Structural, microstructural and dielectric properties of $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{(1-x/4)}\text{O}_3$ prepared by sol gel method

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Detailed structural and dielectric properties of Lanthanum-doped barium titanate $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{(1-x/4)}\text{O}_3$ ceramic powders BLTx (where $x = 0.00; 0.10; 0.20; 0.30$ and 0.40)/BT, BLT10, BLT20, BLT30 and BLT40, synthesized by the sol gel process, calcined at 900°C for 3 h and sintered at 1250°C for 6 h, have been investigated. The phase formation and crystal structure of the samples were checked by X-ray diffraction (XRD) and Raman spectroscopy. The samples crystallize in the pure perovskite structure that transforms from tetragonal to pseudocubic under doping with La; results that have been confirmed by Rietveld Refinement technique. The estimated average crystallite size of the samples was about 23 nm. Dielectric parameters (dielectric permittivity and losses) were determined in the temperature range room temperature (RT) — 280°C and in the frequency range 500 Hz–2 MHz. La doping gives rise to a strong decrease of the ferro-to-paraelectric transition temperature, and the frequency dependence of the permittivity shows that the samples with $x = 0.00$ and $x = 0.10$ reach their resonance frequency. The frequency dependence of impedance and electric modulus properties were studied over a wide frequency range from 1 kHz to 2 MHz at various temperatures to confirm the contributions from grains and grain-boundaries. The complex impedance analysis data have been presented in the Nyquist plot which is used to identify the corresponding equivalent circuit and fundamental circuit parameters; it was found that the grain boundaries resistance is dominant at room temperature. The frequency dependence of the parameters permittivity, losses and AC conductivity reveals that the relaxation process is of the Maxwell–Wagner type of interfacial polarization.

Keywords: $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{(1-x/4)}\text{O}_3$ ceramics; Rietveld refinement; PTCR effect; dielectric properties; complex impedance.

1. Introduction

Barium Titanate (BaTiO_3) and its solid solutions are an important class of materials that show remarkable piezoelectric response. It includes ferroelectric behavior below 130°C , spontaneous polarization and nonlinear optical coefficients, high dielectric constant and low dielectric loss that are useful for technological applications, such as gate dielectrics, ultrasonic transducers, ferroelectric random access memories FRAM's, Multilayer Ceramic (MLCCs), detection of gaseous pollutants like CO, Positive temperature coefficient resistors (PTCR), optical data storage at high density, pyroelectric security surveillance systems, waveguide modulators, IR detectors, etc.^{1–12}

BaTiO_3 is a typical ferroelectric with three phase transitions in which crystallographic structure changes with temperature, from rhombohedral (R3m) to orthorhombic (Amm2) around -80°C ; from orthorhombic to tetragonal (P4mm) around 5°C ; and from tetragonal to cubic (Pm-3m) around 130°C .¹³

Multiple-ion occupation of Ba and/or Ti sites in BaTiO_3 perovskite system are expected to bring changes in its Curie temperature, structural, dielectric and ferroelectric properties.¹⁴ It is also known that lanthanum which is a donor-dopant occupies the Ba sites in the crystal lattice of BaTiO_3 . On the other hand, substitution of La^{3+} on Ba^{2+} sites creates charge defects. Three compensation mechanisms are possible: barium vacancies, titanium vacancies, and electrons. In this type of materials, the main doping mechanism is the ionic compensation one. However, the controversy remains whether the dominant ionic mechanism is a result of the creation of barium or titanium vacancies.^{15–17} Doping BaTiO_3 with La produces a change in symmetry of barium titanate from tetragonal to cubic, and a change in grain size and in electrical resistivity.^{18–20} Thus, in this study, the influence of lanthanum doping (up to 40 at.%) on the structure, microstructure, dielectric and impedance properties of barium titanate ceramics, which were prepared by the sol gel method, are investigated. Our interest is also in optimizing the

calcination temperature that leads to a decrease in the crystallite size. The synthesized powders whose chemical formula is $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$, were elaborated using the sol gel process through the destabilization of colloidal solution (DCS) method, and were calcined at 900°C for 3 h before sintering at 1250°C for 6 h. The data extracted from dielectric measurements has been used to calculate and analyze the AC impedance of the sintered $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ceramics.

The analysis of impedance at high temperatures shows the presence of both grain interior and grain boundary contributions to the resistivity of the samples. Weak PTCR effect was also observed in the pure barium titanate sample.

2. Experimental Procedure

2.1. Samples preparation

Lanthanum-doped barium titanate powders, $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ (BLT_x) (where $x = 0.00, 0.10, 0.20, 0.30$ and 0.40), were prepared by the sol gel route using titanium(IV) isopropoxide: $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (purity $\geq 97\%$), Barium acetate $\text{C}_4\text{H}_6\text{BaO}_4$ (purity 99%) and lanthanum(III) acetate hydrate $\text{C}_6\text{H}_9\text{LaO}_6 \cdot x\text{H}_2\text{O}$ (purity 99%) as precursors, in adequate proportions. Distilled water, acetic acid CH_3COOH and ethanol $\text{C}_2\text{H}_5\text{OH}$ were used as solvents.

The following flow chart details the experimental procedure of the preparation of the samples.

