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# Dielectric properties of $Na_{1-x}Li_xNbO_3$ ceramics from powders obtained by chemical synthesis

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**Abstract**

Ultra-fine powders of $Na_{1-x}Li_xNbO_3$ ($x=0$; 0.06; 0.09; 0.12 ) were synthesized by the Polymeric Precursors Method. Such powders had their orthorhombic structures determined by X-ray diffraction and their surface area determined by BET isotherms (less than 10 $m^2 g^{-1}$). Densification was followed by dilatometric study. The powders, calcined at 700°C for 5 h, were sintered at 1290°C during 2 h under ambient atmosphere with no application of extra pressure. The samples with relative densities higher than 95% were analyzed by impedance spectroscopy at room temperature, under a signal amplitude of 1 $V_{rms}$. Dielectric constants of about 180 and dielectric loss factor of about 0.03 were measured showing small dependence with frequency. The electrical properties were similar to those obtained for samples sintered by hot pressing. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

*Keywords:* Sodium and lithium niobate; Polymeric precursors; Dielectric

## 1. Introduction

Since the discovery of the piezoelectric phenomenon in 1880 by the brothers Pierre and Paul-Jacques Curie, extensive investigations have been carried out with several materials that display such property [1,2].

From the decade of 1950 on some perovskites of the type $A(B'B'')O_3$ and $(A'A'')BO_3$ were developed aiming the optimization of electronic properties of these materials for several technological applications such as piezoelectric devices, capacitors or semiconductors [3,4].

For the applications in high frequency (over 30 MHz), the fabrication of resounding elements becomes difficult due to the small dimensions required, leading to search new materials, such as niobate based perovskites. Some compositions involving the system $(A'A'')NbO_3$, where A represents an alkaline metal, have been prepared by solid state reaction aiming the electrical properties optimization of dielectric devices based on these systems. These properties should have high dielectric constant, high coefficient of planar coupling and low Curie temperature [5,6]. The system $Na_{1-x}Li_xNbO_3$ is a solid solution of sodium niobate and lithium niobate, named LNN, displaying dielectric characteristics different from the two pure niobates. Lithium niobate is ferroelectric at room temperature showing a rhombohedral structure whereas the sodium niobate is antiferroelectric showing orthorhombic structure. The presence of small amounts of $LiNbO_3$ dissolved in $NaNbO_3$ modify its dielectric characteristics [7], however, only a small number of papers are dedicated to investigate the electric properties of ceramic materials based on LNN [8].

In this paper, powders of lithium and sodium niobates, $Na_{1-x}Li_xNbO_3$ ($x=0$; 0.06; 0.09; 0.12) were synthesized using the polymeric precursors method [9]. The polymeric precursors method, based on a Pechini patent, make possible the synthesis of a powder with superior properties compared to the conventional methods. Several ceramics have been synthesized using this method such as: $SrTiO_3$, $BaTiO_3$ and $Pb(Zr_{1/2}Ti_{1/2})O_3$, (PZT). Recently sodium niobates with high stoichiometric control was synthesized using this method given small particles (< 1.0 μm) at relatively low calcining temperature [10].

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## 2. Experimental procedure

Powders with stoichiometry $Na_{1-x}Li_xNbO_3$ ($x=0$; 0.06; 0.09; 0.12) were prepared by the polymeric precursors method or Pechini method. The starting salts used were $NH_4H_2[NbO(C_2O_4)_3]\cdot 3H_2O$, $Na_2CO_3$ and $Li_2CO_3$, all analytical grade, as described in Table 1. An aqueous solution of ammonium niobium oxalate was prepared and ammonium hydroxide was dropped upon it thereafter. The precipitated of niobium hydroxide was filtered and washed aiming the elimination of all oxalate ions and dissolved back with a previously prepared citric acid aqueous solution. The niobium content in the solution was determined by thermogravimetric method resulting 2.55% of $Nb_2O_5$.

This solution was divided into four equal parts and it was added over them the carbonates of sodium and lithium, according to the desired stoichiometries, together with ethylene glycol. The resins were polymerized by the elimination of the solvent at temperature of 120°C for 12 h, and were pre-calcined at 350°C for 2.5 h. The pre-calcined powders were calcined at 700°C for 5 h and at 1000°C for 1 h over alumina slabs in an electric furnace. They were analyzed by X-ray diffraction in a Siemens D5000 diffractometer at room temperature using the CuK$\alpha$ radiation and a graphite monochromator. BET adsorption and desorption isotherms were obtained in a Micromeritics ASAP 2000 as well as the dilatometric analyses in a Netzsch 402 ES dilatometer.

