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Structural and optical studies of manganese doped modified sodium potassium lithium niobate lead complex ceramic

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Abstract

We report the Structural and Optical properties of $(Na_{0.5}K_{0.5})_{0.934}Li_{0.066}NbO_3$ (NKLN934) and $(Na_{0.5}K_{0.5})_{0.936}Li_{0.064}NbO_3$ (NKLN936) ceramics obtained from Rietveld analysis of X-ray diffraction data and its effect on the band gap on doing with MnO_2 doping. Diffraction analysis reveals that the materials synthesized are tetragonal (space group; P4mm). Results predict that MnO_2 doping shows a uniform trend for both the systems: the band gap decreases with increase in MnO_2 doping. **PAC No:** 61.05, 78.20.Ci

Key words: XRD, Reitveld analysis, bandgap

Introduction

There are immense research interests in perovskite materials, because of their varied structure, compositional and physical structure. Owing to their significant to both the fundamental research and the high tegnological applications, perovkite have attracted intense research activities in many applied and fundamental areas of advanced material research. Today electronic ceramics play a pivotal role in any modern technological society that only two decades ago were inconceivable; applications ranging from ceramic engines to optical communications, electro-optic devices to laser materials, and substrates in electronic circuits to electrodes in electrochemical devices. In recent years, the complex Perovskite oxides have attracted the attention of material researchers with increasing interest in obtaining physical properties that are useful for technological applications $PbTiO_3$-$PbZrO_3$ (PZT) based materials have been employed in many piezoelectric applications for the last seven decades [1]. This is due to increasing needs of high-tech industries of new lead-free ferroelectric materials, which would reduce environmental contamination. ABO_3 type compounds have attracted attraction due to their relatively simpler structure. Sodium Niobate based solid solutions are interesting both from fundamental and practical view point. Pure $NaNbO_3$ has a perovskite structure and undergoes one of the most complicated sequences of phase transition as a function of temperature [2]. The Li doped Sodium Niobate system, with chemical formula (Li_xNa_{1-x}) NbO_3 (LNN) is of practical importance because of its low density (~ 4.5g/cm^3).

LNN also have high sound speed (> 5 Km/s), and wide range of curie temperatures, dielectric constants, and acceptable piezoelectric characteristic. Solid solution based on Potassium Sodium Niobate ($(K_xNa_{1-x})NbO_3$) are promising lead-free candidate for replacing the lead based piezoelectric ceramics. It is believed that in these ceramics exhibit remarkable properties close to the Morphotropic Phase Boundary (MPB).

Alkaline Niobate systems are, nowadays, considered as very promising candidates for technological applications. Compared to other Bi-based alkaline systems are preferable due to high leakage current. It has been experimentally found that the MPB is very different in the lead-based compounds in KNN-based ceramics because it shows strong temperature dependence [3], making them interesting candidate not only from the technological point view, but also as fundamental to the understanding of the inpact of doping (both A and B site), grain size, etc. on or around the MPB. .

From the technological point of view, in order to achieve the desired properties and sintering of these samples, additional hardening dopant is also explored, like Li, Ta, Zr, Mn, W based dopants have been used to obtain the optimal piezoelectric properties in these and PZT-based and other ceramics [13]. MnO_2 doping in $(Na_{0.5}K_{0.5})NbO_3$ (NKN) has led to enhanced piezoelectric and electromechanical properties. These results are appreciable and comparable to the PZT ceramics [4-7].

It has earlier been reported that Alkaline Niobate systems, Li-doped NKN ceramics show relatively high curie temperatures (T_c) and good electrical properties with a T_c of 463 ^{o} C and is believed to lie close to MPB [8]. we have further studied the

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MnO_2 doped in NKLN935 composition and have reported the corresponding X-ray diffraction (XRD) patterns with peak-indexing as well as various electrical properties [9]. It was found that MnO_2 could be a useful dopant in NKLN systems for power applications, as it leads to harder ceramics with lower relative permeability and loss values, higher quality factors and electromechanical coupling factors. Recently we have carried we have also carried systematic studies on its structure, electrical and optical properties [10]. Therefore, in this article we concentrate on two neighboring compositions, $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936). We will explore the structural and optical properties of these compositions at y= 0.934 and 0.936, *i.e*, $(Na_{0.5}K_{0.5})_{0.934}Li_{0.066}NbO_3$ (NKLN934) and $(Na_{0.5}K_{0.5})_{0.936}Li_{0.064}NbO_3$ (NKLN936). In particular, we have carried out a detailed analysis of the structural properties through Reitveld analysis of X-Ray Diffraction (XRD) patterns.