2.2. Characterization equipment

The crystal structure of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ powders was determined by X-ray diffraction (XRD) with a scanning rate of $0.02^\circ/\text{min}$ for 2θ range 20° – 80° , using a $\text{CuK}\alpha$ radiation

Fig. 1. Flow chart of the preparation of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ samples.

wavelength $\lambda = 1.54059 \text{ \AA}$ (Diffractometer system= XPERT-PRO) operating at 30 mA and 40 kV, FTIR spectra (VERTEX 70) and Raman spectra (SENTERRA). Microstructure of the ceramics were characterized using a scanning electron microscope (SEM) (Quanta 200 FEI). For dielectric measurements, the powders were uniaxially pressed into discs with a diameter of about 12 mm and a thickness of about 1.2 mm at a pressure of 9 MPa in a stainless steel die. The pressed discs were sintered in air at 1250°C for 6 h.

Dielectric measurements were performed using an impedance analyzer (HP 4284A), in the temperature and frequency ranges [ambient, 270°C] and [500 Hz, 2 MHz], respectively.

3. Results and Discussion

3.1. Structural characterizations

Figure 2(a) illustrates the diffractograms of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ powders calcined at 900°C during 3 h, and shows that all the samples crystallize in the pure perovskite phase, without any presence of traces of impurities.

Furthermore, since the lanthanum-doping rate was increased, the diffraction peaks slightly shift toward higher angles, as shown in Fig. 2(b). Indeed, a zoom in on the peak (111) in the range $37^\circ < 2\theta < 40^\circ$ shows clearly that La-doping moves the position of this peak to high angles, indicating a reduction of the unit cell volume that is consecutive to the incorporation of La atoms in BaTiO_3 lattice. As expected, as the ionic radii of Ba^{2+} and La^{3+} are 1.49 and $1.172 \text{ \AA}$, respectively, then a lattice distortion would be induced. La-doping gives rise to a gradual transformation from quadratic (pure BT) to pseudo-cubic phase as revealed by the zoom on the peak (200) (Fig. 2(c)) in the range $44^\circ < 2\theta < 47^\circ$, showing that this large and asymmetric peak indicates the existence of two complementary peaks with intensities of 13.70% and 22.22%, observed around $2\theta = 45^\circ 09'$ and $2\theta = 45^\circ 36'$ in the pure sample ($x = 0.00$), and these two peaks tend to merge, as observed for the three other compositions while maintaining relatively large FWHM. The fact that no impurities have been detected on XRD spectra suggests that the solubility of La in BaTiO_3 lattice could be greater than 40%.

Structural refinement was carried out for the $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ($x = 0.00; 0.10; 0.20; 0.30$ and 0.40) ceramic powders calcined at 900°C during 3 h using Rietveld refinement program Fullprof and the final output is shown in Fig. 3.

The starting structural model for the tetragonal crystal system and the initial parameters are taken from the crystallography open Database. The refinement model, which employs the $P4mm$ space group and the Thompson–Hastings pseudo-Voigt profile function, which intrinsically considers internal strain effects on the diffraction patterns, produced satisfactory agreement factors which are listed in Table 1. In this table, the fitting parameters (R_p , R_{wp} , R_{exp} and χ^2) show a

Fig. 2. (a) XRD pattern of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ powders calcined at 900°C for 3 h, (b) zoom in on (111) peak and (c) zoom in on (200) peak.

good agreement between the observed and calculated patterns in the Rietveld refinements of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ceramics with different compositions.

The XRD patterns, refined by the Rietveld method (Fig. 3), confirm the structure type of the crystalline phases

through the determination of the lattice parameters. On the other hand, detailed information such as, Wyckoff position and atomic positions of fit parameters are given in Table 2.

The evolution of the tetragonal unit cell parameters ' c ' and ' a ' with La content is shown in Fig. 4(a) and Table 1. It can be seen that both ' c ' and ' a ' decrease, in a similar linear behavior with increasing La content, leading to a decrease in the tetragonality expressed by the c/a ratio (Fig. 4(b) and Table 1); increase in La content tends to change the unit cell symmetry from tetragonal to pseudo cubic, as a consequence of electrostatic repulsions between $3d$ electrons of Ti^{4+} ions and $2p$ electrons of O^{2-} ions.²¹ On the other hand, and as said above, the elementary cell volume is also reduced with La doping as seen in Table 1, owing to the smaller ionic radius of La^{3+} ($1.172 \text{ \AA}$) compared to that of Ba^{2+} ($1.49 \text{ \AA}$).

The average crystallite size (ACS) of the $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ samples was calculated using Scherrer's formula²²:

$$D = k * \lambda / \beta * \cos \theta, \quad (1)$$

where D is the average crystallite size, k depends on the shape of crystallite size ($k = 0.9$ for spherical grains), $\lambda = 0.154059 \text{ nm}$ is the X-ray wavelength of the source used, and β is the full width at half maximum (FWHM) of the most intense peak on the 2θ scale.

Table 1 and Fig. 4(b) show the estimated average crystallite size of the as-prepared $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ nanopowders calcined at 900°C for 3 h, assuming spherical-shaped particles. It is observed that the ACS decreases with an increase in La content. This quite linear evolution may be approached by the approximate following equation:

$$\text{ACS} = -29.75x + 29.84. \quad (2)$$

Moreover, the variation of the crystallite size seems to be in correlation with that of the unit cell volume (Fig. 4(b)) and also with the grain size, as shown below.

