Na$_{1-x}$Li$_x$NbO$_3$ ceramics studied by X-ray diffraction, dielectric, pyroelectric, piezoelectric and Raman spectroscopy

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A B S T R A C T

Na$_{1-x}$Li$_x$NbO$_3$ ceramics with composition 0.05 $\leq x \leq$ 0.30 were prepared by solid-state reaction method and sintered in the temperature range 1100–1150 °C. These ceramics were characterised by X-ray diffraction as well as dielectric permittivity measurements and Raman spectroscopy. Dielectric properties of ceramics belonging to the whole composition domain were investigated in a broad range of temperatures from 300 to 750 K and frequencies from 0.1 to 200 kHz. The Rietveld refinement powder X-ray diffraction analysis showed that these ceramics have a single phase of perovskite structure with orthorhombic symmetry for x $\leq$ 0.15 and two phases coexistence of rhombohedral and orthorhombic above x=0.20. The evolution of the permittivity as a function of temperature and frequency showed that these ceramics Na$_{1-x}$Li$_x$NbO$_3$ with composition 0.05 $\leq x \leq$ 0.15 present the classical ferroelectric character and the phase transition temperature $T_c$ increases as x content increases. The polarisation state was checked by pyroelectric and piezoelectric measurements. For x=0.05, the piezoelectric coefficient $d_{33}$ is of 2pC/N. The evolution of the Raman spectra was studied as a function of temperatures and compositions. The results of the Raman spectroscopy study confirm our dielectric measurements, and they indicate clearly the transition from the polar ferroelectric phase to the non-polar paraelectric one.

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1. Introduction

ABO$_3$ perovskite compounds, having interest for technological applications, are usually A or B substituted solid solutions with a composition close to the so-called morphotropic phase boundary. Whereas, the number of studies carried out on ferroelectrics during many years underlines the great interest of the materials both on the fundamental point of view and for application [1–3]. They were investigated by many authors [4–6] from the fundamental scientific and industrial points of view [7], owing to their interesting and important properties, such as a diffuse phase transition and frequency dependence of the dielectric permittivity.

Sodium lithium niobate Na$_{1-x}$Li$_x$NbO$_3$ (hereafter referred to as NLN) is a solid solution based on mixture of NaNbO$_3$ and LiNbO$_3$. It is considered as an advanced ferroelectric ceramic for high frequency applications [8,9]. The studies based on alkaline niobates as new dielectric materials have been carried out by other researchers in order to obtain suitable materials for high performance applications, which require a combination of advanced characteristics such as low dielectric loss, low aging coefficient, high permittivity and planar coupling coefficient. Although NaNbO$_3$ is ferroelectric only around 163 K, the NLN system has been found to be ferroelectric at room temperature for $x \geq$ 0.02 [10,11]. Reports on optical studies in the Na$_{0.95}$Li$_{0.05}$NbO$_3$ single solid solution have described five phase transitions between 163 and 940 K with the transition temperature found around 640 K [12]. Recent studies have shown that lithium niobate (LiNbO$_3$) is a very important material for optical and other applications. Possible applications include electric wave guides, optical storage, amplitude modulators, second harmonic generators and acoustic wave transducers. The structures and electrical properties of those two crystals NaNbO$_3$ and KNbO$_3$ are different from those of LiNbO$_3$. At room temperature, LiNbO$_3$ [13] and KNbO$_3$ [14] are ferroelectrics; however NaNbO$_3$ is anti-ferroelectric with orthorhombic distorted perovskite structure. NaNbO$_3$ and KNbO$_3$ undergo successive phase transitions from low temperatures through high temperatures (10–1500 K), but LiNbO$_3$ remains in the same state until 1523 K, at this point it becomes cubic. Wang et al. [15] have shown that dielectric and...
piezoelectric properties of \((K_{0.50}Na_{0.50})NbO_3\) have been strongly modified by substituting \((K_{0.50}Na_{0.50})\) with Li, Ag and Sb. Lithium substituted sodium niobate compounds NLN, have perovskite type structure and present several structural phase transitions of the antiferroelectric–ferroelectric (AFE–FE) [16], antiferroelectric–paraelectric (AFE–PA) [16], ferroelectric–paraelectric (FE–PA) [17], ferroelectric–ferroelectric (FE–FE) [18] and ferroelastic–paraelastic (FE–EL) [19] types.

