Dielectric, pyroelectric and piezoelectric properties in the 
\((1 - x)(0.1\text{BaTiO}_3 - 0.9\text{NaNbO}_3) - x\text{LiNbO}_3\) system

F. Benabdallah\textsuperscript{a,b,*}, A. Aydi\textsuperscript{a}, N. Abdelmoula\textsuperscript{a}, H. Khemakhem\textsuperscript{a}, A. Simon\textsuperscript{b}, R. Von Der Mühll\textsuperscript{b}, M. Maglione\textsuperscript{b}

\textsuperscript{a}Laboratoire des Matériaux Ferroélectriques, UR. 05/UR/15-04, Faculté des Sciences de Sfax, Université de Sfax, BP. 1171, 3000 Sfax, Tunisia

\textsuperscript{b}CNRS, Université de Bordeaux, ICMCB, 87 Avenue Dr A. Schweitzer, Pessac 33608, France

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Abstract
New lead free piezocermics with the given compositions \((1 - x)(0.1\text{BaTiO}_3 - 0.9\text{NaNbO}_3) - x\text{LiNbO}_3 (0.01 \leq x \leq 0.125)\) were prepared by solid-state reaction technique. XRD patterns revealed a single perovskite-structured phase only for \(0.01 \leq x < 0.05\). The dielectric, pyroelectric and piezoelectric responses were investigated for compositions with \(x = 0.01\) and 0.02. For both compositions, \(\varepsilon_r\) exhibited a sharp peak with no frequency dependence (classical ferroelectrics). Losses displayed a strong dispersion at low frequencies in the paraelectric phase which was attributed to Li ionic conductivity in these compositions. The spontaneous polarization was found to be 35 and \(= 22 \mu \text{C cm}^{-2}\) for \(x = 0.01\) and 0.02 respectively. The transverse piezoelectric coefficient \(d_{31}\) measured for \(x = 0.01\) reached value of 37 pC/N at room temperature while the planar coupling factor was about 0.23.

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1. Introduction

The quest for novel lead-free piezocermics has been widely intensified because of environmental issues over the last few years. The aim of these investigations is mainly to replace lead–zirconate-titanate (PZT) as the major material for electromechanical devices such as actuators, sensors and transducers. For this purpose, solid solutions derived from \((\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3)\) \[1\], \((\text{KNbO}_3, \text{NaNbO}_3)\) \[2,3\] and \((\text{BaTiO}_3)\) \[4–7\] based perovskite compounds are largely studied. Very attractive dielectric and piezoelectric properties have been reported in all these materials. However, these enhanced responses depend on many factors including the processing method (conventional sintering, hot pressing, spark plasma sintering...), the chemical modifications (doping, substitution) and using promising perovskite end members for the construction of phase diagrams suitable for a morphotropic phase boundary (MPB) with lead-free piezocermics. It is noteworthy that the concept of MPB between two crystal structures may be extended to reaching flat Gibbs free energy curves by combining solid solutions among end members of three different crystal structures \[8\]. In the present work, we have investigated the dielectric, pyroelectric and piezoelectric properties of \(\text{BaTiO}_3 - \text{NaNbO}_3 - \text{LiNbO}_3\) ternary system which consists of compounds with different crystal structures at room temperature.

Barium titanate was the first perovskite oxide identified as being ferroelectric. At high temperature, it has a paraelectric cubic perovskite structure \((\text{Pm}3\ \text{m})\). When the temperature is lowered from the latter phase, \(\text{BaTiO}_3\) exhibits successive ferroelectric transitions to the tetragonal state \((\text{P4mm})\) at 393 K, to the orthorhombic state \((\text{Amn}2)\) around 278 K and then to the rhombohedral state \((\text{R}3\text{m})\) at 183 K. \(\text{BaTiO}_3\) has become a very important material with widespread use in the electronic industry owing to its high dielectric constant and piezoelectric and ferroelectric properties \[9,10\].

For lithium niobate \((\text{LiNbO}_3)\), the paraelectric phase has a rhombohedral unit cell of \(R3\ c\) symmetry where the oxygen octahedra have been rotated around [111] crystallographic direction. At 1483 K, it undergoes a phase transition into \(R3\ c\) ferroelectric state by displacements of the cations along [111], breaking the mirror-plane symmetry and resulting in a nonzero spontaneous polarization.

