Unambiguous evidence of three coexisting ferroelectric phases in a lead-free Li$_x$Na$_{1-x}$NbO$_3$ system

Abhinav Kumar Singh, Digvijay Nath Dubey, Gurvinderjit Singh, and Saurabh Tripathi

1Department of Physics, Indian Institute of Technology (BHU), Varanasi, 221005, India
2Laser and Functional Materials Division, Raja Ramanna Centre for Advanced Technology, Indore, 452013, India

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We report here the presence of three coexisting ferroelectric phases in a lead-free Lithium Sodium Niobate (Li$_3$(Na$_x$N$\alpha$)O$_3$; LNNx) system stable for 0.15 $\leq$ x $\leq$ 0.80, which contrasts the review report of Dixon et al. [C. A. Dixon and P. Lightfoot, Physical Review B 97, 224105 (2018)]. More importantly, we have identified LNN20 as an important composition for technological applications, due to its high dielectric permittivity, low loss, and high ferroelectric response. The anomalous dielectric and ferroelectric responses in LNN20 have been attributed to the MPB like nature around this composition.

Lead-based materials are known to have detrimental effects on health/environment for a long time, and therefore, international efforts are continuously increasing to restrict the use of such toxic materials from everyday life. However, most of the piezoelectric devices based industries still use lead zirconate titanate (PZT), due to its unrivaled high electromechanical response, which has inspired researchers to look for lead-free alternatives. Most of the research for such applications are focussed on the perovskite materials; BaTiO$_3$, NaNbO$_3$, LiNbO$_3$, KNN, NaBiO$_3$, SrTiO$_3$, their solid solutions, and derivatives. Alkali Niobates have drawn considerable interest after the discovery of high piezoelectric properties in Na$_x$K$_{3-x}$NbO$_4$. Sodium Niobate (NN) and Lithium Niobate (LN) are some of the important materials falling under this category having several technological applications, such as high-density optical data storage, nonlinear photonics, electro-optic devices, SAW (surface acoustic wave) devices, laser modulators, piezoelectric devices, optical wave-guides etc. NN has an anti-ferroelectric orthorhombic Pnma (OAFE) structure at room temperature and shows a series of phase transitions as a function of temperature with complex structures (supercells), as a function of composition (x). Many controversies have been reported in LNNs about the exact region of phase coexistence and Morphotropic Phase Boundary (MPB). Nitta et al. have reported a single phase for x $\leq$ 0.14, and an additional lithium niobate like rhombohedral (R$_m$) phase for LNN11. Whereas, Jankowska et al. have observed an MPB like behaviour at x $\approx$ 0.04, based on dielectric anomaly. LNNx with x=0.12, has been identified as an MPB composition, based on dielectric properties, radial coupling coefficients, polarization, electromechanical response, and synchrotron X-ray diffraction measurements. On the other hand, Mitra et al. have reported an MPB at LNN14 based on coexistence of R$_m$, R$_g$, and O$_{PC}$ phases, facilitating easy polarization rotation, similar to PZT. On the other hand, Franco et al. didn’t observe any MPB like behaviour in the region 0 $\leq$ x $\leq$ 0.12. Pozdnyakova et al. carried out a detailed structural phase transition studies in the regions 0 $\leq$ x $\leq$ 0.14 and 0.95 $\leq$ x $\leq$ 1.00 and reported a single phase (O$_{PC}$) for x $\leq$ 0.0125; two phases (O$_{AFE}$, O$_{PC}$) for 0.0125 $\leq$ x $\leq$ 0.07; two phases (O$_{AFE}$, R$_m$) for 0.08 $\leq$ x $\leq$ 0.13; single phase (O$_{PC}$) for x = 0.14 and again a single phase (R$_m$) for x $\geq$ 0.95. Recently, Dixon et al. revised the composition-dependent phase diagram for 0.05 $\leq$ x $\leq$ 0.95, using a combination of X-ray diffraction, neutron diffraction and $^{23}$Na solid-state NMR spectroscopy techniques. They have reported a single phase (O$_{PC}$) for x = 0.05, two phases (O$_{AFE}$, R$_m$) for 0.08 $\leq$ x $\leq$ 0.20, two phases (R$_m$ and R$_g$) for 0.25 $\leq$ x $\leq$ 0.90, and finally, a single phase for (R$_m$) in the region 0.95 $\leq$ x $\leq$ 1.00. They have also pointed out that the phase diagram depends on the synthesis conditions, such as annealing temperature, cooling rate etc.

