Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2009, Article ID 928545, 6 pages
doi:10.1155/2009/928545

Review Article

Dielectric Spectroscopy Analyses of $SrBi_4Ti_4O_{15}$ Films Obtained from Soft Chemical Solution

A. Z. Simões[1] and C. S. Riccardi[2]

[1] *Universidade Federal de Itajubá—Unifei, Campus Itabira, Rua São Paulo, 377, Bairro: Amazonas, 35900-37 Itabira, MG, Brazil*
[2] *Laboratório Interdisciplinar em Cerâmica, Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista, Bairro: Quitandinha, 14800-900 Araraquara, SP, Brazil*

Correspondence should be addressed to A. Z. Simões, alezipo@yahoo.com

Received 22 June 2009; Revised 14 September 2009; Accepted 9 October 2009

Recommended by Zoe Barber

$SrBi_4Ti_4O_{15}$ (SBTi) thin films were deposited by the polymeric precursor method on Pt bottom electrodes. The obtained films were characterized by X-ray diffraction, scanning electron microscopy, Raman spectroscopy, and dielectric spectroscopy analyses. The capacitance-voltage (C-V) characteristics of perovskite thin film showed normal ferroelectric behavior. The remanent polarization and coercive fields were 5.4 μC/cm^2 and 85 kV/cm, respectively. Dielectric spectroscopy was employed to examine the polycrystalline behavior of ferroelectric material and the mechanisms responsible for the dielectric performance of the thin film.

1. Introduction

Dielectric thin films have attracted much attention mainly due to the possibilities for applications in various electronic devices, especially such as memory cell capacitors. Dielectric films usually have rather poor electrical properties when compared with bulk crystalline materials. For polycrystalline devices, grain boundaries, twin boundaries, or dislocation networks, all of them possessing space charge nature, appear to be the major elements contributing to the total dielectric response. This is because microstructural and electronic control of the latter can be effectively performed by high-temperature annealing as well as impurity doping, whereas for thin-film materials many restrictions apply, that have their origin in deposition processes and heat treatments. In recent years, ferroelectric thin films have attracted much attention because the progress of sophisticated thin film processing methods and materials. This allows integration of ferroelectric thin films in a complementary metal oxide semiconductor circuits (CMOS) as high-speed nonvolatile ferroelectric random access memories (NVFRAM) [1–3]. Understanding the nonlinear conduction behavior in ferroelectric thin films is critical to accurate analysis of the nonlinear ferroelectric-based properties such as permittivity and polarization hysteresis.

Bismuth layered perovskites belonging to the Aurivillius family, denoted $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n-1})^{2-}$, where $n = 2, 3, 4,$ and 5, have received attention as ferroelectric materials with excellent fatigue-resistant properties [4]. These materials are constructed by stacking n perovskite units between $(Bi_2O_2)^{2+}$ layers. Among them $SrBi_2Ta_2O_9$ or $SrBi_2Nb_2O_9$ and $Bi_4Ti_3O_{12}$ or $Bi_{4-x}La_xTi_3O_{12}$, which have two and three perovskite units, respectively, have been extensively studied so far [5–14]. But $SrBi_4Ti_4O_{15}$ (SBTi) thin films have some drawbacks, for example, a low Curie temperature (310°C) [15], which may induce a drift in temperature of ferroelectric properties, [16] and a high processing temperature (800°C) [4]. For the memory applications, electrical properties of thin films should be investigated thoroughly. In the thin film structure, high electric fields are produced even for low applied voltages. These high electric fields cause nonlinear electrical behaviors; especially non-ohmic characteristics. In this way, the use of impedance spectroscopy analyses is being used to study the mechanisms

responsible for the dielectric properties of polycrystalline materials, [17–20], particularly to obtain information on non-intrinsic dielectric effects. The purpose of using dielectric spectroscopy analysis [21, 22] instead of the traditional impedance spectroscopy approach is to demonstrate that dielectric complex diagrams of the frequency response of polycrystalline materials can sometimes reveal more about the relaxation processes involved with grain boundaries and dielectric dipolar relaxation than impedance diagrams can.

