Structural, Ferroelectric, Pyroelectric, and Dielectric Study of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ Ceramics synthesized with Precursors Obtained by Sol-Gel Method doped with Lanthanum

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Abstract

In this work, the ferroelectric, pyroelectric and dielectric properties of La-doped bismuth sodium titanate ceramics ($\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{La}_x\text{TiO}_3$ (BNLT) using amounts from 0 to 6.7 at.% La were studied. The precursor powders used to make dense BNLT ceramics were obtained by the sol-gel method using the acetic acid route. All samples were calcined at 700°C for 1hr and sintered at 1150°C for 30 min in an encapsulated crucible to avoid Na and Bi volatilization, obtaining relative densities equal or higher than 94%. The obtained X-ray diffraction patterns typical of the perovskite structure, confirm the incorporation of lanthanum into the lattice, evolving from rhombohedral phase to a mixture of rhombohedral and cubic structure for higher concentrations. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) results indicate that the crystallization of precursors powders of BNT takes place between 500 and 700°C. Additionally, the Scanning Electron Microscopy (SEM) micrographs reveal a decrement of grain size from 4.5 to 0.5 μm with increasing La content. The ferroelectric hysteresis curves show that the best ferroelectric properties were obtained for BNT 1.3% La, where the obtained values of remnant polarization and coercive field were $P_r=29 \, \mu\text{C/cm}^2$ and $E_c=39 \, \text{kV/cm}$ respectively. Also, at this concentration, the pyroelectric response shows the higher value, 4 times the pyroelectric signal of the pure BNT.

Keywords: sol–gel, lead-free ferroelectrics, dielectrics, pyroelectrics.
1 Introduction

Nowadays, lead-based electro-ceramics as PZT are the most used due they have excellent piezoelectric \( (d_{33}=590-610 \ \text{pC/N}) \) and dielectric \( (\varepsilon_r=1700-1790) \) properties [1,2]. However, considering the high toxicity of lead and its volatility at high temperatures, required for the synthesis of lead-based ceramics, there is a trend towards the development of lead-free ferroelectric systems [3]. Since its discovery by Smolenskii et al., in 1960 [4], the bismuth sodium titanate \( \text{Na}_0.5\text{Bi}_0.5\text{TiO}_3 \) (BNT) perovskite system has emerged as a good candidate to replace lead-based systems, due to its high remnant polarization \( (P_r=38\mu\text{C/cm}^2) \) and Curie temperature \( (T_c=320^\circ\text{C}) \) [5, 6]. However, it is well known that the BNT is considered as a hard ferroelectric, due to its high coercive field values \( (E_c \approx 73 \ \text{kV/cm}) \) [7], also presents relatively high leakage currents, hindering the polarization process. Being the latest, limiting characteristics for the use of this system in several applications [3,8].

Notwithstanding the above, the BNT has been widely studied as a modified system through use of BNT-based solid solutions in order to improve its properties with another systems such as \( \text{BaTiO}_3 \) (BT) \( (d_{33}=83\text{pC/N}, \ \kappa_p=15.9\% \ \text{for pure BNT system to } d_{33}=155\text{pC/N}, \ \kappa_p=36.7\% \ \text{for } 0.4\text{BNT}-0.06\text{BT}) \) [9], \( \text{SrTiO}_3 \) (ST) \( (\text{piezoelectric improvement until } d_{33}^* \approx 620 \ \text{pC/N for } 0.72\text{BNT–0.28ST}) \) [10], \( \text{K}_0.5\text{Na}_0.5\text{TiO}_3 \) (KNN) \( (\text{piezoelectric improvement until } d_{33}=94 \ \text{pC/N and } \kappa_p\approx27\% \ \text{for } 0.94\text{BNT}-0.06\text{KNN}) \) [11], and \( \text{Bi}_0.5\text{K}_0.5\text{TiO}_3 \) BKT \( (\text{piezoelectric and dielectric improvement until } d_{33}=115 \ \text{pC/N and } \varepsilon_r=1660 \ \text{for } 0.82\text{BNT}-0.18\text{BKT}) \) [12].

The modification of the BNT system by ion-doping is another method to improve its piezoelectric and ferroelectric properties [13]. Particularly, the addition of \( \text{La}^{3+} \) in certain concentrations has led to an improvement on pyroelectric and dielectric properties into systems such as PZT \( (\text{maximum energy density improvement from } 799.5 \ \text{J}^{-1} \ \text{per cycle for } 5/65/35 \ \text{PLZT to } 1014 \ \text{J}^{-1} \ \text{per cycle for } 7/65/35 \ \text{PLZT}) \) [14], BT \( (\varepsilon_r=900 \ \text{for undoped BT to } \varepsilon_r=1450 \ \text{for } 8 \ \text{at.}\% \ \text{La}) \) [15] and BNT \( (\varepsilon_r=350 \ \text{for undoped BNT to } \varepsilon_r=928 \ \text{for } 5 \ \text{at}\% \ \text{La}) \) [16].

It should be noted that the starting powders, used during the synthesis process, have a strong influence on the final properties of the ferroelectric systems. The precursor powders can be obtained from different ways: raw powders (oxides and carbonates), by the co-precipitation
method, and sol-gel method, to mention just a few of them. Particularly the precursor powders derived from the sol-gel method have many advantages like a high compositional homogeneity [17] and great dispersibility [18]. Additionally, nanosized powders obtained by the sol-gel method decrease significantly temperatures and times of processing stages of calcination and sintering [19].

