Evaluation of structure, dielectric and electrical properties of (Li/Ta/Sb) modified (Na, K) NbO₃ lead-free ceramics with excess Na concentration

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Polycrystalline perovskite structured (Li_{0.04} (Na_{0.54+x} K_{0.46})_{0.96} (Nb_{0.81} Ta_{0.15} Sb_{0.04}) O₃ ceramics with $x = 0.00, 0.005$ and 0.01 mole excess Na concentration were prepared by solid state sintering method. The present study relates the role of excess Na addition with the stoichiometry, density, structure, dielectric and ferroelectric properties of the samples. X-ray diffraction (XRD) pattern exhibits single phase orthorhombic structure. The characteristic Raman modes were observed due to translational modes of cations and vibrational modes of NbO₆ octahedra and no structural phase transition were observed. This confirms the formation of single phase perovskite structure and is consistent with XRD results. The dielectric permittivity increases about two times, while dielectric loss decreases by four times for $x = 0.01$ composition. The electrical measurements carried by Complex Impedance spectroscopic analysis suggest negative temperature coefficient of resistance (NTCR) behavior.

Keywords: Perovskite; dielectric properties; negative temperature coefficient of resistance (NTCR); ferroelectric properties; leakage current.

1. Introduction

Recent environmental concerns and legislation imposed on lead-based materials were limiting their use and it was an urge among the researchers to look for feasible alternative replacement of lead-based materials.¹ Among the available lead-free materials, (Na_{1-x}K_x) NbO₃ (KNN) has been widely studied due to excellent electromechanical coupling, high Curie temperature and piezoelectric properties.² In 2004, Saito *et al.*³ studied the textured (K, Na) NbO₃-LiTaO₃-LiSbO₃ system by reactive templated grain growth (RTGG) method and were successful in achieving excellent piezoelectric coefficient value ($d_{33} \sim 416$ pC/N). It is believed that this high piezoelectric property could be achieved because of the morphotropic phase boundary (MPB) among rhombohedral, tetragonal or monoclinic phases.^{4,5} Any modification in this phase boundary proves to be powerful technique for promotion of improved piezoelectric and dielectric properties.⁶ This thermodynamic equivalent phase permits almost continuous rotation of polarization under external vector fields which enhances the dielectric, piezoelectric and electromechanical properties.^{7,8} Polymorphic phase boundary (PPB) particularly in KNN system has achieved considerable interest because of the enhanced properties achieved in this region,¹ and this enhancement in PPB region can be attributed to intrinsic and extrinsic contribution as (a) polarization rotation and polarization extension due to electric field-induced phase transformation are associated to linear distortion in lattice with significant modification in

polarization of the unit cell, (b) other responses not included in intrinsic contribution can be stated as the extrinsic contribution.⁹ Ochoa *et al.*¹⁰ showed that extrinsic (domain wall) contribution along with intrinsic contribution influences the PPB significantly and enhances the functional properties.

Although a large number of significant publications and extensive research on bulk densification and reproducible electrical properties in KNN¹¹-based system has been carried over the past few decades, its utilization for commercial purpose has been restricted due to difficulty in processing of the bulk.¹² Non-stoichiometry and poor density occurring due to loss of alkali species at elevated temperatures during solid state sintering process,¹³ result in poor performance of the KNN system.¹⁴ To overcome these problems, different processing methods have been adopted to achieve high density ceramics, such as sol-gel¹⁵ microwave sintering,¹⁶ hot-pressed sintering,¹⁷ spark plasma sintering,¹⁸ molten salt method¹⁹ and cold isostatic sintering,²⁰ etc. But these methods are too expensive and are not appropriate for large-scale industrial applications. To avoid these difficulties, different doping elements as sintering aids, such as CuO,²¹ MgO,²² HfO₂²³ and CaZrO₃,²⁴ etc. have been used in KNN ceramics for achieving densified ceramics with enhanced physical properties. Li substitution at A-site and Ta and/or Sb at B-site induces changes in the lattice parameters and ameliorate the phase transitions. Furthermore, addition of Li/Ta/Sb improves the stability, piezoelectric properties and

modifies the Curie (T_c) temperature in KNN system. Ever since then, Li/Ta/Sb-modified KNN system has been extensively studied.