In previous works, our group have reported the preparation of thin films by the polymeric precursor method [23]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [24]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. The polymeric precursor method presents many advantages, such as the possibility to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments).

Considering that literature reports no data about the dielectric spectroscopy analyses of $SrBi_4Ti_4O_{15}$ thin films deposited by a spin-coating process using a polymeric solution, in this work, the main goal is to describe the response of the dielectric and non-Ohmic properties of a ferroelectric thin film.

2. Experimental Procedure

The coating solution was prepared by the polymeric precursor method, which is based on the chelation of cations with citric acid in an aqueous solution. Ethylene glycol was added to the metallic citrate formed and the heating of this mixture led to polymerization and resulted in a homogeneous resin. The viscosity of the coating solution was adjusted to 20 cPs by the controlled evaporation of water. SBTi thin films were spin coated on $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 5000 rpm for 30 seconds (spin coater KW-4B, Chemat Technology). Through this process, we have obtained thickness values of about 270 nm, reached by repeating the spin-coating and heating treatment cycles. The films were characterized by X-ray diffraction (XRD) using Cu Ka radiation (RIGAKU, 20-2000), 40 kV and 150 Ma from 10 to 60°. Microstructural characterization of the films was carried out using a scanning electron microscopy (SEM) with a TOPCOM SM-300 microscope equipped with an energy dispersive spectrometer (EDS). Raman measurements were performed using an ISA T 64 000 triple monochromator. An optical microscope with 80 X objective was used to focus the 514.5-nm radiation from a Coherent Innova 99 Ar^+ laser on the sample. The same microscope was used to collect the back-scattered radiation. The scattering light dispersed was detected by a charge-coupled device (CCD) detection system = 0.3 mm. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace under oxygen atmosphere at 300°C for 1 hour. Here, the desired effect was to decrease eventually present oxygen vacancies. The capacitance-voltage characteristic was measured in the metal-ferroelectric-metal (MFM) configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology 6000 A). The dielectric spectroscopy measurements were taken with a frequency response analyzer (HP 4294 A), at frequencies ranging from 40 Hz to 110 MHz with an amplitude voltage of 1 V.

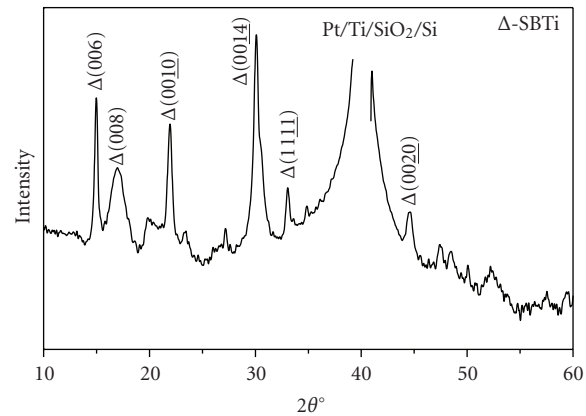

Figure 1: X-ray diffraction of SBTi film annealed deposited by the soft chemical method at 700°C for 2 hours.

3. Results and Discussion

The X-ray diffraction of $SrBi_4Ti_4O_{15}$ thin films deposited on platinum coated silicon (111) substrates and annealed at 700°C for 2 hours in static air is shown in Figure 1. Platinum coated silicon (111) substrate peak was observed in the range of $38° < 2\theta < 41°$ and no impurity phase was identified, indicating that the polymeric precursor method allows to obtain a single perovskite phase. The broad pattern revealed that the SBTi thin films were polycrystalline with a strong *c*-axis (00$\underline{14}$) orientation while non-*c*-axis orientation is the (1111) [25].