The equivalent mean particle diameter was determined from the relative densities of the powders and from their surface areas, determined by BET isotherms, according to the relation,

$$D_{\mathrm{BET}} = \frac{6}{\rho_{\mathrm{T}} S_{\mathrm{BET}}} \qquad (1)$$

where $D_{\mathrm{BET}}$ is the equivalent mean diameter and $S_{\mathrm{BET}}$ is the surface area determined by BET, $\rho_{\mathrm{T}}$ is the theoretical density of each composition, calculated as,

$$\rho_{\mathrm{T}} = (1-x)\rho_{\mathrm{Na}} + x\rho_{\mathrm{Li}} \qquad (2)$$

where $\rho_{\mathrm{Na}}$ is the sodium niobate density ($4.757\,\mathrm{g\,cm^{-3}}$) and $\rho_{\mathrm{Li}}$ is the lithium niobate density ($4.472\,\mathrm{g\,cm^{-3}}$) with $x=0$; 0.06; 0.09 and 0.12.

Table 1
Reagents used for synthesis of $Na_{1-x}Li_xNbO_3$ ($x=0$; 0.06; 0.09; 0.12) by the polymeric precursor method

| Reagent | Supplier | Purity |
|---|---|---|
| $NH_4H_2[NbO(C_2O_4)_3]\cdot 3H_2O$ | CBMM Brazil | 98% |
| NH4OH | Merck, Brazil | 98% |
| $Na_2CO_3$ | Merck, Brazil | 99% |
| $Li_2CO_3$ | Carlo Erba, Italy | 99% |
| Citric acid | Merck, Brazil | 99% |
| Ethylene glycol | Merck, Brazil | 99% |

The calcined powders were conformed in 8 mm diameter pellets and isostaticaly pressed at 210 MPa. The samples were then sintered at 1290°C for 2 h over alumina slabs using ambient atmosphere in an electric Lindberg furnace model Blue M 1524. The sintered pellets were thereafter polished and prepared with conductive silver paste (Degussa) at 450°C during 30 min for electrodes as needed for the electrical measurements. The samples were placed in a Keithley 3327 sample holder and impedance spectroscopy were performed at room temperature for frequencies from 120 Hz to 100 kHz in a Keithey 3330 LZC meter under a signal amplitude of 1 $V_{\mathrm{rms}}$.

## 3. Results and discussion

### *3.1. Characterization of the LNN powders*

The surface areas were determined by BET isotherms at 700°C for 5 h under ambient atmosphere. These surface areas for each composition and the equivalent mean diameters are shown in Table 2 and these results are compared with those from Nobre and co-workers [10] for pure $NaNbO_3$ synthesized by the polymeric precursor method in the same conditions of calcination and characterization.

Data for powder synthesized by solid state reaction were not found in the literature. Nevertheless, it is known that powders synthesized by chemical route show higher surface area when compared to synthesized by solid state reaction [11]. The spread in the results of surface areas and equivalent diameters emphasizes the great influence of the processing properties of powders prepared by the polymeric precursor method.

The orthorhombic phase (JCPDS#33-1270) was observed as shown in Fig. 1, for all the powders no matter the amount of added lithium. Henson and co-workers proposed that for the composition $Na_{0.88}Li_{0.12}O_3$ the orthorhombic and tetragonal phase co-exist [6]. However the diffractograms of powders of pure sodium niobate and sodium niobate doped with 6%, 9% and 12% lithium, calcined at 1000°C for 1 h, display for all the samples the orthorhombic phase of

Table 2
Surface area of the powders calcined at 700°C for 5 h and equivalent mean diameters for all compositions of $Na_{1-x}Li_xNbO_3$

| Composition | Surface area ($m^2\,g^{-1}$) | | $D_{\mathrm{BET}}$ (nm) |
|---|---|---|---|
| $NaNbO_3$ | 14.21 | ±0.07 | 94.04 |
| $Na_{0.94}Li_{0.06}NbO_3$ | 9.72 | ±0.01 | 138.0 |
| $Na_{0.91}Li_{0.09}NbO_3$ | 9.70 | ±0.01 | 149.8 |
| $Na_{0.88}Li_{0.12}NbO_3$ | 11.15 | ±0.03 | 125.0 |
| $NaNbO_3$[a] | 21.70 | ±0.01 | 60 |

[a] M.A.L. Nobre, Matter. Letters 28 (1996) 215.