Apart from these methods, addition of excess of alkali species (Na/K) at A/B site in KNN system has been found to be effective in suppressing the loss of alkali species at elevated temperatures, improves the density and the properties²⁵ as well as it is cost-effective. K^+ substitution prevents the formation of metastable states and stabilizes the ferroelectric phase, while Na^+ addition lowers the orthorhombic to rhombohedral transition temperature to lower temperature side without altering the other higher transitions in KNN system.²⁶

Progress made in the line of research is elaborated with more extensive research on (Li/Ta/Sb)-modified (Na, K) NbO_3 system making it more viable lead-free system known to date. In order to achieve enhanced ferroelectric properties and better device performance, it is required to understand the phenomenon related directly to the structure at the scale of unit single cell. Keeping in view, the above mentioned details, we report in this work (Li, Na, K) (Nb, Ta, Sb) O_3 ceramics with 0%, 5% and 10% excess Na in the starting precursor and investigated the effect of additional excess alkali species on density, structure, dielectric and ferroelectric properties.

2. Experimental Details

In this experiment (Li/Ta/Sb)-modified (Na, K) NbO_3 ceramics have been prepared with excess of Na according to the chemical formula $(Li_{0.04}(Na_{0.54+x}K_{0.46})_{0.96}(Nb_{0.81}Ta_{0.15}Sb_{0.04})O_3$ with $x = 0.00, 0.005$ and 0.01 , hereby designated as KNNLST. Analytical grade reagents Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Sb_2O_3 , Nb_2O_5 and Ta_2O_5 with more than 99% purity from Sigma-Aldrich were used as starting materials. The starting precursors were weighed according to the stoichiometric calculations. The powders of the ingredients were mixed with 2-propanol and ball milled for 72 h with zirconia balls as the milling media. The powders so obtained were dried overnight and then calcined at $1020^\circ C$ for 12 h. The powder thus obtained was compressed into cylindrical pellets of ~ 1 mm thickness and 15 mm diameter using Polyvinyl alcohol (PVA) (10% mol. wt.) as the binder. These pellets were sintered in air at $1080^\circ C$ for 2.30 h. For electrical measurements, the sintered pellets were silver fired on both sides and heated at $500^\circ C$ for 30 min.

X-ray diffractometer (Bruker D2 Phaser) with $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) was utilized to identify the crystal structure. Room temperature Raman scattering spectroscopy was performed using excited Ar^+ radiation 488 nm operating at 25 mW (Micro-Raman spectrometer from Jobin Yvon Horibra LABRAM-HR) and spectrum was recorded in a range of 150 cm^{-1} to 1000 cm^{-1} . Scanning electron microscopy (SEM) was performed in SE mode by Zeiss

instrument. Polarization–Electric field hysteresis measurements were made on Radiant Technologies, USA at room temperature and at 10 Hz. Dielectric constant, loss tangent and impedance parameters of the samples were measured using a PSM1735 Impedance Analyzer in a frequency range of 100 Hz to 1 MHz from room temperature to $500^\circ C$ with the samples being heated in a Carbolite (MTF9/15/130) tube furnace. The density was measured by Archimedes Principle using Mettler Toledo instrument.

3. Results and Discussions

Figure 1 shows the room temperature X-ray diffraction (XRD) pattern of KNNLST ceramics. The absence of any secondary tetragonal tungsten bronze (TTB) structure confirms the formation of single phase perovskite structure, since TTB is a common secondary phase in KNN-based system arising due to the volatilization of alkali species. All the samples exhibit orthorhombic symmetry. Narrow and sharp peaks were observed in the XRD results which indicate good crystallization and homogeneity of the samples. Least square refinement method was employed for the determination of the lattice parameters and the indexing of the reflection peaks were done by using inter-planer spacing d . No significant changes were observed in the lattice parameters with respect to excess Na.