The last end member \((\text{NaNbO}_3)\) in the current studied ternary system was originally reported as ferroelectric but is in fact antiferroelectric with an orthorhombic symmetry \((\text{Pb}n\text{a}2)\) at room temperature \[11\].

Khemakhem et al. have reported good dielectric and pyroelectric responses for \(0.1\text{BaTiO}_3 - 0.9\text{NaNbO}_3\) composition but relatively
low transverse piezoelectric coefficient \(d_{31} = 30.8 \text{ pC/N at room temperature}\). Moreover, one of the most interesting feature of this material is the elevated Curie temperature \(T_c \approx 500 \text{ K}\) opening the door to a large-volume applications over an extended temperature regime \([12,13]\).

Based on the previous research, we have examined the effect of lithium addition on the stability of the perovskite-structured solid solution and the evolution of properties such as dielectric permittivity, polarization, piezoelectric coefficient and electromechanical coupling factor in the \((1-x)(0.1\text{BaTiO}_3-0.9\text{NaNbO}_3)-x\text{LiNbO}_3\) system \((0.01 \leq x \leq 0.125)\).

2. Experimental

The polycrystalline ceramics were elaborated by the conventional solid state route using BaCO\(_3\), Na\(_2\)CO\(_3\), TiO\(_2\), Li\(_2\)CO\(_3\) and Nb\(_2\)O\(_5\) high-purity powders (99.99\%) as starting materials. To prepare stoichiometric compositions, the powders were dried at 150 °C during 15 h then weighed with respect to the following equation:

\[
0.1(1-x)\text{BaCO}_3 + x/2\text{Li}_2\text{CO}_3 + 0.45(1-x)\text{Na}_2\text{CO}_3 + 0.1(1-x)\text{TiO}_2 + (0.05x + 0.45)\text{Nb}_2\text{O}_5
\]

\[
\rightarrow \text{Ba}_{0.1(1-x)}\text{Na}_{0.9(1-x)}\text{Li}_1\text{Ti}_{0.1(1-x)}\text{Nb}_{0.1x+0.9}\text{O}_3 + (0.55 - 0.05x)\text{CO}_2
\]

In the following, the desired compositions corresponds to \(0.01 \leq x \leq 0.125\). ‘x’ represents the molar fraction of lithium niobate in the complex perovskite structure.

After being mixed by ball-milling for 1 h using alcohol as the milling medium, the obtained powders were dried and calcined at temperature going from 800 to 1000 °C (depending on the compositions) for 12 h under oxygen atmosphere. After calcination, powders were crushed and ball-milled again in order to break the agglomerates, pressed under 100 MPa into disk-shaped samples. To prepare stoichiometric compositions, the powders were dried at 150 °C during 15 h then weighed with respect to the following equation:

\[
0.1(1-x)\text{BaCO}_3 + x/2\text{Li}_2\text{CO}_3 + 0.45(1-x)\text{Na}_2\text{CO}_3 + 0.1(1-x)\text{TiO}_2 + (0.05x + 0.45)\text{Nb}_2\text{O}_5
\]

\[
\rightarrow \text{Ba}_{0.1(1-x)}\text{Na}_{0.9(1-x)}\text{Li}_1\text{Ti}_{0.1(1-x)}\text{Nb}_{0.1x+0.9}\text{O}_3 + (0.55 - 0.05x)\text{CO}_2
\]

The electromechanical coupling factor \(k_p\) and the transverse piezoelectric coefficient \(d_{31}\) were determined by the resonance method according to IEEE standard using an impedance analyser (HP 4194 A) \([16]\). It should be noted that the poling of the ceramics for piezoelectric characterizations were done with the same protocol as described above for pyroelectric experiments.

3. Results and discussion

3.1. Phase structure and microstructure

X-ray diffraction (XRD) patterns of \((1-x)(0.1\text{BaTiO}_3-0.9\text{NaNbO}_3)-x\text{LiNbO}_3\) ceramics sintered at 1200 °C/3 h/O\(_2\) are shown in Fig. 1. For compositions with \(0.01 \leq x \leq 0.05\), the XRD patterns reveal a single perovskite-structured phase with tetragonal symmetry. However, a small amount of a secondary phase, which was identified as Li\(_4\)Na\(_2\)Ti\(_4\)Ba\(_4\)Nb\(_6\)O\(_{30}\), was observed when \(x \geq 0.05\). Thus, different thermal treatments (by varying the heating rate, the sintering temperature and the sintering time) were done to avoid the formation of the latter phase of tungsten bronze structure. Unfortunately, these processes have been determined to be no efficient. In the following, we focused our attention on compositions with single perovskite phase \((x = 0.01\) and 0.02\).