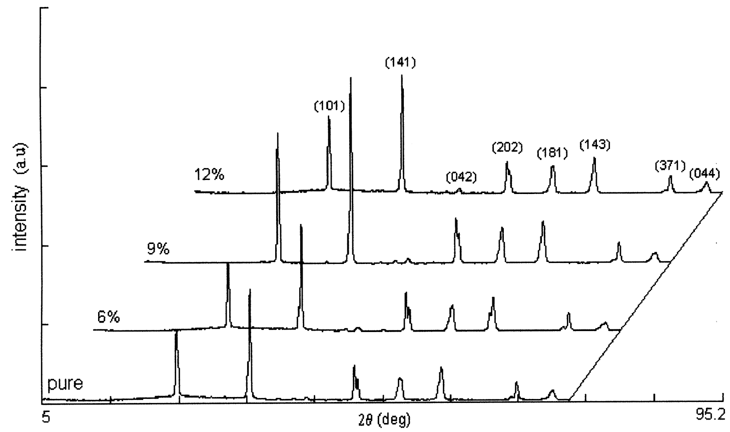

Fig. 1. X-ray diffratograms of the powders having the composition $Na_{1-x}Li_xNbO_3$, with $x$ in mole = 0; 0.06; 0.09; and 0.12, calcined in ambient atmosphere at 1000°C for 1 h.

sodium niobate, free from the lithium niobate phase. In a recent study of low temperature phase transition in LNN crystals, Zhong and co-workers [12] describe the occurrence of a morphotropic phase boundary (MPB), between the orthorhombic and tetragonal phases at room temperature for $x = 0.12$ based only in the piezoelectric results. They synthesized the powder by solid state reaction, however no diffractograms were shown.

The use of polymeric precursors route leads to materials with rigorous stoichiometric control, with no local stoichiometric deviations, and higher reactivity, when compared with powder synthesized by conventional route. A major obstacle to the synthesis of LNN powders by solid state reaction method is the formation of nonstoichiometric intermediate phases, rich in lithium or rich in sodium. The absence of tetragonal phase in the diffractograms of Fig. 1 results from a complete reaction of the powders prepared by chemical route. The presence of both tetragonal and orthorhombic phases reported by in Refs. [6] and [12] for LNN with $x = 0.12$ could be due to incomplete solid state reaction and therefore the presence of a lithium rich tetragonal phase.

Table 3 presents the lattice parameters of the synthesized LNN powders and compared with the sodium niobate diffractogram reference (JCPDS#33-1270) as well as with the results obtained by Zhong and co-workers [12] for the system $Na_{0.94}Li_{0.06}NbO_3$. The cell volume of pure sodium niobate reference value is close to those obtained by us, but smaller than those obtained by Zhong and co-workers [12]. Probably in their work the reaction for formation of LNN was not completed and the chemical equilibrium was not reached. The decrease in the unit cell dimensions with the addition of lithium suggests the formation of a solid solution with the substitution of sodium by lithium in the crystalline lattice. Nobre and co-workers [10] found that the nucleation of sodium niobate phase occurs between 400° and 500°C without the presence of an intermediate phase, during the synthesis using the polymeric precursor method. Otherwise, we observed the presence of sodium niobate and lithium niobate phases by X-ray diffraction in the powders calcined at 700°C for 5 h. This indicates that both phases are formed during the elimination of organic material when calcined at relatively low temperatures . This temperature is quite low when compared with the one used by Wang and co-workers [8] for the synthesis of $Na_{0.94}Li_{0.06}NbO_3$ by solid state reaction at 850°C for 4 h. For high calcination temperatures, the lithium solubilization in the sodium niobate is more uniform leading to a single orthorhombic phase as indicated by Fig. 1.

