

Synthesis, structural and dielectric properties of Li-doped BaTiO₃ nanopowders by sol-gel method

F. Krimech^a, S. Sayouri^{a,*} and T. Lamcharfi^b

^aLaboratory of Physics, Theoretical and Applied, FSDM B.P. 179, Fez, Morocco

^bLaboratory of signals systems and components FST Street Immouzar, B.P. 2202 Fez, Morocco.

Li-doped BaTiO₃ nanoparticles with Li⁺ mole fraction, x , such as $0 \leq x \leq 0.30$ (BL _{x} T) have been successfully synthesized by the sol-gel method and their structure examined with X-ray diffraction (XRD) technique. The latter showed that these materials, heat treated at 1000 °C during 4hrs; crystallize in the pure tetragonal phase for the undoped sample (BT), which transforms into pseudo-cubic phase for $x \geq 0.05$. These results were confirmed by Raman analysis. The thermal behavior of the permittivity and the conductivity was studied and in particular the thermal behavior of the latter revealed the PTCR effect.

Key words: Sol gel, Structure analysis, Dielectric properties, PTCR effect.

Introduction

The lead-based perovskite Pb (Zr, Ti)O₃ (PZT) ceramics have attracted much attention for their dielectric characteristics [1, 2]. However, such materials contain lead, which is an unfavorable material because of its harmful effects to human being and environment. Recently, many research works have concerned lead-free piezoelectric materials in place of PZT for environmental protection. BaTiO₃ (BT) has become one of the most important ferroelectric materials used in the electronics ceramic industry.

BaTiO₃ is known by its Curie transition T_c of 120 °C [3] which defines two dielectric states: ferroelectric state for $T < T_c$ in which the material crystallizes in the tetragonal system and paraelectric state for $T \geq T_c$, where BT structure transforms to cubic one. Multiple dopants may be added to BaTiO₃ to adapt some of its properties for specific applications: Sr²⁺ to decrease its transition temperature T_c , Pb²⁺ to increase T_c and Co²⁺ to mitigate losses inherent to intense electric fields without affecting its piezoelectric constant [3].

Usually, BaTiO₃ (BT) based ceramics are fabricated using the conventional solid-state method. Several synthesis methods have been used to prepare BT powders including nonconventional ones such as, oxalate, hydrothermal synthesis and polymeric precursors method. Recently, considerable research efforts have been devoted to the preparation of materials by various wet chemical methods, such as solvothermal process [4], citrate method [5], emulsion method [6] and composite-hydroxide-mediated

method [7].

In the present study, Li-doped BaTiO₃ ceramics, Ba_{1- x} Li _{x} Ti_{1+ x /4}O₃ (BL _{x} T) (with $x = 0, 0.05, 0.1, 0.15, 0.2, 0.25$ and 0.3), were produced by the sol gel process. The choice of this method of processing was based on its various advantages, low processing temperature, high purity, homogeneity and an excellent control of the stoichiometry of the products [8].

We have investigated the structure and microstructure of the samples using X-ray diffraction (XRD), Raman Spectroscopy and scanning electron microscopy (SEM). We have also performed dielectric measurements for temperatures such as $30 < T < 200$ °C

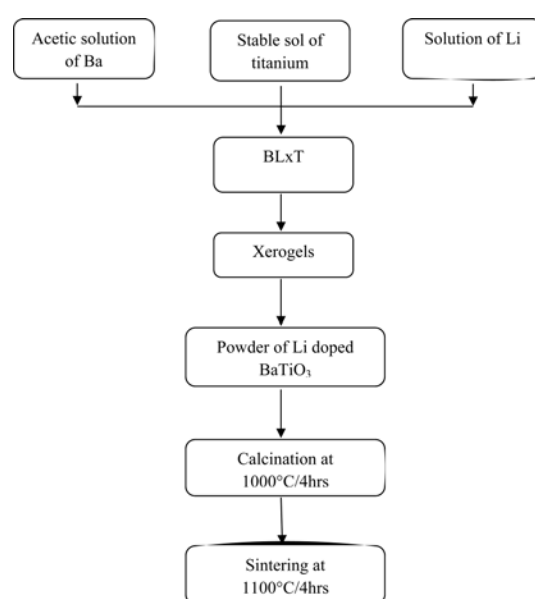


Fig. 1. Flow chart of the Li doped BaTiO₃ synthesis by the sol gel process.

*Corresponding author:
Tel : +212673785288
E-mail: ssayouri@gmail.com

and frequency range of [10 kHz, 2 MHz].

Experimental

Li doped BaTiO₃ powders Ba_{1-x}Li_xTi_{1+x/4}O₃ (BL_xT) were prepared by the sol gel method through the destabilization of colloidal solution (DCS). Barium acetate, titanium isopropoxide and lithium acetate were used as starting materials (all are 99% purity). Fig. 1 shows the flow chart of the sol gel process used for the preparation of the powders.