The optical properties of these compositions, measurements of diffuse reflectance spectroscopy (DRS) of a powdered sample with a UV-Visible (UV-Vis) spectrophotometer. It is used for the determination of the absorption properties and optical band gap [11, 12]. We have performed the UV-Vis spectroscopy and experimentally determined the optical band gaps for these compositions along with the effect of MnO_2 doping on the band gap using the Kubelka-Munk Function.

1. Experimental Details

In analogy to our previous work [10], the polycrystalline samples of $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) were prepared by solid-state reaction method. The starting materials were high purity (99.9%) powders of KCO_3, KCO_3 (99%), Nb_2O_5(99.9%) and $LiCO_3$ (99.99%), MnO_2 (99.99%). All these materials were dried at 150°C, dried in air, and then calcined at 900°C for 5 hours. After the calcination, the calcined powder was crushed and the calcined powder was then mixed with a small amount of manganese oxide (MnO_2), represented by the formula (1-x) $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) + x MnO_2 (x = 0.01, 0.015, 0.02). The MnO_2 added to $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) were mixed for another10 hours to homogeneously distribute the dopant. The dried powder was compacted into disks in a die plunger having tungsten carbide tips. We put it in the furnace and these pellets were sintered at 1050^0 C for $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936). Sintering was carried in the temperature range of 1050 -1070 ^{0}C for the MnO_2 doped in $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) in the programmable high temperature oven.

The crystal structure details of the samples using the X-ray diffraction (XRD; D-8 Advance Brokers). Diffuse reflectance measurements of the powder samples were done with Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer equipped with a 150 mm integrating sphere. The spectra were measured in the wavelength range 200-2500 nm.

Rietveld refinement details

Rietveld refinement of these compositions was carried out using the XRD data with a Rietveld refinement program FULLPROF [13]. The background was fitted with 6-Cofficient polynomial function, while the peak shapes were described by pseudo-Voigt profiles. In all the refinements, scale factor, lattice parameters, positional coordinates (*x, y, and z*) and thermal parameters were varied. Occupancy parameters of all the ions were kept fixed during refinement. No correlation between the positional and thermal parameters was observed during refinement and as such it was possible to refine all the parameters together.

2. Results and discussion

The powder of $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) compositions were prepared by calcining the stoichiometric amounts of various constituents at 900^0C. These powders were sintered at 1050 -1070 ^{0}C to obtain the ceramic pellets of good quality and high densities. All the reflection peaks of the X-ray profile were indexed. Figs. 1 & 2 show the X-ray diffraction (XRD) patterns of the present compositions and all the reflection peaks of the X-ray profile are indexed. The structure is tetragonal (space group P4mm) for both the compositions NKLN934 & NKLN936. The K^{1+}/Na^{1+} ions occupy 1 (a) sites at (0, 0, z), L^{1+} /$Nb^{5+}$and O_I^{2-} occupy 1 (b) sites at (1/2, 1/2, z), and O_{II}^{2-} occupy 2(c) sites at (1/2, 0, z). For the refinement, the initial values of the lattice parameters were obtained from our XRD data by least squares method. In this structure, K^{1+}/Na^{1+} coordinates were fixed at (0, 0, and 0) in our refinement. Fig. [1 & 2] depicts the observed, calculated and difference profiles for the refined structure after removing the peaks corresponding to the Cu-kα_2 wavelength. The fit is found to be quite good. The refined structural parameters and the positional coordinates of these compositions for NKLN934 & NKLN936 are given in Table 1 & 2.

Table caption:

Table 1.
Refined structural parameters of NKLN 934 using tetragonal (space group; P4mm) model.

Ions	Positional coordinates x	y	z	thermal parameters B(Å^2)
Na^{1+} / K^{1+}	0.00	0.00	0.00	0.0717(5)
Li^{1+} / Nb^{5+} /	0.50	0.50	0.5453(5)	0.0382(3)
O_I^{2-}	0.00	0.50	0.477(5)	0.0418(1)
O_{II}^{2-}	0.50	0.50	0.087(2)	0.0022(1)

a = b = 3.9622(4)Å, c = 4.074(5) Å, R_P = 6.63, R_{wp} = 8.89, R_{exp} = 5.43, R_B = 7.90, R_f = 8.94, Vol. = 62.911(1) and χ^2 = 2.68

Table 2.
Refined structural parameters of NKLN 936 using tetragonal (space group; P4mm) model.