Raman Scattering Spectra were recorded at room temperature to further analyze the KNNLST ceramics with $x = 0.00, 0.005$ and 0.01 . For KNN system $4A_1 + 4B_1 + 3B_2 + A_2$, Raman active optical phonon modes are observed out of which A_2 is IR mode as predicted by theoretical calculations and previous works.²⁷ Modes in lower wavenumber $< 170 \text{ cm}^{-1}$ were assigned to the translational modes arising due to Na^+/K^+ cations and vibrational modes of the NbO_6 octahedral units. The vibrational modes $1A_{1g}(V_1)$, $1E_g(V_2)$,

Fig. 1. Room temperature XRD patterns of KNNLST (where $x = 0.00, 0.005, 0.01$) ceramics.

$2F_{1u}(V_3, V_4)$, $F_{2g}(V_5)$ and $F_{2u}(V_6)$ along with $F_{1g} \times F_{2g} = F_{2g}(V_1 + V_5)$ observed in the range of $170\text{--}900\text{ cm}^{-1}$ were assigned as the main unit of perovskite for $(\text{Na}, \text{K})\text{NbO}_3$.²⁸ In the present study, similar behavior was observed for all the compositions. Raman spectra were fitted with the sum of Lorentzian peak fitting as shown in Figs. 2(a)–2(c). The triply degenerated symmetric O–Nb–O mode observed at 250 cm^{-1} is attributed to $F_{2g}(V_5)$, which is relatively strong because of nearly perfect octahedral symmetry. At 613 cm^{-1} , $1A_{1g}(V_1)$ mode represents the double degenerate symmetric O–Nb–O stretching vibrations.²⁹ Raman modes observed at wavenumber 863 cm^{-1} are assigned as the irreducible coupling mode of $F_{2g}(V_1 + V_5)$. Another vibrational mode was observed at 572 cm^{-1} $1E_g(V_2)$.³⁰ These results are in good agreement with XRD results.

Figures 3(a)–3(c) show the SEM micrographs of the fractured samples of KNNLST with $x = 0.00, 0.005$ and 0.01 in SE mode. All the samples exhibit the typical morphology of alkaline niobate ceramics. The ceramics show a bimodal microstructure with cube shape distribution of grain size.

Fig. 2. Room temperature (300 K) Lorentzian Fitted Raman spectra of KNNLST (where $x = 0.00, 0.005, 0.01$) as a function of wavenumber.

(a)

(b)

(c)

Fig. 3. (a)–(c) SEM (SE Mode) of KNNLST (where $x = 0.00, 0.005, 0.01$) ceramics.

Fig. 4. (a) Variation of real part of dielectric constant (ϵ') of KNNLST (where $x = 0.00, 0.005, 0.01$) with temperature at frequency 10 kHz. (b) Variation of dielectric loss ($\tan \delta$) of KNNLST (where $x = 0.00, 0.005, 0.01$) temperature at frequency 10 kHz.

The ceramics with $x = 0.01$ composition show denser microstructure than for $x = 0.00$ and 0.005 . This is because the smaller grains fill up the gaps among the larger ones for $x = 0.01$, while this process does not occur for $x = 0.00$ and $x = 0.005$ samples, giving rise to poorer microstructure with gaps. This can be corroborated by the fact that physical density of ceramics increases with increase in Na concentration. The average grain size of the samples ranges from 250 nm to 400 nm for all the compositions. The density calculated was found to be $> 95\%$ of theoretical value for $x = 0.01$ sample, while it remained up to 90% for samples with 0.005 and 0.00 compositions. It can be inferred from the above observation that adding excess mole concentration of alkali species densifies the KNNLTS system and effectively compensates the loss of alkali species.

Figures 4(a) and 4(b) show the temperature-dependent variation of dielectric permittivity and dielectric loss of KNNLTS ceramics at 1 KHz. The real part of the dielectric permittivity curves for all the samples exhibits ferroelectric phase transition from orthorhombic to tetragonal structure at about 173°C while the ferroelectric–paraelectric phase transition from tetragonal to cubic structure is at about 332°C for $x = 0.00$ to 347°C for $x = 0.010$ sample. The value of the dielectric constant increases twice for $x = 0.00$ to $x = 0.010$ composition. The maximum value of the dielectric permittivity ($\epsilon'_{\max}$) at 10 KHz is ~ 7023 . Transition temperature shifts by 20°C towards the higher temperature side. The dielectric loss reduced by four times for samples $x = 0.010$ and this may be attributed to the compensation of alkali (Na) loss in KNNLST ceramics.