(BL_xT) samples with $x = (0, 0.05, 0.1, 0.15, 0.2, 0.25 \text{ and } 0.3)$ were prepared, and calcined at 1000 °C during 4 hrs and annealed at 1100 °C during 4hrs with a heating rate of 5 °C/min. For SEM analysis and dielectric measurements, the samples in pellet shapes were prepared and obtained by pressure with a uniaxial pressure of 8 tons/cm². The microstructure of the ceramics was examined by scanning electron microscopy (SEM) (Quanta 200 FEI model EDAX).

The crystallinity and phases of the powders were examined using an X-ray diffractometer (XRD) with CuK α ($\lambda = 1.5405 \text{ \AA}$) radiation and a Raman spectrometer.

Results and Discussion

X-ray diffraction study

Fig. 2(a) shows the XRD patterns of BL_xT ($x=0-0.30$) ceramics calcined at 1000 °C for 4hrs. Inspection of the peak intensities clearly demonstrates that the main phase for the as-prepared samples is a simple

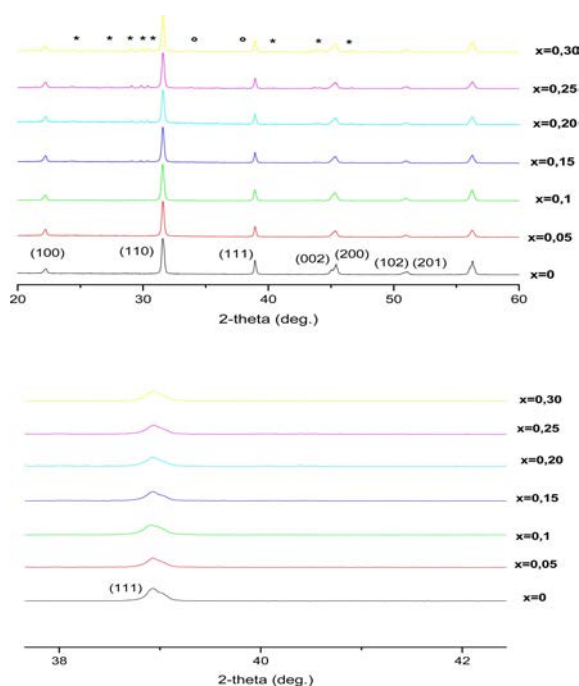


Fig. 2. (a) XRD patterns of Li doped BaTiO₃ for different concentration in Li+calcined at 1000 °C for 4hrs, (b) zoom in on the peak (111).

Table 1. Lattice parameters, tetragonality (c/a) and volumes of undoped BaTiO₃ and Li-doped BaTiO₃ ceramics ($x = 0-0.30$) calcined at 1000 °C for 4hrs.

x (%)	a (Å)	c (Å)	(c/a)	V
0	3,9970	4,0120	1,0037528	64,0957
5	3,9962	4,0036	1,0018518	63,9364
10	3,9966	4,0015	1,001226	63,9152
15	3,9975	4,0004	1,0007255	63,9264
20	3,9981	4,0001	1,0005002	63,9408
25	3,9989	3,9996	1,000175	63,9584
30	3,9984	3,9986	1,00005	63,9264

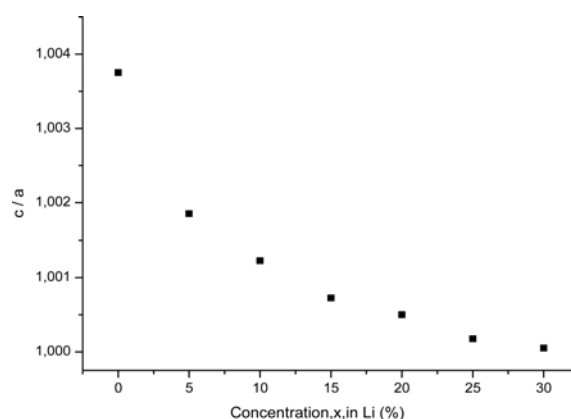


Fig. 3. c/a ratio vs Li content of the BL_xTcalcined at 1000 °C/ 4 hrs.

