completely removed when propanediol is used. In addition, in the same spectrum, a small band around 739 cm^{-1} appears that might be assigned to the Ti–O–Ti linkage formation by expanding the coordination of Ti; this also indicates that propylene glycol is not completely effective in stabilizing this alkoxide.¹⁴

TG spectra are shown in Figure 3. Similar curves were obtained, although it is clearly seen that for the ethylene glycol derived spectra, the total weight loss is less than that for the propylene glycol derived dried gel. The weight losses

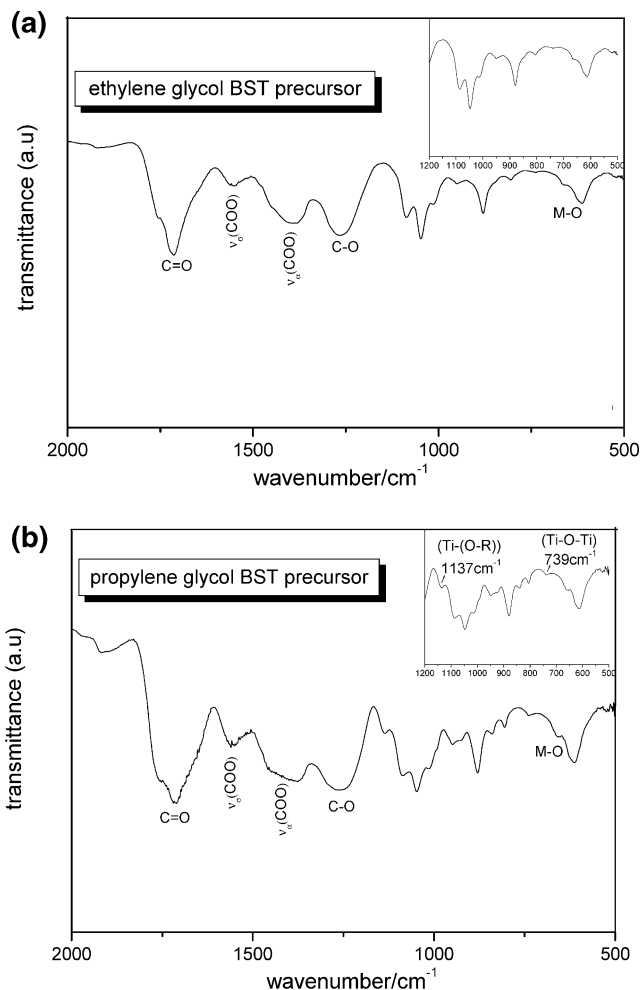


Figure 2. FTIR spectra of diol-sols obtained at the last preparation step for both glycol-derived gels: (a) ethylene glycol derived BST sol and (b) propylene glycol BST sol.