The variation of dielectric constant with frequency at room temperature is shown in Fig. 5 for KNNLST with $x = 0.00, 0.005, 0.01$ compositions. With increasing frequency, the dielectric constant decreases exhibiting dipole relaxation at low frequencies. Dielectric values obtained at

Fig. 5. Show the room temperature dielectric permittivity (ϵ') of KNNLST (where $x = 0.00, 0.005, 0.01$) at different frequencies.

higher frequencies remain constant, while at lower frequency, the dielectric values decrease rapidly exhibiting dispersion phenomenon. The nature of graph suggests that the addition of Na favors the enhancement of dielectric properties of KNNLST samples. These variations can be explained on the phenomenological theory model proposed by Koop³¹ and Space charge polarization model given by Maxwell and Wagner.³² Dielectrics are supposed to be formed from poor conducting grain boundaries which are very effective at low frequencies and highly conducting grains which are dominant at higher frequencies. This particular trend may arise due to the hopping of electrons at the octahedral sites. When an electric field is applied, electrons hop and follow the field from these conducting grains towards the poorly conducting grain boundaries. At the proximity of the boundary, large resistance is offered, and electrons unable to pass through these boundary assemblies and large space charge polarization

is obtained, hence resulting in larger dielectric constant at the boundary. With further increase in the frequency, the direction of flow is precluded inside the dielectric medium, accumulation of charges occurs now at the grain boundaries and as a result, there is an overall decrease in the dielectric constant value at higher frequencies.³³

To further explore the ferroelectric behavior of the samples, polarization–electric field hysteresis measurements were carried out for different compositions at 10 Hz and at room temperature as shown in Fig. 6. With the applied electric field, the ferroelectric domains favorably orient themselves along the field whereas the domain wall motion occurs along less favorably oriented domain. The nature of the curve changes with increase in Na content. The maximum remnant polarization $P_r \sim 7.8 \mu\text{C}/\text{cm}^2$ at an applied electric field of 27.5 kV/cm is observed for $x = 0.01$ composition. With increasing Na content, the oxygen vacancies are compensated leading to the decrease in defect dipoles and enhance the ferroelectric properties.

Further investigation of the intrinsic contribution of defects and oxygen vacancies arising due to the volatilization of alkali species was carried out by leakage current measurements at room temperature and at 10 Hz for all the samples. Figure 7 shows the variation of current density with applied electric field and the curves are found to be symmetrical in nature with low leakage current values. Leakage current decreases with increase in Na content and also it is seen that the value of leakage current of all the samples remains low at an applied field of 10 kV/cm. Domain wall and grain boundary are considered as the primary reasons for the leakage current mechanism in the samples.³⁴ With increasing Na concentration, the dense morphology and good crystallization are obtained which not only decrease the grain boundary proportions, but also reduce the leakage current

Fig. 6. Room temperature polarization–electric field hysteresis loop measured at 10 Hz of KNNLST (where $x = 0.00, 0.005, 0.01$) ceramics.

Fig. 7. Leakage current characteristics of KNNLST (where $x = 0.00, 0.005, 0.01$) at 10 Hz.

density and enhance the ferroelectric property. This enhancement can also be attributed due to the reduction in defects such as oxygen vacancies created due to volatilization of alkali species.

Figure 8 exhibits the variation of real part (Z') of impedance with frequency at different temperatures. Initially, the real value of impedance Z' decreases with frequency at all temperatures, which is due to slow dynamic relaxation process as a result of space charge in the material. At temperatures $> 300^\circ\text{C}$, a low frequency plateau region is seen. This may be due to dc conductivity property of the material. At higher frequencies $> 10 \text{ kHz}$, all the curves merged, which may be attributed to the release of space charge,³⁵ as a result of lowering the barrier properties of the materials at high temperatures in the high frequency region. Negative Temperature Coefficient of Resistance (NTCR) behavior is exhibited by samples because of the decreasing trend of Z' with increasing temperature. It was observed that the real part of the impedance Z' increased first with the temperature in the low frequency region followed by relative decrease in it at higher temperatures. This may be due to the change in the charge ordering behavior with temperature and this effect is prominently exhibited in the low frequency region.³⁶