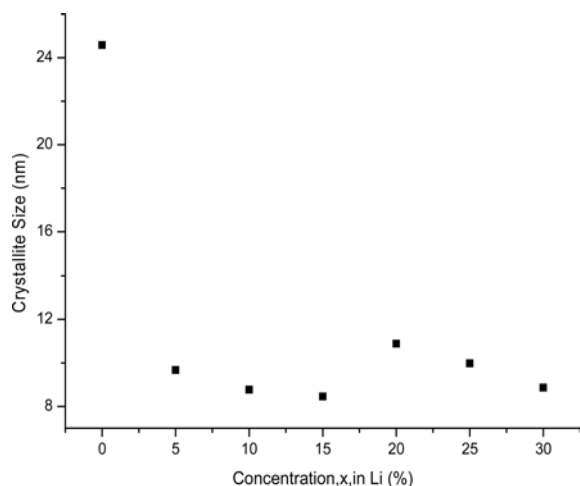
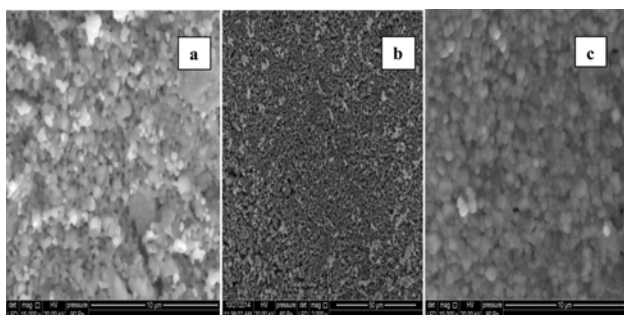
perovskite phase. Zoom in on the peak (111) (Fig. 2(b)) shows a shift of its position toward larger angles, which is indicative of incorporation and effect of Li on BT structure. Moreover, the intensity of this peak slightly decreases with increasing the mole fraction Ba/Li, due to the difference between ionic radii of Ba and Li. For low Li content ($x < 0.10$), we observe the presence of (200) and (002) peaks around $2\theta = 45.36^\circ$ and 45.05° , respectively, which are characteristic of the quadratic phase. Increasing x (Li content) tends to merge these two peaks, and for $x > 0.10$, they are practically undistinguishable, indicating a decrease in the tetragonality of the BT matrix and hence a gradual transition from tetragonal to pseudo cubic phase.

Besides, for $x > 0.10$, very weak peaks corresponding to two secondary phases appearing around 24.55° , 27.19° , 29.06° , 29.84° , 30.38° , 40.10° , 43.95° and 46.40° (*), and around 33.79° and 37.65° (°) are associated with Li₂ Ba₃ Ti₈ O₂₀ (JCPDS 049-0189) and with Li₂O phases. The influence of the incorporation of Li has been followed by calculation of lattice parameters. This calculation was done using the software X-powder. The values obtained are gathered in Table 1. It is clearly seen that introduction of Li stabilizes the pseudo-cubic phase (Table 1, Fig. 3).

The crystallitesize was estimated using Scherrer's equation:

Table 2. Crystallite size of Li doped BaTiO₃, calcined at 1000°C (4 hrs)

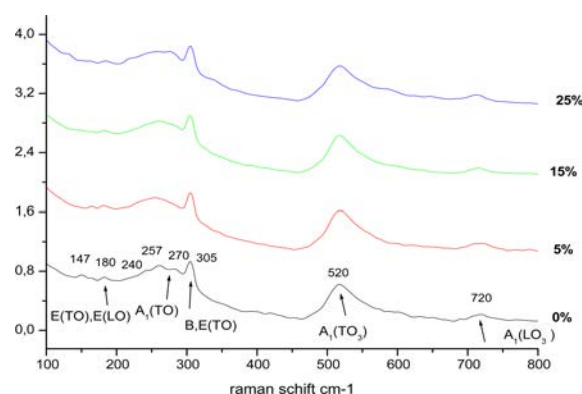
x (%)	Crystallite Size (nm)
0	24.5824
5	9.6739
10	8.7707
15	8.4543
20	10.8839
25	9.9749
30	8.8668

**Fig. 4.** Evolution of the crystallite size of BLxT ($0 \leq x \leq 0.30$) calcined at 1000 °C (4 hrs).**Fig. 5.** SEM images of Li-doped BaTiO₃ sintered at 1100 °C for 4 hrs. The Li molar fraction: (a) 0, (b) 0.15, and (c) 0.25.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the X-ray wavelength (1.5406 Å), β is the full-width-at-half-maximum (FWHM) of a characteristic diffraction peak and θ the diffraction angle (the value is calculated from FWHM of the most intense line at the diffraction angle). The estimated values for our samples, heat treated at 1000 °C during 4 hrs are given in Table 2.

It is clearly observed that incorporation of Li ($x = 0.05$) abruptly diminishes the crystallite size from about 24.6 nm to 9.7 nm and then its value fluctuates around a mean value (9.4 nm) (Fig. 4). This can be explained by the fact that lithium has an ionic radius (0.076 nm) smaller than that of barium (0.16 nm).