Figure 5 shows the Raman spectra at room temperature of the $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ nanopowders, recorded for different La content and for frequencies ranging from 100 to 1400 cm^{-1} . It is well known that Raman spectroscopy is highly sensitive to local crystal structure and local symmetry because the structural changes alter the vibrational modes.^{23,24} For BaTiO_3 , the tetragonal phase is usually characterized by a sharp band at 305 cm^{-1} and asymmetric broader bands at 261 , 523 and 715 cm^{-1} . The corresponding peak positions for all ceramics are listed in Table 3. All the Raman spectra show a sharp peak at around $305\text{--}308 \text{ cm}^{-1}$ which is a characteristic peak for the tetragonal phase and whose intensity slightly decreases with an increase in x . The presence of the mode at 305 cm^{-1} along with the overlapping of E(TO) and E(LO) is observable for all compositions; this mode is associated with the tetragonal-to-cubic phase transition. This overlapping may be due to random orientation of crystallites. The same observation is valid for the peak around 715 cm^{-1} , which arises from phonons propagating along the

Fig. 3. The structural refinement patterns of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ using X-ray powder diffraction data for a mixture of tetragonal and cubic phases. Inset: 3D rendering in the ball-and-stick and polyhedron models, using the VESTA program.

Table 1. Cell parameters for BT, BLT10, BLT20, BLT30 and BLT40 samples.

Samples		BT	BLT10	BLT20	BLT30	BLT40
Elementary cell parameters	a (Å)	4.0023	3.9948	3.9868	3.9811	3.9775
	c (Å)	4.0135	4.002	3.9918	3.9857	3.9819
	Ratio c/a	1.0028	1.0014	1.0013	1.0012	1.0011
	V (Å) ³	64.29	63.84	63.49	63.17	63.00
Average crystallite size (nm)		29.8401	26.0819	24.5335	19.4008	17.9381
Calculated density ρ (g/cm ³)		6.022	6.038	6.048	6.047	6.036
Rietveld analysis parameters	R_p [%]	11.20	13.90	30.70	18.90	23.50
	R_{exp} [%]	6.96	9.80	16.98	10.77	14.52
	R_{wp} [%]	9.66	9.96	17.00	13.70	16.00
	χ^2 [%]	1.92	1.03	1.00	1.27	1.10

c axis (the corresponding mode is extremely broad and weak in the cubic phase).

The two bands at 305 and 715 cm⁻¹ tend to disappear for the sample with $x = 0.40$, indicating that the sample structure is very close to the cubic one, in conformity with XRD results (Table 1). A decrease in intensity and broadening in the

$A_1(LO_3)/E(LO)$ mode is observed for $x > 0.20$; this mode is extremely broad and weak in the cubic phase.

Two asymmetric, broad intense bands around 261 [A₁(TO₂)] and 523 cm⁻¹ [A₁(TO₃)] (optical modes) are observed, the mode A₁(TO₃) is also associated with a modification in the Ti–O–Ti bond.²⁵

Table 2. Atomic positions of the tetragonal phase of (Ba_{1-x}La_x)Ti_(1-x/4)O₃, as obtained from the Rietveld crystal structural refinements.

Sample	Site (wyckoff position)	Atomic positions			Occ	U_{iso}
		x	y	z		
BT	Ba(1a)	0.0000	0.0000	0.0000	1.0000	0.0098
	Ti(1b)	0.5000	0.5000	0.5243	1.0350	0.0125
	O1(1b)	0.5000	0.5000	0.0458	1.2286	0.0255
	O2(2c)	0.5000	0.0000	0.4664	1.1121	-0.0004
BLT10	Ba(1a)	0.0000	0.0000	0.0000	0.1250	0.0257
	La(1a)	0.0000	0.0000	0.0000	0.0056	0.0257
	Ti(1b)	0.5000	0.5000	-1.4609	0.1245	0.5395
	O1(1b)	0.5000	0.5000	-1.3092	0.1849	0.0053
	O2(2c)	0.5000	0.0000	2.4273	0.5059	0.0283
BLT20	Ba(1a)	0.0000	0.0000	0.0000	0.0085	0.0982
	La(1a)	0.0000	0.0000	0.0000	0.1165	0.0381
	Ti(1b)	0.5000	0.5000	0.5542	0.1168	0.0472
	O1(1b)	0.5000	0.5000	0.1107	0.1889	0.0223
	O2(2c)	0.5000	0.0000	0.4277	0.2270	0.0982
BLT30	Ba(1a)	0.0000	0.0000	0.0000	0.1250	0.0406
	La(1a)	0.0000	0.0000	0.0000	0.1301	0.0406
	Ti(1b)	0.5000	0.5000	2.5806	0.1665	0.0253
	O1(1b)	0.5000	0.5000	-0.0357	0.3943	0.0556
	O2(2c)	0.5000	0.0000	-2.6417	0.2388	0.0434
BLT40	Ba(1a)	0.0000	0.0000	0.0000	0.0166	0.1295
	La(1a)	0.0000	0.0000	0.0000	0.1084	0.1295
	Ti(1b)	0.5000	0.5000	0.4962	0.0961	0.0218
	O1(1b)	0.5000	0.5000	1.8010	0.1633	0.0261
	O2(2c)	0.5000	0.0000	0.5867	0.2964	-0.0188

Notes: Number of space group: 99 Herman–Mauguin symbol: P 4mm Hall symbol: P 4-2.