Raman spectra of SBTi film evidenced vibrational modes located at 60, 117, 270, 543, and 855 cm^{-1} (Figure 2). The modes located below 200 cm^{-1} can be addressed to different sites occupied by bismuth within the perovskite layer. On the other hand, the vibrational modes located at 270, 543, and 855 cm^{-1} result from the TiO_6 octahedral (Ti = 5 or Ti = 6). Slight changes which occur above 200 cm^{-1} can be associated to structural distortion and reduction of vibrations in the TiO_5 octahedra. The position occupied by strontium on the bismuth site within the perovskite structure has marginal influence in the interactions between the $(Bi_2O_2)^{2+}$ layers and perovskite.

Figure 3 shows the surface of the SBTi film deposited on platinum coated silicon (111) substrates and annealed at 700°C for 2 hours in static air. The grains are not uniform

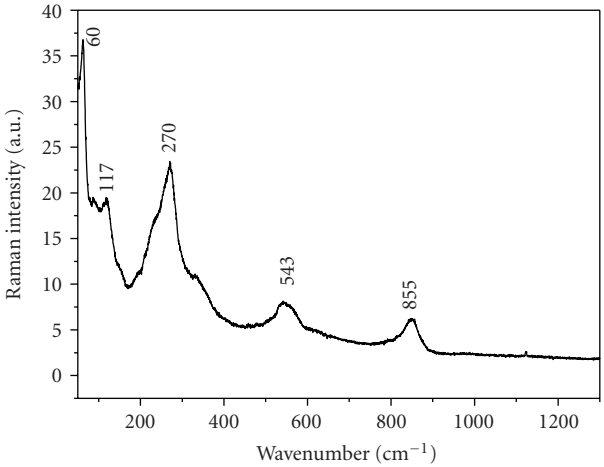

Figure 2: Micro Raman spectra of SBTi film annealed deposited by the soft chemical method at 700°C for 2 hours.

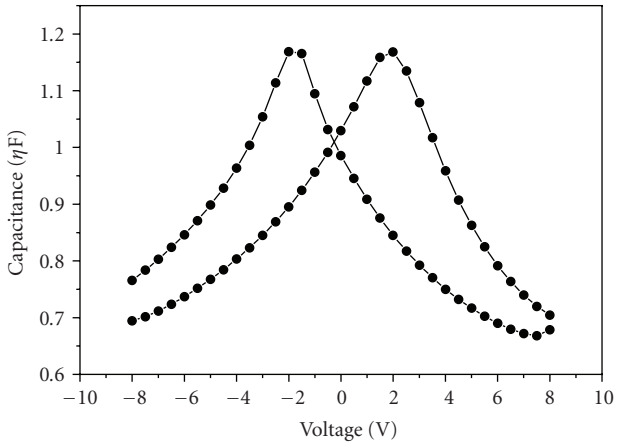

Figure 4: C-V curve of SBTi film annealed deposited by the soft chemical method at 700°C for 2 hours.

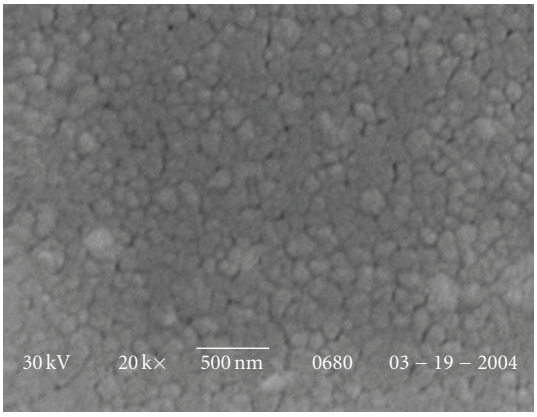

Figure 3: SEM micrograph of SBTi film annealed deposited by the soft chemical method at 700°C for 2 hours.