Ions	Positional coordinates x	y	z	thermal parameters B(Å^2)
Na^{1+} / K^{1+}	0.00	0.00	0.00	0.31(2)
Li^{1+} / Nb^{5+} /	0.50	0.50	0.51897(1)	0.042(3)
O_I^{2-}	0.00	0.50	0.46(1)	0.7595(1)
O_{II}^{2-}	0.50	0.50	0.08733(1)	0.145(5)

a = b = 3.961196(2)Å, c = 4.09995(2) Å, R_P = 11.7, R_{wp} = 14.7, R_{exp} = 5.95, R_B = 5.43, R_f = 3.24, Vol. = 62.921(1) and χ^2 = 6.09

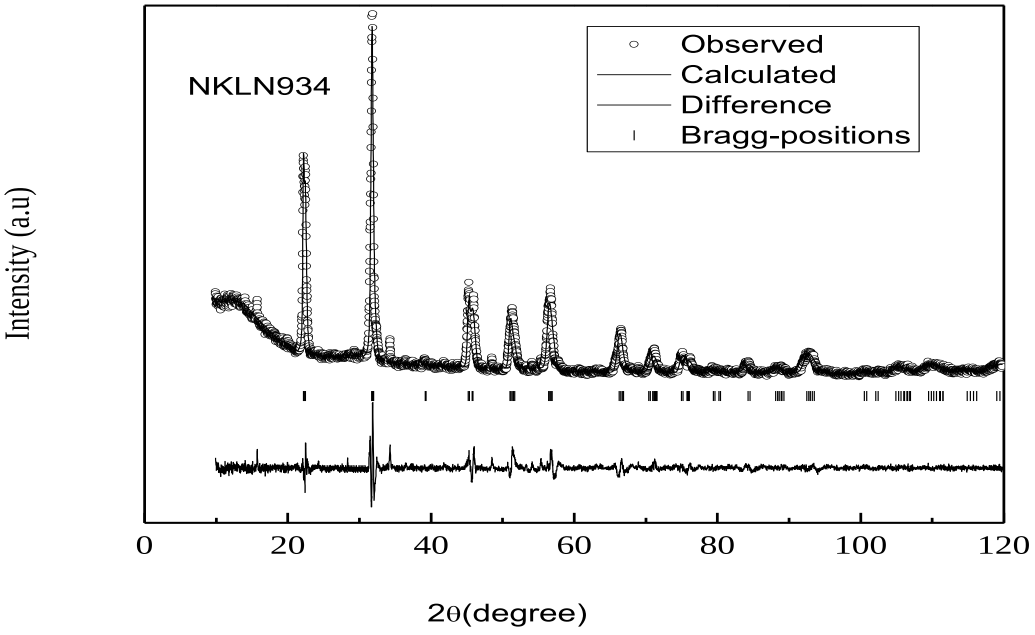


Fig.1 Observed (circle), Calculated (continuous lines), and difference (bottom of the figure) profiles in the 2θ range 20-120 degree for the given composition for the NKLN934.

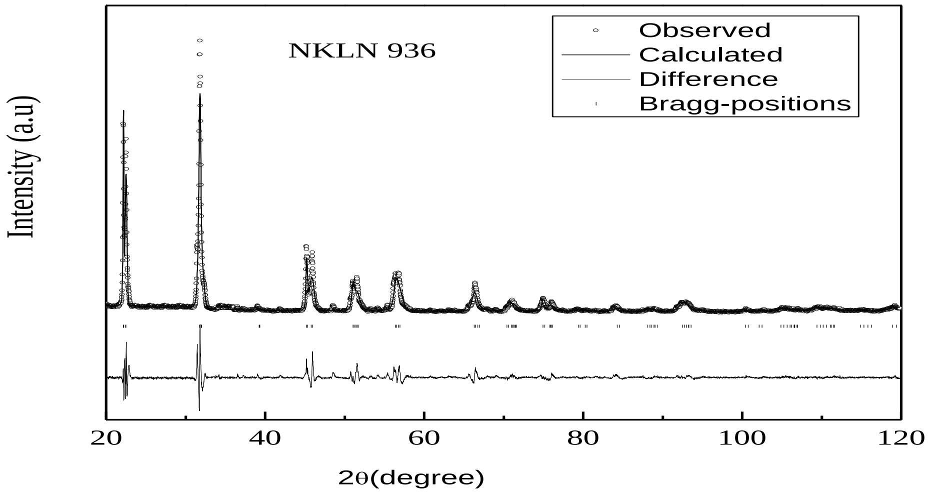


Fig.2: Observed (circle), Calculated (continuous lines), and difference (bottom of the figure) profiles in the 2θ range 20-120 degree for the given composition for the NKLN936.

