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Phase Transition Characteristics in A-Site La^{3+} Modified Bi-Layered Aurivillius-Type Structure $\text{SrBi}_2\text{Nb}_2\text{O}_9$ Ferroelectric Ceramics

J. D. S. GUERRA,^{1,2,*} I. C. REIS,^{2,3} A. C. SILVA,^{2,3}
E. B. ARAÚJO,³ R. GUO,¹ AND A. S. BHALLA¹

¹Multifunctional Electronic Materials and Devices Research Lab, Department of Electrical and Computer Engineering, College of Engineering, The University of Texas at San Antonio, San Antonio, TX 78249, USA

²Grupo de Ferroelétricos e Materiais Multifuncionais, Instituto de Física, Universidade Federal de Uberlândia, 38400-902 Uberlândia-MG, Brazil

³Departamento de Física e Química, Universidade Estadual Paulista, 15385-000. Ilha Solteira-SP, Brazil

The phase transition characteristics have been investigated in lanthanum modified bismuth layer structured $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) ferroelectric ceramics, obtained from the conventional sintering method. In particular, structural, ferroelectric and dielectric properties have been analyzed taking into account the influence of the lanthanum content. Results of Raman spectroscopy as well as dielectric response suggested an evolution from normal ferroelectric-paraelectric phase transition to a relaxor-like behavior of the SLBN system, with the increase of the lanthanum concentration. The compositional cationic disorder has been considered as the main cause for the observed behavior, affecting the evolution of the long-range polar ordering in the studied system.

Keywords Aurivillius; dielectric permittivity; phase transition; relaxors

Bismuth layered structure ferroelectrics (BLSFs), known as Aurivillius systems [1], have strong potential for practical applications in the electronic industry because of its very interesting physical properties [2]. For instance, their insertion in electronic devices, such as capacitors, memories and sensors, has been considered in the past [3]. The crystal structure of the BLSFs family is basically composed of $(\text{Bi}_2\text{O}_2)^{2+}$ layers interleaved with perovskite-like blocks of $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ type, having the general chemical formula $\text{A}_{m-1}\text{Bi}_2\text{B}_m\text{O}_{3m+3}$. The parameter m is the number of perovskite layers and A and B refer to the A- and B-sites of the perovskite structure, which can be occupied by high atomic radius ions as well as smaller atomic radius elements, respectively. In order to improve their physical properties, many works have been focused on the influence of doping with different elements either in the bismuth layers or in the perovskite units [4, 5]. Such substitutions consider the inclusion of mono-, di- and trivalent ions in either the A-site [2, 4] or Bi^{3+} site, as well as the inclusion of tetra-, penta- and hexavalent ions in the B-site [4, 5] of the perovskite structure. In this way, improved responses such as high spontaneous

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*Corresponding author. E-mail: jose.guerra@utsa.edu; santos@infis.ufu.br

polarization, fatigue-free behavior and low leakage currents, can be achieved in these materials, which make them promising for using in nonvolatile ferroelectric memories devices [3]. However, there have been reported only few works considering the A-site substitution by rare-earth elements in $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN). In fact, not much attention have been paid to the substitution of the A-site with the lanthanum (La^{3+}) cation. Therefore, more detailed investigations regarding the ferroelectric properties as well as the phase transition characteristics should be taken into account for those cases.

The objective of the present work is to investigate the structural and dielectric properties in bi-layered Aurivillius-type structure $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ferroelectric ceramics, obtained from the conventional sintering method. The effect of the lanthanum doping on the structural, ferroelectric and dielectric properties has been taken into account in $\text{Sr}_{1-3x/2}\text{La}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ (SLBN) samples, where $x = 0, 0.10, 0.20$ and 0.30 . Specially, the influence of the lanthanum content on the ferroelectric-paraelectric phase transition characteristics has been discussed.