Crystal system: Tetragonal Angle(°): $\alpha = \beta = \gamma = 90^\circ$ Laue class: 4/mmm.

Fig. 4. Variation of (a) unit cell parameters, inset: Tetragonality (c/a), (b) Cell volume (v) and average crystallite size ($\langle D \rangle$) as a function of x for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ceramic powders calcined at 900°C for 3 h.

The observed anti-resonance effect at 192 cm^{-1} as an interference arises because of the coupling between the sharp $A_1(\text{TO}_1)$ and $A_1(\text{TO}_2)$ broad modes.

3.2. SEM characterization

Figures 6(a)–6(c) show the SEM micrographs of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ($x = 0.10, 0.30$ and 0.40) samples sintered at 1250°C for 6 h. These images show well-developed grain morphology and a dense microstructure.

Fig. 5. Raman spectra of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ calcined at 900°C for 3 h.

Table 3. Peak position of Raman spectra for BT, BLT10, BLT20, BLT30 and BLT40 samples calcined at 900°C for 3 h.

Composition	A1 (TO1)	A1 (TO2)	B1,E (TO+LO)	A1 (TO3)	A1(LO)/ E(LO)
BT	192	261	305	523	715
BLT10	186	257	306	523	717
BLT20	183	258	307	521	719
BLT30	189	258	306	522	716
BLT40	194	255	308	523	718

The doped ones are found to be dense with clearly visible grains of much smaller size than that of the undoped BaTiO_3 and with well-defined grain boundaries. Thus, for the ceramic with $x = 0.10$, a more uniform microstructure consisting of small grains and a rather spherical grain size distribution is observed (Fig. 6(a)). With an increase in La^{3+} ion content, the average grain size decreases, and was estimated for the whole range of x to be $1.2\text{ }\mu\text{m}$ ($x = 0.00$), $1.06\text{ }\mu\text{m}$ ($x = 0.10$), 872 nm ($x = 0.20$), 687 nm ($x = 0.30$) and 534 nm ($x = 0.40$). This result may be probably associated with the substitution of the larger Ba^{2+} ion by the smaller La^{3+} ion, structural defects, or the formation of agglomerates and barium and/or titanium vacancies. The grain size (G. S.) may be approximately approached by the following linear equation:

$$\text{G. S.} = -1.705x + 1.211. \quad (3)$$

As mentioned above, the behavior of the three parameters, unit cell volume, crystallite size and grain size is linear particularly indicating the good incorporation of La ions in the BaTiO_3 structure.

SEM analysis provides an estimate of the aggregates, and the sizes of these aggregates are higher than those calculated with specific surface area values or XRD analysis and this may be due to the fact that XRD provides information about the crystallites or crystallographic domain size.²⁶

3.3. Dielectric studies

The real permittivity was calculated with the help of the following relation:

$$\epsilon' = \frac{cd}{A\epsilon_0}, \quad (4)$$

where c is the capacitance of the pellet, d the thickness of the pellet, A the area of the cross-section of the pellet and $\epsilon_0 = 8.85 \times 10^{-12}\text{ F/m}$ is the permittivity of the vacuum.

(a)

(b)

(c)

Fig. 6. Scanning Electron Micrographs (SEM) for BLT10 (a), BLT30 (b) and BLT40 (c).

(a)

(b)

(c)

Fig. 7. Variation of the real part of permittivity (ϵ_r') with temperature at different frequencies, (a) BT (500 Hz–100 KHz), (b) BT (100 KHz–1 MHz) and (c) BLT10 (500 Hz–1 MHz) sintered at 1250°C for 6 h.

The dielectric properties of BT and BLT10 samples were studied as functions of temperature (ambient — 270°C) at different frequencies (500 Hz–1 MHz). Figures 7(a)–7(c) show the thermal behavior, for different frequencies, of the real part of the permittivity (ϵ_r') for BT and BLT10 samples.

Fig. 8. Variation of dielectric permittivity with frequency for the samples (a) BT and (b) BLT10 sintered at 1250 °C for 6 h.

Fig. 9. Variation of the real part of permittivity (ϵ_r) with frequencies at different temperature (28–240 °C) for the $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ sintered at 1250 °C for 6 h.

Fig. 10. Variation of dielectric losses ($\tan \delta$) with frequencies at different temperature (28 – 240°C) for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ sintered at 1250°C for 6 h.

It is observed in Fig. 7(a) that the permittivity of the pure BT decreases with an increase in frequency, as usually observed in such materials.²⁷ However, above the frequency 100 kHz (Fig. 7(b)), the permittivity increases with an increase in frequency, which indicates that the sample

approaches its frequency of resonance. This resonance might be of a mechanical nature involving the whole sample in a natural vibrational mode. Indeed, Fig. 8 indicates that the samples reach their resonance frequency (f_r) at the frequencies between 1.72 and 1.99 MHz and between 1.71 and

2.46 MHz) for BT (Fig. 8(a)) and BLT10 (Fig. 8(b)), respectively, also showing the effect of La doping on the f_r parameter.