To analyze the structure of these compositions $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936), we have concentrated on the 200, 220, 222 pseudo-cubic X- ray diffraction profiles. It is known that, around the MPB composition, the structure is either rhombohedral, or tetragonal, or there is a coexistence of these two phases. In our case, we expect that the structure of $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) compositions may be one of the above. For the rhombohedral structure, the 200 reflection appears as a singlet where as 220 and 222 appears as doublet with weaker reflection on the lower 2θ side. For the rhombohedral structure, the 200 reflection peak appears as a singlet, where as the 220 and the 222 peaks appear as doublet with weaker reflection on the lower 2θ side. For a tetragonal structure, while the 200-peak is a doublet with weaker reflection on the lower 2θ side, the 220 peak is also a doublet with weaker reflection on the higher 2θ side whereas the 222 peak is a singlet. For a monoclinic structure, all the three reflection peaks *viz.* the 200, 220, and 222 peaks show splitting [13]. For the present composition, we analyze this set of peak profiles. We find that the 200 peak is a doublet with weaker reflection on the lower 2θ side, the 220 peak is also a doublet with weaker reflection on the higher 2θ side, and the 222 peak is a singlet. Hence, it is evident that the structure of this composition is tetragonal, the space group being P4mm, as obtained from the Rietveld refinement.

Furthermore, we also find that the NKLN936 has more tetragonal distortion that the NKLN934 composition, as indicated by the corresponding *c/a* ratio. In the tetragonal distortion, the unit cell gets elongated along one direction, which leads to change in hybridization between the participating B-site cation and O atoms. This further leads to change in electronic and optical properties of the compound. The values of the *c/a* ratio for these compositions are found to be 1.028 and 1.035 for the NKLN934 and NKLN936 compositions, respectively. These changes are clearly exhibited in the optical band gap of these samples.

The Optical band gaps of $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) and also the MnO_2 doped (at x = 0.01, 0.015, 0.02) samples were determined by the diffuse reflectance spectroscopy (DRS). The result, thus obtained, reflectivity spectra can be converted to an equivalent absorption spectra using the Kubelka-Munk (KM) function [15]. The KM function at any wavelength is given as:

$$F(R_\infty)=\frac{(1-R_\infty)^2}{2R_\infty}=\frac{\alpha}{s} \quad .$$

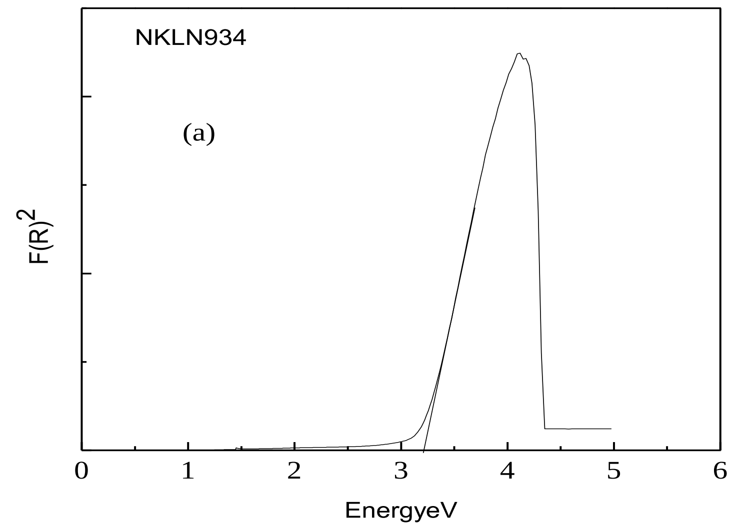
……………… (1)