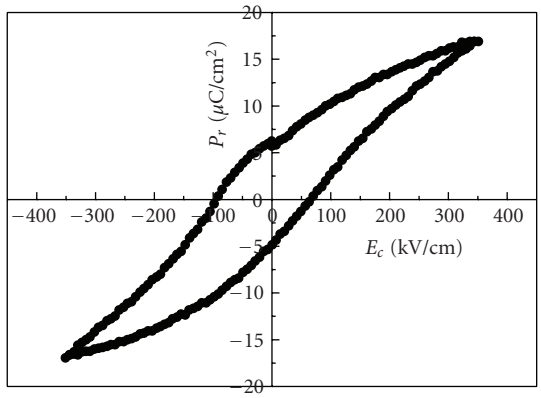

Figure 5: P-E curve of SBTi film annealed deposited by the soft chemical method at 700°C for 2 hours.

in size and there are voids among the grains. Tiny pores less than 10 nm in size are present within the grains and along the grain boundaries. The average grain size of the SBTi film was about 46 nm and is spherical in shape. The grains formed grew as single grains from the bottom electrode to the surface of film. However, SEM images do not provide clear information on the orientation of the grains. A detailed analysis reveals that the film is free of pyrochlore structure due the suppression effect of the Pt bottom. This result is in agreement with those reported in literature [26] and with those previously reported by our group [27–29].

Figure 4 displays the typical C-V curve for the MFM capacitors. Capacitance dependence on the voltage is strongly nonlinear, which confirms the ferroelectric properties of the film. The two peaks, which characterize spontaneous polarization switching, are clearly shown in Figure 4. Also, the C-V curve displays symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The capacitance changes from 0.69 to 1.16 ηF with the voltage applied in the +10 to −10 V range resulting in a dielectric permittivity calculated from C_{max} of about 175.

Figure 5 shows the polarization versus electric field (P-E) hysteresis loops of SBTi film. As can be seen, SBTi films showed poor ferroelectric properties. The hysteresis loop was not saturated even at 350 kV/cm; the remnant polarization (P_r) was only 5.4 μC/cm^2, and the coercive field (E_c) was as high as 80 kV/cm. These results were similar to those reported by Watanabe et al. [30]. Recently, Irie and Miyayama reported on ferroelectric properties of the $SrBi_4Ti_4O_{15}$ single crystals [31]. They indicated that $SrBi_4Ti_4O_{15}$ single crystals in a- and b-axis orientations showed typical ferroelectric behavior with P_r of 29 μC/cm^2, whereas dielectric behavior was observed for c-axis orientation. This indicates the remnant polarization of polycrystalline film is strongly dependent on the orientation of grains. It was reported that SBTi thin film with a lower c-axis ratio showed better saturated hysteresis loops than that with a higher c-axis ration due to the weak ferroelectricity of bismuth-layered ferroelectrics along the c-axis.

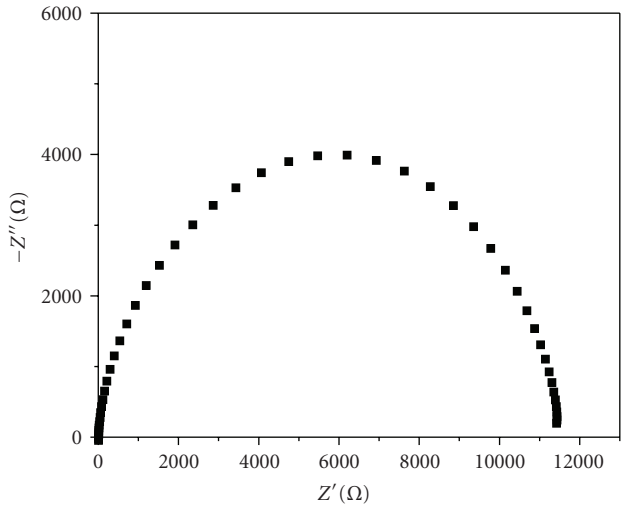

Figure 6: Nyquist diagram obtained at 300°C for SBTi film deposited by the soft chemical method and annealed at 700°C for 2 hours.