**Fig. 6.** Raman spectra of Li-doped BaTiO₃ samples calcined at 1000 °C/4 hrs.

Characterization by scanning electron microscopy

The SEM micrographs of BLxT ($x = 0, 0.15, 0.25$) ceramic samples sintered at 1100 °C for 4 h are shown in Fig. 5. The estimated grain sizes were about 447 nm and 535 nm for $x = 0.15$ and $x = 0.25$, respectively. For all samples, we have observed that the fine particles aggregate into grains presenting a quite regular morphology in shape throughout all the compositions.

Raman investigations

Fig.6 shows Raman spectra of the barium titanate (BT) and BLxT powders calcined at 1000 °C/4 hrs. BaTiO₃ has five atoms and fifteen degrees of freedom per unit cell. In the cubic phase it has Oh symmetry, and the 15 degrees of freedom are divided into the optical representations $3F_{1u} + F_{2u}, F_{1u}$; the latter symmetry mode corresponds to an acoustical branch. At room temperature BaTiO₃ is tetragonal and has C_{4v} symmetry.

The frequency-covered range was from 200 cm⁻¹ to 800 cm⁻¹. Based on the crystallography, Raman-active modes for tetragonal BaTiO₃ (P4mm) are $4E(TO + LO) + 3A_1(TO + LO) + B_1(TO + LO)$, while no Raman-active mode is predicted for the cubic phase (Pm3m) [9].

The spectrum of BT shows the three modes (B₁ / E (TO₁LO), (E (TO) / A₁(TO₃) and (A₁(LO) / E (TO) located at around 268 cm⁻¹, 305 cm⁻¹, 520 cm⁻¹ and 720 cm⁻¹, respectively. For BLxT ($x = 0.05, 0.15$ and 0.25), a slight weakening of the intensity of the mode located around 720 cm⁻¹ is observed which may be associated with the crystallographic transformation from the tetragonal to the pseudo cubic phase in agreement with XRD results.

Dielectric constant and loss tangent

Temperature dependence of the real part of the dielectric permittivity (ϵ_r) and the dielectric losses, at frequencies ranging from 10 kHz to 2 MHz were performed for the compositions $x = 0, x = 0.1, x = 0.15$ and $x = 0.20$; these dependences are displayed in

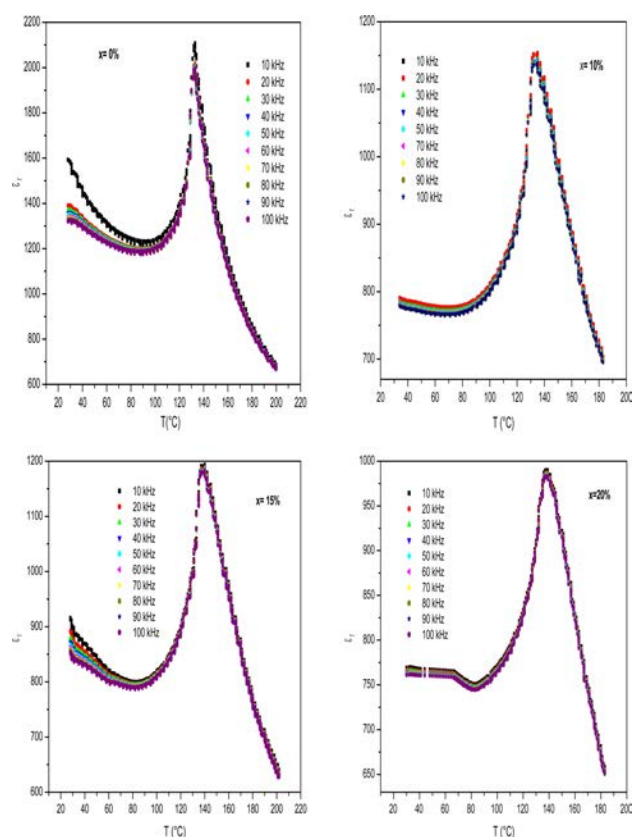


Fig. 7. Thermal variations of ϵ_r for frequencies ranging from 10 kHz to 100 kHz.