$\text{Sr}_{1-3x/2}\text{La}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ (SLBN) ceramic samples, with $x = 0.0, 0.10, 0.20$ and to 0.30 , were synthesized from the conventional sintering method, from high purity raw materials. After mixing in stoichiometric proportions, the powders were ball milled for 34 hours and calcined at 850°C for 30 min. After that, the samples were uniaxially pressed and then sintered in air atmosphere at 1100°C for 1 hour. The samples have been named as SBN, SLBN10, SLBN20 and SLBN30, for $0.0, 0.10, 0.20$ and 0.30 compositions, respectively. The structural properties were investigated at room temperature from x-ray diffraction (XRD) analysis by using a Shimadzu XRD-6000 diffractometer, with a $\text{CuK}\alpha_1$ (1.5406 \AA) radiation. Raman spectra were also collected at room temperature from a Raman BX51-Voyage and Nikon Eclipse 80i microscope, by using an Ar+ laser with 785 nm excitation line (150 mW), covering the spectral range of $100\text{--}2510 \text{ cm}^{-1}$. Silver electrodes were applied on the opposite faces of the samples in order to investigate the electric properties. Ferroelectric hysteresis loops were obtained at room temperature from a modified Sawyer-Tower circuit, using a Trek PM04014 High Voltage AC/DC Generator. The dielectric measurements were carried out by using a HIOKI 3532-50 LCR HiTESTER, in the frequency and temperature range of $100 \text{ Hz--}1 \text{ MHz}$ and $25\text{--}550^\circ\text{C}$, respectively.

Figure 1 shows the x-ray diffraction measurements obtained for the SBN, SLBN10, SLBN20 and SLBN30 powdered ceramic samples. Results confirmed the orthorhombic ($A2_{1am}$) ferroelectric phase (represented by indexed peaks), with perovskite structure layers placed between the bismuth layers, for all the cases without the presence of any secondary phases. The XRD patterns have been confirmed from the ICSD-088476 data for the $\text{SrBi}_2\text{Nb}_2\text{O}_9$ system [12]. On the other hand, detailed information on the structural characteristics were investigated after structural refinement of the experimental data from Reitveld refinement method analyses, carried out by using the GSAS-EXPGUI software [6]. Results revealed significant structural changes in the SBN ceramics with the inclusion of the lanthanum ion. Since the lanthanum cation (La^{3+}) has ionic radius around 1.032 \AA [7], it is assumed that it could easily occupy the A-site, substituting the strontium cation (Sr^{2+}) with ionic radius of 1.180 \AA [8].

Table 1 shows the obtained values for the structural parameters obtained after the refinement analyses for all the studied compositions. It can be seen that both the tetragonality (c/a) and the volume of the unit cell parameters decrease with the increase of the lanthanum content, which can be explained on the basis of ionic radius. Lanthanum ions with smaller radius can easily enter into the crystal lattice of the as-prepared SBN Aurivillius structure-type samples and locate itself in the A-site with adequate space. The replacement of Sr^{2+} ions in A-sites by La^{3+} ions will cause the contraction of the unit cell, resulting in the reduction of the unit-cell volume.

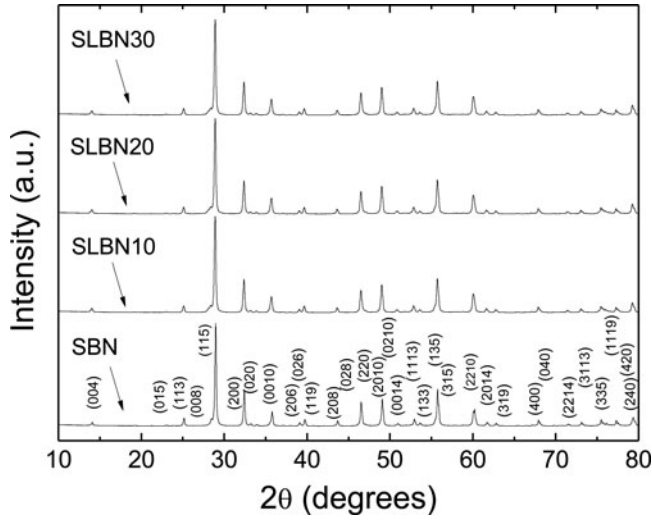


Figure 1. X-ray diffraction (XRD) patterns obtained at room temperature for the SBN, SLBN10, SLBN20 and SLBN30 compositions.

Figure 2 shows the Raman spectroscopy results obtained at room temperature for the studied samples. As can be seen, well defined localized vibrational modes around 178 cm^{-1} , 210 cm^{-1} , 450 cm^{-1} , 575 cm^{-1} and 840 cm^{-1} respectively were obtained for all the cases, which can be related to the orthorhombic ferroelectric phase vibrational modes. These results are in agreement with previously reported results in the literature [9, 10]. Specifically, the observed peak around 210 cm^{-1} can be attributed to vibrations of both Bi^{3+} and La^{3+} ions, according to the reported results by Liu et al. [11]. It can also be noticed that, with the increase of the lanthanum content, the 178 cm^{-1} and 210 cm^{-1} vibrational modes tend to overlap, and can be attributed to the structural disorder promoted by the A-site occupation for higher lanthanum concentrations.