In this letter, we have carried out detailed structural investigation using X-ray diffraction profiles for LNNx system, and strove to resolve the ambiguities present in the composition-dependent phase diagram of this system. Rietveld and Le-bail refinements revealed unambiguous evidence of three phase coexistence for region 0.15 $\leq$ x $\leq$ 0.80. Composition-dependent dielectric and polarization measurements have shown anomalously high response for LNN20, similar to an MPB composition. These high responses near MPB compositions are related to the least energy barrier with flattened nature of free energy profile between the different phases, facilitating easy polarization rotation, similar to PZT.

The LNNx (0 $\leq$ x $\leq$ 1.00) ceramics were prepared using conventional solid-state reaction route (see the supplementary material for the details of synthesis). For phase transition studies, X-ray diffraction measurements were carried out.
using a X-ray diffractometer (Rigaku MiniFlex 600), with Cu-Kα radiation. Diffraction data were collected at scan rate of 2°/minute and step interval of 0.02° in the 2θ range of 20°-120°. The room temperature dielectric permittivity (ε) and loss (tanδ) measurements were performed on an impedance analyzer (HP4194A), at 100 kHz. The P-E hysteresis loops measurements of unpoled samples were carried out using Radiant Technology’s Precision Material Analyzer Workstation based on virtual ground system at 10 Hz and an alternating voltage of about 70 kV/cm waveform.

X-ray diffraction studies confirm the formation of solid-solution for the entire composition range with a trace amount (<1%) of secondary phase i.e., Na3Nb5O14 (Space group: Pbnm) [89], due to alkali loss during sintering. Fig.1 shows composition-dependent evolution of powder X-ray diffraction patterns in the 2θ range of 20°-65°. The reflections have been indexed in terms of doubled pseudocubic perovskite cell. Exclusive reflections of all categories viz; main perovskite reflections represented by all (q=1/2,1/2,1/2), (supercell q=1/2,1/2,0), and (0001) reflections corresponding to the Glazer’s simple tilt system with ferroelectric displacements [42–44]. These reflections can be classified into two major subgroups (even or odd) integers, and superlattice reflections represented by one or more odd integer (s) such as (eeo), (ooe) or (000), and (or) fractional integers. Furthermore, (000) and (000) types of reflections represent out-of-phase and in-phase tilting of oxygen octahedra [42–44]. The X-ray diffraction patterns for x = 0.00, and x = 1.00, have been indexed with an orthorhombic anti-ferroelectric phase (OAFE) having a compound tilt system (a’-b’-a’’), having tilt system $\sqrt{4a_p} \times 4b_p \times c_p$, having tilt system $\sqrt{4a_p} \times 0 \times c_p$, respectively, consistent with the literature [19,24,42,43,45]. For a small amount of Li+ substitution (x = 0.05), the structure of LNN transforms to a ferroelectric OFE phase, showing evolution of R3m & O3m phases. The reflections are indexed with respect to doubled perovskite cell. Exclusive reflections of all the different phases are shown by arrow marks.

![Fig. 1. X-ray diffraction pattern of the LNNx ceramics with varying Li content. The reflections are indexed with respect to doubled pseudocubic perovskite cell and unique reflections of different phases are shown by arrow marks.](image1.png)

