Dielectric relaxation and modulus spectroscopy analysis of $(\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06})\text{NbO}_3$ ceramics

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We have investigated the structure, dielectric and electrical properties of lead-free polycrystalline $(\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06})\text{NbO}_3$ ceramics as a function of temperature and frequency in order to understand the intrinsic contribution of grain/bulk and grain boundary effects toward the dielectric response as well as the electrical conduction mechanism in the samples fabricated by microwave sintering method. X-ray diffraction analysis exhibits perovskite structure with orthorhombic symmetry, which is well supported by the Raman spectroscopic analysis. A minor secondary impurity phase of tungsten bronze structure was observed for samples sintered at 1050°C, which gets weaker for samples sintered at 1150°C. Dielectric permittivity was enhanced by 50%, although there was a reduction in the dielectric loss by about 50% at Curie temperature (450°C) for samples sintered at 1150°C. Complex impedance spectroscopic analysis indicated non-Debye-type dielectric relaxation present in the samples, and this phenomenon followed thermally activated process related to hopping mechanism. Nyquist plot showed the negative temperature coefficient of resistance, characteristic of the samples.

Keywords: Lead-free piezo-ceramics; dielectric properties; AC impedance spectroscopy; dielectric relaxation; negative temperature coefficient of resistance (NTCR).

1. Introduction

In recent times, research on health-cautious green technologies based on piezoelectric and ferroelectric materials has become more focussed and intensified. The urge to replace lead-based toxic materials such as lead zirconium titanate has dominated the commercial market for past few decades.¹ One of the challenges currently faced by industry is that most of the dielectric materials are not able to work properly at temperatures higher than 125°C,^{2,3} whereas the advance of technology demands electronic devices which can be used under harsh environments (>200°C) such as in automobile and aircraft industries.⁴ Sodium potassium niobate (Na, K) NbO_3 (KNN) is one of the prominent members of lead-free family, which has been studied extensively for past few decades because of its high Curie temperature, good electro-mechanical coupling effect and piezoelectric and ferroelectric properties.^{5,6} With extensive research followed by a large number of scientific publications every year on KNN-based bulk ceramics, it is still very difficult to densify ceramics whose electrical properties could be reproduced,^{7,8} thus hindering commercial realization. Retaining stoichiometry and high density has been the major issue related

to successful fabrication of KNN ceramics, which is caused by the loss of volatile alkali species present at elevated temperatures during the fabrication process.^{9,10} Nonstoichiometry leads to the formation of defects such as A-site vacancies, space charge polarization and oxygen vacancies and some intermediate secondary phase, which results in poor ferroelectric and electrical properties.¹¹ Different defects are also responsible for dielectric relaxation at higher temperatures.

It is very difficult to fabricate dense ceramics by conventional sintering process because of the limitations of phase stability of KNN above 1140°C, due to volatility of alkali species at A-site (Na/K ratio) leading to oxygen vacancies and nonstoichiometry, which in turn give rise to conductivity of the samples. Kosec and Kolar¹² proposed that the acceleration of slow-moving species (A-site cation) can lead to densification of the sample and promotion of sintering process. Several synthesis techniques such as solid-state reaction,¹³ sol-gel¹⁴ and hydrothermal¹⁵ and various sintering methods such as field-assisted sintering technique,¹⁶ pressureless sintering¹⁷ and hot pressing¹⁸ have been developed to densify and enhance electrical properties in KNN systems. However, these sintering techniques have their limitations

such as low efficiency, high cost and time-taking process. Microwave (Mw) sintering technique, in contrast, is cost-effective, nonpolluting and very effective than the conventional technique. In this process, there is volumetric absorption of electromagnetic energy, which is transformed into heat because of microwave radiation. Core heating, utilization of energy supplied up to 80–90% and heating rates could be induced up to several degrees in a second,^{19,20} which are the additional advantages over conventional sintering methods.