In a previous work [20] we explored the BNT system doped with La in a concentration range of 0 to 6% at. However, it was necessary to use an excess of 100% of the Na source in the initial precursors to be able to compensate the volatilization of Na in the calcination and sintering stages, to obtain samples with appropriate ferroelectric characteristics of the doped BNT, this because in the calcination and sintering process did not use the encapsulation stage. In this work, we added this encapsulation stage in the synthesis process, which it is possible to obtain samples with high densification and good ferroelectric properties, without the need to add excess of Na or Bi in the initial precursors.

The aim of the present work is the study of the effect of Lanthanum doping in low range concentrations to avoid the formation of secondary phases, range from 0 to 6.7 % at. on structural, ferroelectric, pyroelectric, and dielectric behavior of a modified BNT system, obtained using precursor powders derived by the sol-gel method.

2 Materials and methods

(Bi,Na),La,TiO (0, 0.003, 0.007, 0.01, 0.013, 0.033, and 0.067) powders were prepared by a sol-gel process. The precursor solution was prepared by dissolution of an appropriate amount of anhydrous sodium acetate, (CH₃COONa, 99%, Golden Bell), bismuth (III) acetate ((CH₃COO)₃Bi, 99.99%, Sigma Aldrich), and lanthanum acetate ((CH₃COO)₃La, 99.99%, Sigma Aldrich) in glacial acetic acid (99.7%, Sigma Aldrich) and deionized water under stirring and heating at 80 °C for 30 min. Secondly, Ti (IV) isopropoxide (Ti (OCH (CH₃) 2) 4, 97%, Sigma Aldrich) is dissolved in 2-propanol (99.5%, Sigma Aldrich) in a ratio of 1 to 5. Then, stabilizing agent (acetylacetone, 99%, Sigma Aldrich) was added in the resulting solution for 15 min to promote a complete reaction. Finally, a stoichiometric amount of the titanium complex solution was added drop by drop to the solution of acetates under constant stirring at 80°C, where the molar ratio of
Ti:H₂O=1:5. After this process, a transparent and stable yellow precursor solution was obtained. The BNLT sol was dried in a hot plate at 180°C for 4 h and calcined in an oven at 700°C for 1 h to obtain the BNT in its corresponding perovskite phase. The calcined powders were ground to obtain fine powders with homogenous size after that were uniaxially pressed at 275 MPa for 5 min to obtain pellets with 10.14 mm of diameter and 0.5 mm of thickness followed by sintering at 1150°C for 30 min using encapsulation to minimize loss of volatile elements such as bismuth and sodium.

Thermal behavior and decomposition of metalorganic compounds were obtained by thermogravimetric analysis (TGA) and differential thermal analysis (Mettler Toledo STARTe, Mettler Toledo 822). The structural characterization of BNLT samples was obtained by X-ray diffraction (Rigaku Dmax2100) using Cu Kα radiation. Raman spectra were collected using a Spex-double spectrometer model 1403, using an excitation line at 488.0 nm of an argon-ion laser, Lexel laser Inc. model 95. The dielectric properties as a function of temperature were measured using an impedance analyzer (Agilent 4294A) and a homemade oven with controlled temperature. The ferroelectric hysteresis loop at room temperature was measured using an equipment Precision LC-materials analyzer Radiant Technology coupled with a high voltage amplifier Trek model 609E-6. The pyroelectric response was determined with a photothermal experimental set-up. In which the ceramic sample, with Ag contacts, previously poled is heated periodically with a diode laser source, and the induced AC voltage due to the pyroelectric effect is measured in amplitude and phase with a lock-in amplifier. The pyroelectric response is directly the amplitude of the AC signal as a function of modulation frequency. This signal is proportional to the pyroelectric coefficient (p), and the pyroelectric coefficient is related with the spontaneous polarization (Pₛ) by the next relation, \( p = \left( \partial P_S / \partial T \right)_{E,X} \), where the electric field (E) and stress (X) are remained constant [21]. More details about the measurement method were previously published [22, 23]

3 Results and Discussion
3.1 DSC and TG Analyses
Fig. 1 shows the TG and DSC curves of dried xerogel of pure BNT. Exothermic peaks, accompanied by three mass loss steps, are appreciated around 98°C, 311°C, and 500°C. However, DSC curve shows an endothermic peak around 605 °C which is belonging to a solid-state reaction of BNT. There is not a weight loss above 650 °C. The weight loss and the exothermic peaks obtained at 98 °C, 311°C, and 500°C were due to the residual solvents and volatile organics. The first step mass loss of 10.7% in the xerogel is associated with the residual solvents. The second step has 24.6% of mass loss obtained around 200 to 400°C, which is related to loss of remnant water, acetone, and carbon dioxide [24]. Finally, even though during the BNT crystallization it must not show weight losses, the TG curve shows a mass loss of 1.2%, which is associated with the volatilization of residuary CO₂.

Fig. 1. The TGA and DSC curves of BNT xerogel show the temperatures at which occur the principal transformations.