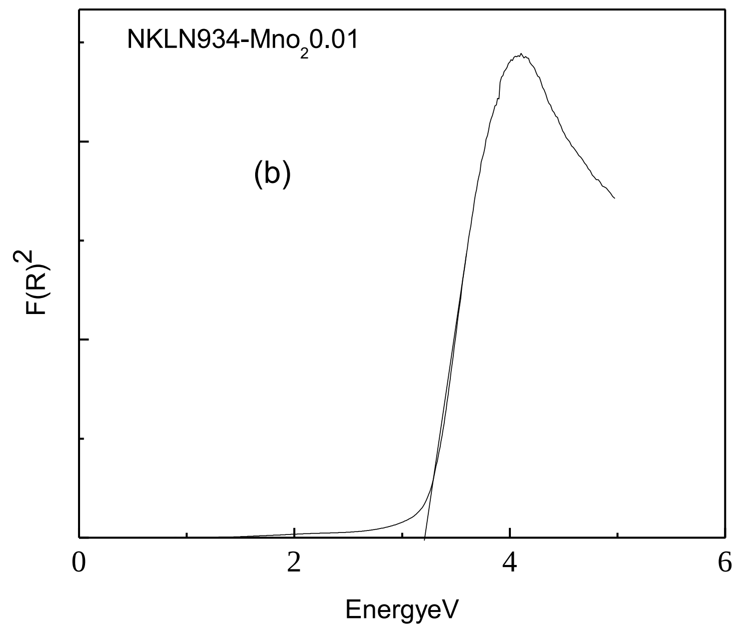
Here, $F(R_\infty)$ is the remission or Kubelka-Munk function, R_∞ is the reflectance of the sample relative to the reference material ($(R_\infty = R_{sample}/R_{splectron})$, α is the absorption coefficient and s in the scattering coefficient. Here $F(R_\infty)$ is be assumed to be proportional to the absorption spectrum [16]. The energy dependence of the adsorption coefficient near the absorption edge can be expressed as

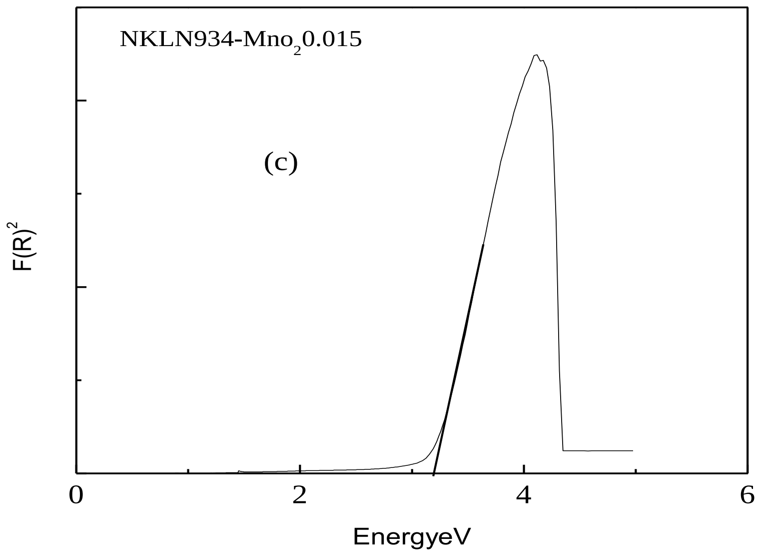
$$\alpha \propto \frac{(h\nu - E_g)^n}{h\nu},$$

………… (2)

As suggested by Davis and Mott [16]. Here $h\nu$ is the photon energy and E_g is the energy of the optical transition corresponding to the optical band gap. Value of the exponent *n* depends on the nature of the optical transition and takes the value ½, 2, 3/2, or 3 for direct-allowed, indirect-allowed, direct- forbidden or indirect forbidden transitions, respectively. With an appropriate value of *n*, the plot of $(\alpha h\nu)^{1/n}$ vs hυ is linear near the absorption edge and the value of the optical band gap can be determined from the slope of the linear part or alternatively by directly plotting the appropriate power of the Kubelka-Munk, $[F(R_\infty)]^n$ as a function of the energy/frequency of incident photons, where *n* taked the values as above [10,17, 18]. We have used the second method to obtain the band gap for above compositions. The optical band gap values for the samples $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) and MnO_2 doped (at x = 0.01, 0.015, 0.02) for n=2 is given in the Table 3 & 4. Figs. 3 and 4, respectively, show the behavior of $[F(R_\infty)h\nu]^2$ with increasing energy of the incident photon. $h\nu$. We have plotted the corresponding functions for all the above values of *n* (not shown). However, the best fit was found to be for the value of *n=2*. This implies that both the above compositions have direct band gaps. Due to insulating behavior of these compositions, the values of the plotted function is zero in the low energy limit and has linearly increasing non-zero values for energy values greater than a threshold energy of the incident photon. As mentioned above, the value of the optical band gap is obtained from intercept of low energy linear behavior of this function, as also shown in the corresponding figures.




NKLN934-Mno$_2$0.01
(b)
F(R)^2
0
2
4
6
EnergyeV


NKLN934-Mno$_2$0.015
(c)
F(R)^2
0
2
4
6
EnergyeV

..