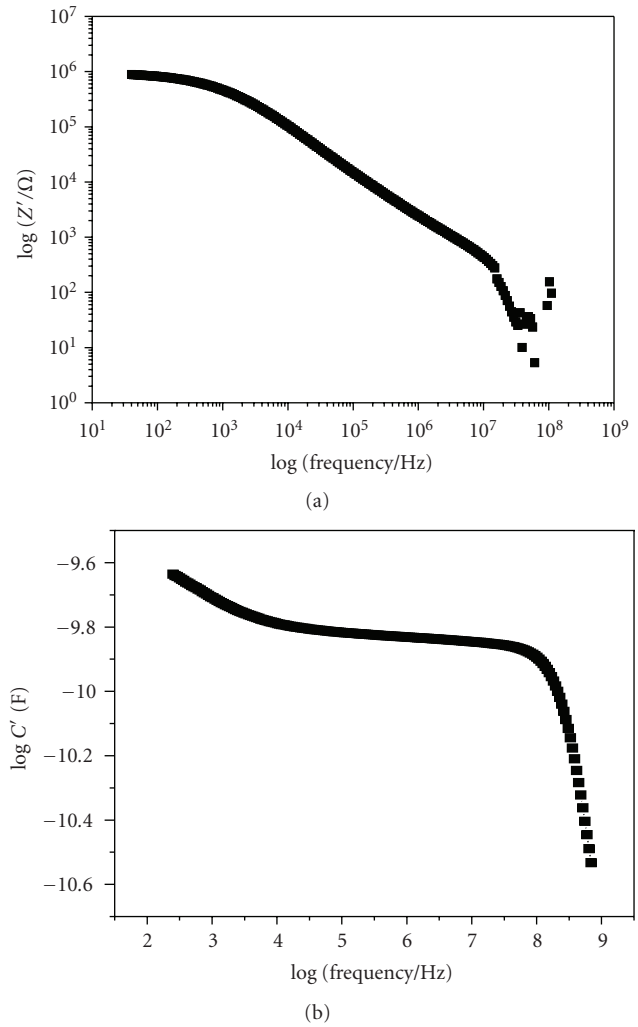

Figure 7: Bode capacitive diagrams for the SBTi film, logarithm of real part of the complex capacitance as a function of frequency.

Figure 6 illustrates the impedance spectroscopy response of SBTi film at 300°C. Usually, the conductivity of oxide materials is highly dependent upon both the carrier concentration and mobility. The semicircular arc in the complex plane yield to an arc, with the center displaced below the real axis, due to the presence of distributed elements and a relaxation process resulting from the trapped states. There exists one semicircle with a tail at the low frequency end. The semicircle is ascribed to originate from the grain boundary and nonzero intercept corresponding to the resistance of the grain, with no semicircle corresponding to electrode-sample interface. There is a relaxation relating to the grain boundary which is probably due to a Schottky-type barrier existing in this type of polycrystalline material. The Bode capacitive diagram in Figure 7 provides a better vision of the different relaxations existing in this polycrystalline system and their respective frequency ranges. The SBTi film exhibited a resistivity in the range of 10^{14}–10^{13} $\Omega \cdot$ cm when a bias voltage of 5–10 V was applied to the capacitor. The estimated low conductivity suggests that the film is a very good insulator.