A sharp peak (maximum of $\varepsilon'_r(T)$) is observed for $x = 0.00$ at $T_c = 134.5^\circ\text{C}$ ($\varepsilon'_r = 5278$ at 1 kHz) (Figs. 7(a) and 7(b)); however, for $x > 0.00$, the temperature corresponding to the ferro-to-paraelectric phase transition (FPPT) is lower than room temperature (Fig. 7(c)).²⁸

The variations of the permittivity (ε'_r) and dielectric loss ($\tan\delta$) with frequency (1 kHz–2 MHz) at various temperatures (ambient, 240°C) for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ samples are shown in Figs. 9 and 10, respectively.

It can be noticed that the two parameters ε'_r and $\tan\delta$ decrease for all the investigated samples with the addition of La, and show an increasing behavior with frequency accompanied with a dispersion in the lower frequency range. One possible reason for the significant reduction in the dielectric constant of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ may be the presence of less polarizable La^{3+} ions that substitutes for the more polarizable Ti^{4+} ions. The high values of the parameters dielectric constant and dielectric loss at low frequencies are explained on the basis of the excitation of bound electrons, lattice vibration dipole orientation, and accumulation of space charge polarization between the sample and the electrodes, i.e., Maxwell–Wagner polarization and interfacial polarization in the material.²⁹

The high values of permittivity are not usually intrinsic, but rather are associated with a heterogeneous conduction in the grain and grain boundary structure of the compounds, which arises ascribable to the materials consisting of grains separated by more insulating inter grain barriers as in a boundary layer capacitor. The observed variation of ε'_r with frequency can be attributed to the frequency relaxation in the material. This behavior is observed in dielectric materials in which a conduction mechanism of the hopping type is present.³⁰ On the other hand, the ionic-doping mechanism involves partial replacement of Ba^{+2} (ionic radius 1.49 Å) with the smaller La^{+3} (ionic radius 1.172 Å) ions on the A-site with creation of B-site vacancies. The B-site vacancy introduces void inside O_6 octahedra. It is known that in ABO_3 perovskite, ferroelectric phenomena are related to the shifting of B-site cation from its equivalent position. In the present

case, both A-site replacement and B site vacancy reduce the permittivity.

The high relative dielectric constant at room temperature is 3177 for $x = 0.10$ at 1 kHz while the dielectric loss is 0.23. It is found that $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ with $x = 0.40$ has a low value of the relative dielectric constant and loss, which might be attributed to the high levels of oxygen vacancies thanks to the formation of the pseudocubic phase.

The clear evidence of the existence of the resonance phenomenon mentioned above can be noticed. Table 4 gathers values of the real permittivity at different temperatures and frequencies, and Table 5 compares our values of the parameters unit cell volume, crystallite size and grain size to some of published works.

Table 4 shows in particular that for 10% in La, for the temperature 40°C and for the frequencies studied (10, 40, 200 and 600 kHz), an increase in the permittivity that is followed by a dramatic decrease for $x > 10\%$, while for $T = 100^\circ\text{C}$ and 140°C , the permittivity decreases, but this decrease is strongly marked for concentrations greater than 10% in La. An opposite behavior has been reported for BT-doped with low concentrations in La ($<0.2\%$ in La)³¹; indeed, very weak values of the permittivity were recorded.

Moreover, for BT, BLT10, and for all the temperatures and frequencies considered, ε_r decreases, however, for the other concentrations in La, values of this parameter remain practically temperature and frequency-independent.

3.4. Conductivity study

The electrical conductivity, σ , can be determined from dielectric data with the help of the following relation:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'', \quad (5)$$

where f is the frequency (Hz), ε_0 is the permittivity of vacuum (8.85×10^{-12} F/m) and ε'' is the imaginary part of the dielectric permittivity.

Figure 11 shows the frequency dependence of the conductivity, at different temperatures, for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ samples, with $x = 0.00, 0.10, 0.20$ and 0.30 . It is noted on this figure that for the samples BT and BLT10, as the frequency increases, σ shows an almost frequency-independent behavior followed by a dispersion above a certain frequency

Table 4. Value of the real part of permittivity (ε_r) with temperature at different frequencies (10–40–200 and 600 KHz) for the $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ (Fig. 7(c)).

Sample	ε'_r (at 10 KHz)			ε'_r (at 40 KHz)			ε'_r (at 200 KHz)			ε'_r (at 600 KHz)		
	40°C	100°C	140°C	40°C	100°C	140°C	40°C	100°C	140°C	40°C	100°C	140°C
BT	1684	1663	2902	1610	1621	2815	1541	1594	2790	1595	1683	3181
BLT10	2070	1531	1433	1858	1359	1241	1695	1258	1119	1654	1250	1105
BLT20	71.68	66.32	61.99	71.56	66.22	61.89	71.38	66.03	61.75	71.25	65.88	61.67
BLT30	124.34	103.34	96.65	119.18	102.94	96.28	115.33	102.54	95.99	113.51	102.35	96.03
BLT40	49.01	45.24	43.32	48.45	45.18	42.98	48.04	45.10	40.23	47.93	45.04	37.19

Table 5. Some $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ structural and dielectric parameters obtained with other studies.