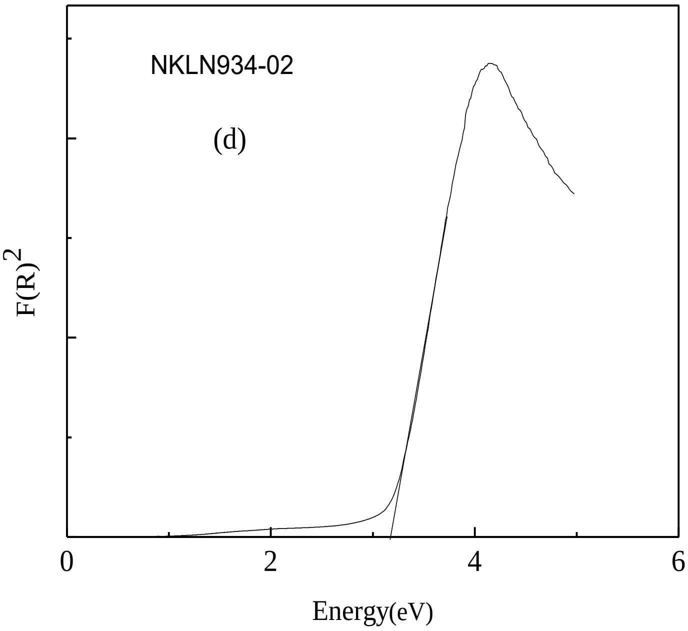
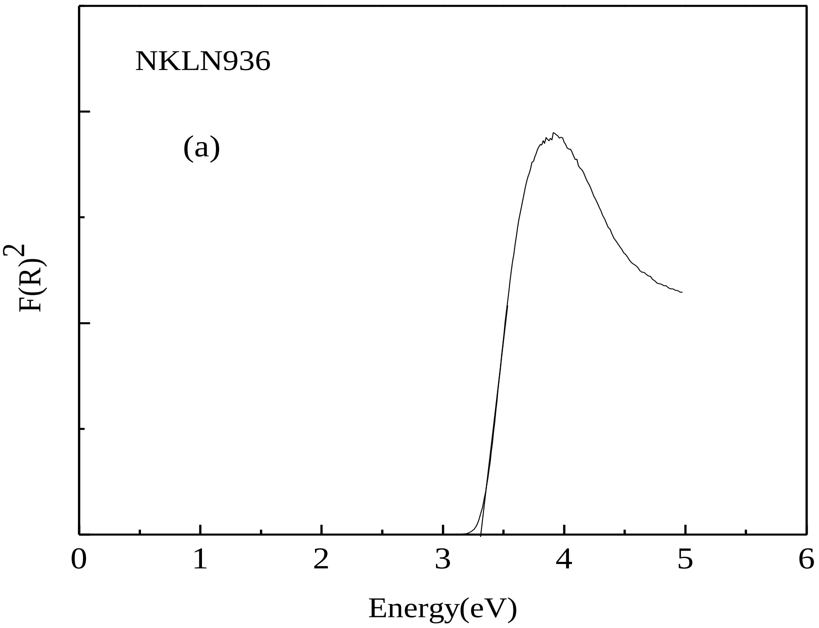
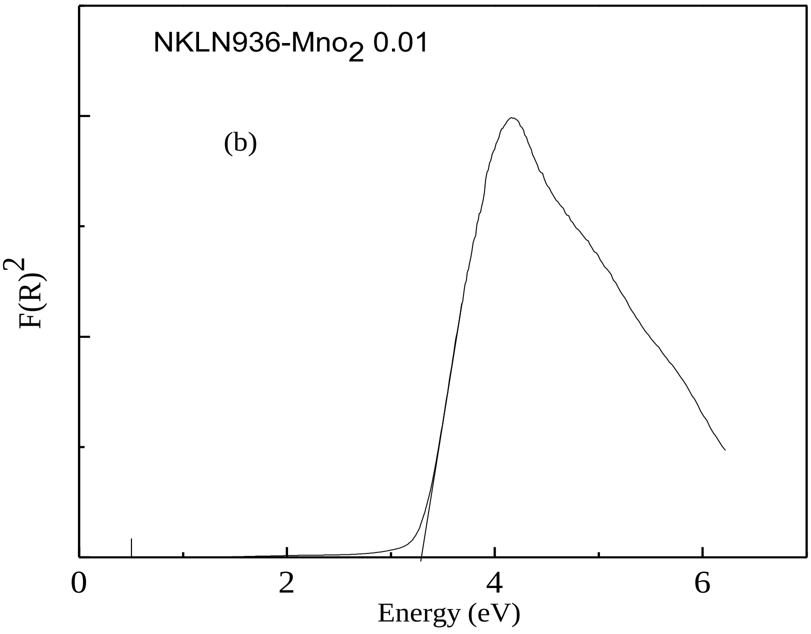
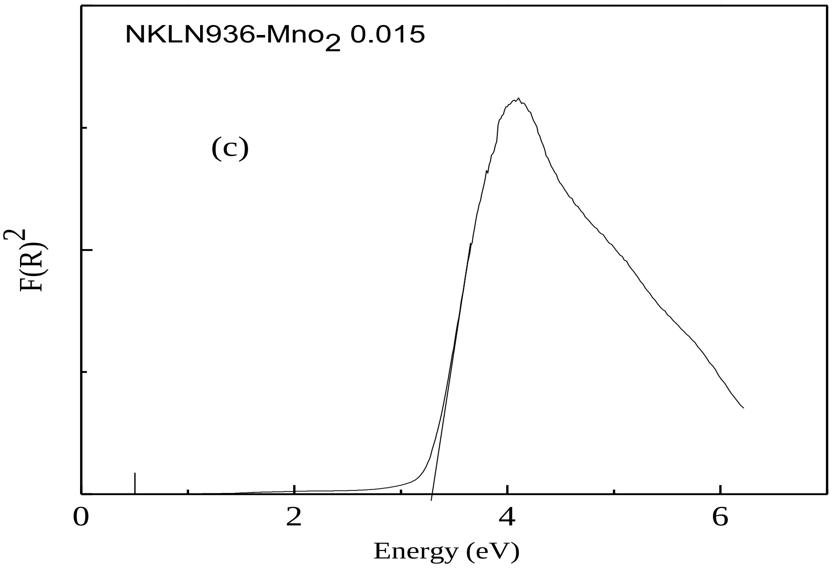