The aim of the present work is principally the study of the \(Na_{1-x}Li_xNbO_3\) solid solution by X-ray diffraction (XRD) which permits the characterisation of the second phase in this material for the high percent of composition. Additionally, the Raman spectroscopy technique was used as a principle element for characterising the ferroelectric–paraelectric phase transition and the effect of the Na–Li substitution on the lattice dynamic. The lead-free perovskite ceramics NLN system with different compositions \((x=0.05, 0.10, 0.15, 0.20, 0.25\) and \(0.30\)) derived from NaNbO_3 and mixed with LiNbO_3 was prepared and elaborated by traditional solid-state sintering process. The effects of LiNbO_3 on the structure and dielectric properties of NaNbO_3 were investigated. These lead-free compounds could be of great interest as respectful materials for the environment in the scope of applications as dielectrics for capacitors or actuators. The temperature and frequency dielectric responses of NLN ceramic samples were correlated with the unit cell symmetry and parameters obtained by XRD. Scanning Electron Microscopy (SEM) was used to characterise the microstructure.

2. Experimental

\(Na_{1-x}Li_xNbO_3\) ceramics \((x=0.05, 0.10, 0.15, 0.20, 0.25\) and \(0.30\)) were synthesised by means of a conventional mixed oxide route. High-purity oxides and carbonates, \(Nb_2O_5\) (99.9%) and \(Na_2CO_3\) (99.5%), \(Li_2CO_3\) (99.98%), were used as starting materials with the chemical reaction:

\[
(1-x)Na_2CO_3 + \frac{x}{2}Nb_2O_5 + \frac{x}{2}Li_2CO_3 \rightarrow Na_{1-x}Li_xNbO_3 + xCO_2
\]

These powders were placed in an oven at 120°C for 2 days and then stored in a moisture-free vessel. The weighed powders were mixed by a planetary ball-mill in an anhydrous alcohol for 12 h. After drying, the calcination was carried out at the temperature 1000°C for 12 h according to the compositions in a covered alumina crucible. The calcined powders were ground in an agate mortar and then calcined once again in order to improve the compositional distribution. The well-calcined powders were ball-milled again. After drying, powders were pressed under 100 MPa into discs of 8 mm in diameter and about 1 mm in thickness. These pellets were sintered for 2 h at either 1150°C for \(x=0.15\) or 1100°C for \(x=0.10\). Sintered bulk specimens were ground, polished and examined by XRD using Cu Kα radiation \((λ=1.54056\text{ Å})\) at room temperature on a Philips PW 3040/00 XPERT diffractometer. The scanning record was run at preset 2θ ranges from 5 to 110° with 0.02° step and 10 s counting time.

The experimental density \(d_{exp}\) was determined from the weight and geometrical dimensions of the cylindrical pellets and then compared to the theoretical density \(d_{theor}\) determined from XRD. The compactness is thus calculated as the ratio \(C=d_{exp}/d_{theor}\), the value obtained for the sintered specimens is about 0.96. The microstructure was observed by a SEM (JEOL JED 2300). A SEM picture of the ceramic rough surface with the composition \(x=0.30\) is reported on Fig. 1. The average grain size of the ceramic sample was about 2 μm.

Dielectric measurements were performed on the ceramic discs after deposition of gold electrodes on the circular faces (polished pellets) by cathodic sputtering. Heating or cooling rate was 2 K/min. The real relative permittivity was determined under helium as a function of both temperature (400–750 K) and frequency (10^2–2 x 10^5 Hz) using a Wayne-Kerr 6425 Component Analyser. Raman scattering data was collected in the frequency range 50–1000 cm\(^{-1}\) using a Raman spectrometer (Horiba HR 800, Jobin Yvon).

3. Results and discussion

3.1. X-ray diffraction study

Although both LiNbO_3 and NaNbO_3 have NbO_6 octahedra as their basic structure units, they crystallise in different ways. The XRD experiments were undertaken at room temperature in order to determine the crystal structure. At room temperature, LiNbO_3 is an excellent ferroelectric and exhibits the “lithium niobate-type” rhombohedral structure with space group R3c, while NaNbO_3 is an antiferroelectric and has the perovskite orthorhombic structure with space group Pbnm. The value of the lattice and profile parameter was determined using a global profile-matching method with the software “FullProf” [20].