![Fig. 2. Zoomed up view of portions of the X-ray diffraction patterns, showing evolution of R3m & O3m phases. The reflections are indexed with respect to doubled perovskite cell. Exclusive reflections of all the different phases are shown by arrow marks.](image2.png)
phonon mode of \(Pm\bar{3}m\) space group, related with the quadrupling of \(b_0\) unit-cell parameter. Example of such reflections are \((31/21), (25/20)\) at \(2\theta \approx 37^\circ\) and \((43/22), (37/21)\) at \(2\theta = 55.5^\circ\) (Fig.1 and Fig.2). The \(O_{FE}\) to \(O_{Li}\) transition is also reported by Pozdnyakova et al.\textsuperscript{34} and Yuzuyuk et al.\textsuperscript{35}. Furthermore, the most intense reflection \((200)\) and the exclusive reflection \((040)\) of \(O_{Li}\) phase at \(2\theta = 22.9^\circ\) and 47.0° respectively, disappears at \(x = 0.95\), suggesting a single \(R_{Li}(a_2, a_2, a_2)\) tilt system in the modified Glazer’s notation\textsuperscript{36} phase, for \(x \geq 0.95\), similar to the reports by Pardo et al. and Pozdnyakova et al.\textsuperscript{34,39}. On the other hand, the most intense peak of LiNbO\(_3\) (\(R_{Li}\) phase) corresponds to \((020)\) reflection at \(2\theta \approx 23.6^\circ\) (Fig.1), survives till \(x \approx 0.15\), asserting the existence of \(R_{Li}\) phase in the region \(0.15 < x < 1.00\). The presence of \(R_{Li}\) phase in this region is also supported by Nitta et al. and Pardo et al.\textsuperscript{26,49}. On the other hand, Mishra et al. found a small phase fraction \((\approx 2\%)\) of \(R_{Li}\) phase even at \(x = 0.12\).\textsuperscript{50} The evolution of \((000)\) reflection \((13 \cdot 1)\) of LN at \(2\theta = 40^\circ\) corresponding to \(R_{Li}\) phase, survives till \(x = 0.20\), however for \(x = 0.15\), it seems to have merged with background due to the small phase fraction of \(R_{Li}\). Moreover, on close inspection of diffraction pattern of LNN5, we find that the reflection at \(2\theta \approx 39.4^\circ\) can not be indexed with \(O_{FE}\) or \(O_{Li}\) phase. Presence of such reflections have been previously reported by Yuzuyuk and Mishra et al. in the vicinity of LNN12. They claimed that, this phase was similar to the low temperature rhombohedral \(R_{Na}(a_3, a_3, a_3)\) phase in modified Glazer’s notation\textsuperscript{34} phase of NaNbO\(_3\)\textsuperscript{15,30}. The evolution of \(R_{Na}\) phase is shown by its exclusive reflection \((222)\) at \(2\theta = 39.4^\circ\), as clearly depicted in Fig. 2. The existence of reflection corresponding to \(R_{Na}\) phase for \(0.05 \leq x \leq 0.80\) clearly shows that this composition range can not be indexed with \(O_{FE}\) phase or two phase model \((O_{FE} + R_{Li})\). Moreover, the possibility of indexing these structures with two phase model \((R_{Na} + R_{Li})\), as reported by Peel et al.\textsuperscript{35} can be ruled out from the evolution of \(O_{FE}\) reflection at \(2\theta = 46.82^\circ\) (Fig.2). The evolution of this exclusive reflection confirms the presence of \(O_{FE}\) phase from \(x = 0.05\) to \(x = 0.80\). Therefore, for compositions \(0.15 \leq x \leq 0.80\), we have undoubtedly three coexisting ferroelectric phases, \(O_{FE}, R_{Na}\) and \(R_{Li}\). Also, the relative intensity of the \(R_{Li}\) phase most intense and exclusive reflection in LNN20 is \(\approx 0.0369\) or \(3.69\%\) at \(2\theta = 23.72^\circ\) (marked by the arrow in Fig.1). Similarly, the relative intensity of the exclusive reflection corresponding to \(R_{Na}\) phase is \(\approx 0.0074\) or \(0.74\%\) in LNN20 at \(2\theta = 39.36^\circ\) (marked by arrow in Fig.2).

To further ascertain the composition-dependent phase diagram, we have performed Rietveld refinements of X-ray diffraction data, using a structure refinement program “FULLPROF”\textsuperscript{48}. The Pseudo-Voigt function was chosen for peak profile fitting in the refinements. The Background was described in terms of linear interpolation between a set background points with refinable heights. The lattice parameters, zero correction, half width parameters (U, V and W), atomic coordinates and thermal parameters were refined to get least square (chi square) fit between the observed and simulated powder diffraction pattern. In order to confirm three