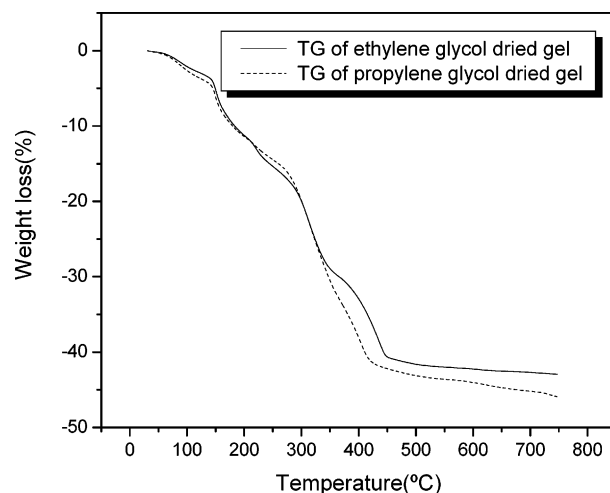


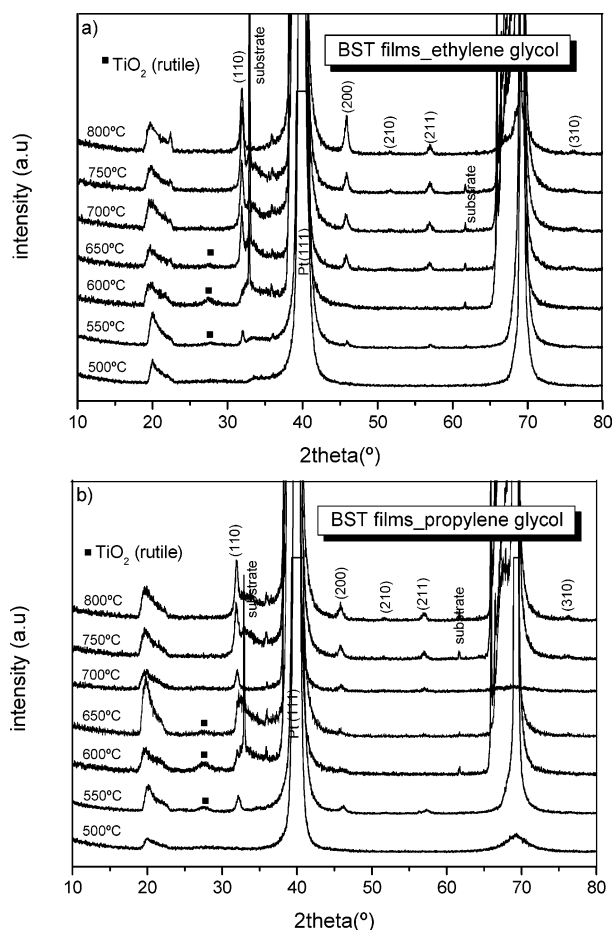
Figure 3. (a) TG of dried gels; (b) DTA of dried gels.

observed in the temperature range between 200 and 400 °C are attributed to the decomposition of most of the organic species. No more weight loss is observed in the range 400–700 °C that corresponds to the phase-crystallization step.

The phase-formation process was investigated by XRD analysis. XRD patterns of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films prepared with ethylene glycol and propylene glycol solvents and annealed at different temperatures are depicted in Figure 4. Below

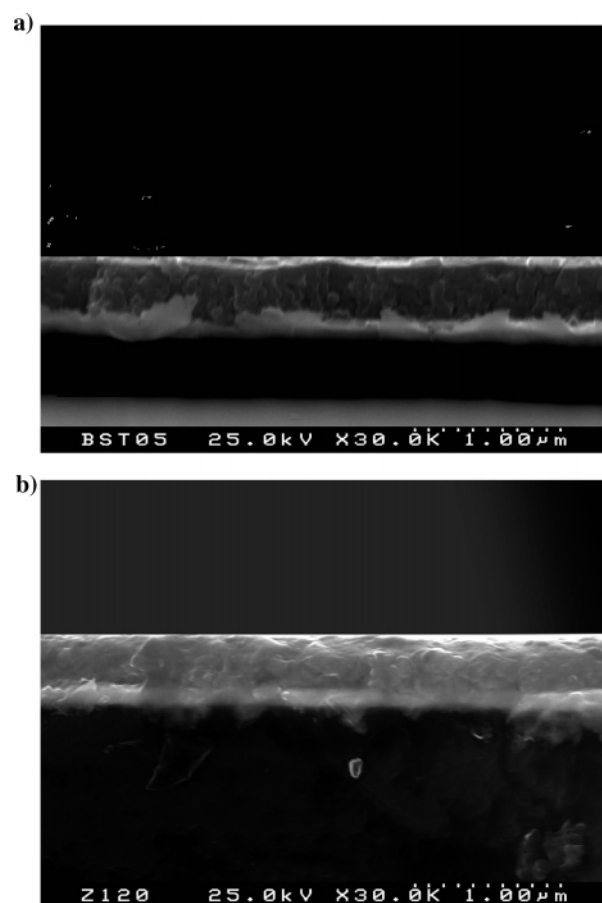
Table 1. Summary of the Dielectric Response of BST Films Prepared by Different Deposition Methods

composition	method	thickness (nm)	dielectric permittivity	dielectric losses	ref
Ba _{0.5} Sr _{0.5} TiO ₃	sol–gel ethylene glycol	~350	459 (1 kHz)	0.07	this work
Ba _{0.5} Sr _{0.5} TiO ₃	sol–gel propylene glycol	~390	302 (1 kHz)	0.1	this work
Ba _{0.5} Sr _{0.5} TiO ₃	sol–gel 2-methoxyethanol	1100	133 (10 kHz)	0.053	Irzaman et al. ²⁰
Ba _{0.5} Sr _{0.5} TiO ₃	excimer laser ablation	500	467 (100 kHz)	0.02	Saha et al. ²¹
Ba _{0.5} Sr _{0.5} TiO ₃	sol–gel butanol:water	~250	~400 (Hz ^a)	^a	Gust et al. ²²
Ba _{0.7} Sr _{0.3} TiO ₃	sol–gel HAc, 2-methoxyethanol ethylene glycol (additive)	120	400 (100 kHz)	0.024	Giridharan et al. ¹⁸