BLTx	a (Å)	c (Å)	V (Å) ³	A.C.S (nm)	G.S (μm)	T_C (°C)	ϵ'_{max} (at T_C)	Method and reference
$x = 0.00$	3.9957	4.0256	64.270	—	50	117	5520 (10 kHz)	Solid state ¹⁸
	4.00835	4.02840	64.723	31.56	0.850	144	900 (1 K)	Sol gel ³²
	4.0023	4.0135	64.29	29.840	1.2	134.5	5278 (1 K)	Sol gel (This work)
$x = 0.001$	3.9931	4.0318	64.28	—	25	125	3405 (20 K)	Solid state ³³
$x = 0.0025$	3.9934	4.0330	64.32	—	—	125	4446 (20 K)	
$x = 0.005$	3.9896	4.0296	64.14	—	—	110	2608 (20 K)	
$x = 0.01$	3.9908	4.0234	64.08	—	—	100	1374 (20 K)	
$x = 0.025$	3.9896	4.0156	63.92	—	55	60	1689 (20 K)	
$x = 0.03$	4.00638	4.01840	64.499	29.52	0.200	28.5	1050 (1 K)	Sol gel ³²
$x = 0.04$	3.9953	4.0073	63.968	—	—	45	6000 (10 K)	Solid state ¹⁸
$x = 0.05$	4.00409	4.00409	64.197	28.87	—	12	1235 (1 K)	Sol gel ³²
$x = 0.06$	3.9985	3.9985	63.930	—	—	20	8630 (10 K)	Solid state ¹⁸
$x = 0.08$	4.00060	4.00060	64.029	27.45	—	−41	1450 (1 K)	Sol gel ³²
$x = 0.10$	3.9950	3.9950	63.760	—	5	−100	9900 (10 K)	Solid state ¹⁸
	3.9948	4.002	63.84	26.082	1.06	—	—	Sol gel (This work)

Fig. 11. Variation of conductivity as a function of frequency for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ceramics, with $x = 0.00, 0.10, 0.20$ and 0.30 .

(region where σ is sensitive to both frequency and temperature)³⁴; the observed increase may be attributed to the relaxation phenomenon. Moreover, for a given frequency, σ increases ($T > 60^\circ\text{C}$) with temperature ($x = 0.00$) until the

ferro-to-paraelectric transition temperature and then decreases indicating the existence of the PTCR effect.

It is also observed in Fig. 11 that for $x > 10\%$, the conductivity exhibits an almost linear behavior which may be

Fig. 12. Variation of the conductivity as a function of $1000/T$ for BaTiO_3 ceramic.

Fig. 13. Thermal variation of resistivity at various frequencies of BaTiO_3 pellet sintered at 1250°C for 6 h.

due to the increase of the conductive character of the samples for such concentrations in La.

Figure 12 displays the variation of $\ln(\sigma)$ as a function of $1000/T$ (T is the absolute temperature) at different frequencies (500 Hz–100 KHz), for BT below and above the transition temperature. It is observed that σ first increases (below T_c) with increasing temperature, and then decreases (above T_c). This behavior, in accordance with that observed in Fig. 11, may be explained as due to the existence of the PTCR effect.

Indeed, as revealed by the curves corresponding to thermal variations of resistivity (Fig. 13), the latter decreases until T_c and then increases. The dc activation energy, E_a , was calculated from the slope of the graph (Fig. 12) using the Arrhenius formula:

$$\sigma = \sigma_0 \exp(-E_a/K_B T). \quad (6)$$

Hence, $\ln(\sigma) = \ln(\sigma_0) - E_a/K_B T$.

Here, σ_0 stands for the pre-exponential term, σ is the ac conductivity, K_B is the Boltzmann constant and T is the temperature (in Kelvin). Activation energy (E_a) values are listed in Table 6 for various frequencies.

The values of E_a (associated with the dc conductivity) for the pure sample obtained for the ferroelectric (tetragonal structure $T < T_c$) and paraelectric (cubic structure $T > T_c$) region, ranging from 0.0024 to 0.076 eV and 0.018 to 0.582 eV, may be explained as due to the hopping charge mechanisms.³⁵ At lower temperature, the oxygen vacancies exhibit low mobility; however, with the increase in temperature, they are activated and contribute to the observed electrical behavior. It can be noticed that the obtained activation energy may be associated with single-ionized oxygen vacancies.^{36,37} Figure 13 shows the variation of resistivity with temperature (28–255 °C) for the sintered BaTiO_3 ceramics. The resistivity decreases with increasing temperature which indicates the semiconducting nature of the samples. However, a break is observed in the linear variation around the Curie temperature ($T_c = 134.5^\circ\text{C}$), and a weak PTCR effect arises, which is frequency dependent. There are two regions in the resistivity plot: the first region observed at low temperatures is due to impurities and may be attributed to the ordered state of the ferroelectric phase, and the second region that occurs at higher temperature which is due to polaronic hopping may be attributed to the disordered paraelectric state.³⁸

Table 6. Activation energy of conduction at different frequencies.