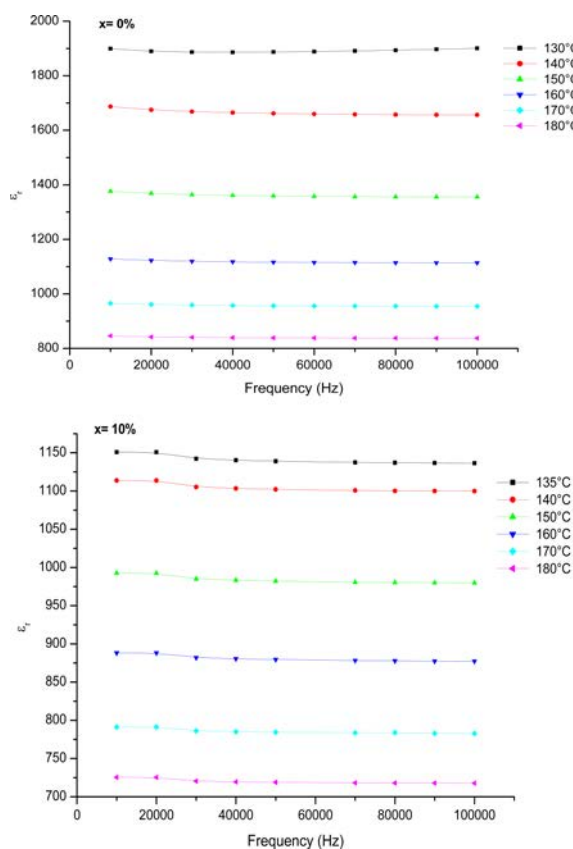


Fig. 8. Frequency dependences of ϵ_r for different temperatures.

Table 3. Values of the temperature, T_m , of the maximum of (ϵ_r).

x (%)	T_m (°C)
0	131 (T_c)
10	133
15	138
20	138

(figures 7-11). It is seen that the pure BT sample behaves as a classical ferroelectric, with a Curie temperature $T_c = 131$ °C. For BLxT ($x > 0$) samples, the value of the temperature, T_m , of the maximum of ϵ_r increases slightly (Table 3) in relation to T_c , accompanied with a diffuse character of the ferro-to-paraelectric transition (Fig. 7). Moreover thermal variations of the permittivity for frequencies (f_r) ranging from 10 kHz to 2 MHz show that for $f_r \leq 100$ kHz these variations are almost frequency independent for BT and BLxT ($x = 0.1, 0.15$ and 0.20) (Figs. 7 and 8).

For $f_r \geq 100$ kHz, we observe an unusual increase of the maximum of the permittivity (ϵ_r) with increasing frequency (Fig. 9). This increase with frequency of ϵ_r indicates that we are approaching frequency resonance of the sample (Fig. 10 and Table 4). Indeed, resonance frequencies are theoretically expected above very high

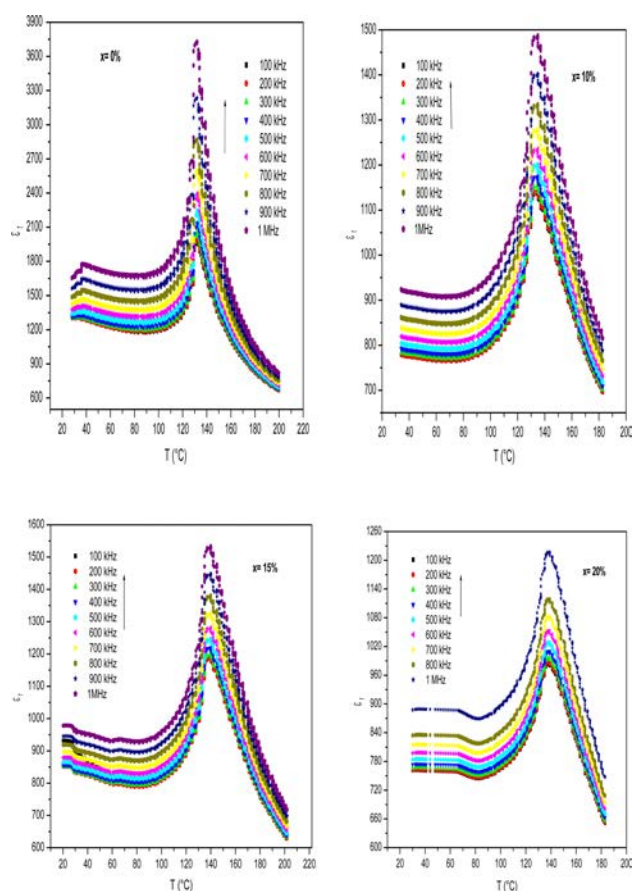
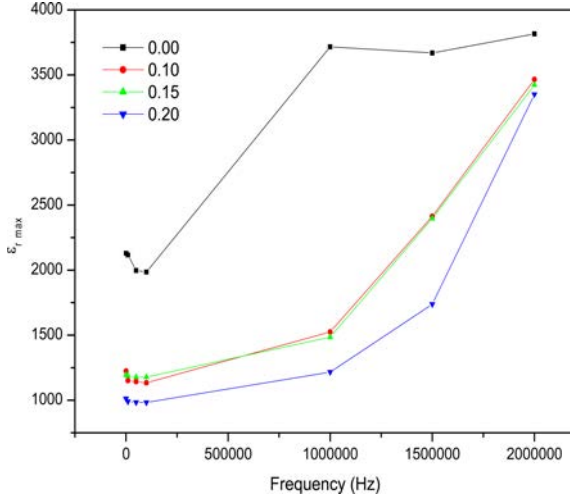
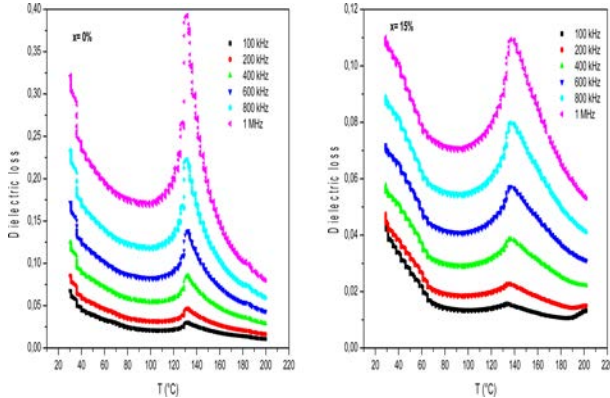