^a Value was not reported in reference.**Figure 4.** XRD of BST films: (a) ethylene glycol derived and (b) propylene glycol derived.

550 °C, BST films are amorphous. At 550 °C, the gel films crystallize and an intermediate phase TiO₂ (rutile) was identified. At 700 °C, the pure perovskite structure was detected for both kinds of gels. Above 700 °C, the intensity of the peaks corresponding to the perovskite phase of films prepared with ethylene glycol increased when compared with those of films prepared with propylene glycol, suggesting an enhanced crystallinity for the former films, despite the small differences in the film thickness. A preferential (*h*00) orientation is observed for the ethylene glycol films when the annealing temperature is increased from 700 to 800 °C.

Figure 5 presents the cross sections of BST films prepared with glycol solvents. Dense and uniform films were obtained. The thickness measured by SEM was 350 and 390 nm for BST films prepared from ethylene glycol and propylene glycol, respectively. The disparity in the thickness might be related to the precursor viscosity difference, as shown in Figure 1 and Table 2. Although none of the prepared films

**Figure 5.** Cross-section microstructure of BST films prepared with (a) ethylene glycol and (b) propylene glycol solvents at 800 °C.**Table 2. Physical and Chemical Data of Ethylene and Propylene Glycol Solvents^a**

solvent	mol wt	BP (°C)	LHV (cal/g)	η (Pa s)	d (g/mL)	ST (dynes/cm)
ethylene glycol (C ₂ H ₆ O ₂)	62.07	197.6	195	0.021	1.115	48.4
propylene glycol (C ₃ H ₈ O ₂)	76.10	188.2	170	0.045	1.04	40.1

^a BP = boiling point, LHV = latent heat of vaporization, η = viscosity, d = density, ST = surface tension.

exhibit a columnar grain type growth, as observed in other CSD prepared films,¹³ the microstructure of ethylene glycol derived films shows elongated grains in an out-of-plane direction not visible in propylene glycol films.

The microstructure differences between the two types of films become clearer in the AFM topographic analysis (Figure 6). Films prepared with ethylene glycol and annealed at 800 °C have smaller grain sizes ($G = 50$ – 100 nm) than the films prepared with propylene glycol ($G = 120$ – 180 nm). The surface roughness (RMS) for ethylene glycol derived

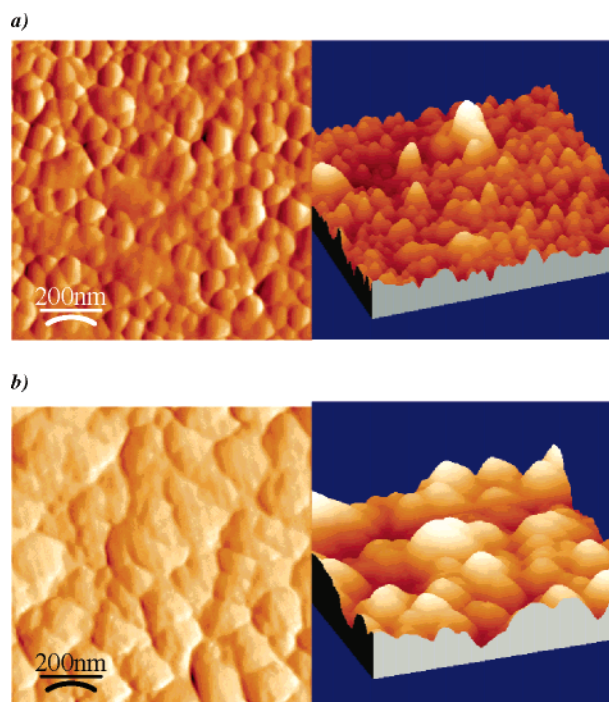


Figure 6. Topography images by AFM of BST films from glycol solvents: (a) ethylene glycol derived and (b) propylene glycol derived.

films is also lower ($\text{RMS} = 5 \text{ nm}$) when compared with values obtained for the propylene glycol derived films ($\text{RMS} = 8.14 \text{ nm}$).