Addition of suitable sintering aids and doping (such as Li^+ , Ta^{5+} , Sb^{5+}) at the A- or B-site in the KNN system have been studied,²¹ which proved to be effective in suppressing the volatility of the alkali species and in improving the density and piezoelectric and ferroelectric properties as well. Doping with 6% Li^+ at the A-site leads to significant reduction in the polymorphic phase boundary occurring between orthorhombic and tetragonal phase transitions around 200°C to room temperature (RT).^{22,23} A small amount of Li substitution is considered to be sufficient to affect the BO_6 octahedra and thereby increase the Curie temperature,²⁴ with highest value reaching up to 500°C for 10%mol concentration.²⁵

Complex impedance spectroscopy is a versatile and very effective technique for analyzing electrical responses in polycrystalline materials in different frequency ranges as a function of temperature. An alternating voltage signal is applied to the material, and the corresponding current responses are measured. This technique is widely used for analyzing the relationship between electrical properties and microstructure of the material, intrinsic contributions from grain, grain boundary and materials electroding and their total contribution toward conductivity of the samples. A detailed analysis of the electrical properties (dielectric constant/loss, conductivity, etc.) carried out using relaxation frequency ($\omega_{\max}$) gives unambiguous results when compared with those obtained at arbitrarily selected fixed frequencies. Any ambiguity or error can be eliminated by the application of impedance spectra arising due to stray frequency effects. Both the reactive and resistive components can be easily analyzed from Nyquist plot (complex plane plot).²⁶ In complex impedance spectroscopy, frequency-dependent behavior of the materials may be expressed in terms of complex impedance (Z), complex electric modulus (M), complex dielectric constant (ϵ') and tangent loss ($\tan \delta$), which are related to each other.²⁷

It is therefore very crucial to gain a fundamental understanding of the conductivity mechanism. Therefore, in this work, we doped (Na, K) NbO_3 ceramic with Li, and the samples were microwave-sintered at different temperatures — 1050°C and 1150°C — in order to study the effect of different microwave sintering temperatures on the structure, dielectric and electrical properties of the samples.

2. Materials and Methods

Lead-free ($\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}$) NbO_3 hereby designated as KNNL ceramics and microwave-sintered at 1050°C and

1150°C was prepared by conventional solid-state heating process using analytical grade reagents from Sigma Aldrich with more than 99% purity (Na_2CO_3 , K_2CO_3 , Nb_2O_5 and Li_2CO_3 were used as the starting materials). The raw materials were weighed according to stoichiometric proportion and then mixed with 2-propanol and ball-milled for 72 h with zirconia balls as the milling media. The powder thus obtained was dried overnight, grinded and calcined at 850°C for 2 h and the calcined powder was grinded and then compressed into cylindrical disk of 10 mm diameter and 1 mm thickness. These samples were microwave-sintered using a microwave heater (UMF-01, 2.54 GHz, Unicera, Korea) at 1050°C and 1150°C, respectively, for 2 h at a heating rate of 50°C/min.

X-ray diffraction patterns were recorded at RT (Bruker D8 Discover) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) to identify the crystal structure of the ceramics. Raman spectroscopic study was performed using 488 nm Ar^+ radiation at 25 mW (Micro Raman spectrometer from Jobin Yvon Horibra LABRAM-HR) at RT recorded from the range of 150–1000 cm^{-1} . Dielectric constant, loss tangent and impedance parameters of the samples were measured using a PSM1735 Impedance Analyzer in the frequency range of 100 Hz to 1 MHz at RT to 500°C in a Carbolite (MTF9/15/130) tube furnace.

3. Results and Discussion

Figure 1 shows the RT X-ray diffraction pattern of the KNNL microwave-sintered samples. The diffraction pattern exhibits perovskite structure with minor secondary phase indexed as $\text{K}_3\text{LiNb}_6\text{O}_{17}$ (JCPDS-360533) for samples sintered at 1050°C, which weakens for samples sintered at 1150°C. Using a standard computer program package POWD,²⁸ the indexing and unit cell configurations were calculated. Orthorhombic unit cell was selected on the basis of the observed and

Fig. 1. RT X-ray diffraction pattern of KNNL sintered at (a) 1050°C and (b) 1150°C.

calculated inter-planer spacing d . The lattice parameters were found to be consistent with the earlier results for the KNNL system.²²