Figure 9 exhibits the variation of (Z'') imaginary part of impedance with temperature for KNNLST ceramics. The value of Z'' decreases with increase in frequency at low temperatures. As temperature increases above 300°C , a weak dielectric relaxation phenomenon is observed and the spectrum shows a monotonous decreases with dispersive nature of pattern in low frequency region. At higher frequencies, a plateau region is observed suggesting the presence of electronic, dipolar and space charge polarization in the samples.³⁷ It is observed that the peaks with asymmetric broadening are shifting towards higher frequency side with rise in temperature. It has also been observed that the spectra merge at higher

Fig. 8. Variation of real part (Z') of impedance with frequency at different temperatures of KNNLST (where $x = 0.00, 0.005, 0.01$) ceramics.

frequencies irrespective of the temperature. The relaxation species may possibly be electrons or immobile charges at low temperatures and oxygen vacancies or defects at higher temperatures. Therefore, it can be inferred that the electrical

conduction in these materials arises only by hopping of electrons, oxygen vacancies among the available localized sites.

Figure 10 shows the complex impedance spectrum (Nyquist plot) of the samples at different temperatures i.e.,

Fig. 9. Variation of imaginary part (Z'') of impedance with frequency of KNNLST (where $x = 0.00, 0.005, 0.01$) ceramics.

Fig. 10. Nyquist plot of KNNLST (where $x = 0.00, 0.005, 0.01$) ceramics at different temperatures.

Table 1. Lattice parameters, cell volumes and the variation of electrical parameters (bulk/grain) as a function of compositions (Na concentration).

Compositions	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)	R _b (KΩ)	C _b (pF)
$x = 0.00$	3.94	5.64	5.67	125.996	0.785	2.014
$x = 0.005$	3.96	5.62	5.66	125.664	1.068	8.720
$x = 0.01$	3.97	5.70	5.45	123.328	1.120	8.948

200°C, 300°C, 400°C and 500°C. The impedance spectrum consists of semicircular arcs. At lower temperature region, an arc appears which gets resolved into a semicircular arc with increasing temperature and the depression of the arc may be interpreted as the static distribution of the relaxation times. The intercept of the semicircular arcs on the real-axis appears to approach towards the origin of the complex plane plot suggesting a decrease in the sample barrier properties with rise in temperature. These semicircular arcs of the impedance spectrum at elevated temperatures have been attributed to the grain interior contribution, which are consistent with the brick layer model for a polycrystalline material. Appearance of single circle arc intercepted and with the center lying below x -axis (Z') demonstrates that bulk resistance offers major contributions to the conductivity of the materials. The slope of the curve is found to be decreasing and bending towards real (Z')-axis with temperature exhibiting a typical semiconducting behavior i.e., NTCR. Above 300°C, the center of the curve lies below x -axis suggesting the relaxation to be poly-dispersive and non-Debye type, which is due to the

presence of grain size, defects, oxygen vacancies, stress-strain phenomenon and elemental distribution in materials electrode system.³⁸ The values of the resistance and capacitance due to the grain/bulk contribution can be evaluated from the impedance spectrum. The values of bulk resistance R_b and bulk capacitance C_b obtained by standard software ZSimpWin software³⁹ are listed in Table 1.

4. Conclusion

In this work, lead-free ferroelectric KNNLST ($x = 0.00, 0.005$ and 0.01) ceramics prepared by solid state synthesis route with excess of Na concentration have been investigated for ferroelectric, dielectric and electrical properties. All samples showed single phase perovskite structure with orthorhombic symmetry. An increase in density reveals that excess Na addition at A-site suppresses the volatility of alkali elements in the ceramics. A high remnant polarization and low leakage current were found for $x = 0.01$. The electrical

property indicates that the materials exhibit (a) high dielectric constant value $\epsilon'_{\max} \sim 7023$ for $x = 0.01$ composition, (b) T_C is shifted to higher temperature, (c) NTCR behavior, (d) weak dielectric relaxation above 300°C , (e) bulk conduction at lower temperature and (f) decrease in leakage current with increase in Na content. It is evident from the results that the composition $x = 0.01$ possesses very good dielectric and ferroelectric properties which could be exploited for device applications.

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