Table 3
Calculated lattice parameters for all compositions of $Na_{1-x}Li_xNbO_3$ powders

| Composition | a (Å) | b (Å) | c (Å) | Volume (Å$^3$) |
|---|---|---|---|---|
| $NaNbO_3$ | 5.568 | 15.53 | 5.507 | 476.1 |
| $Na_{0.94}Li_{0.06}NbO_3$ | 5.565 | 15.52 | 5.500 | 475.0 |
| $Na_{0.91}Li_{0.09}NbO_3$ | 5.562 | 15.50 | 5.509 | 475.0 |
| $Na_{0.88}Li_{0.12}NbO_3$ | 5.564 | 15.52 | 5.504 | 475.3 |
| $NaNbO_3$[a] | 5.5687 | 15.523 | 5.504 | 475.84 |
| $Na_{0.94}Li_{0.06}NbO_3$[b] | 5.523 | 15.564 | 5.556 | 477.6 |

[a] File JCPDS#33-170.

[b] W.L. Zhong, Phys Rev. B 46 (1992) 10583.

## 3.2. Characterization of the sintered samples

Fig. 2(a) shows the shrinkage curves for pure and lithium doped sodium niobate powders with 6 and 9 mol% of lithium. The samples were compacted and sintered with heating rate of 10°C min$^{-1}$ from 600°C to 1300°C under synthetic air atmosphere. Maximum shrinkage rate temperature for each composition was obtained by the first derivative of the shrinkage curves. Two regions of shrinkage can be observed for all curves in the Fig. 2. The low temperature region (between 800 and

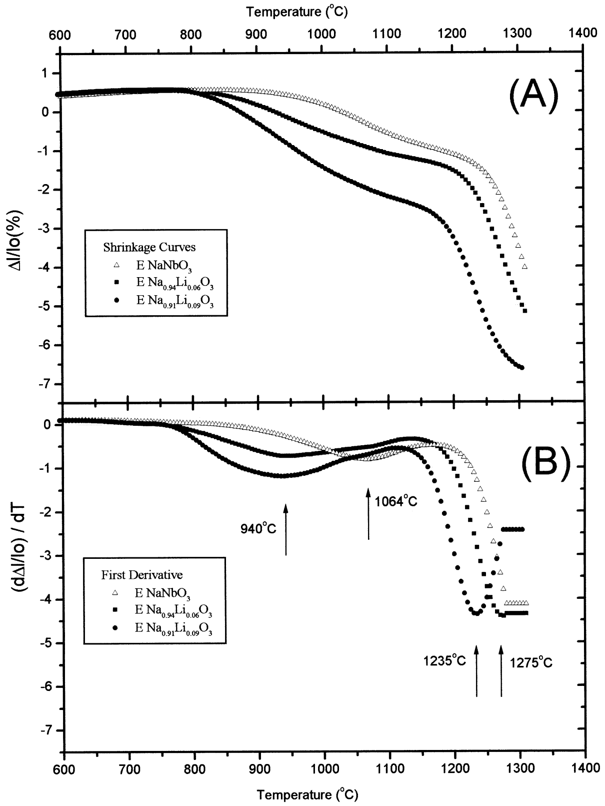

Fig. 2. (a) Shrinkage curves of the powders having the composition $Na_{1-x}Li_xNbO_3$, with $x=0$; 0.06; 0.09; and 0.12, calcined in ambient atmosphere at 1000°C for 1 h, and sintered from 600 to 1300°C with heating rate of 10°C min$^{-1}$. (b) First derivative of the shrinkage curves of Fig. 2a, indicating the maximum shrinkage rate temperatures.

1200°C) corresponds to densification of agglomerates. The maxiumum shrinkage rate of these agglomerates depends on the lithium concentration. Undoped $NaNbO_3$ ceramics has the maximum shrinkage rate of agglomerates around 1064°C whereas for the doped $NaNbO_3$ the maximum shrinkage rate of the agglomerates is about 940°C. After the densification of the agglomerates the shrinkage rate increase sharply with temperature, reaching a maximum at temperatures which depend on the lithium concentration as shown in Fig. 2(b). Then the increase in lithium concentration decrease the temperature for sintering LNN ceramics.