As is well known, KNN undergoes a sequence of phase transitions starting from high-temperature cubic phase (Pm3m, O1h) to tetragonal phase (P4mm, C^{14v}), followed by the RT orthorhombic phase (Amm2, C_{2v}¹⁴) and finally to the low-temperature rhombohedral phase (R3m, C^{53v}).^{29,30} All the XRD patterns have been further analyzed by the Rietveld refinement technique using orthorhombic perovskite space group Amm2, C_{2v}¹⁴. The FullProf program, version May 2016, has been used. The Rietveld refined patterns for the samples sintered at 1050°C and 1150°C are shown in Fig. 2. The pattern with open circle corresponds to the experimental XRD pattern, the pattern with solid line corresponds to theoretically generated XRD pattern, vertical lines correspond to Bragg's position of the given space group and bottom line corresponds to the difference between theoretical and experimental XRD pattern. The Rietveld refinement is a least-square fitting technique, which helps to generate a theoretical XRD pattern close to that of the experimental pattern. Here, in the refinement of the XRD pattern of KNaLiNbO₃, oxygen occupancy has been kept fixed and remaining elements' occupancy was allowed to vary at A and B sites of the perovskite structure. The major free parameters in our iteration are lattice parameter, occupancy, scale factor, isothermal

parameter, shape profile parameter and peak shape function. The two important parameters which show the quality of agreement between experimental and theoretical XRD pattern during iteration with FullProf program are (i) weighted profile factor (Rwp) and (ii) reduced χ^2 (X^2). The values of obtained Rwp and X^2 are listed in Table 1. The observed value of Rwp of samples sintered at 1150°C is in agreement with the recent report on KNN crystalline materials,³¹ whereas Rwp value for the samples sintered at 1050°C is on the higher side, which is due to the presence of impurity phase. Moreover, acceptable X^2 has been obtained for samples sintered at 1150°C, which is the goodness of fit. The lattice parameters, unit cell volume, Rwp and X^2 obtained for both the samples are shown in Table 1.

The density of the sample was calculated by Archimedes' method. The density was found to be >95% of theoretical value for sample sintered at 1150°C and it was about 90% for sample sintered at 1050°C.

Figure 3 shows the RT Raman scattering spectra of the samples. The effect of sintering temperatures and the doping at A-site causing the deformations in the local structure of perovskites due to tilting of NbO₆ octahedra or lattice deformations and distortion caused by cationic displacements can be effectively investigated using Raman spectroscopic study. According to theoretical predictions, there are total 12 Raman modes and 11 IR modes observed in the KNN

Fig. 2. XRD patterns along with the Rietveld refined data of samples sintered at (a) 1050°C and (b) 1150°C. The pattern with black corresponds to the experimental data and red line corresponds to the theoretically fitted data. Vertical lines represent the Bragg's position and the pattern at the bottom represents the differences between experimental and theoretical data. Asterisks denote positions of peaks due to minor levels of secondary phase.

Table 1. Lattice parameters, cell volume, Rwp and X^2 values of the KNNL samples.

Sintering temperature (°C)	Lattice parameter (a) Å	Lattice parameter (b) Å	Lattice parameter (c) Å	Unit cell volume (Å ³)	Rwp	X^2
1050	3.99	3.97	3.81	60.35	28.7	12.6
1150	3.71	3.79	3.44	48.36	19.2	1.92

Fig. 3. RT Raman spectra of KNNL sintered at (a) 1050°C and (b) 1150°C.

spectra. The NbO_6 octahedra exhibit Oh symmetry and a total of six normal modes are observed.³² The observed Raman spectra here indicate that the crystal structure is orthorhombic. Three distinct and signature peaks are observed here. The doubly degenerate symmetric O-Nb-O stretching vibrational mode is observed at 611 cm^{-1} (V_5), whereas a triply degenerate bending vibration of O-Nb-O symmetry is observed at 256 cm^{-1} (V_1). The discontinuity observed in the full width at half maximum (FWHM) for V_1 and V_5 peaks agrees well with the evidence of morphotropic phase boundary in KNN-based systems from earlier works.³³ The peak observed around 862 cm^{-1} represents the coupling mode ($V_1 + V_5$). Both X-ray diffraction and Raman study confirm the stabilization of the orthorhombic symmetry in the samples.