The \(0-\theta\) scan profiles for compositions \(x = 0.01\) and 0.02 could be indexed in the tetragonal symmetry \((P4m m\) space group\). The unit cell parameters were computed at room temperature using a profile-match to the FullProf software and presented along with the cell volume in Table 1. A result of great importance to the piezoelectric characterizations was done with the same protocol as described above for pyroelectric experiments.

Fig. 1. X-ray diffraction patterns of \((1-x)\) BTNN-x LN ceramics sintered at 1200 °C/3 h under oxygen atmosphere. The black stars point to peaks of Al (substrate). The blue ones correspond to the secondary phase with bronze structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
SEM micrograph of 0.99BTNN-0.01LN ceramic sintered at 1200 °C for 3 h is shown in Fig. 2. We obtain dense ceramic with a bulk density reaching 90% of the theoretical value. The grain sizes are in the range of 2–15 μm. It is worth mentioning that high performance materials with high density and uniform microstructure could only be achieved if both composition and grain growth are controlled. However, several difficulties inherent in the sintering process such as the volatility of alkali elements (Li and Na) and phase instability at high temperatures (formation of alkali-deficient secondary phase of tungsten bronze structure) will lead to poor densification and abnormal grain growth with compositional inhomogeneity, especially for $x \geq 0.05$.

3.2. Dielectric properties

The temperature dependence of the real part $\varepsilon'_r$ and the imaginary part $\varepsilon''_r$ of the relative dielectric permittivity in the frequency range from $5 \times 10^2$ Hz to $2 \times 10^5$ Hz are shown for 0.99BTNN-0.01LN and 0.98BTNN-0.02LN ceramics in Fig. 3a and b respectively. Only one dielectric anomaly has been observed for both compositions which is originated from phase transition from a cubic paraelectric to a tetragonal ferroelectric state. Moreover, the real part of the dielectric permittivity exhibits a sharp and narrow peak at $T_c$ with no frequency dependence. This feature is typical of classical ferroelectrics. The Curie temperature increases with the augmentation of the lithium content ($x$) and reaches values of 526 K and 531 K for $x = 0.01$ and 0.02 respectively.

It is well known that for a standard ferroelectric material, the dielectric constant above $T_c$ follows the Curie-Weiss law described by the following relation:

$$\varepsilon'_r = \frac{C}{T - T_0}$$

where $C$ is the Curie constant and $T_0$ is the Curie–Weiss temperature.

Fig. 4 shows the inverse of $\varepsilon'_r$ as a function of temperature at 1 kHz fitted to Curie–Weiss law for 0.99BTNN-0.01LN ($x = 0.01$) and 0.98BTNN-0.02LN ($x = 0.02$). The Curie constant $C$ was found to be 1.49 $10^5$ K and 1.45 $10^5$ K for $x = 0.01$ and 0.02 respectively. $T_0$ is almost the same for both compositions ($= 511$ K).

In the paraelectric phase, strong frequency dispersion is observed for both compositions and systematically related to the ionic conductivity. This phenomenon is a thermally activated process— the material has thermally created lattice defects through which host ions can move— following the empirical equation given by:

$$\sigma = \sigma_0 e^{-E_a/kT}$$

$\sigma_0$, $k$ and $E_a$ are the preexponential factor, the Boltzmann constant and the activation energy respectively. The variation of the conductivity versus temperature for 0.98BTNN-0.02LN is plotted in Fig. 5, showing an Arrhenius behaviour with an activation energy $E_a$ value of 0.36 eV.

Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>$x = 0.00$</th>
<th>$x = 0.01$</th>
<th>$x = 0.02$</th>
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</thead>
<tbody>
<tr>
<td>Unit cell parameters</td>
<td>$a = b = 3.919(8)$</td>
<td>$a = b = 3.919(0)$</td>
<td>$a = b = 3.920(3)$</td>
</tr>
<tr>
<td>($\text{Å}$)</td>
<td>$c = 3.954(3)$</td>
<td>$c = 3.963(8)$</td>
<td>$c = 3.981(5)$</td>
</tr>
<tr>
<td>Tetragonality ($c/a$)</td>
<td>1.009</td>
<td>1.01</td>
<td>1.015</td>
</tr>
<tr>
<td>Unit cell volume ($\text{Å}^3$)</td>
<td>60.737</td>
<td>60.878</td>
<td>61.190</td>
</tr>
</tbody>
</table>

3.3. Pyroelectric and piezoelectric properties

Fig. 6 displays the temperature dependence of the spontaneous polarization $P_s$ for polarized samples with $x = 0.01$ and 0.02. We remark that $P_s$ increases in continuous way in the ferroelectric phase and reaches a value of 35 μC cm$^{-2}$ for $x = 0.01$ but fall down to 22 μC cm$^{-2}$ for $x = 0.02$. In both cases, the measured polarization is comparable to the one reported for BaTiO$_3$ but still smaller.
than that of LiNbO₃ at room temperature [19,20]. Naturally, lithium has the potential to off-centre on the A-site in the perovskite structure, enabling high internal polarization. However, large rotations of the oxygen octahedra may destabilize this effect as the lithium content increases [21].

Importantly, one can see that the Curie temperatures $T_c$ presented in $P_x-T$ curve (≈ 560 K for $x = 0.01$ and ≈ 590 K for $x = 0.02$) are much higher than those mentioned in dielectric measurements respectively for the same compositions. This could be attributed to the fact that a small residual polarization is still existing in the paraelectric phase after poling the sample and upon heating, which causes artificially $T_c$ to shift to higher temperatures.

The Piezoelectric measurements were performed on disk-shaped ceramics with composition $x = 0.01$ and 0.02. At different temperatures, the conductance ($G$) and susceptance ($B$) were measured versus frequency around the main radial resonance mode (Fig. 7). The material constants were computed using impedance equations and equivalent circuit recommended by the IEEE Standard on Piezoelectricity. The piezoelectric coefficient $d_{31}$ was found to be 37 pC/N, $K_p = 0.23$ and $Q_m$ (mechanical quality factor) = 153 for $x = 0.01$ at room temperature. However, this piezoelectric response dropped significantly in the case of $x = 0.02$ reaching values of $d_{31} = 6$ pC/N, $K_p = 0.07$ and $Q_m = 77$.

A possible explanation of these minor properties was that the material was difficult to pole due to high leakage currents together with the high coercive field. Moreover, it is well known that the electromechanical response of the material is greatly influenced by its microstructural characteristics including: densification, grain size, defects, morphology, etc... which are difficult to control in this case by using conventional sintering technique. By way of illustration, hot-isostatic pressing or spark plasma sintering could be a powerful processing technique to obtain fully-dense ceramics
and piezoelectric properties were obtained for \( x = 0.01 \) after sintering at 1200 °C for 3 h. The properties for this material can be summarized as follows: \( T_c = 526 \text{ K}, P_s = 35 \mu \text{C cm}^{-2}, d_{31} = 37 \text{ pC/N}, K_p = 0.23 \) and \( Q_m = 153 \).

The drop of the spontaneous polarization with increasing the lithium content \( \text{"x"} \) could be attributed to large rotations of the oxygen octahedra leading to a drastic lowering of the internal polarization generated by the off-centring of an A ion (in this case lithium) in the perovskite structure. Furthermore, poor densification and several extrinsic effects (high leakage currents, high coercive field, stable ferroelectric domains...) limit the piezoelectric response in the investigated compositions.

Finally, it may be interesting to explore other regions in the BaTiO\(_3\)–NaNbO\(_3\)–LiNbO\(_3\) phase diagram which could possibly provide an MPB, giving rise to good piezoelectric properties.

4. Conclusions

Lead-free \((1-x)\) BTNN-x LN \((0.01 \leq x \leq 0.125)\) solid solutions were designed using solid–state reaction method. Effects of the addition of lithium on the phase structures, dielectric, pyroelectric and piezoelectric properties were systematically investigated. Lithium diffused into the BTNN lattice to form a perovskite-structured solid solution with tetragonal symmetry in the composition range \(0.01 \leq x < 0.05\). The increase of the unit cell parameters together with the Curie temperature can be ascribed to lattice distortions (tilting of the oxygen octahedra). The best pyroelectric

![Fig. 8. Thermal evolution of the transverse piezoelectric coefficient and the planar coupling factor for the composition with \( x = 0.01 \).](image)

References