3.2 Microstructural Analyses

The density of the sintered samples, with different atomic concentrations of La (0, 0.003, 0.007, 0.01, 0.013, 0.033, and 0.067) was determined by the Archimedes method. The results presented in Table 1 show an increase in density up to a concentration of 1.0 at % of La, which decreases for higher concentrations, but in all cases the relative density is equal or
higher than 94%. The shrinkage percentage of the diameter of sintered samples, concerning their diameter before sintering, was also determined between 10.1 and 14.1%.

Table 1. Dependence of contraction, grain size, and relative density in sintered pellets of BNT system as a function of Lanthanum content.

| X    | 0.0  | 0.003 | 0.007 | 0.01 | 0.013 | 0.033 | 0.067 |
|------|------|-------|-------|------|-------|-------|-------|
| Contraction (%) | 12.7 | 11.2 | 11.3 | 13.6 | 14.1 | 10.1 | 11.4 |
| Average Grain size (μm) | 4.5 | 3.3 | 2.0 | 1.1 | 0.6 | 0.5 | ---- |
| Relative density (%) | 94.5 | 95 | 95.6 | 97.0 | 94 | 94.5 | 95.3 |

Fig. 2 show the SEM micrographs of fractured surface of representative samples, in which is observed long-round shape without well-defined faces for pure BNT. This is an important difference in the microstructure of samples obtained with powders obtained by sol-gel, respect to the microstructure obtained with carbonates and oxides precursors, where in general the shape of the grain is well defined. Nevertheless, in the case of precursors obtained by sol-gel, when La-concentration increases, the shape of the grains are better defined.

Table 1 shows the evolution of the grain size with the concentration of La. The addition of lanthanum into the BNT system leads to a large decrease of grain size from 4.5 μm for undoped BNT until 0.5 μm corresponding to La-doped BNT with 3.3 at.%. Grain size belonging to the highest La-concentration (6.7 at.%) was not possible to estimate due to the presence of grains fusion.

A similar effect of grain size reduction has also been observed in other ferroelectric systems in addition to BNT, such as in the case of BaTiO₃ and PZT [25-27]. The effect of La doping in the A sites of the BNT perovskite structure, substituting Na and Bi, leads to a decrease in grain size, and for higher concentrations, it is expected also that it contributes to the appearance of an additional phases [25-27].
Fig. 2. SEM Micrographs of (Bi$_{0.5}$Na$_{0.5}$)$_{1-x}$La$_x$TiO$_3$ system sintered at 1150°C; (a) pure BNT, (b) with 1.3 at.% La$^{3+}$, (c) with 3.3 at.% La$^{3+}$.

3.3 X-ray diffraction results

Fig. 3 shows the X-ray diffraction patterns (XRD) of BNT ceramic samples with different concentrations of La ($0 \leq x \leq 6.7$ at%), sintered at 1150°C by 30 min. The sharp peaks in the XRD patterns indicate that the obtained samples had good crystalline quality, free of secondary phases, even in the samples with the highest La concentration. This result was achieved thanks to the encapsulation stage during the sintering process, without the need to add excess Na to compensate for its volatilization, when encapsulation is not included. The crystalline phase identified according to the crystallographic file (ICDD-PDF # 36-0340) for pure BNT corresponds to the R3c Rhombohedral structure [9, 28,29].

The samples with a low concentration of La ($0 \leq x \leq 1.3$% at) show a good correspondence with the rhombohedral phase. However, for samples with a higher concentration of La ($3.3 \leq x \leq 6.7$% at), the diffraction peaks (012) and (110) that are presented in the inset of Fig. 2 show an evolution that allows identifying the presence of a mixture of crystalline phases, rhombohedral (R3c) and cubic (Pm-3m group).
Fig. 3. Comparison of X-ray diffraction patterns for pure BNT and Lanthanum doped BNT. The inset shows the evolution peaks (012) and (110) with La content.

Previous studies about La-doping into perovskite structures have suggested that La\textsuperscript{3+} replaces preferably A-sites due to their close radii [25,27]. D. Shannon [30] reports the next ionic radius for Na\textsuperscript{+}(r\textsubscript{Na}=1.39Å, CN=12), La\textsuperscript{3+}(r\textsubscript{La}=1.36Å, CN=12) and for Bi\textsuperscript{3+} only gives ionic radii for coordination 8, Bi\textsuperscript{3+}(r\textsubscript{Bi}=1.17 CN=8). In coordination XII Blessington et al. [29] report a value of 1.36 Å for Bi, Liu et al and F. Yang et al. [31,32] report a value of 1.38 and 1.39 Å respectively. As can be seen, the ionic radius are very close and taking in consideration the oxidation state of La\textsuperscript{3+} then the probability to the La\textsuperscript{3+} occupy Bi\textsuperscript{3+} sites in the lattice is higher than occupy sites of Na, where a disbalance charge 2+ is expected. However, the synthesis method intrinsically results in the samples showing a high density of defects, in the case of pure BNT (Na, Bi, and O vacancies), for which is expected that the initial effect of the introduction of La in the range of low concentrations is the compensation of defects of Na and Bi and later with the increase in the concentration of La, the preferential substitution by Bi\textsuperscript{3+} should manifest, and for concentrations greater than 10% it will lead to Bi-rich phase
segregation, as observed in previous work [20] In the evolution of the XRD patterns it was possible to observe a proportional shift in the main diffraction peak located in $2\theta$ region (32.1°-33.1°) with the La amount added into the BNT system, which suggests a distortion on the lattice. First, an increase in lattice parameter until La concentration of 1.0% at, and after that, change to a mixture of rhombohedral and cubic structures for higher La concentrations. To describe that changes into lattice parameters, the diffraction patterns of pure BNT and La-doped BNT samples were analyzed by profile fitting method using the Fullprof Suite program [33]. Fig. 4 shows the Rietveld refinement for sample of BNT doped with 1.0% at La, in this case, the adjustment was realized considering only the rhombohedral phase. X-ray diffraction of sintered samples to undoped BNT and BNT with low La concentration ($\leq$1.3 at. %) were indexed as a single rhombohedral phase belonging R3c group. Nevertheless, for higher La concentration ($\geq$3.3 at.%), it was necessary to use in addition to the rhombohedral phase a cubic phase for the adjustment to the diffraction patterns, indicating the coexistence between the rhombohedral phase (R3c group) and non-ferroelectric cubic phase (Pm-3m group )[27].