Figure 7(a) shows the Bode complex impedance diagram for the SBTi film. The feature at the highest measuring frequency is characteristic of *R-L* resonance form, the measuring leads and electrode itself. On the other hand, the region of lower frequencies shows an inverse behavior. This range accounts for grain-grain junctions and controls the global conductivity response, being strongly related to the dielectric mechanism. Moreover, the complex capacitive diagram indicates that the capacitance of the electrodes is hardly affected by the structure of the ferroelectric material. Figure 7(b) shows the Bode capacitive diagrams, confirming the effects of the interface on the capacitance from intermediate to low frequencies. Such a relaxation pattern can be described by an equivalent circuit consistent with three parallel contributions: the "high frequency" limit related to grain boundary capacitances, the complex incremental capacitance at intermediate frequencies related to the relaxation of the particular structure found in the space charge region, and finally, in the low frequency region, the term representing the dc conductance of the multijunction device. The high frequency region of the complex capacitance diagrams shows the presence of a dipolar relaxation process possessing a near-Debye pattern (see Bode capacitive diagrams of Figure 7). It is important to emphasize here that, in the present discussion, because the dielectric properties may be strongly related to the a multijunction domain, [32, 33], it is inappropriate to use parameters such as dielectric permittivity or susceptibility, since it is almost impossible to know enough about the geometry, that is, the thickness of the region in question (domain boundaries existing in the grain), to determine the complex permittivity. That is why we prefer to express the response in terms of complex capacitance (C^*) instead of complex dielectric form (ε^*) [34]. Responses due the sample-electrode interfaces, which have very high polarization both due the thin film geometry of the interface

and the high charge density due to any space charge effects, are evident and appear at the lowest measuring frequencies. For practical applications, the films are preferred to be less conductive. As previously verified in early work of our group [35], the oxygen vacancies concentration is affected by the annealing atmosphere. The thermal treatment in oxidant atmosphere in materials with p-type conductivity increases defects as Bi or Ti vacancies. This results in an increase in conductivity with increasing oxygen content indicating that the mobile carriers are positively charged and that the possibility of hopping through the Bi ion can be considered. Taking into account that we have annealed the SBTi film in static air, the oxygen vacancies are ordered, avoiding oxygen ions to migrate and therefore reducing conductivity. Thus, less conditions for the trapping of electrons result in a highly resistance film.

4. Conclusions

In summary, we investigated the dielectric spectroscopy analysis of SBTi films obtained by the polymeric precursor method. The multilayer thin films consisted of fine grains of approximately 46 nm, with a film thickness of 270 nm. The C-V characteristics showed a typical butterfly loop that confirms the ferroelectric properties of the film, which are related to ferroelectric domain switching. The films showed a remanent polarization of P_r equal to $5.4\,\mu C/cm^2$ and a coercive field of equal to 85 kV/cm. The low conductivity of the SBTi film is a consequence of oxygen vacancies ordering, avoiding oxygen ions to migrate, and less conditions for the trapping of electrons. These results suggest that the technique can be adapted to produce large area thin films from a variety of materials which form stable aqueous solutions of the required chemical composition, without exposure to hazardous chemical reagents.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq, and CAPES.

References

[1] J. F. Scott and C. A. Paz de Araujo, "Ferroelectric memories," *Science*, vol. 246, no. 4936, pp. 1400–1405, 1989.

[2] O. Auciello, J. F. Scott, and R. Ramesh, "The physics of ferroelectric memories," *Physics Today*, vol. 51, no. 7, pp. 22–27, 1998.

[3] C. A. Paz de Araujo, J. D. Cuchlaro, L. D. McMillan, M. C. Scott, and J. F. Scott, "Fatigue-free ferroelectric capacitors with platinum electrodes," *Nature*, vol. 374, no. 6523, pp. 627–629, 1995.

[4] E. C. Subbarao, "A family of ferroelectric bismuth compounds," *Journal of Physics and Chemistry of Solids*, vol. 23, no. 6, pp. 665–676, 1962.

[5] Y. Kim, H. K. Chae, K. S. Lee, and W. I. Lee, "Preparation of $SrBi_2Ta_2O_9$ thin films with a single alkoxide sol-gel precursor," *Journal of Materials Chemistry*, vol. 8, no. 11, pp. 2317–2319, 1998.

[6] K. Amanuma, T. Hase, and Y. Miyasaka, "Preparation and ferroelectric properties of $SrBi_2Ta_2O_9$ thin films," *Applied Physics Letters*, vol. 66, no. 2, pp. 221–223, 1995.