All diffraction spectra were measured at room temperature. For the NLN compound, the XRD patterns indicated the following orthorhombic unit cells and the space groups: \(Pbnm\) ‘‘P-phase’’ for \(x=0\) and \(P2_1/m\) ‘‘Q-phase’’ in the regions \(x=0.05\)–0.10; these results are well consistent with previous studies of \(P\) and \(Q\) phases in NaNbO_3 [21–23] and NLN [24–26]. In the orthorhombic \(P\) and \(Q\) phases, the NbO_6 octahedra are tilted in a different manner. Following Glazer’s [27] structural description, the phase \(P\) has pairs of alternating layers: \(a^- b^+ a^- a^- b^+ a^-\) while in the \(Q\)-phase the tilting can be described as \(a^- b^- c^+\). Whereas for \(x=0.15\), the analyses show that the NLN system is a single phase perovskite solid solution with an orthorhombic structure. The observed and calculated spectrum of \(Na_{0.95}Li_{0.05}NbO_3\) \((x=0.05)\) is given on Fig. 2 as an example. The refined parameters are summarised in Table 1. The decrease of the lattice parameters and the unit cell volume can be due to the substitution of the sodium by the lithium and should be related to the values of ionic radii [28]: \(r(Na^+)\) = 1.18 Å quite higher than \(r(Li^+)\) = 1.08 Å in an eight fold coordination.

Because of the difference in crystal structure of NaNbO_3 (orthorhombic) and LiNbO_3 (rhombohedral), the single phase solid solutions \(Na_{1-x}Li_xNbO_3\) can be obtained only in the Na-rich region: it is orthorhombic for \(x≤0.15\) [9] or in the Li-rich region: it is rhombohedral for \(x≥0.95\) [29]. In addition, the analyses show that two phases coexist above \(x=0.20\) confirming the results.
The coexistence of phases, the ferroelectric $Q$ with space group $Pmnm$ giving rise either to composition fluctuations producing regions with different Na content or to the appearance of incommensurate phases between two structurally different antiferroelectric $P$ phases (monoclinic and orthorhombic) [32]. Following [28], on increasing the mean $Li^+$ content, larger ferroelectric phase stability is induced in such a way that minority regions of the AFE $P$-phase embedded in a majority of Q-like phases, undergo a phase transition to the Q-like phase producing a structurally homogeneous ferroelectric.

### 3.2. Dielectric properties

The temperature dependence of the real part permittivity $\varepsilon'_r$ was determined for $Na_{0.75-x}Li_xNbO_3$ ceramics with compositions $x=0.05$, 0.10 and 0.15. We can observe one anomaly corresponding to the tetragonal-cubic phase transition. The high temperature peak corresponds to the ferroelectric–paraelectric phase transition: it is given by the maximum of $\varepsilon'_r(T)$ and it is called Curie temperature $T_C$. Fig. 4 shows the evolution of the real part dielectric permittivity $\varepsilon'_r$ as a function of temperature and frequency for $Na_{0.95-x}Li_xNbO_3$ ($x=0.05$) ceramic with $T_C=600$ K given as an example. This study shows that for compositions $0.05 \leq x \leq 0.15$, the value of $T_C$ is not depending on frequency. The temperature of the $\varepsilon'_r$ maximum remains stable when the frequency increases, this behaviour corresponds mainly to the classical ferroelectric type.

All these results of the transition temperatures $T_C$ corresponding to the ferroelectric–paraelectric phase transition are summarised in Table 2. These results show that, for $0.05 \leq x \leq 0.15$, the introduction of the lithium (Li) instead of the sodium (Na) in NaNbO$_3$ leads to the increase of the transition temperature.

### 3.3. Pyroelectric measurements

In order to confirm dielectric results, we carried out pyroelectric measurements on the classical ferroelectric $Na_{0.95-x}Li_{0.05}NbO_3$ ($x=0.05$) specimen. A dc electric field of 1.5 kV/mm was applied between 540 and 625 K during 5 min in dry helium atmosphere.

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>$T_C$ (K)</th>
</tr>
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<tbody>
<tr>
<td>0.05</td>
<td>600</td>
</tr>
<tr>
<td>0.10</td>
<td>690</td>
</tr>
<tr>
<td>0.15</td>
<td>740</td>
</tr>
</tbody>
</table>
The two electrodes were then short-circuited for several minutes in order to eliminate any residual space charges. The pyroelectric depolarisation current was measured on heating at a rate of about 2 K/min from 310 to 675 K.