![Fig. 4](image)

**Fig. 4** Rietveld profile fitting of BNT sample doped with 1.0% at La. The profile fitting of the crystalline structure was made considering the rhombohedral structure (R3c group).

Table 2 shows the adjust parameters such as, rhombohedral and cubic lattice parameter ($a_R$, $c_R$, $a_c$), unit-cell volume ($V_{R}$, $V_{C}$), phase percentage concentration (% phase), and the
goodness of fit ($\chi^2$), which should be $\leq 1.5$ for a good fit [33]. However, high backgrounds of X-ray diffraction patterns for all compositions contributed to reaching higher $\chi^2$ values. As observed in Table 2, low La$^{3+}$ concentrations $\leq 1.0$ at. % into the BNT system led to an increase of the unit-cell volume; for 1.3 at% La is observed a slightly volume decrease, and for higher La concentration, there is observed strong structural changes, appear the cubic phase as the majority crystalline phase for 3.3% of La, and for 6.7% of La, the sample is practically constituted by cubic phase with 98.41 phase concentration.

**Table 2.** Rhombohedral and Cubic lattice parameters of (Bi$_{0.5}$Na$_{0.5}$)$_{1-x}$La$_x$TiO$_3$ ceramics sintered at 1150$^\circ$C for 30 min where x=0, 0.003, 0.007, 0.01, 0.013, 0.033, and 0.067.

| %at. La | Rhombohedral R3c | Cubic Pm-3m | %phase R3c Rombohedral | %phase Pm-3m Cubic | Re | Re$^*$ | Resp | $\chi^2$ |
|---------|------------------|-------------|------------------------|-------------------|----|-------|------|-------|
| 0       | 5.4899 13.5854 354.599 | ----- | 100 | 0 10.2 13.3 6.05 2.11 |
| 0.3     | 5.4923 13.6097 355.419 | ----- | 100 | 0 12.2 15.7 5.91 2.62 |
| 0.7     | 5.4956 13.6126 356.038 | ----- | 100 | 0 14.5 18.5 8.89 2.03 |
| 1       | 5.5003 13.6094 356.572 | ----- | 100 | 0 13.3 17.1 9.10 1.84 |
| 1.3     | 5.4981 13.5196 356.284 | ----- | 100 | 0 11.2 14.3 6.63 2.10 |
| 3.3     | 5.4875 13.5196 352.531 | 3.9304 60.716 89.59 10.41 11.6 14.6 6.56 2.23 |
| 6.7     | 5.4942 13.4745 350.512 | 3.8918 58.947 1.57 98.41 12.4 16.4 6.36 2.55 |

This particular lattice distortion behavior, also observed in Pr$^{3+}$-doped BNT and La$^{3+}$-doped PZT systems [26,34], has been related to generation of micro-strain and cation-vacancies respectively. Both mechanisms could happen when vacancies in A-sites are generated in order to neutralize the positive charge into the unit cell and a subsequent distortion into the lattice in order to stabilize the perovskite structure. As previously indicated, the ionic radii of Na$^{1+}$, Bi$^{3+}$, and La$^{3+}$ are similar. La can enter isovalently by Bi, and as a donor by Na with an excess of 2+ electrical charge. For very low concentrations of La, it is expected that initially the vacancies of the A site will be compensated, as the concentration of La increases, there will be a competition between substitution for Bi and Na. The substitution by Na will give rise to Na vacancies to compensate for the electrical charge excess of La. These will
lead to a distortion of the lattice, which in this case is observed as a linear increase of cell volume, up to concentrations of La close to 1.0%. However, a continued increase of La-concentrations (≥1.3 at.%) reveals a decrease of cell-volume and change to cubic structure. Hence, higher La-concentrations could finally, lead to an equilibrium into \( A(Bi^{3+}/Na^+) \)-site substitution therefore a decrease in cation-vacancy concentration. Additionally, a constant shrinkage of \( a \) and \( c \) lattice parameters and unit-cell volume are related with a continuous evolution to higher cell symmetry for the BNT system [27,35] therefore a continuous transition from rhombohedral to cubic phase.