[7] T. J. Boyle, C. D. Buchheit, M. A. Rodriguez, et al., "Formation of $SrBi_2Ta_2O_9$—part I: synthesis and characterization of a novel "sol-gel" solution for production of ferroelectric $SrBi_2Ta_2O_9$ thin films," *Journal of Materials Research*, vol. 11, no. 9, pp. 2274–2281, 1996.

[8] S. D. Bu, B. H. Park, B. S. Kang, S. H. Kang, T. W. Noh, and W. Jo, "Influence of the laser fluence on the electrical properties of pulsed-laser-deposited $SrBi_2Ta_2O_9$ thin films," *Applied Physics Letters*, vol. 75, no. 8, pp. 1155–1157, 1999.

[9] H. N. Al-Shareef, D. Dimos, T. J. Boyle, W. L. Warren, and B. A. Tuttle, "Qualitative model for the fatigue-free behavior of $SrBi_2Ta_2O_9$," *Applied Physics Letters*, vol. 68, no. 5, pp. 690–692, 1996.

[10] B. S. Kang, B. H. Park, S. D. Bu, S. H. Kang, and T. W. Noh, "Different fatigue behaviors of $SrBi_2Ta_2O_9$ and Bi_3TiTaO_9 films: role of perovskite layers," *Applied Physics Letters*, vol. 75, no. 17, pp. 2644–2646, 1999.

[11] B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, "Lanthanum-substituted bismuth titanate for use in nonvolatile memories," *Nature*, vol. 401, no. 6754, pp. 682–684, 1999.

[12] P. C. Joshi and S. B. Krupanidhi, "Structural and electrical studies on rapid thermally processed ferroelectric $Bi_4Ti_3O_{12}$ thin films by metallo-organic solution deposition," *Journal of Applied Physics*, vol. 72, no. 12, pp. 5827–5833, 1992.

[13] K. Tani, T. Yamanobe, H. Matsuhashi, and S. Nishikawa, "Formation of c-axis-oriented $Bi_4Ti_3O_{12}$ films with extremely flat surface by spin-coating," *Japanese Journal of Applied Physics*, vol. 36, no. 3, pp. 1460–1464, 1997.

[14] T. Kijima, S. Satoh, H. Matsunaga, and M. Koba, "Ultra-thin fatigue-free $Bi_4Ti_3O_{12}$ films for nonvolatile ferroelectric memories," *Japanese Journal of Applied Physics*, vol. 35, no. 2, pp. 1246–1250, 1996.

[15] K.-H. Hellwege and A. M. Hellwege, Eds., *Landolt-Börnstein—Group III Condensed Matter*, vol. 3, Springer, Berlin, Germany, 1969.

[16] A. Furuya and J. D. Cuchiaro, "Compositional dependence of electrical characteristics of $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ thin-film capacitors," *Journal of Applied Physics*, vol. 84, no. 12, pp. 6788–6794, 1998.

[17] D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, "$CaCu_3Ti_4O_{12}$: one-step in-internal barrier layer capacitor," *Applied Physics Letters*, vol. 80, no. 12, p. 2153, 2002.

[18] T.-T. Fang and H.-K. Shiau, "Mechanism for developing the boundary barrier layers of $CaCu_3Ti_4O_{12}$," *Journal of the American Ceramic Society*, vol. 87, no. 11, pp. 2072–2079, 2004.

[19] J. R. Macdonald, *Impedance Spectroscopy*, John Wiley & Sons, New York, NY, USA, 1987.

[20] A. R. West, T. B. Adams, F. D. Morrison, and D. C. Sinclair, "Novel high capacitance materials:- $BaTio_3$:La and $CaCu_3Ti_4O_{12}$," *Journal of the European Ceramic Society*, vol. 24, no. 6, pp. 1439–1448, 2004.

[21] C. J. F. Böttcher and P. Bordewijk, Eds., *Theory of Electric Polarization*, vol. 2, Elsevier, Amsterdam, The Netherlands, 1992.