The temperature dependence of the pyroelectric coefficient \( p \) was calculated from the rate of variation of the temperature \( b \) and pyroelectric current \( i \) following the relation: \( p = \frac{i}{s b} \), where \( s \) is the area of the electrode. The spontaneous polarization \( P_s \) was calculated by integration of the value of \( p \) versus \( T \) [33]. Results are shown in Fig. 5. From this figure, it can be seen that the pyroelectric coefficient \( p \) has a broad maximum close to 600 K and then decreases until zero around 675 K. These results indicate that the polar state of the sample disappears at a temperature close to 650–675 K. The spontaneous polarization \( P_s \) presents a constant value at low temperature before the phase transition and then decreases quickly close to \( T_c \). The non-zero value of polarization above phase transition temperature can be connected according to Smiga et al. [34] to the existence of the polar region in paraelectric phase in NaNbO 3–LiNbO 3 solid solutions. These evolutions provide the evidence of the ferroelectric classical behaviour.

In addition, in the ferroelectric zone, the spontaneous polarization has a maximum value \( P_s = 3 \mu C/cm^2 \) for the composition \( x = 0.05 \). This value is significantly lower compared to that obtained by Jiménez et al. [35] which is of 6 \( \mu C/cm^2 \) but for this study, the variation of \( P_s \) at low temperature is not constant. So it decreases progressively from the value 6–3 \( \mu C/cm^2 \). This behaviour can be explained by the two different polarization procedures [35]. The same for the pyroelectric coefficient which is maximum at \( T_c \) having \( p = 50 nC/cm^2 K \) value for the composition \( x = 0.05 \).

### 3.4. Piezoelectric study

Piezoelectric resonance measurements of the admittance and the susceptance versus frequency were undertaken with an HP 4194A impedance analyser for the NLN ceramic with composition \( x = 0.05 \). For \( x = 0.10 \) and 0.15, the piezoelectric response is very weak. The main radial electromechanical resonance was recorded at various temperatures. The calculation of piezoelectric parameters, such as the radial resonance frequency \( f_r \), the longitudinal propagation speed \( v_L \), the electromechanical coupling factor \( k_p \) and the piezoelectric coefficient \( d_{31} \) given in Table 3, were done with a home-made software following the IEEE [36] specifications. The full fitting of the admittance lead to the transverse piezoelectric coefficient value \( d_{31} \) at room temperature of 2 pC/N.

![Fig. 5. Thermal variation of pyroelectric coefficient \( p \) and spontaneous polarization \( P_s \) in Na_{0.05}Li_{0.95}NbO_3 (x=0.05).](image)

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Piezoelectric characteristics of Na_{1-x}Li_xNbO_3 (x=0.05) ceramic at T=300 K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x=0.05 )</td>
<td>( f_r ) (kHz)</td>
</tr>
<tr>
<td>( x=0.10 )</td>
<td>( f_r ) (kHz)</td>
</tr>
<tr>
<td>( x=0.15 )</td>
<td>( f_r ) (kHz)</td>
</tr>
<tr>
<td>( x=0.20 )</td>
<td>( f_r ) (kHz)</td>
</tr>
<tr>
<td>( x=0.25 )</td>
<td>( f_r ) (kHz)</td>
</tr>
<tr>
<td>( x=0.30 )</td>
<td>( f_r ) (kHz)</td>
</tr>
<tr>
<td>( k_p )</td>
<td>0.0062</td>
</tr>
<tr>
<td>( d_{31} ) (pC/N)</td>
<td>2</td>
</tr>
</tbody>
</table>

![Fig. 6. Raman spectra of several compositions of the Na_{1-x}Li_xNbO_3 system over the wave number range 50–1000 cm\(^{-1}\).](image)