The room-temperature dielectric constant and dissipation factor as a function of the frequency for BST films annealed at different temperatures for 1 h are depicted in Figure 7. Films derived from the ethylene glycol stabilized solution exhibit enhanced dielectric responses. The dielectric constant and the dissipation factor values at 1 kHz are 459 and 0.07, respectively, for films prepared with ethylene glycol and annealed at 800°C . For equivalent films prepared with propylene glycol, the dielectric constant and the dissipation factor are 302 and 0.10, respectively. The effect of the annealing temperature on the dielectric constant at 1 kHz for BST films prepared with both solvents is clearly seen in Figure 8. Increasing the annealing temperature from 600 to 800°C leads to an increase in the dielectric constant for films prepared with both solvents, as expected, with the dielectric constant values for BST films prepared with ethylene glycol solvent always higher than for those prepared with propylene glycol. An increase in the dissipation factor to frequency values close to 1 MHz for higher temperatures may be related to space charge conductivity effects.¹⁹

The dielectric properties of the prepared films are summarized and compared with some literature reference data in Table 1. The dielectric properties reported in this work for films derived from the ethylene glycol solvent precursor are superior to those reported by Irzaman et al.²⁰ for 1100 nm BST (50:50) sol-gel films and similar to those properties reported by Saha et al.²¹ for 500 nm BST films prepared

using Excimer Laser Ablation and to those reported by Gust et al.²² for 250 nm sol-gel BST films using Ba-Ti and Sr-Ti methoxypropoxide precursors. Giridharan et al.¹⁸ also reported values of the dielectric constant, using sol-gel 70:30 BST films prepared with ethylene glycol, that are lower than the values reported here.

Figure 9 shows the dependence of the capacitance on the bias voltage of BST films prepared with both solvents and annealed at 750°C . The C - V curves suggest that both films are paraelectric at room temperature. It is obvious that the C_{max} values are higher for BST films prepared with the ethylene glycol solvent, in accordance with the dielectric permittivity curves. The capacitance changes from 1.65 to 2.05 nF with the applied voltage, in the -5 to 5 V range for BST film prepared with ethylene glycol and from 1.35 to 1.625 nF for propylene glycol derived films. The C - V curves are asymmetrical with respect to the 0 V point, and the maximal values of capacitance C_{max} are shifted toward the negative bias region, which could be related to the difference between the top and bottom electrode work function.²³

IV. Discussion

Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$) belong to the same family of organic solvents, named diol. In diols, each alcohol functional group consists of an O atom bonded to a C atom and an H atom via σ bonds. Both the C-O and the O-H bonds are polar because of the high electronegativity of the O atom. The presence of two OH groups in these molecules increases their polar nature. This property is important in defining the boiling point and aqueous solubility. Diol compounds have quite a high boiling point and are infinitely soluble in water. The chemical and physical characteristics and the molecular structure of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$) are depicted in Table 2 and Scheme 2.

The molecular structure of ethylene glycol is linear when compared with the branched molecular structure of propylene glycol. During the stabilization process of titanium alkoxide, the linearly structured molecule of ethylene glycol will easily react with the alkoxide to form a stable precursor molecule, as was observed by IR analysis (Figure 2), and will also act as the template for a dense and linearly aligned structure of the precursor molecules. On the other hand, with the branch-structured propylene glycol molecule, the alkoxide stabilization is more difficult because of the fact that carbon chains cannot line up as close to each other as they can in unbranched chains. Hence, when the reaction with the titanium alkoxide takes place, less contact between atoms and fewer opportunities for the creation of permanent dipoles occur, leading to the following: (i) a noncomplete stabilization of the titanium precursor, as observed in IR (Figure 2;