Table 4 presents the values of relative densities of the sintered samples in relation to the theoretical densities for each composition. According to Hardiman and co-workers [13] the electro-mechanic properties of the LNN system are deeply dependent of the density of the samples. Zeyfang and co-workers and Henson and co-workers [5,6] have electrically characterized a LNN system using ceramics sintered under hot pressing, and they obtained values of about 95% of the theoretical density.

Table 4
Relative densities of the samples sintered at 1290°C for 1 h for all compositions of $Na_{1-x}Li_xNbO_3$

| Composition | Theoretical density (g cm$^{-3}$) | Density % |
|---|---|---|
| $NaNbO_3$ | 4.757 | 94.4% |
| $Na_{0.94}Li_{0.06}NbO_3$ | 4.741 | 93.9% |
| $Na_{0.91}Li_{0.09}NbO_3$ | 4.726 | 87.0% |
| $Na_{0.88}Li_{0.12}NbO_3$ | 4.709 | 91.5% |

The different powders, calcined at 700°C for 5 h were sintered without any extra pressure at 1290°C for 2 h under ambient atmosphere with heating rate of 10°C min$^{-1}$. Due to the high reactivity of the powder synthesized by the polymeric precursors route, relative densities in the order of 95% were obtained, even without the use of an extra pressure during sintering. The electric properties were similar to those obtained for samples sintered under pressure, as will be discussed below.

### 3.3. Electrical characterization of the sintered samples

The values of dielectric constant, $\varepsilon_r$ , dielectric loss factor, tan $\delta$, and capacitance, $C$, were measured in the frequency range from 120 Hz to 100 kHz, using a potential of 1.0 $V_{rms}$ at room temperature. The dependence of the dielectric constant, $\varepsilon_r$, with the lithium amount in the fixed frequency of 1 kHz was studied by Henson and co-workers for the LNN [6]. They observed that the addition of a small amount of lithium reduces the dielectric constant in relation to pure sodium niobate, further additions of lithium, on the other hand, increases the dielectric constant, nevertheless the influence of the applied frequency on the dielectric behavior was not reported. Wang and co-workers [8] studied the influence of temperature in the range 120 K to 320 K on the dielectric behavior of LNN ceramics having $x=0.06$, but with a fixed frequency of 10 kHz.

Fig. 3 shows the dependence of dielectric constant, $\varepsilon_r$ , and Fig. 4 the dependence of the dielectric loss factor, tan $\delta$, of the non polarized ceramic samples, with the frequency in the range from 120 Hz to 100 kHz, at room temperature and using several lithium concentrations. Fig. 3 reveals a small dependence of $\varepsilon_r$ with the variation of frequency for each of the studied compositions, indicating a small decrease in $\varepsilon_r$ with increasing frequencies, with no apparent anomaly. The dielectric behavior observed by Henson and co-workers [6] in the LNN ceramics at frequency of 1 kHz is similar to that observed in this work for the whole range of frequencies.

Pure sodium niobate samples displayed value of $\varepsilon_r$ of 182 at 1 kHz and a low dependency of $\varepsilon_r$ with frequency as shown Fig. 3. This same behavior is observed for the dielectric loss factor, tan $\delta$, as observed in Fig. 4. For frequencies over 10 kHz, the dielectric loss factor for LNN, with different lithium contents, have the tendency to level off, with tan $\delta=0.015$. Nevertheless, for frequencies below 1 kHZ the amount of lithium deeply influences tan $\delta$.

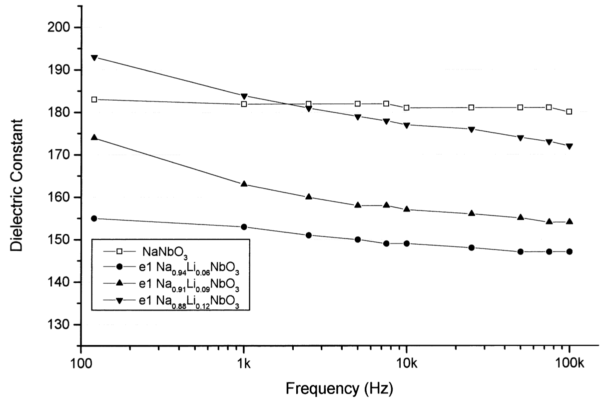

Fig. 3. Dielectric constant, $\varepsilon_r$ , as a function of the frequency measured at room temperature in samples having the composition $Na_{1-x}Li_xNbO_3$, with $x=0$; 0.06; 0.09; and 0.12, calcined in ambient atmosphere at 1000°C for 1 h, and sintered from 600 to 1300°C with heating rate of $10°Cmin^{-1}$.