Frequency (KHz)	1	5	10	20	50	100	200	500	800	1000
$E_a(\text{ferro})\text{eV}$	0.076	0.033	0.017	0.0047	0.003	0.0024	0.0032	0.016	0.027	0.034
$E_a(\text{Parra})\text{eV}$	0.462	0.351	0.276	0.201	0.105	0.018	0.106	0.333	0.482	0.582

Fig. 14. Z'' as a function of Z' for the ceramics $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$. Inset Equivalent circuit.

3.5. Complex impedance and electrical modulus studies

The electrical properties of a material are normally determined from the dielectric data with the help of the following relations:

Complex permittivity:

$$\varepsilon^* = \varepsilon' - j\varepsilon''.$$

(7)

Dielectric loss:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{Z'}{Z''} = \frac{M''}{M'}.$$

(8)

Complex impedance:

$$Z^* = \frac{\varepsilon''}{C_0\omega(\varepsilon'^2 + \varepsilon''^2)} + j\frac{-\varepsilon'}{C_0\omega(\varepsilon'^2 + \varepsilon''^2)} = Z' + jZ'', \quad (9)$$

Complex electrical modulus:

$$M^* = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + jM'' \quad (10)$$

where $\omega = 2\pi f$ is the angular frequency, C_0 is the capacitance of the cell in vacuum, (ε', Z', M') and $(\varepsilon'', Z'', M'')$ are the real and imaginary components of permittivity, impedance and modulus, respectively.

In the perovskite lattice, the main mode of charge transport is a multiple jump process. This jumping process occurs especially among the potential barriers that exist within the structure and the local atoms/ions environment.

In order to understand better the nature of conduction, we studied the complex impedance spectra (Nyquist plot) of $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ samples. Figure 14 shows the impedance spectra ($Z'' = f(Z')$) of BLTx samples, which are sintered at 1250°C for 6 h, and measured at relatively high temperatures, from 200 to 400°C. For each temperature, the curves corresponding to the pure sample appear in the form of two depressed semicircular arcs, suggesting the presence of both bulk and grain boundary effects in the studied sample. In contrast, whereas, the single semicircle observed for the doped samples indicates that the grain boundary resistance is dominating over grain resistance.³⁹ It is observed in Fig. 14 that the slope of the lines decreases with increasing temperature, and hence they bend towards Z' axis, and that the corresponding radius of curvature decreases with increasing temperature due to the increase of the conductivity of the samples. Moreover, each semicircle may be represented by an

RC circuit, corresponding to an individual component (grain or grain boundary) of the samples and providing a real representation of their electrical properties.

By fitting the curves using Zview analysis software (version 3.1c), values of the equivalent circuits' parameters were extracted and they are given in Table 7.

Results from impedance spectra have been approached by an equivalent circuit composed of two parallel elements (R, CPE) connected in series, as shown in Fig. 14. R and CPE represent the resistance and the constant phase element, respectively. Indeed, the fitting results show that the measured $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ capacitance response throughout the frequency range is not ideal, i.e., the as-prepared samples do not behave as pure capacitors, which may be due to the distribution of various relaxation times.⁴⁰

Hence, the effect of the grains (bulk) and the grain boundaries are represented by the parallel combinations $R_g\text{-CPE}_g$ and $R_{gb}\text{-CPE}_{gb}$, respectively.

The frequency dependence of real part Z' and imaginary part Z'' of the impedance at different temperatures is shown in Fig. 15. It is observed that the magnitude of Z' decreases with increasing frequency and temperature, indicating the increase in ac conduction (σ_{ac}) in the samples. This increase in conduction may be explained as due to the contribution of defects such as oxygen deficiencies, and hence at high temperature, the contribution due to the latter is more dominant. At low frequencies, a significant decrease of Z' with increasing La content is observed. At high frequency, the value of Z' appears to be frequency independent (constant value)

Table 7. The estimated values of the equivalent circuits' parameters.

T (°C)	x = 0.00						x = 0.10					
	R_g (KΩ)	CPE-g (10 ⁻⁹ F)	n_1	R_{gb} (KΩ)	CPE-gb (10 ⁻⁹ F)	n_2	R_g (KΩ)	CPE-g (10 ⁻⁹ F)	n_1	R_{gb} (KΩ)	CPE-gb (10 ⁻⁹ F)	n_2
200	342.59	1.797	0.98	4812	5.12	0.97	14	25.44	0.79	4015	1.28	0.99
250	255.00	1.115	0.99	3820	9.931	0.89	11	35.15	0.80	1124	3.62	0.90
300	61.00	1.180	0.97	2955	17.950	0.90	8	32.76	0.76	35.50	19.31	0.86
350	5.888	6.046	0.87	93.761	19.830	0.80	3.62	60.23	0.72	27.06	81.71	0.77
400	1.491	3.107	0.98	62.027	88.705	0.67	1.51	89.74	0.70	8.082	98.96	0.77
T (°C)	x = 0.20						x = 0.30					
	R_g (KΩ)	CPE-g (10 ⁻⁹ F)	n_1	R_{gb} (KΩ)	CPE-gb (10 ⁻⁹ F)	n_2	R_g (KΩ)	CPE-g (10 ⁻⁹ F)	n_1	R_{gb} (KΩ)	CPE-gb (10 ⁻⁹ F)	n_2
200	350	0.937	0.99	34930	0.0255	0.99	100	2.973	0.99	21820	0.0456	0.99
250	112	0.154	0.99	29000	0.0432	0.97	70	0.325	0.97	4965	0.0542	0.99
300	65	0.413	0.99	22300	0.164	0.87	35	1.091	0.92	2681	0.656	0.82
350	35.35	0.211	0.99	16464	0.0351	0.97	17	0.821	0.91	1083	0.713	0.82
400	8	0.401	0.99	7272	0.0224	0.99	15.5	0.155	0.99	999.8	0.4985	0.85
T (°C)	x = 0.40											
	R_g (KΩ)	CPE-g (10 ⁻⁹ F)	n_1	R_{gb} (KΩ)	CPE-gb (10 ⁻⁹ F)	n_2						
200	59	6.13	0.99	72000	0.0242	0.99						
250	34.2	0.0242	0.99	33000	0.0241	0.99						
300	24	0.219	0.99	4940	0.0957	0.90						
350	12.6	0.534	0.99	6362	0.0314	0.97						
400	8.5	0.808	0.99	5587	0.0312	0.96						