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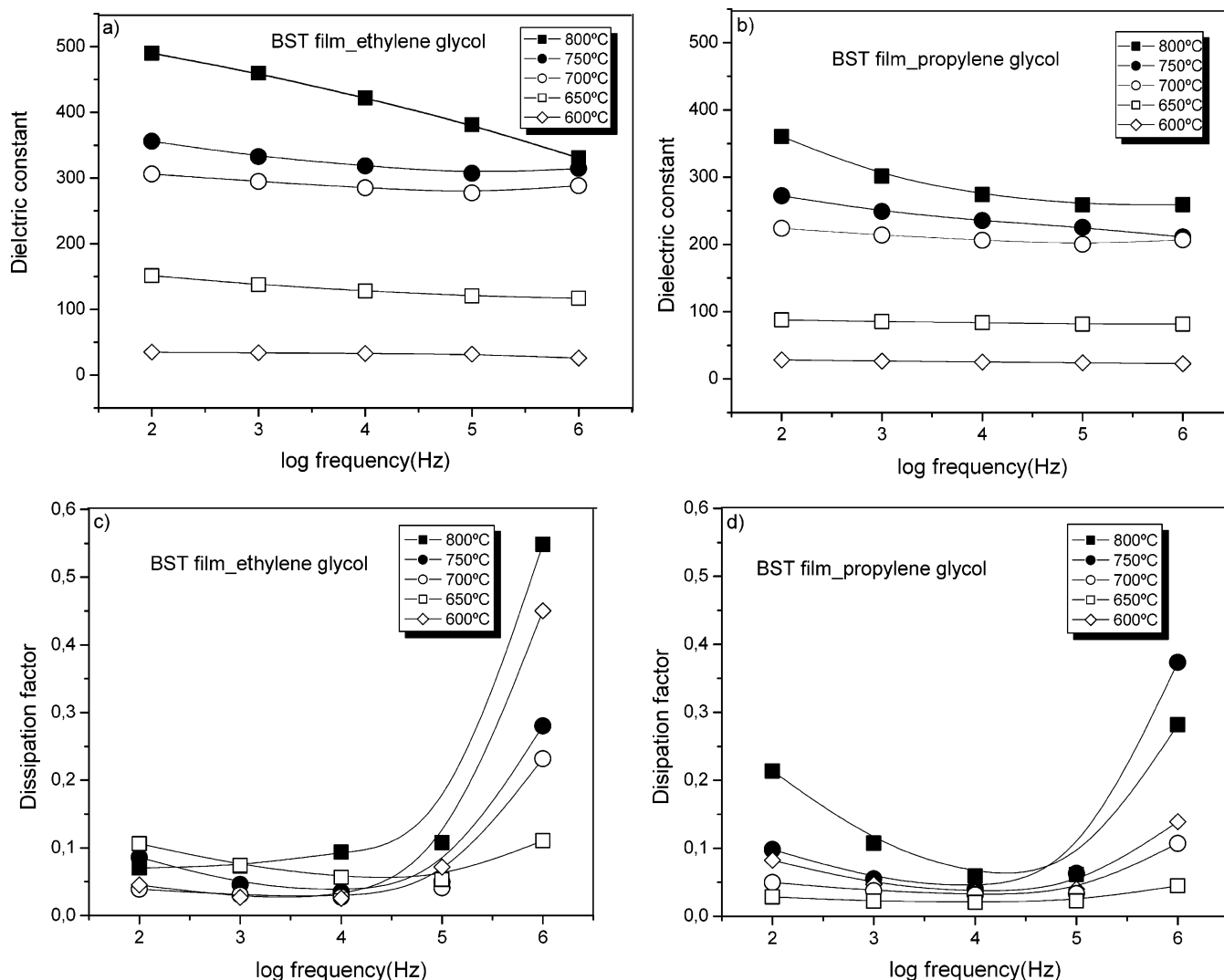


Figure 7. Dielectric constant and dissipation factor of BST films derived from ethylene glycol and propylene glycol solvents and annealed at different temperatures: (a) dielectric constant vs frequency for the ethylene glycol derived film, (b) dielectric constant vs frequency for the propylene glycol derived film, (c) dissipation factor vs frequency for the ethylene glycol derived film, and (d) dissipation factor vs frequency for the propylene glycol derived film.