### 3.4 Raman Characterization

The Raman spectra at room temperature using an excitation line of argon ion laser at 488.0 nm for the set of sintered samples are showed in Fig. 5-a. The spectra of BNT system shows Raman modes overlapped in four main bands identified as \( A_1 \)TO in the range of 109-187 cm\(^{-1}\) which are dominated by Bi-O and Na-O vibrations, [29,36]. ETO\(_2\) in the range of 200-450 cm\(^{-1}\) associated with Ti–O vibrations, TO\(_3\) in the range of 450-700 cm\(^{-1}\) associated with stretching and breathing vibrations of the octahedral TiO\(_6\) [29]. Finally, the band LO\(_3\) in the highest frequency Raman modes located at 770 and 830 cm\(^{-1}\) which can be correlated to oxygen vacancies. [37], doping BNT with Cr in site B, give place to oxygen vacancies, this oxygen vacancies increase with Cr concentration, giving place to an increase intensity of the broad Raman band centered around 800 cm\(^{-1}\), showing that the intensity of this band is related with oxygen vacancy concentration [37].

The plot was normalized for the highest intense band corresponding to the second main band. According to XRD results at room temperature, the BNT system belongs to a rhombohedral structure (space group R3c) which is observed until 1.3% of La, for higher La concentrations the cubic phase appears and also increase its phase concentration. Figure 5B shows 12 individual Raman modes obtained by deconvoluting of fitted Raman spectra within the measured region (100-1000 cm\(^{-1}\)) using a Gaussian-Lorentzian function. The Raman active phonon modes expected for a rhombohedral R3c phase with A-site disorder (e.g. Bi/Na sites into BNT system) are 13, 4A1+9E, actives also in IR [29,38-43]. On the other hand, the cubic paraelectric phase (Pm3m) has four optical modes 3F\(_{1u}\)+1F\(_{2u}\) where only 3 modes with F\(_{1u}\) symmetry are IR active and F\(_{2u}\) is a silent mode, in principle those modes are not Raman
actives modes [38,39], nevertheless, the distortions in the lattice, impurities and vacancies can give place to Raman bands in the cubic phase.

Fig. 5 A) Raman spectra of (Bi$_{0.5}$Na$_{0.5}$)$_{1-x}$La$_x$TiO$_3$ sintered samples measured at room temperature where $x=0, 0.003, 0.007, 0.01, 0.013, 0.033$, and $0.067$. B) Deconvoluted modes obtained by fitting of overlapped A-D bands.

The number of individual modes obtained by deconvolution process, were close to that of the factor-group analysis of R3c space-group, in general the literature show lower number of deconvoluted modes, in our case is the band A$_1$TO$_1$ in the region of 109-187 cm$^{-1}$ where we found 2 additional modes, in the rest of the bands was found the same number modes reported in the literature [39], this region is associated with vibrations of Bi-O, Na-O, and with the introduction of La in sites A, it is expected the influence of La in those vibrations and also the contribution of La-O vibration.

Figure 6A shows the evolution of the frequency shift of the deconvolved modes as a function of the doping of La, in Figure 6B the evolution of the width at half the maximum (FWHM) of the bands of greater intensity obtained from the deconvolution is shown. In them, it can be observed that the greatest changes in frequency shift and in width at half the maximum, occur for concentrations of La greater than 1.3%, which corresponds to concentrations where the cubic phase appears, for higher concentrations, the majority of the modes shows a
broadening, which can be attributed to the coexistence of the rhombohedral and cubic phases, as well as disorder in the A sites, due to the random substitution of La in the Bi/Na sites [41].

**Fig. 6** A) Modes frequency shift and B) FWHM of principal deconvoluted bands as a function of La concentration.

The changes observed at concentrations lower than 1.3% of La are related to local changes within the rhombohedral structure due to the introduction of La in the A sites of the network. The lower frequency band located near 140 cm\(^{-1}\) splits into three individual modes (at about: 135, 151, and 161 cm\(^{-1}\)) for the pure BNT. Those modes shift to lower frequencies for low La\(^{3+}\) concentrations (≤ 1.3 at. %) and when Lanthanum content increase to 3.3 at. %, there is a shift to higher frequencies. However, for highest dopant concentrations (6.7 at. %) one individual mode disappears, and the frequencies decrease to about 135 and 152 cm\(^{-1}\), for the highest La concentration, the XRD results indicate that the crystalline majority phase is cubic. The FWHM of the mode at 135 cm\(^{-1}\) show an interesting behavior, where firstly, for low La concentration, show a decrease and after that show a quasi-linear increase with La concentration of 3.3%, and again show a decrease for the highest La concentration. The introduction of La with intermediate atomic mass between Na and Bi (\(m_{\text{Bi}}=208.98\), \(m_{\text{Na}}=22.99\), and \(m_{\text{La}}=138.91\)), in A sites, imply a distribution vibration of Na-O, Bi-O and La-O, which are manifested in this region as a shift to lower frequencies, for lower concentrations, while for higher concentrations (>1.3%), the influence of the cubic phase is observed. In principle in the cubic phase is not expected Raman bands, nevertheless for 3.3% and 6.7% of La concentration we have a mixture of rhombohedral and cubic phases, and also in this pervoskites structures is common that the introduction of dopants like La in A
sites, give place to a substitutional disorder, breaking the Raman selection rules and show Raman bands in the same region of the coexistence crystalline phase, in this case rhombohedral phase [42].