The possible inclusion of the La^{3+} ions in the Bi_2O_2 layers can also contribute for the overlapping of the 178 cm^{-1} and 210 cm^{-1} vibrational modes, leading to a possible relaxor-like SLBN structure. On the other hand, the widening of the peak around 840 cm^{-1} with the increase of the lanthanum content, can be an evidence of the stretching of the NbO_6 octahedral in the a - b plane related to the vacancies probably induced by the charge compensation mechanism, due to the different valences of the La^{3+} and Sr^{2+} ions [10].

Table 1

Lattice parameters (a , b and c) and volume (V) of the unit cell, for the studied samples

Sample	a (Å)	b (Å)	c (Å)	c/a	V (Å ³)
SBN	5.5157	5.5159	25.0636	4.5440	762.5362
SLBN10	5.5143	5.5120	25.0494	4.5426	761.3720
SLBN20	5.5086	5.5137	25.0138	4.5408	759.7383
SLBN30	5.5111	5.5049	24.9660	4.5301	757.4199

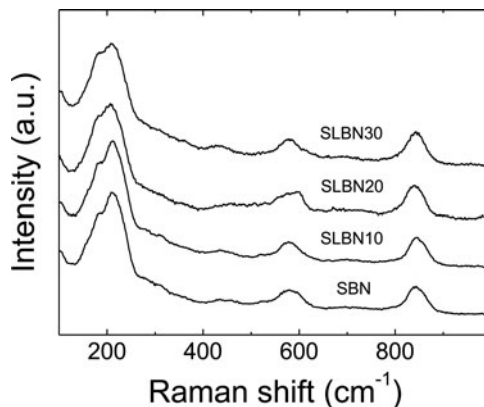


Figure 2. Raman spectra obtained at room temperature for of the SBN, SLBN10, SLBN20 and SLBN30 compositions.

Figure 3 shows the ferroelectric hysteresis loops for SLBN10, SLBN20 and SLBN30 samples obtained at room temperature. It can be observed that the macroscopic polarization is strongly affected by the inclusion of the lanthanum cation. As depicted in the inset of Fig. 3, the remnant polarization (P_r) decreases with the increase of the lanthanum content (from $1.0 \mu\text{C}/\text{cm}^2$, for the SLBN10 sample, to $0.38 \mu\text{C}/\text{cm}^2$, for the SLBN30 composition), showing the hysteresis loops shapes indeed a tendency from a normal ferroelectric hysteresis to slim hysteresis loop. This result could be an indicative of the relaxor characteristics for the highest lanthanum content composition (SLBN30), and is in agreement with the previously obtained results from Raman spectroscopy. For some perovskite structure-type ferroelectric systems the lanthanum doping is known to break the long-range interaction between the

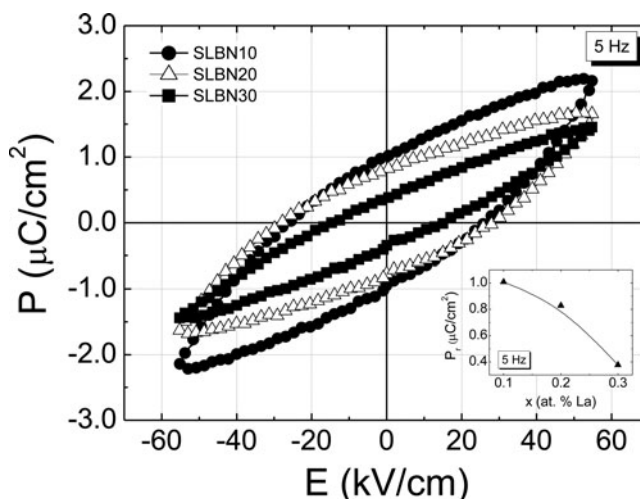


Figure 3. Ferroelectric hysteresis loops obtained at room temperature, for the SLBN10, SLBN20 and SLBN30 compositions; the inset shows the lanthanum concentration (x) dependence of the remnant polarization (P_r).