Fig.3: Kubelka -Munk transformed reflectance spectra of function; (a) NKLN934, (b) NKLN 934-MnO$_2$-0.01 , (c) NKLN 934-MnO$_2$ -0.015, (d) NKLN 934-MnO$_2$- 0.02




NKLN936-Mno$_2$ 0.01
(b)
F(R)^2
0
2
4
6
Energy (eV)


NKLN936-Mno$_2$ 0.015
(c)
F(R)^2
0
2
4
6
Energy (eV)

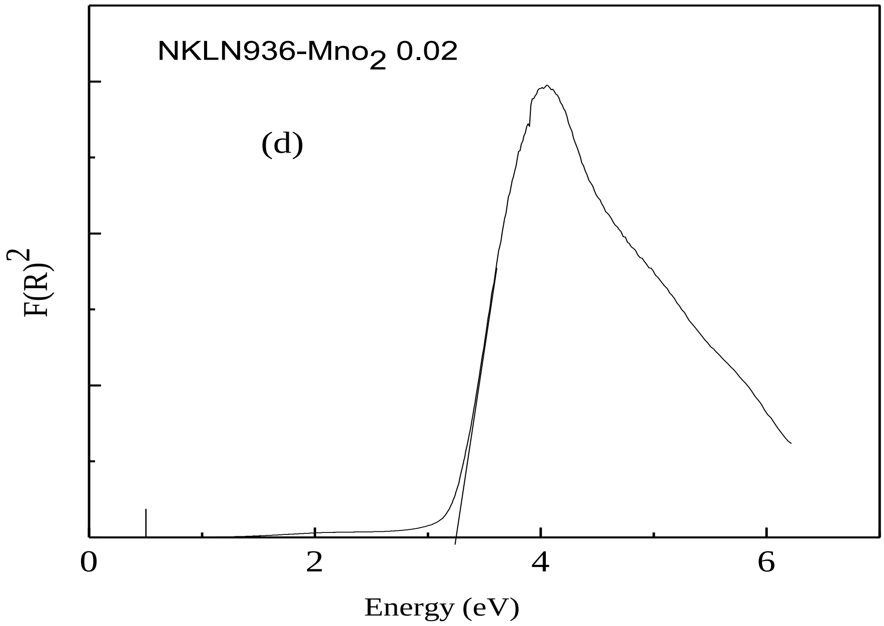


Fig.4: Kubelka -Munk transformed reflectance spectra of function; (a) NKLN934, (b) NKLN 934-MnO_2- 0.01 , (c) NKLN 934-MnO_2 -0.015, (d) NKLN 934-MnO_2 -0.02