### 3.5. Raman scattering

Raman spectroscopy measurements were done using a Horiba HR 800 monochromator. The spectrometer had a wave number resolution better than 3 cm\(^{-1}\) and equipped with a microscope (Olympus BX41), with the Helium ion laser 633 nm emission line at a power of 15 mW and with a CDD detector. The Raman spectra of Na_{1-x}Li_xNbO_3 at various concentrations (\( x = 0.05, 0.10, 0.15, 0.20, 0.25 \) and 0.30) are shown in Fig. 6. The spectra exhibit continuous changes on passing from Na_{0.95}Li_{0.05}NbO_3 (\( x = 0.05 \)) to Na_{0.7}Li_{0.3}NbO_3 (\( x = 0.30 \)) ceramic. It is noted that some peaks with clearly distinct changes are observed, especially in the low frequency region. Based on the model proposed by Ross [37], the only previous attempt to separate the vibrations of such a system into internal modes of a coordination polyhedra and translational modes of an isolated cation is the study by Last [38] on NaNbO_3 [32] and KNbO_3 [39], which have structures resembling that of perovskite. The octahedral molecule NbO_6 with the symmetry \( O_4 \) has 15 internal vibrational degrees of freedom or six normal vibrational modes \( \nu_r \). They can be represented from theoretical group as

\[
\Gamma_{vib} = A_{1g}(R) + E_g(R) + 2F_{1u}(IR) + 2F_{2g}(R) + F_{2u}(inactive)
\]

where the subscripts \( g \) and \( u \) represent symmetric and antisymmetric vibrations, respectively. Of these, \( (A_{1g} + E_g + F_{1u}) \) are stretching and the rest are bending modes. Thus, there might be three characteristic Raman (\( R \)) peaks and two strong characteristic infrared (IR) absorption bands belonging to the internal vibration modes of the NbO_6 octahedra. Last [38] observed a strong, broad doublet at 660, 550 cm\(^{-1}\) and another band at 375 cm\(^{-1}\) in the infrared spectrum of NaNbO_3. He attributed these to the \( F_{1u} \) stretching and bending modes, respectively. However, the vibrational modes of the NLN crystals can be classified as internal modes of the NbO_6 octahedron and the lattice transitions involving motion of the cation. The vibrational
modes of an isolated NbO$_6$ octahedron can be decomposed into two-pure bond stretching vibrations of symmetry $A_{1g}(v_1)$ and $E_g(v_2)$, two interbond angle bending vibrations $v_3$ and $v_6$ of symmetry $F_{2g}$ and $F_{2u}$, respectively, and two vibrations $v_4$ and $v_5$, considered as combinations of stretching and bending, both of $F_{1u}$ symmetry, respectively.

The high frequency vibrational modes observed at 605 and 560 cm$^{-1}$ on NLN Raman spectra are assigned as the $v_1$ and $v_2$ stretching mode in NbO$_6$, respectively. The observed mode wavenumbers and proposed assignments are given in Table 4. The internal stretching modes of NLN caused by the vibration of NbO$_6$ octahedron are similar to those in NaNbO$_3$ crystal. Generally, both types of clusters may break the IR and Raman selection rules of the cubic symmetry. Particularly, the effect of polar clusters is complicated because of their anisotropy: in IR effective medium treatment of the average dielectric response, in Raman appearance of LO (Longitudinal Optic) modes and averaging over orientational phonon dispersion which may shift the observed peaks from TO (Transverse Optic) and LO mode frequencies. The effect of cluster formation on the dielectric response is complex and not understood quantitatively. It is clear, therefore, that the IR response contributes to the static permittivity only by several hundred, much less than its total value.

Fig. 6, which represents the evolution of Raman spectra as a function of compositions, shows that the mode at 612 cm$^{-1}$ (LO) observed for $x=0.10$, originating mainly from the vibration of atoms inside the NbO$_6$ octahedron, could be assigned as $v_1$. This peak ($v_1$) is attributed to the symmetric Nb–O stretching vibration. The mode at 570 cm$^{-1}$ (TO) should be assigned as $v_2$, which indicates the doubly degenerate symmetric O–Nb–O stretching vibrational mode. They split into longitudinal (LO) and transverse (TO) components due to the long-range electrostatic forces associated with lattice ionicity. The peak at 250 cm$^{-1}$ (TO) could be assigned as $v_3$, indicating the triply degenerate symmetric O–Nb–O bending mode ($F_{2g}$). Its shape is wide and strong for $x \leq 0.15$, and has split into two peaks 234 and 258 cm$^{-1}$ for $x \geq 0.20$. They anomaly broaden at 250 cm$^{-1}$ suggesting a large distortion of the octahedra. The mode at 189 cm$^{-1}$ (TO–LO) assigned as $v_6$ is Raman inactive according to the $O_h$ symmetry of NbO$_6$. It is observed because of the octahedron distortion.