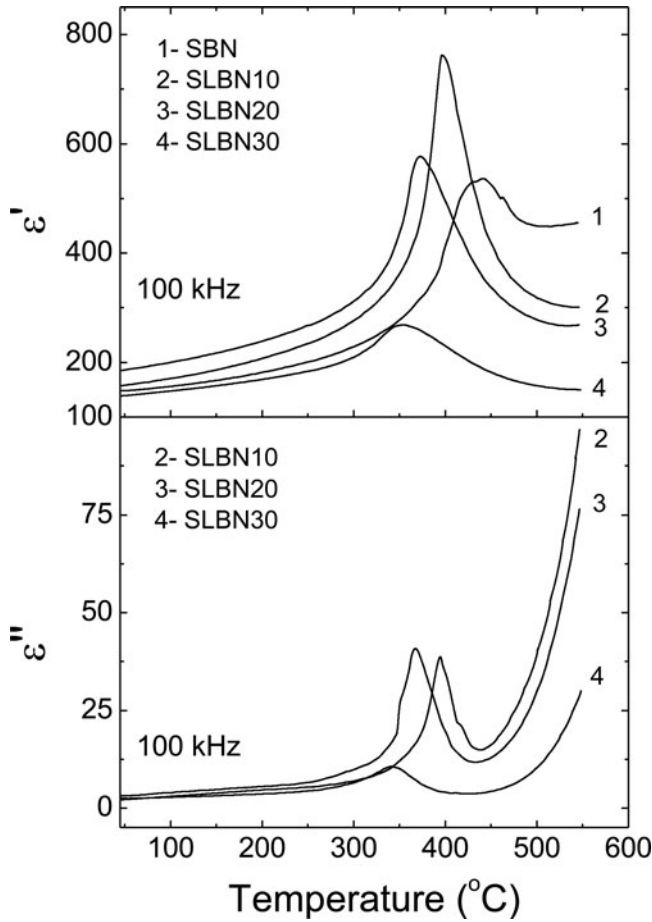


Figure 4. Temperature dependence of the real (ϵ') and imaginary (ϵ'') components of the dielectric permittivity, for the studied SBN, SLBN10, SLBN20 and SLBN30 samples, at 100 kHz.

ferroelectrically active ions, thus preventing the macroscopic transformation into a long-range ferroelectric state [12]. Accordingly, for higher lanthanum concentrations a state with nanometer scale local polar regions may take place. It is important to point out that, although the obtained remnant polarization values seems to be lower than those reported for classical ferroelectric systems (i.e. BaTiO_3 , PbZrTiO_3 , etc.), they are higher than those reported for typical bismuth layer structured $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) ferroelectric ceramics, showing P_r values between $0.18 \mu\text{C}/\text{cm}^2$ and $0.30 \mu\text{C}/\text{cm}^2$ [10, 13]. On the other hand, non-saturated hysteresis loops were observed for all the cases for an applied electric field close to $55 \text{ kV}/\text{cm}$, which is an indicative of the conductivity contribution in the samples. Thus, higher electric fields seem to be needed for domains switching and saturation of the polarization, which could result in the electrical breakdown of the samples.

Figure 4 shows the temperature dependence of the real (ϵ') and imaginary (ϵ'') components of the dielectric permittivity, for the studied SBN, SLBN10, SLBN20 and SLBN30 samples, obtained at the frequency of 100 kHz. Typical behaviors of ferroelectric-paraelectric phase transitions, characterized by the peak in the dielectric permittivity for

Table 2

Real and imaginary component of the dielectric permittivity obtained at room temperature (ϵ'_{RT} and ϵ''_{RT} , respectively), maximum real and imaginary dielectric permittivities (ϵ'_m and ϵ''_m) and their corresponding temperatures (T_m and $T_{\epsilon''_m}$, respectively) values for the studied samples, at 100 kHz

Sample	ϵ'_{RT}	ϵ''_{RT}	ϵ'_m	T_m ($^{\circ}\text{C}$)	ϵ''_m	$T_{\epsilon''_m}$ ($^{\circ}\text{C}$)
SBN	148	1.32	537	440	—	—
SLBN10	159	2.19	762	396	39.12	395
SLBN20	187	3.17	578	372	40.91	368
SLBN30	138	2.55	268	353	10.74	342

temperatures around the transition temperature (T_m), were obtained for all the samples [14, 15]. The obtained value of T_m for the pure SBN sample is in agreement with that reported in the literature [16]. On the other hand, an anomalous behavior characterized by a continuous increase in the imaginary component of the dielectric permittivity was observed for temperatures higher than 450°C . This behavior can be associated to the conductivity losses, which become prominent at low frequencies [17].

Table 2 shows the dielectric parameters obtained from the experimental results of Fig. 4. As can be seen, the temperature of the maximum real dielectric permittivity (T_m) decreases with the increase of the lanthanum content, showing a linear-like dependence for compositions higher than $x = 0.10$, which confirms the solubility of the lanthanum ion in the SBN crystalline lattice.