The band located around 200-450 cm\(^{-1}\) also splits into three modes at 262, 302, and 313 cm\(^{-1}\) and survive for higher La concentrations where the principal crystalline phase is cubic. With the introduction of La, all modes show shift to lower frequencies until 1.3\% of La, and for higher concentration (\(\geq 3.3\%\)) the behavior is a shift to higher frequencies. The FWHM of the 262 cm\(^{-1}\) mode, show a slight decrease until 1.0\% of La, for 1.3\% the reduction is higher, and for higher concentration the FWHM show a linear increase. This region is associated with Ti–O vibrations, the shift to lower frequencies by the introduction of La imply a decrease in the strength in the Ti-O bonds, until 1.3\% of La, and for higher concentration the shift to higher frequencies imply an increase of the Ti-O strength bonds associated with the change to cubic phase. The overlapping main band around 450-700 cm\(^{-1}\) are split into three components located at 486, 531, and 600 cm\(^{-1}\). This region is associated with vibration of the octahedral TiO\(_6\), as breathing and stretching modes [43]. It is expected that the introduction of La induce very weak changes, as can be observed in Fig 5A, these modes do not show appreciable changes until 1.3\% of La, for higher concentration where is present the cubic phase these modes shift to higher frequencies, which imply an increase in the strength bonds in the TiO\(_6\) octahedra. The FWHM of the mode at 531cm\(^{-1}\) show a monotonically decreasing with La concentration until 2\%, and for higher concentration change to an increasing behavior. This broadening can be associated with a distribution of TiO\(_6\) octahedral structures in rhombohedral and cubic phases, under the influence of Bi, Na and La in sites A. Finally, the highest frequency band consists of three individual modes (at 784, 810, and 860 cm\(^{-1}\)), which correspond to oxygen vacancies where an increase in its intensity is related with a higher vacancy concentration. The pure BNT show these bands due to losses of high volatile elements such as bismuth oxide [37]. However, the intensity of this band diminished when La was added, especially with large La concentration (\(\geq 3.3\) at. \%). This behavior indicate that oxygen vacancies are reduced with the introduction of La. It could be produced for vacancies in Bi\(^{3+}\)-sites created during the high temperature steps, but the introduction of isovalent La\(^{3+}\) ion, in this range of concentration, reduce the generation of oxygen vacancies.
3.5 Dielectric characterization

The temperature dependence of losses and permittivity in samples of \((\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{La}_x\text{TiO}_3\) system varying La-concentration of \(x= 0, 0.003, 0.007, 0.01, 0.013, 0.033, \) and 0.067 at four different frequencies (1kHz, 10kHz, 100kHz, and 1 MHz) are sown in Fig 7. The dielectric function shows small dispersion with frequency. Only two main peaks can be appreciated within temperature range from 25°C to 450°C. They are located around at 220°C and 350°C for undoped BNT which are belonging to a ferroelectric-antiferroelectric phase transition \((T_D)\) and an antiferroelectric-cubic phase transition \((T_{\text{max}})\) respectively [9,44].

The value of the dielectric function at \(T_{\text{max}}\) was around 2665 for pure BNT. Nevertheless, with the introduction of La, the maximum value decreased to 1845 for 1.3% of La and for 6.7% of La the maximum falls to 855. For the 3.3% concentration, the transition peak from the antiferroelectric to paraelectric phase shows an appreciable broadening, at this concentration, according to the XRD results, there is a mixture of rhombohedral and cubic phases in a ratio of approximately 90 to 10 respectively, and for the 6.7% concentration of La, the dielectric function shows a more uniform value around 760, for this composition the proportion of crystalline phases is 1.57 rhombohedral and 98.41 cubic phase, and the maximums associated with \(T_D\) and \(T_{\text{max}}\) are much less pronounced. On the other hand, the dielectric function at room temperature fluctuates between 600 and 700 up to a La concentration of 1.3%. For the concentration 3.3, it reaches its maximum around 1000 with little dispersion with frequency, and for the highest concentration of La (6.7%), the dispersion with frequency increases slightly, fluctuating around a value close to 710.

\(T_{\text{max}}\) increase linearly with increasing the (see Fig. 8) La-concentration, reaching a maximum at 1.3 at% \((T_{\text{max}}\approx 365^\circ \text{C})\) and then drops to lower temperatures with higher concentrations \((\geq 3.3 \text{ %at})\). Furthermore, \(T_D\), known as depolarization temperature, decreases slightly with La-concentration increment from 220°C for undoped BNT to 207°C for BNT 1.3at%, for sample with 3.3% of La it was not possible to determine \(T_D\), because the peak at \(T_{\text{max}}\) was very broad and the maximum for \(T_D\) was not distinguishable, see Fig.7.
Fig. 7 Temperature dependence on dielectric constant and loss at 1kHz, 10 kHz, 100kHz, and 1 MHz for pure BNT and BNLT samples.