As shown in Fig. 6, the peaks observed for $x=0.05$ at 118 and 142 cm$^{-1}$ gradually in intensity, becomes one peak at 140 cm$^{-1}$ for $x=0.15$ and finally disappear as the concentration $x$ is increased (for $x \geq 0.20$). These peaks can be assigned as the translational modes involving Na$^+$ and/or Li$^+$ cation motion against the NbO$_6$ octahedron. So for the high percent of Li$^+$ in this solid solution, the high conductivity of Li$^+$ induced an important disorder in the lattice and the peaks become broader. But on the other hand, it induces a degeneration of the central peak at 250 cm$^{-1}$. It can be noted that the spectra of samples with the compositions $x \leq 0.15$ are different to the other spectra corresponding to $x \geq 0.20$. The peaks observed in the region 100–300 cm$^{-1}$ for $x \geq 0.20$ are assembled like one broad peak. However, this interpretation is not linked to the second point of view deduced by the XRD which suggests the presence of a secondary phase in the compositions for $x \geq 0.20$. Also, uncertain impurity band at 875 cm$^{-1}$ appears in all ceramic samples, this band was also observed by Juang et al. [40] and assigned to overtone. This band is independent of the Li content and was excluded in the following discussion.

Figs. 7–9 show the temperature dependence of the Raman spectra of NLN ceramic for $x=0.05$, 0.10 and 0.25 respectively, close to the ferroelectric–paraelectric phase transition in the frequency range 50–1000 cm$^{-1}$. From the Raman spectra evolution
for three selected compositions ($x = 0.05$, $x = 0.10$ and $x = 0.25$), we can point out these observations:

- For all compositions, the normal modes, which are normally not active in the paraelectric phase are observed. So the presence of these modes can be linked to the fact that there are some polar clusters that are still retained at the paraelectric phase.

- All peaks present travel at low frequencies and the most intense peaks are observed at around 250 and 600 cm$^{-1}$. We can deduce that these peaks are assigned to the bands in the direction of polarisation. It therefore marks the transition from the polar ferroelectric phase to the non-polar paraelectric one.

4. Conclusions

Dense ceramics with compositions Na$_{1-x}$Li$_x$NbO$_3$ (0.05 $\leq x \leq 0.30$) were obtained via classical solid-state route. It was shown by XRD at room temperature that the structure of compounds for $x = 0.15$ is of perovskite type with a single phase of orthorhombic symmetry. In the regions $x = 0.05–0.10$, we have confirmed a previously reported transition to the orthorhombic ferroelectric 'Q-phase' with space group $P2_1ma$ and two phases coexistence of rhombohedral and orthorhombic above $x = 0.20$. These symmetry characteristics originate in both intrinsic mechanisms of NaNbO$_3$ phase transition and Li$^+$ doping. Dielectric measurements show that the permittivity peak is sharp for the compounds with $0.05 \leq x \leq 0.15$, without frequency dependence: it is of classical ferroelectric type. For $x = 0.05$, pyroelectric measurements show that the polar state of the compound disappears between the temperatures 650 and 675 K. The spontaneous polarization presents a constant value at low temperature before the phase transition and decreases quickly close to the transition temperature. These evolutions confirm the evidence of the ferroelectric classical behaviour. The calculation of piezoelectric parameters such as mainly the $d_{31}$ coefficient of 2 pC/N was obtained at room temperature for Na$_{0.35}$Li$_{0.65}$NbO$_3$ ($x = 0.05$) compound given as an example.

The observed spectra are discussed following the separation of modes into internal stretching modes of the NbO$_6$ octahedron and cation translation modes. The 118 and 142 cm$^{-1}$ peaks are proposed due to the translational modes of Na$^{+}$ and Li$^+$ cation. The difference of the Raman spectra observed in the region 100–300 cm$^{-1}$ is not linked to the existence of the secondary phase deduced by XRD. The evolution of the Raman spectra studied as a function of temperatures and compositions confirm our dielectric results, so it marks clearly the transition from the polar ferroelectric phase to the non-polar paraelectric one.

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**References**