It can also be noticed from Fig. 4 that the width of the peak around T_m increases with the increase of the lanthanum content, revealing a broadened response for the SLBN30 composition. Similar result were reported for lanthanum modified $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics [18], and can be related to compositional inhomogeneities due to the inclusion of structural defects for higher lanthanum concentrations, where the same crystallographic site can be occupied by two different ions. As can be seen, the difference between the temperature for the maximum imaginary dielectric permittivity ($T_{\epsilon''_m}$) and the temperature for the maximum real dielectric permittivity increases with the increase of the lanthanum concentration. This behavior, which can be better observed in the Table 2, shows additional evidences for the relaxor-like character of the ferroelectric-paraelectric phase transition as the lanthanum content increases. In order to better clarify this fact, the temperature dependence of the real and imaginary component of the dielectric permittivity has been investigated for the SLBN30 composition, as a function of the frequency. Results are shown in Fig. 5 and reveal a strong frequency dispersion of the dielectric response, which becomes more evident for temperatures around T_m . Indeed, the maximum value of ϵ' decreases with the increase of the frequency, whereas its corresponding temperature (T_m) shifts to higher temperatures.

This result shows evidences of the relaxor-like behavior with a diffuse character of the ferroelectric-paraelectric phase transition (DPT), revealing that for higher lanthanum concentration compositions (SBN30) the compositional disorder of cations on A-sites of the perovskite blocks affects the evolution of the long-range polar ordering [19, 20]. In fact, both the relaxor behavior and DPT effects could have not been completely reached and seem to be overlapped for the higher lanthanum concentration sample. This behavior has been also attributed to the compositional fluctuation induced by La^{3+} , partly in the perovskite blocks and partly in the in $(\text{Bi}-2\text{O}_2)^{2+}$ layers [21]. In addition, the increase of

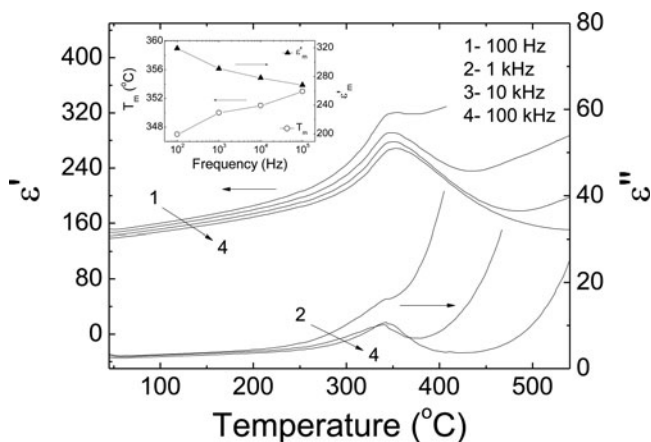


Figure 5. Temperature dependence of the real (ϵ') and imaginary (ϵ'') component of the dielectric permittivity, for the studied SLBN30 composition, at several frequencies. Inset shows the variation of the maximum dielectric permittivity (ϵ'_m) and its corresponding temperature (T_m) with the frequency.

both real and imaginary component of the dielectric permittivity for temperatures higher than 370°C is also ascribed to the DC conductivity mechanisms in these samples [17]. The obtained results for the dielectric response confirm the previously discussed results for the Raman spectroscopy and ferroelectric hysteresis loops measurements and suggest an evolution from normal ferroelectric-paraelectric phase transition to a mixed diffuse ferroelectric-paraelectric phase transition and relaxor behavior with the increase of the lanthanum content. For a better comprehension of the obtained results further investigations, which include detailed analyses of the dielectric response for the studied samples as well as new additional SLBN compositions, are in progress. Results will be reported in the near future.

In summary, the physical properties of bismuth layer structured $\text{Sr}_{1-3x/2}\text{La}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ (SLBN) ferroelectric ceramics, obtained from the conventional sintering method, have been investigated taking into account the lanthanum concentration ($x = 0.00, 0.10, 0.20$ and 0.30). Structural analysis revealed a contraction in the volume of the unit-cell as the lanthanum content increases, which can be explained on the basis of the ionic radii. On the other hand, the La substitution on Sr site promoted the decrease of the Curie temperature, showing a linear-like behavior, which is a strong evidence of the high solubility of the La in the SBN crystalline lattice. The Raman spectroscopy analysis, ferroelectric response as well as dielectric properties results suggest an evolution from normal ferroelectric-paraelectric phase transition to a mixed diffused and relaxor ferroelectric-like behavior of the SLBN system, with the increase of the lanthanum concentration.

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