| Composition | Phases                        |
|-------------|-------------------------------|
| \(x = 0.05\) | \(O_{Li}\)                    |
| \(0.05 \leq x \leq 0.12\) | \(O_{Fe} + R_{Na}\)          |
| \(0.15 \leq x \leq 0.80\) | \(O_{Fe} + R_{Na} + R_{Li}\)|
| \(x = 0.90\) | \(O_{Fe} + R_{Li}\)          |
| \(0.95 \leq x \leq 1.00\) | \(R_{Li}\)                    |
phase coexistence, we have carried out Rietveld refinements of LNNx, as shown in Fig. 2(a)-(d). Fig. 3(a) shows fitted profile of LNN15 using two phase model (O_{FE} + R_{Li}), similar to the reports by Nitta et al. and Pardo et al. However, we could not index the reflections present at 2θ = 39.4° and 57.1° (marked with *), by using this two phase model. Similarly, Fig. 3(b) shows fitted profile with two phase model (R_{Na} + R_{Li}), which results in even worse fit, as is clearly evident from the poor profile fitting and the absence of peak in the simulated pattern corresponding to O phase at 2θ = 46.8°. Furthermore, we have refined the profile of LNN15 with the widely reported two phase model (O_{Na} + R_{Li})^{32,35,37,50}. This model could not index the reflection at 2θ = 23.7° corresponding to R_{Li} phase, as shown by + mark in the inset of Fig. 3(c). Therefore, it is clear that none of the two phase model could index all the reflections present in LNN15. Fig. 3(d) shows the fitted profile with three phase model (O_{Na} + R_{Na} + R_{Li}), giving the best fit with lowest agreement factors. Although, for compositions 0.15 ≤ x ≤ 0.80, the best fit has been achieved by three phase (O_{Na}, R_{Na} and R_{Li}) model, we observed an extra reflection with very low intensity in the vicinity of (2θ = 36.4°) for compositions 0.15 ≤ x ≤ 0.25. This reflection may be due to the presence of an incomensurate modulation or long-range ordering which requires high-resolution neutron/synchrotron diffraction data to fix the structure. The revised phase diagram as confirmed from Rietveld and Le-bail refinements, can be seen from Table I.

The variation of room temperature dielectric permittivity (ε') and loss (tanδ) as a function of composition is shown in Fig. 4. The ε' values of undoped NN and LN are 207 and 80, the best fit values in literature for compositions 0.15 ≤ x ≤ 0.80 unlike Dixon et al. reports, where they find a single report for LNNx, showing similar anomalies in dielectric permittivity with such high dielectric response. Furthermore, the dielectric loss (tanδ), exhibit small values (< 0.018) for compositions x ≤ 0.40, which is of the same order as reported by Mitra et al.

We have performed the room temperature PE hysteresis loop measurement for various compositions 0.10 ≤ x ≤ 0.40 in the vicinity of LNN20 (Fig. 5). The variation of remnant polarization (P_r) for 0.10 ≤ x ≤ 0.40, clearly shows the presence of high P_r values in LNNx for 0.15 ≤ x ≤ 0.25 (Fig. 5). LNN15 and LNN20, both have comparable P_r (7.26 & 8.60 μC/cm² respectively), but high value of coercive field (E_c = 35.5 kV/cm) makes LNN15 inappropriate for applications. The high E_c in LNN15 is linked with lower experimental density of LNN15 (4.463 gm/cc) w.r.t. LNN20 (4.528 gm/cc). The polarization values are in close agreement with Mitra et al. Note that, LNNx ceramics become highly conductive at high voltage of around 70 kV/cm, and therefore, saturation could not be achieved for many compositions and hence, P_r values are compared at a field of 70 kV/cm.

In conclusion, composition-dependent X-ray diffraction analysis reveals several phase transitions in LNNx ceramics, along with three coexisting ferroelectric phases stable in region 0.15 ≤ x ≤ 0.80 unlike Dixon et al. reports, where they have reported a coexistence of O_{FE} and R_{Na} phases for 0.15 ≤ x ≤ 0.20 and R_{Na} and R_{Li} phases for 0.20 < x ≤ 0.90. Room temperature dielectric and polarization measurements have shown an anomaly at LNN20 and is attributed to the MPB-like behaviour near this composition, which is further confirmed by the temperature-dependent X-ray diffraction studies of LNN20 showing the existence of all the three phases up to 423K (see Fig. S1 in supplementary materials). The MPB-like
behaviour is related with the least energy barrier between the different phases, facilitating easy polarization rotation, similar to PZT system, where the tetragonal phases (P4mm+R3m) coexist over the composition range 0.451 < T(x) < 0.488, but the highest properties has been observed for \( T(x) = 0.485 \pm 0.059 \). These results suggest an MPB like behaviour for LNNx at \( x = 0.20 \), against widely reported MPB at \( x = 0.12 \).

**SUPPLEMENTARY MATERIAL**

See supplementary materials for the materials synthesis procedure, temperature-dependent X-ray diffraction analysis, and the variation of dielectric permittivity and loss with composition (x) for LNNx ceramics.

The data that supports the findings of this study are available within the article and its supplementary material.
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**Graph Description:**
- The graph shows the polarization ($\mu$C/cm$^2$) as a function of the electric field (kV/cm) for various compositions (x).
- The polarization values are indicated for different LNN compositions: LNN10, LNN12, LNN15, LNN20, LNN25, LNN30, and LNN40.
- The inset graph illustrates the composition (x) vs. $P_r$ ($\mu$C/cm$^2$) relationship.