Fig. 9. Thermal variations of (ϵ_r) for frequencies ranging from 100 kHz to 1 MHz.

Table 4. Temperature of the maximum of ϵ_r of Li-doped BaTiO₃ at various frequencies.

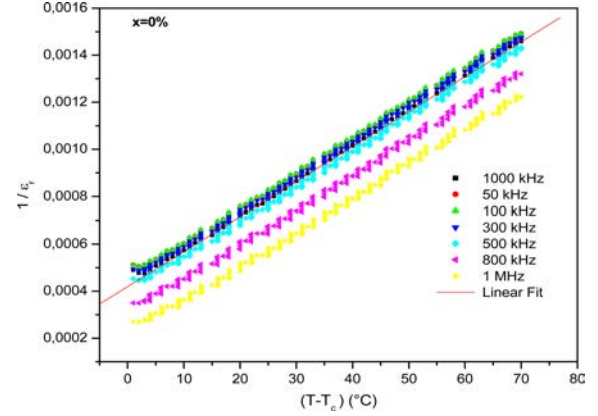
BL _x T	500 Hz	10 kHz	50 kHz	100 kHz	1 MHz	1.5 MHz
x = 0	2130	2116	1997	1985	3716	3916
x = 0.1	1224	1151	1143	1134	1525	2413
x = 0.15	1193	1188	1178	1178	1485	2397
x = 0.2	1013	990	984	983	1216	1738

**Fig. 10.** Frequency dependences of ϵ_r for the BC_xT ceramics at 10 kHz.**Fig. 11.** Temperature dependence of the dielectric losses for frequencies ranging from 100 kHz to 1 MHz.**Table 5.** Values of dielectric losses and temperature of their maximum of Li-doped BaTiO₃ at various frequencies.

BL _x T	50 kHz	500 kHz	800 kHz	1 MHz	T _m (°C)
x = 0	0.02	0.10	0.21	0.39	131 (T _c)
x = 0.1	0.01	0.04	0.08	0.11	133
x = 0.15	0.01	0.04	0.08	0.10	138
x = 0.2	0.01	0.03	0.06	0.08	138

values, but doping may lower these values as reported here and other works [10].

Thermal variations of dielectric losses are shown in Fig. 11. Weak values of these losses are observed (Table 5), with their maximum located at temperatures slightly higher than the corresponding ones in the thermal variations of ϵ_r (Table 5).

**Fig. 12.** The plot of the inverse dielectric constant vs temperature at different frequencies for the BT (x = 0).

The same thermal behavior of ϵ_r is observed for losses; the latter decrease for $f_r \leq 100$ kHz and then are slightly increasing for $f_r \geq 100$ kHz.

For a classical ferroelectric, the dielectric permittivity above the Curie temperature follows the well known Curie-Weiss law:

$$\epsilon_r = \frac{C}{T - T_C} \quad (T > T_C) \quad (2)$$

Where T_C refers to the Curie temperature and C to Curie Weiss constant.

Fig. 12 shows the plots of the inverse dielectric permittivity versus temperature at different frequencies for the pure BT. This plots show that the Curie -Weiss law is well respected for the pure barium titanate.

As shown in Fig. 7, the addition of Li gave rise to the appearance of a diffuse character of the ferro-to-paraelectric transition and then this behavior deviates from the typical Curie-Weiss observed for the sample with x = 0 (pure BT), and can be well described by the modified Uchino's law [11].

$$\frac{1}{\epsilon_r} = \frac{1}{\epsilon_{r \max}} \left[1 + \frac{(T - T_m)^\gamma}{2\delta^\gamma} \right] \quad (3)$$

Where γ and δ are the relaxor and diffuse parameters, respectively (Tables 6 and 7). A good fitting of the experimental data was performed (Fig 13), and allowed determination of the parameters γ and δ . Values of γ are characteristic of a diffuse character. Indeed, $\gamma = 1$ indicates a normal transition, $1 < \gamma < 2$ indicates a diffuse character and $\gamma = 2$ is obtained for relaxor materials.