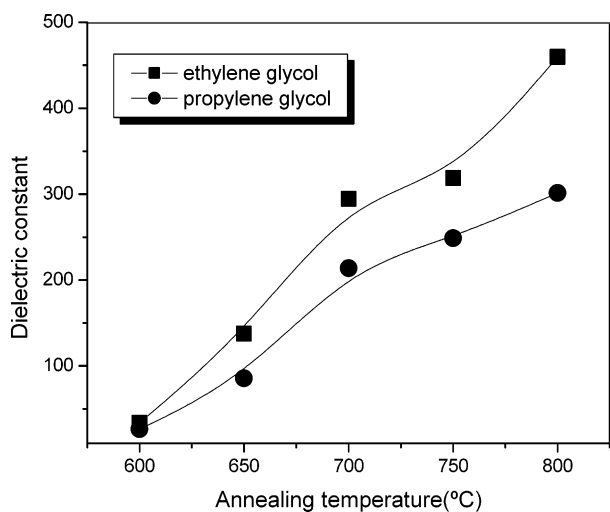


Figure 8. Dielectric constant vs annealing temperature for BST films derived from ethylene glycol and propylene glycol solvents at 1 kHz.

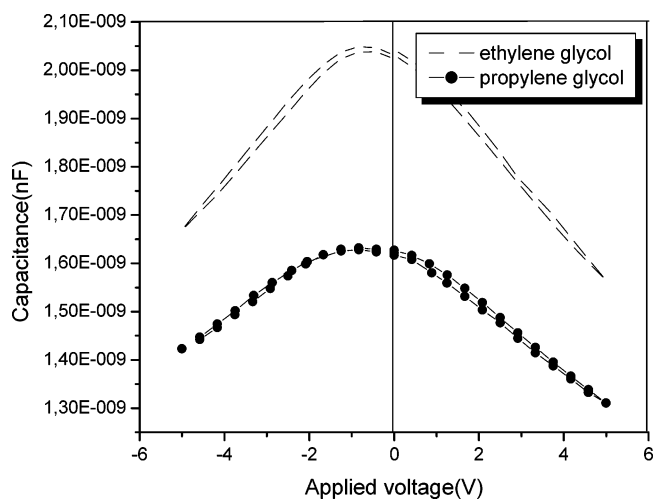
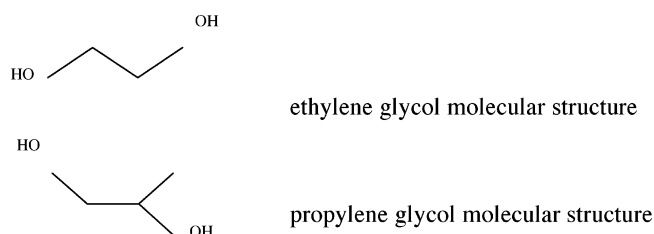


Figure 9. C-V characteristics for BST films derived from ethylene glycol and propylene glycol solvents at 5 kHz.

the band at 1137 cm^{-1} attributed to $\text{Ti}(\text{-OR})$, which was not observed in films derived from ethylene glycol, is evidence of the existence of some heterogeneities at the molecular level and of an incomplete stabilization of the

alkoxide); and (ii) a high rate of irreversible entanglement of molecules during the deposition process, which results in the formation of rigid structures that might complicate the densification of the film and later result in nonhomogeneous

Scheme 2. Molecular Structure of Diol Solvents.

microstructures. Indeed, propylene glycol derived films are less dense than ethylene glycol derived ones.

The structural differences between the studied solvents also affect the crystallization behavior of the films. Although the perovskite phase was detected at the same annealing temperature for both derived glycol films, a higher content of the second phase, identified as TiO_2 (rutile), was observed (Figure 4) in the propylene glycol derived ones. Chen et al.²⁴ also observed this intermediate phase in their sol–gel BST films and attributed it to some inhomogeneities in the solution precursor. In the present work, this intermediate phase appears at lower temperatures and in a higher concentration in films derived from propylene glycol, which somehow correlates it to the incomplete stabilization of the titanium precursor by this solvent, as observed in the IR spectra (Figure 2) and supported by the results of Chen et al.²⁴ Because the higher content of this second phase will inhibit the formation of the pure perovskite phase, the degree of crystallinity of films prepared from propylene glycol might be inferior, as was in fact observed (Figure 4). A higher degree of crystallinity is indicated by the increasing intensity of the (200) peak for ethylene glycol solvent derived films above 600 °C. Moreover, a preferential ($h00$) orientation is observed for these films heat-treated at 800 °C. As reported for lead titanate films,²⁵ the growth of longer linear polymeric chains in an ethylene glycol derived precursor may help the crystallization of the film along a certain preferential crystallographic direction, in this case ($h00$).