That temperature shift of $T_D$ towards lower temperature has a relation with increment of ionic radii of Lanthanides [45] where Lanthanum ionic radius belonging to a coordination number 12 (CN) has one of the biggest radii of them therefore, it could be expected to observe changes in that temperature with addition of Lanthanum. Additionally, dielectric curves show broader shape which are related with replacement of A sites (Bi/Na site) which leads to a local heterogeneity in cation distribution promoting a greater diffuse dielectric behavior [9,44,45]. For the highest La-concentration (6.7 at.%), a large $T_D$ shift towards low temperatures near 71°C was observed (Fig. 8). It could imply to have an antiferroelectric behavior at close room Temperature due to addition of Lanthanum [44,46,47].
Fig. 8 Dependence of \( T_m \) temperature where dielectric function shows a maximum and Ferroelectric-antiferroelectric transition temperature \( T_D \) as a function of La concentration in the BNT system at 100 Hz.

Fig. 7 also is shown the dependence of dielectric losses with La-concentration in the BNT system. The addition of Lanthanum in concentration between 0.3 to 1.3 at.% shows a reduction in dielectric losses concerning the undoped sample. Increasing the La concentration the dielectric losses increase showing the maximum losses for the sample with the highest La concentration, where the donor character of Na substitution by La is manifested. Nevertheless, always the losses are lower than 0.4. Raman results show a reduction in oxygen vacancies with the introduction of La. Then, the reduction in losses at lower La concentration, imply a reduction in electrical conductivity until 1.3% of La, and the interpretation of the reduction of oxygen vacancies is reinforced [48,49].

3.6 Hysteresis Loops
The hysteresis loops (P vs E) were measured at room temperature for all compositions. Fig. 9-a shows clearly that ferroelectric properties of BNT system were considerably affected by addition of La. Continuous change of ferroelectric loop behavior from a normal ferroelectric (0-1.3 at.% La) to thin hysteresis loop (≥3.3 at.% La) suggests a phase transition from ferroelectric to non-ferroelectric phase, the hysteresis loop for 6.7%at of La show a dielectric behavior. It is known that relatively high concentrations of Lanthanum can lead a phase transition from ferroelectric phase to pseudocubic phase in BNT system and BNT-based solutions [27,34]. Our XRD results show a concentration close to 90% of cubic phase for 6.7% at of La. However, compositions with small Lanthanum quantities show the best ferroelectric characteristics, at around 1.3 at.% of La, where is observed the maximum remnant polarization $P_r$ ($28.3 \mu$C/cm$^2$) and lower coercive field of $E_c$ ($38$ kV/cm) than pure BNT ($51$ kV/cm) system. Fig. 9-b shows that after the maximum remanent polarization at 1.3 at.% La there follows an appreciable decrease in remnant polarization and the coercive field for La concentrations greater than 3.3 at.%. The high remnant polarization showed by doped samples with low La concentrations (≤ 1.3 at.% La) could be related to the contribution of La-O bonding additional of Na-O and Bi-O bondings due to aleatory introduction of La$^{3+}$ in A sites. Also is expected the compensation of native Bi/Na vacancies besides substitution of Bi$^{3+}$ or Na$^+$. Since ionic dielectric polarizability $[50]$ of Na$^+$($\alpha=1.8$) is considerably lower than La$^{3+}$ ($\alpha=6.07$) and the polarizability of Bi$^{3+}$ ($\alpha=6.04$) is close to that La$^{3+}$, then it is expected an increase in the dipolar moment of the unit cell when Na$^{1+}$ is substituted by La$^{3+}$ than Bi$^{3+}$ substitution. The morphological results by SEM micrographs shows a reduction of grain size from around 4.5 $\mu$m for pure BNT to 0.6 $\mu$m for sample with 1.3%at of La. The increase in the polarizability of the unit cell, give place to increase in remnant polarization. The reduction in grain size and therefore an increase of grain boundaries as a function of La concentration it could be expected an easier domain switching therefore an increase in mobility of domain wall, making easier the domain switching and therefore, a reduction in the coercive field, facilitating the polarization process caused by relaxation of inner stress generated from the electrostriction $[9]$. Both effects, increasing the polarizability of the unit cell, and reduction of grain size, give place to an improvement ferroelectric behavior analogous to the "soft" PZT systems doped with donor dopants where vacancies at site A are generated to balance the charge of the cell $[51]$.
Fig. 9 A) P–E hysteresis loops at room temperature for BNT and La-doped BNLT samples and B) Evolution of remnant polarization (Pr) as a function of La concentration at 3.3Hz and 80 kv/cm

3.7 Pyroelectric response

Fig. 10 show the pyroelectric response measurements. For these measurements, the samples with a thickness of around 500 μm with Ag contacts, were poled with a field of 50 kV/cm during 30 minutes at room temperature. The poled samples were heated periodically with a modulated diode laser with a constant power of 35 mW, the periodic heating of the sample give place to AC signal due to the pyroelectric effect. The amplitude of the pyroelectric signal was acquired as function of modulation frequency in the range of 5 to 40 Hz. The inset of Fig. 10 shows the pyroelectric signal at 10 Hz as a function of the La concentration. The introduction of La increase the pyroelectric signal, the maximum pyroelectric response is obtained for the sample with 1.3% at of La, respect to pure BNT sample the signal is increased close to four times, after that at 3.3% the amplitude signal is reduced to half of the pure BNT sample, for 6.7% the signal is very small. The behavior of the pyroelectric signal with La concentration, show a similar behavior of the remnant polarization with La concentration, evidencing the direct relation between these parameters. For 3.3% at of La, the remnant polarization shows a drastic reduction, and for 6.7% the Pr is close to 0, similar drastic reduction is observed in the pyroelectric signal.
Performing an analysis of the set of results presented in the BNT system doped with La, we found the following relevant aspects.