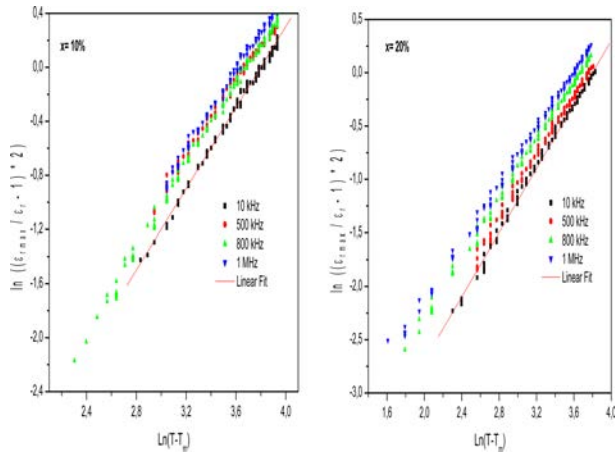


Fig. 13. Plot of $\ln\left(\frac{\epsilon_{\max}}{\epsilon_0} \cdot f\right)$ as a function of $\ln(T-T_0)$ at different frequencies for the Li⁺ doped BaTiO₃ (x = 0.1 and x = 0.2).

Table 6. γ value for the Li-doped BaTiO₃ (x = 0.1, x = 0.15 and x = 0.2) at different frequencies.

Frequencies kHz	x = 10%	x = 15%	x = 20%
10	1.32	1.52	1.55
500	1.27	1.36	1.45
800	1.31	1.53	1.57
1000	1.25	1.48	1.54

Table 7. δ value for the Li-doped BaTiO₃ (x = 0.1, x = 0.15 and x = 0.2) at different frequencies.

Frequencies kHz	x = 10%	x = 15%	x = 20%
10	41.15	44.60	44.66
500	37.84	39.91	42.44
800	34.66	39.69	40.17
1000	32.15	37.16	40.58

Thermal behavior of the conductivity

Thermal behavior, for different frequencies, of the conductivity has been studied using the following relation;

$$\sigma = \omega \epsilon_0 \epsilon_r'' = \omega \epsilon_0 \epsilon_r' \tan(\delta) \quad (4)$$

The activation energies of the electric conduction were evaluated using the following Arrhenius law:

$$\sigma_{ac} = \sigma_0 e^{\frac{-E_a}{k_B T}} \quad (5)$$

σ stands for ac-conductivity, σ_0 is the pre-exponential factor, k_B ($k_B = 1.3806 \cdot 10^{-23} \text{ J/K}$) is the Boltzmann factor, T is the absolute temperature and E_a the activation energy which can be calculated from the slope of σ as a function of $1/T$ plot (Fig. 14). Values of activation energy are gathered in Table 8. E_a shows an

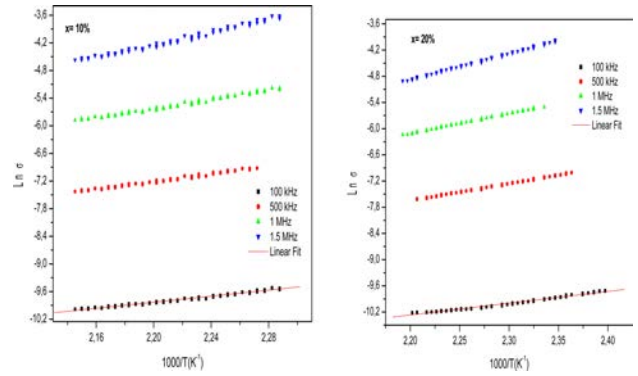


Fig. 14. Arrhenius plots for ac conductivity of Li-doped BaTiO₃ (x = 0.1 and x = 0.2) for different frequencies.

Table 8. E_a (eV) values of Li-doped BaTiO₃ (x = 0.1, x = 0.15 and x = 0.2) at different frequencies.

Frequencies (kHz)	100	500	900	1000	1500
10%	0,28	0,36	0,40	0,43	0,60
15%	0,32	0,37	0,41	0,43	0,58
20%	0,23	0,33	0,36	0,39	0,52

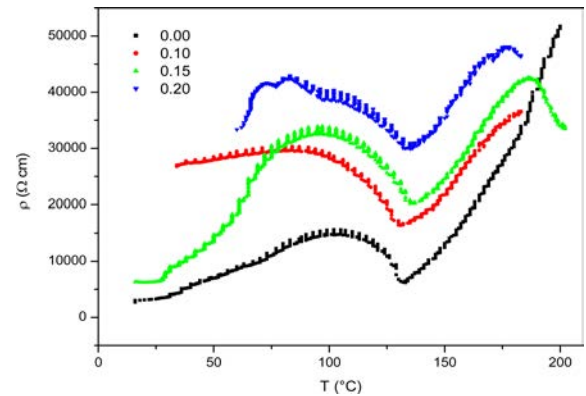


Fig. 14. Resistivity as a function of temperature at 60 kHz of Li-doped BaTiO₃ x = (0, 0.05, 0.1, 0.15 and 0.2).