On the other hand, the structural and chemical differences between ethylene and propylene glycol are also reflected in the film's microstructure. In comparison, ethylene glycol has a higher boiling point and latent heat of vaporization than propylene glycol (Table 2), which is related to its linear molecular structure, in which atoms have more contact between them and thus have more opportunities to create induced or permanent dipoles. The high boiling point and latent heat of vaporization of ethylene glycol might be a benefit for film densification. By avoiding a large change of volume when the wet solution is fired into inorganic oxides during the annealing process, ethylene glycol will reduce the defect formation tendency in the films, as reported.^{18,26} Moreover, the organic decomposition of ethylene glycol precursors is lower (Figure 2). On the other hand, for films derived from propylene glycol, the rapid vaporization of the solvent may favor the capture of some

porosity within the bulk of the film and the creation of defects. This fact is also evidenced in the surface roughness of the obtained films. Films prepared with ethylene glycol present a smaller grain size and a less-rough surface than the films prepared with the propylene glycol solvent. The film surface roughness is important for device performance, because dielectric properties depend not only on a well-defined microstructure but also on the quality of the electrode–film interface.²⁷ A smooth film surface will promote intimate contact between the film and electrode metallization, resulting in lower electric losses. Because of the ethylene glycol derived films' linear molecular structure, the interpenetration and rearrangement of polymeric species during pyrolysis and, later, the crystallization process was favored. This permits it to form a dense and well-aligned crystal structure in the films, which reduces the surface roughness. This is unlike what happens in propylene glycol derived films, in which rigid and entangling polymer species tend to be formed because of its branched molecular nature, which increases film roughness.

Finally, the more-homogeneous and defect-free microstructure of the films prepared from the ethylene glycol precursor gives better dielectric properties. Indeed, films prepared from the ethylene glycol derived precursor with a smaller grain size, denser microstructure, and a less-rough surface exhibit an improved dielectric response. The increase in the ($h00$) orientation can also account for the better dielectric properties, as was observed by Majumder et al.²⁸ in the synthesis of oriented BST films by the sol–gel method. This preferential orientation might be related to the surface energy, which can promote the change of the preferred orientation from random to the ($h00$) direction for temperatures above 600 °C. Indeed, in the perovskite structure, the [100] plane is a closely packed oxygen plane that has the lowest surface energy.²⁹ On the other hand, the fact that the linear molecular structure of ethylene glycol favors the interpenetration and rearrangement of polymeric species during pyrolysis and later in the crystallization process might lead to the growth of a chained structure with a relatively higher degree of preferred orientation in these films.

V. Conclusions

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films were prepared by a diol sol–gel method using ethylene glycol and propylene glycol as solvents. It was observed that the chemical and physical properties of these solvents led to differences in the microstructure and final electrical response of the obtained films. During the phase-formation process, a lower content of the second phase was formed for films derived from ethylene glycol. Microstructure analysis revealed smaller grain size, a more-homogeneous and denser microstructure, and a less-rough surface for these films. Also, an increment of the ($h00$) orientation was developed at high temperatures for the referred films. As a consequence, thin BST films prepared

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with ethylene glycol show enhanced values of dielectric constant and lower values of dielectric losses when compared with films prepared from propylene glycol stabilized solution. Because of the linear molecular structure of ethylene glycol, the interpenetration and rearrangement of polymeric species during pyrolysis and later in the crystallization process is favored. The higher boiling point and latent heat of vaporization of ethylene glycol favors the retention of the atom mobility, reducing the defect-formation tendency. This permits us to obtain films with a dense and defect-free microstructure, to reduce the surface roughness, and to enhance the preferred orientation. In contrast, in propylene glycol derived precursors, rigid and entangling polymer species tend to form because of its branched molecular

nature, which promotes defect formation and an increase in the film roughness. The lower boiling point and latent heat of vaporization of propylene glycol and the higher organic content to be released favor the porosity entrapment in the film microstructure. Consequently, poorer dielectric properties were obtained for these films. It was shown that for the dio-based sol-gel process, ethylene glycol allows for the preparation of BST films with improved dielectric properties.

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