The synthesis of the BNT doped with La obtained from powders of the drying of a precursor solution of BNT using the acetic acid route as solvent of the acetates used and adding an encapsulation step of the samples in the sintering step, allowed us to obtain samples with higher relative densities than 94%. Even for the highest La concentration, it was not observed any segregation of the secondary phase. So, it is possible to study the effect of La in modifying the perovskite lattice of BNT and the evolution of its ferroelectric, dielectric, and pyroelectric properties. The introduction of La$^{3+}$ in the A sites acts as an iso-valent ion in the case of substitution by Bi$^{3+}$, and as a donor when substituting Na$^{+1}$, in the latter case, will lead to the creation of vacancies of Na. The XRD results show a distortion in the lattice, with an increase in the volume of lattice until 1.3%, and for concentrations greater than or equal to 3.3% gives rise to the structural transition from rhombohedral to the cubic crystalline phase, also by the SEM micrographs is observed a reduction in the grain size with increasing

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**Fig. 10** Signal amplitude of the pyroelectric response as a function of the modulation frequency, of the samples doped with La. The inset shows the amplitude of the pyroelectric signal at a fixed frequency of 10 Hz, for the different La concentrations.
La concentration. The improvement of the ferroelectric properties with low La concentrations indicates that in this range of concentrations, La$^{3+}$ initially enters compensating inherent vacancies of Bi and Na, when increasing its concentration initiates a random substitution of Bi and Na, giving place to a distribution of nanoregions rich in Na, Bi, and La that are reflected in the shifts of the characteristic Raman modes of the BNT, where the vibrations of the Na-O, La-O bonds and the vibrations of the TiO$_6$ octahedron are affected.

For La concentrations greater than 1.3%, additional to the reduction of the grain size, is observed the coexistence of the rhombohedral and cubic crystalline phases, the last one rises to a concentration close to 90% for 6.7%at of La, without observing segregation of secondary phases. Additionally, the substitution of La for Na gives rise to greater polarizability of the unit cell, which is related to the increase in the remnant polarization. Also, the decrease of the grain size allows a reduction of the coercive field, both effects result in improved ferroelectric and pyroelectric properties in low concentrations ($\leq$ 1.3%) of La, around 1.3% has obtained the maximum in remnant polarization, and also an appreciable reduction of the coercive field. The direct relationship between the remnant polarization and the pyroelectric coefficient, shows that the pyroelectric response with the incorporation of La, also obtains the maximum pyroelectric response for a concentration of La of 1.3%, and the behavior with La concentration is like that of Pr. This result is of great importance because around this concentration of La is possible the construction of efficient power light detectors, heat flux sensors useful in photopyroelectric techniques, and in thin films, as infrared detectors.

In general, for La concentration greater than or equal to 3.3%, the ferroelectric and pyroelectric properties of BNT are degraded due to the promotion of the cubic phase, which increases for higher La concentrations. Nevertheless, the region of La concentration around 6.7% is also important because, implies the possibility to obtain BNT in the cubic stable phase, where its good dielectric properties can be useful in some devices like capacitors.

4 Conclusions

Stable solutions of pure BNT system and doped with lanthanum using concentrations from 0 to 6.7 at. % were possible to obtain by sol-gel method and the acetic acid route, using
encapsulation of the samples in the sintering step was necessary to obtain bulk samples with high densification values about 94-97 %. An increase of amount of lanthanum produces a suppression in the grain growth where average grain size was diminished from 4.5μm to 0.5μm. The XRD results show that addition of small concentrations (≤ 1.3 at.%) of Lanthanum induce an increase into the volume of BNT cell and a phase transition from rhombohedral to non-ferroelectric phase when concentration increase until 6.7 at.% La. The ferroelectric properties was improved by doping BNT with La (≤ 1.3 at.%) while that for higher La concentrations P, drop quickly. The increase in Lanthanum lead to a change of transition temperature Td to lower temperatures from 220 °C to 71 °C while the dissipation factor tan (δ) and maximum dielectric constant ε max decrease from 0.05 to 0.035 and 2600 to 830 respectively. The incorporation of La in low concentrations in the BNT helps to eliminate the defects and vacancies inherent in the processing of the BNT. The compensation of these vacancies in random sites of Bi and Na maintains the rhombohedral structure and increase the remnant polarization, as well as the pyroelectric response. In this low doping range, a reduction in the coercive field is also obtained, accompanied by a decrease in grain size. 1.3% of La concentration is the appropriate doping region for applications such as heat flux sensors, and power radiation detectors due to its best obtained pyroelectric response. For higher concentrations, a transition from the rhombohedral to cubic phase is promoted, with the consequent degradation of the ferroelectric properties. Additional studies with concentrations of La around 6.7% are interesting because it is likely to induce a complete transformation to the stable cubic structure whose dielectric properties are of technological interest in capacitors.

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