increase as a function of the frequency and its values are similar to those reported in [12] calculated from an empirical Vogel-Fulcher relationship ($T_f = 185 \text{ K}$, $f_0 = 1.18 \cdot 10^{10} \text{ Hz}$, and $E_a = 0.35 \text{ eV}$). It can be noticed that activation energy for conduction behavior of oxygen vacancies in the octahedral of any perovskite structure is 1 eV. Moreover, the plots show that the conductivity of the samples decreases with increasing temperature, whereas it should increase. In fact, this behavior in the temperature range considered may be explained as due to a Positive temperature coefficient resistivity (PTCR) effect as shown on (Fig. 15), depicting the thermal behavior of resistivity of the BLxT samples. PTCR effect show a weakening with increasing Li content (x). This effect has been observed in pure [13] and doped BT [14]. Besides, the increase

of E_a may be linked to that of resistivity.

Conclusions

The sol-gel method was used to obtain Li-doped BaTiO_3 nanopowders (BLxT , $x = 0, 0.10, 0.15, 0.20, 0.25, 0.30$), from which pellets were calcined at $1000^\circ\text{C}/4$ hrs and sintered at 1100°C for 4 hrs. The structural characterization showed that the undoped sample crystallizes in the pure tetragonal phase, and that introduction of Li gives rise to a transformation from tetragonal to pseudo-cubic phase for $x \geq 0.05$. The corresponding XRD spectra show for $x > 0.05$ the presence of few traces of Li_2O_3 and $\text{Li}_2\text{Ba}_3\text{Ti}_8\text{O}_{20}$ phases. Moreover Li diminishes abruptly the crystallite size of BLxT samples which is of the order of 10 nm. Thermal behavior of (ϵ_r) showed that Li increases slightly the ferro-to-paraelectric transition and gives rise to the phenomenon of diffuseness of the corresponding curves. These curves are frequency independent for frequencies, f , inferior to 100 kHz, and for f superior to 100 kHz an unusual phenomenon is observed; indeed, with increasing frequency the maximum (ϵ_r) increases, evidencing that we are near the resonance frequency of the samples. For BLxT , $x > 0$, the ferro-to-paraelectric behavior was well described by the modified Ushino law due to diffuse character of this maximum. Activation energies were calculated from the thermal behavior of ac-conductivity and their values were between 0.25 and 0.60. PTCR effect was revealed from thermal variations of

ac conductivity and resistivity in the temperature range considered (above T_m). Such effect has been observed in pure and doped BT.

References

1. H.G. Haertling, J. Am. Ceram. Soc. 82 (1999) 797-818.
2. H.L. Luo, H. Zhu, S.C. Zhao, X.H. Wang, S.H. Luo, Appl. Phys. Lett. 90 (2007) 052904-52910.
3. G.H. Haertling, J. Am. Ceramic. Soc. 82 (1999) 797-818.
4. K. Kiss, J. Magder, M.S. Vukasovich, R.J. Lockhart, J. Am. Ceram. Soc. 49 (1966) 291.
5. Q. Xu, S. Chen, W. Chen, D. Huang, J. Zhou, H. Sun, et al., J. Mater. Sci. 41 (2006) 6146.
6. Y. Sakabe, Y. Yamashita, H. Yamamoto, J. Eur. Ceram. Soc. 25 (2005) 2739.
7. Y. Xie, S. Yin, T. Hashimoto, Y. Tokano, A. Sasaki, T. Sato, J. Eur. Ceram. Soc. 30 (2010) 699.
8. K. Limame, S. Sayouri, A. El. Ghazouali, L. Hajji, T. Lamcharfi, B. Jaber, A. Housni. Ferroelectrics 371 (2008) 68-81.
9. Jr. Domenic. M, S.H. Wempl, S.P.S. Porto. Physical Review 174 (1968) 522-530.
10. A. Elbasset, T. Lamcharfi and F. Abdi and S. Sayouri, Advances in Physics Theories and Applications 30 (2014) 45-54.
11. N. S. Echadou, T. Lamcharfi, S. Sayouri, L. Hajji, A. Alimoussa, Phys. Chem. News 26 (2005) 40-46.
12. B. Fathi, H. Khemakhem, Ceramics International 39 (2013) 7571-7575.
13. A. Salhi, S. Sayouri, L. Hajji and T. Lamcharfi, Journal of Ceramic Processing Research. 17 (2016) 1-7.
14. M. Rao, K. Ramesh, M. Ramesh and B. Rao, Advances in Materials Physics and Chemistry 3 (2013) 77-82.