The lead-based perovskite Pb (Zr, Ti)O$_3$ (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. BaTiO$_3$ (BT) has become one of the most important ferroelectric materials used in the electronics ceramic industry.

BaTiO$_3$ 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 $T ≥ T_c$, where BT structure transforms to cubic one. Multiple dopants may be added to BaTiO$_3$ to adapt some of its properties for specific applications: Sr$^{2+}$ to decrease its transition temperature $T_c$, Pb$^{2+}$ to increase $T_c$ and Co$^{2+}$ to mitigate losses inherent to intense electric fields without affecting its piezolectric constant [3].

Usually, BaTiO$_3$ (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 BaTiO$_3$ ceramics, Ba$_{1-x}$Li$_x$Ti$_{1+x/4}$O$_3$ (BLxT)(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.
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Experimental

Li doped BaTiO3 powders Ba1−xLi1+4xTi1+2−4xO3 (BLxT) 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.

(BLxT) samples with x = (0, 0.05, 0.1, 0.15, 0.2, 0.25 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 CuKα (λ = 1.5405 Å) radiation and a Raman spectrometer.

Results and Discussion

X-ray diffraction study

Fig. 2(a) shows the XRD patterns of BLxT (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 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° 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 Li2Ba3Ti6O20 (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 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.](image)

![Fig. 3. c/a ratio vs Li content of the BLxT calcined at 1000 °C/4 hrs.](image)

![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).](image)
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).

**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. BaTiO$_3$ 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 BaTiO$_3$ is tetragonal and has C4v symmetry.

The frequency-covered range was from 200 cm$^{-1}$ to 800 cm$^{-1}$. Based on the crystallography, Raman-active modes for tetragonal BaTiO$_3$ ($P4_{mm}$) are $4E$ (TO + LO) + 3$A_1$ (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 (TO/LO), (E (TO) / $A_1$(TO$_3$) and (A$_1$(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 ($\varepsilon_r$) 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
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It is seen that the pure BT sample behaves as a classical ferroelectric, with a Curie temperature $T_c = 131 \, ^\circ$C. For BL$_x$T ($x > 0$) samples, the value of the temperature, $T_m$, of the maximum of $e_r$ 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 BL$_x$T ($x = 0.1, 0.15$ and $0.20$) (Figs. 7 and 8).

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

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

<table>
<thead>
<tr>
<th>$x$ (%)</th>
<th>$T_m$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>131 ($T_c$)</td>
</tr>
<tr>
<td>10</td>
<td>133</td>
</tr>
<tr>
<td>15</td>
<td>138</td>
</tr>
<tr>
<td>20</td>
<td>138</td>
</tr>
</tbody>
</table>

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

Fig. 8. Frequency dependences of $e_r$ for different temperatures.

Fig. 9. Thermal variations of ($e_r$) for frequencies ranging from 100 kHz to 1 MHz.
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 \(\varepsilon_r\) (Table 5).

The same thermal behavior of \(\varepsilon_r\) is observed for losses; the latter decrease for \(f \leq 100\) kHz and then are slightly increasing for \(f \geq 100\) kHz.

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

\[
\varepsilon_r = \frac{C}{T - T_C} \quad (T > T_C)
\]

Fig. 12 shows the plots of the inverse dielectric constant vs 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-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].

\[
\frac{1}{\varepsilon_r} = \frac{1}{\varepsilon_{\text{max}}} \left[ 1 + \frac{(T - T_m)}{2\delta\gamma} \right]^{-1}
\]

Table 4. Temperature of the maximum of \(\varepsilon_r\) of Li-doped BaTiO\(_3\) at various frequencies.

<table>
<thead>
<tr>
<th>BL(_x)T</th>
<th>500 Hz</th>
<th>1 kHz</th>
<th>5 kHz</th>
<th>10 kHz</th>
<th>50 kHz</th>
<th>100 kHz</th>
<th>1 MHz</th>
<th>1.5 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>2130</td>
<td>2116</td>
<td>1997</td>
<td>1985</td>
<td>3716</td>
<td>3916</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x = 0.1</td>
<td>1224</td>
<td>1151</td>
<td>1143</td>
<td>1134</td>
<td>1525</td>
<td>2413</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x = 0.15</td>
<td>1193</td>
<td>1188</td>
<td>1178</td>
<td>1178</td>
<td>1485</td>
<td>2397</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x = 0.2</td>
<td>1013</td>
<td>990</td>
<td>984</td>
<td>983</td>
<td>1216</td>
<td>1738</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Values of dielectric losses and temperature of their maximum of Li-doped BaTiO\(_3\) at various frequencies.

<table>
<thead>
<tr>
<th>BL(_x)T</th>
<th>50 kHz</th>
<th>500 kHz</th>
<th>800 kHz</th>
<th>1 MHz</th>
<th>T(_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>0.02</td>
<td>0.10</td>
<td>0.21</td>
<td>0.39</td>
<td>131 (T(_C))</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>0.01</td>
<td>0.04</td>
<td>0.08</td>
<td>0.11</td>
<td>133</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>0.01</td>
<td>0.04</td>
<td>0.08</td>
<td>0.10</td>
<td>138</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>0.01</td>
<td>0.03</td>
<td>0.06</td>
<td>0.08</td>
<td>138</td>
</tr>
</tbody>
</table>

Fig. 10. Frequency dependences of \(\varepsilon_r\) for the BC\(_x\)T ceramics at 10 kHz.

Fig. 11. Temperature dependence of the dielectric losses for frequencies ranging from 100 kHz to 1 MHz.

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

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

$$\sigma = \sigma_0 e^{-\frac{E_a}{k_BT}}$$

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

$$\sigma ac = \sigma_0 e^{-\frac{E_a}{k_BT}}$$

$\sigma$ stands for ac-conductivity, $\sigma_0$ is the pre-exponential factor, $k_B$($k_B = 1.3806.10^{-23}$ 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 $\sigma$ as a function of $1/T$ plot (Fig. 14). Values of activation energy are gathered in Table 8. $E_a$ shows an increase as a function of the frequency and its values are similar to those reported in [12] calculated from an empirical Vogel-Fulcher relationship ($T_f = 185$ K, $f_0 = 1.18 10^{10}$ Hz, and $E_a = 0.35$ 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 in the conductivity decreases with the increase in the temperature for the samples with lower Li content (x = 0.1 and x = 0.2).
of \( E_a \) may be linked to that of resistivity.

**Conclusions**

The sol-gel method was used to obtain Li-doped BaTiO\(_3\) nanopowders (BL\(_x\)T, \( x = 0, 0.10, 0.15, 0.20, 0.25, 0.30 \)), from which pellets were calcined at 1000 \( ^\circ \)C/4 hrs and sintered at 1100 \( ^\circ \)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\(_2\)O and Li\(_2\)Ba\(_3\)Ti\(_8\)O\(_{20}\) phases. Moreover Li diminishes abruptly the crystallite size of BL\(_x\)T samples which is of the order of 10 nm. Thermal behavior of \( (\varepsilon_r) \) 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 \( (\varepsilon_r) \) increases, evidencing that we are near the resonance frequency of the samples. For BL\(_x\)T, \( x > 0 \), the ferro-to-paraelectric behavior was well described by the modified Ushio law due to diffuse character of this maximum. Activation energies were calculated from the thermal behavior of ac conductivity and resistivity in the temperature range considered (above \( T_m \)). Such effect has been observed in pure and doped BT.

**References**