[22] A. K. Jonscher, "Dielectric characterisation of semiconductors," *Solid-State Electronics*, vol. 33, no. 6, pp. 737–742, 1990.

[23] A. Z. Simões, A. H. Gonzalez, C. S. Riccardi, et al., "Effect of magnesium on the properties of $LiNbO_3$ thin films prepared from polymeric precursors," *Integrated Ferroelectrics*, vol. 43, pp. 123–135, 2002.

[24] A. Z. Simões, A. H. Gonzalez, M. A. Zaghete, et al., "Influence of oxygen flow on crystallization and morphology of $LiNbO_3$ thin films," *Ferroelectrics*, vol. 271, pp. 33–38, 2002.

[25] M. V. Gelfuso, D. Thomazini, and J. A. Eiras, "Synthesis and structural, ferroelectric, and piezoelectric properties of $SrBi_4Ti_4O_{15}$ ceramics," *Journal of the American Ceramic Society*, vol. 82, no. 9, pp. 2368–2372, 1999.

[26] K. Kato, K. Suzuki, K. Nishizawa, and T. Miki, "Comparison of microstructure and ferroelectric properties of alkoxy-derived $MBi_4Ti_4O_{15}$ (M: Ca or Sr) thin films," *Japanese Journal of Applied Physics*, vol. 40, no. 9, pp. 5580–5584, 2001.

[27] A. Z. Simões, C. S. Riccardi, A. Ries, M. A. Ramirez, E. Longo, and J. A. Varela, "Ferroelectric and piezoelectric properties of bismuth layered thin films grown on (1 0 0) Pt electrodes," *Journal of Materials Processing Technology*, vol. 196, no. 1–3, pp. 10–14, 2008.

[28] A. Z. Simões, C. S. Riccardi, M. A. Ramírez, L. S. Cavalcante, E. Longo, and J. A. Varela, "Synthesis and characterization of $CaBi_4Ti_4O_{15}$ thin films annealed by microwave and conventional furnaces," *Solid State Sciences*, vol. 9, no. 8, pp. 756–760, 2007.

[29] A. Z. Simões, M. A. Ramírez, A. H. M. Gonzalez, et al., "Control of retention and fatigue-free characteristics in $CaBi_4Ti_4O_{15}$ thin films prepared by chemical method," *Journal of Solid State Chemistry*, vol. 179, no. 7, pp. 2206–2211, 2006.

[30] H. Watanabe, T. Mihara, H. Yoshimori, and C. A. Paz de Araujo, "Preparation of ferroelectric thin films of bismuth layer structured compounds," *Japanese Journal of Applied Physics*, vol. 34, no. 9, pp. 5240–5244, 1995.

[31] H. Irie and M. Miyayama, "Dielectric and ferroelectric properties of $SrBi_4Ti_4O_{15}$ single crystals," *Applied Physics Letters*, vol. 79, no. 2, pp. 251–253, 2001.

[32] T.-T. Fang and C. P. Liu, "Evidence of the internal domains for inducing the anomalously high dielectric constant of $CaCu_3Ti_4O_{15}$," *Chemistry of Materials*, vol. 17, no. 20, pp. 5167–5171, 2005.

[33] J. Li, A. W. Sleight, and M. A. Subramanian, "Evidence for internal resistive barriers in a crystal of the giant dielectric constant material: $CaCu_3Ti_4O_{15}$," *Solid State Communications*, vol. 135, no. 4, pp. 260–262, 2005.

[34] A. K. Jonscher, "Dielectric characterisation of semiconductors," *Solid-State Electronics*, vol. 33, no. 6, pp. 737–742, 1990.

[35] A. Z. Simões, C. S. Riccardi, A. H. M. Gonzalez, A. Ries, E. Longo, and J. A. Varela, "Piezoelectric properties of $Bi_4Ti_3O_{12}$ thin films annealed in different atmospheres," *Materials Research Bulletin*, vol. 42, no. 5, pp. 967–974, 2007.