for all temperatures, indicating that there is an increase in the concentration of defects with the rise of temperature leading to an increase of conductivity of the samples. The merging of the Z' curves in the higher frequency (above 10 kHz) region is probably due to the release of space charges consequent to the reduction of the barrier properties of the samples. It is also

observed that the frequency at which the curves Z' coincide increases with the increase of the lanthanum content.

On the other hand, it is observed that Z'' increases with frequency, passes through a maximum that shifts towards higher frequencies on increasing both temperature and La content, and then decreases and tends to nearly a constant

Fig. 15. Variation of real part Z' and imaginary part Z'' of impedance as a function of the frequency for ceramics $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$.

value. The width of the maximum may suggest the existence of a distribution of relaxation times and large contribution of space charge polarization at highly resistive interface.⁴¹

For the pure sample, two peaks were observed for Z'' in the low and high frequency regions, that are due to grain boundary and bulk, respectively. In case of the doped samples, only one peak can be seen in the Z'' plots which means

that Nyquist plots (Fig. 14) exhibit only one semicircle corresponding to the grain boundary contribution which probably explains the effect of large grain boundaries of the electrical conduction mechanism.

Table 7 also shows that the grain boundary resistance is increased with La doping at relatively low temperatures (200°C and 250°C), but it is strongly reduced for higher temperatures.

Fig. 16. Variation of M' as a function of frequency for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ceramics.

Fig. 17. Variation of M'' as a function of frequency for $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$ ceramics.

3.6. Modulus spectra

Analysis and interpretation of the dynamic aspects of electric transport phenomena may be carried out with the help of complex modulus which provides information about the electrical processes characterized by the smallest capacity of the materials; the representation of the electric modulus suppresses the undesirable effects of extrinsic relaxation. Indeed, in the M^* formalism, the spatial charge effects

and polarization of the electrodes and the grain-boundary conduction process can be suppressed.^{42,43}

Figure 16 shows the variation of the real part of the electric modulus (M') as a function of frequency, at high temperatures (between 200 °C and 400 °C). Low values of M' are observed in the low frequency region followed by a continuous dispersion with increasing frequency. This dispersion is observed in all samples. It is also observed that the magnitude of M' remains almost constant in the low

frequency region, while at high-frequency region, the values of M' show saturation for all temperatures. This behavior of M' is probably due to the short range mobility of carriers such as ions. Moreover, M' shows a dispersion tending towards $M_{(\text{infini})}$, the asymptotic value of M' at high frequencies.

Figure 17 shows the frequency dependence of the imaginary part M'' of the electric modulus at different temperatures.

M'' exhibits a maximum which shifts to high frequencies with increase in temperature. This peak observed in the plot of M'' as a function of frequency corresponds to a relaxation process. The frequency region below this maximum of M'' gives the extent to which charge carriers are mobile on long distances (Jump conduction process). At the frequencies above this maximum, the carriers are confined to potential wells and hence are mobile on short distances.⁴⁴

Moreover, the widening of the observed asymmetric peak (Fig. 17) may be related to the existence of a distribution of relaxation times.

4. Conclusion

$(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{(1-x/4)}\text{O}_3$, lead free ceramics have been synthesized by the sol gel method. XRD analysis showed that a pure perovskite structure was obtained under heating at 900°C for 3 h, and Rietveld analysis confirms these results. A systematic decrease in tetragonality (c/a) indicates a transformation from the tetragonal to a pseudo-cubic phase with La doping. Raman spectroscopy further confirmed the phase transformation tetragonal-pseudocubic. Moreover, a linear behavior of the parameters cell volume, crystallite and grain size is observed pointing out the good incorporation of La in BaTiO_3 matrix.

Detailed studies of dielectric properties showed that the samples with $x = 0.00$ and 0.10 reached their resonance frequencies and indicate that the materials have mainly two contributions that come from bulk and grain boundary. The activation energy values suggest that the electrical conduction in BaTiO_3 is mainly due to the mobility of the single-ionized oxygen defects via hopping mechanism. The as-prepared samples showed a weak PTCR effect.

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