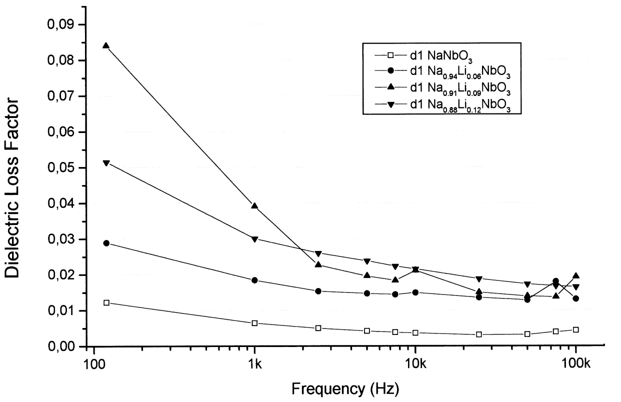

Fig. 4. Dielectric loss factor, tan δ, as a function of the frequency measured at room temperature in samples having the composition $Na_{1-x}Li_xNbO_3$, with $x$ in mole = 0; 0.06; 0.09; and 0.12, calcined in ambient atmosphere at 1000°C for 1 h, and sintered from 600 to 1300°C with heating rate of $10°Cmin^{-1}$.

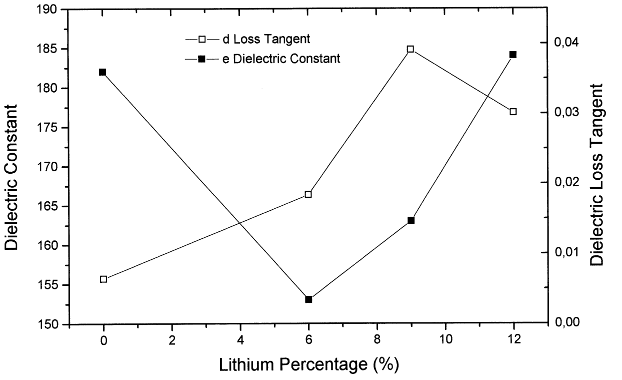

Fig. 5. Dielectric constant and dielectric loss factor, tan δ, as a function of composition measured at room temperature and at 1 kHz in samples having the composition $Na_{1-x}Li_xNbO_3$, with $x$ in mole = 0; 0.06; 0.09; and 0.12, calcined in ambient atmosphere at 1000°C for 1 h, and sintered from 600 to 1300°C with heating rate of $10°Cmin^{-1}$.

Fig. 5 shows the variation of dielectric constant, $\varepsilon_r$, and of the dielectric loss factor as a function of composition for a frequency of 1 kHz. These results are similar to those reported by Henson and co-workers [6] for samples sintered under hot pressing and showing relative densities over 95%. In their work, Henson and co-workers [6] observed an anomaly in region near to $x=0.12$. They related it to the presence of a morphotropic phase boundary (MPB), between the orthorhombic and tetragonal phases at room temperature for this composition. In this work, however, no tetragonal phase was observed for the LNN for lithium up to 12 mol% (Fig. 1). The dielectric constant, $\varepsilon_r$, increases steadily with the amount of lithium and no anomaly was found for compositions near $x=0.12$ (Fig. 5).

## 4. Conclusions

The polymeric precursors method makes possible the synthesis of LNN powders with controlled stoichiometry, $Na_{1-x}Li_xNbO_3$, with $x$ ranging from 0 to 0.12. A single orthorhombic crystalline phase was observed for LNN powders calcined at lower temperatures as compared with powder prepared by solid state reaction.

As a result, powders of high sinterability were obtained with a high surface area, (order of 10 $m^2$ $g^{-1}$) and equivalent diameters of about 130 nm, which allows the sintering of ceramic samples to densities over 95% without the use of hot pressing. The dielectric characteristics of these powders showed a small dependence with the frequency at room temperature. No morphotropic phase boundary, MPB, between orthorhombic and tetragonal phases was identified for LNN compositions near 12 mol% lithium, but a single orthorhombic phase.

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