A comparison of the intercept for pure NKLN934 (Fig. 3a) and NKLN936 (Fig. 4a) show that with increasing Li doping, the band gap increases. The corresponding values of the band gap are 3.22eV and 3.32eV, respectively. This is primarily due to increase in tetragonality of these compositions with increase in Li doping, as mentioned above. This increase in tetragonality leads to larger overlap and, therefore, stronger hybridization of Nb-*d* and O-*p* orbitals. The distribution of the O-*p* orbitals is not isotropic around the Nb atom. There is stronger hybridization between the Nb-dz^2 orbital and the pz orbital of the O1 atoms located at (0, 0, z). Similarly, there is also stronger hybridization between the planar *d* orbital and the planar O-*p* orbital, *px* and *py*.

Interestingly, with MnO_2 doping, the band gaps for both NKLN934 and NKLN936 compositions show uniform trend. Tables 3 & 4, respectively, show the values of the band gap of these compositions, as obtained from the intercepts in Figs. 3 and 4 (Panels (b)-(d)). It is interesting to note that the band gap decreases with increasing concentrations of MnO_2. It is usually considered that the Mn ions occupy the B-site. However, it is not clear whether this substitution for Nb5+ would lead to A-site cation vacancies or Oxygen vacancies to be produced. This situation if further compounded by multiple valence states and large difference in the ionic radii of the Mn and Nb ions. Mn ions are present in both +2 and +4 state, which have the ionic radii of 0.67nm and 0.54 nm. The ionic radius of the Nb^{5+} ion, on the other hand, is 064nm. This difference in valiancy and ionic radii will leads to distortion of the O octahedral surrounding the Nb and Mn ions, eventually leading to different hybridization between the O and B-site ions. For the NKLN935 composition, it has been argued that MnO_2 doping leads to formation of oxygen vacancies. As can be observed from the band gap values, the effective tetragonality of the pure NKLN934 and KNLN936 composition seems to decrease with increase in MnO_2 doping, and is likely to be due to increase in hybridization between the B-site ion and the *pz* orbital of the O1 atoms.

This increase in band gap values is also indicative of enhanced piezoelectric properties of these compositions. Therefore, it is expected that, similar to the NKLN935 [9,10], MnO_2 doping may lead to decrease in dielectric constant, loss tangent and piezoelectric constant d_{33}, an increase in the mechanical quality factor Q_m. Therefore, it is certainly of interest to explore these compositions further, in particular, the dielectric and piezoelectric parameters. Furthermore, other similar compositions should also be explored to locate the MPB as they seem to be excellent and very promising materials for piezoelectric transformer applications [13].

Table 3.

Sample Name	Direct Band gap (eV)
NKLN 934 [Fig. 3(a)]	3.22
NKLN 934-MnO_2 0.01 [Fig.3(b)]	3.21
NKLN 934-$MnO_2$0.015 [Fig. 3 (c)]	3.20
NKLN 934-$MnO_2$0.02 [Fig. 3(d)]	3.18

Table 4:

Sample Name	Direct Band gap (eV)
NKLN 936 [Fig. 4(a)]	3.32
NKLN 936-MnO_2 0.01 [Fig. 4(b)]	3.30
NKLN 936-MnO_2 0.015 [Fig. 4(c)]	3.28
NKLN 936-MnO_2 0.02 [Fig. 4(d)]	3.26

5 Conclusions

In conclusion, we have studied the structural and optical properties of the $(Na_{0.5}K_{0.5})_yLi_{1-y}NbO_3$ (y= 0.934 & 0.936) ceramics (respectively called NKLN934 and NKLN936) and found that both these compositions are tetragonal, similar to the previously studied $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ (NKLN935). The effect of tetragonality, as obtained from the *c/a* ratio, shows that tetragonality increases with Li doping. This further leads to an increase in optical band gap values in these values. Detailed exploration of the optical properties, in terms of the UV-Vis spectrum and Kubelka-Munk function, reveal that the values of the optical band gap is, respectively, 3.22 eV and 3.32 eV, as expected from the relative change in hybridization between the B-site cation and O-p orbital. Furthermore, the MnO_2 doping shows a uniform trend for both the systems: the band gap decreases with increase in MnO_2 doping. This is clearly indicative of the promise of enhanced piezoelectric properties of theses compositions, as required for technological applications like piezoelectric transformers.

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