Figure 4 shows the typical scanning electron micrograph (SEM) of KNNL (fractured and polished) samples in BSE mode sintered at 1150°C. The grain size of the samples is of

the order of $2\text{--}4\text{ }\mu\text{m}$. The fracture surfaces show homogeneous grain and dense structures.

Figures 5(a) and 5(b) show temperature dependence of relative permittivity (ϵ'_r) and loss tangent ($\tan \delta$) at 1 kHz from RT to 500°C. Two phase transitions — orthorhombic to tetragonal T_{0-t} at 160°C and tetragonal to cubic T_{t-c} phase transitions at 420°C — are clearly observed in KNNL ceramics. Thermally induced enhancement of dipole orientation or hopping conduction in the samples enhances the dielectric constant value,³⁴ which increases from 3900 to 5200 for samples sintered at 1150°C. There is a shift in T_{t-c} toward lower temperature by about 10°C for the sample sintered at 1150°C.

Dielectric loss–temperature curve (Fig. 5(b)) is almost constant till 250°C and after that it increases fast. The increase in dielectric loss is due to the presence of space charge polarization, which is prominent at low frequency and high temperature. Frequency-dependent dispersive behavior is seen around T_c . Modification in the crystal structure during phase transitions weakens the carrier transport properties due to scattering effect with probability of the hopping ions to come out of the potential barrier and form electron–hole pair,³⁵ thereby contributing significantly toward the dielectric permittivity and loss. The high loss is attributed to the presence of the nonstoichiometry due to the loss of volatile cations and/or the presence of parasitic secondary phase in the samples sintered at 1050°C. The extent of the loss at RT is almost six times for the samples sintered at 1050°C when compared with the samples sintered at 1150°C.

Figure 6(a) shows the variation of dielectric constant with frequency at Room Temperature (RT) for the ceramics sintered at 1050°C and 1150°C. According to the phenomenological theory proposed by Maxwell-Wagner and Koops model,³⁶ it suggests that contribution from highly conducting grain which constitutes the dielectric medium dominated at the higher frequency region, whereas at the lower frequency

Fig. 4. SEM polished and fractured surface of KNNL sintered at 1150°C.

Fig. 5. Dielectric permittivity as a function of temperature of KNNL sintered at (a) 1050°C and (b) 1150°C at 1 kHz.

region, the contribution is mainly from grain boundary effects. The hopping of electrons at the octahedral sites and their inability to get aligned with the applied field result in decreasing trend of dielectric value with increasing frequency. Large space charge polarization is produced at the grain boundary because of the piling up of the electrons which are unable to pass through poor conduction grain boundaries. With increasing frequency, the charge accumulation at grain boundaries hinders the direction of the flow of electrons inside the dielectric material. This phenomenon results in decreasing dielectric values with increasing frequencies.³⁷

Figure 6(b) shows the variation of dielectric loss with frequency at RT, which appears to be decreasing monotonically with increasing frequency. The relative high dielectric loss for the sample sintered at 1050°C is attributed to the

presence of minor secondary phase, resulting due to the loss of cations/alkali species content in the compounds.

Figure 7 shows the variation of real part of impedance (Z') with frequency at different temperatures. The curve exhibits a decreasing trend with increasing frequency as well as increasing temperature, clearly indicating that there is an increase in the ac conductivity of the sample with increasing temperatures and frequencies. The curve shows a sigmoidal variation at low frequencies, although the saturation region at higher frequencies suggests the mixed nature of electronic, dipolar and orientational present in the samples. A change in the ordering pattern of charge is exhibited at low frequency with temperature. Decreasing Z' with temperature suggests that the sample follows negative temperature coefficient of resistance (NTCR) at low

Fig. 6. (a) Room Temperature variation of dielectric permittivity with frequency of KNNL samples sintered at —■— 1050°C and —●— 1150°C. (b) Room Temperature variation of dielectric loss with frequency of KNNL samples sintered at —■— 1050°C and —●— 1150°C.

Fig. 7. Variation of real part of impedance (Z') of KNNL samples sintered at (a) 1050°C and (b) 1150°C as a function of temperature with different frequencies.

frequencies, while merging of curves at high frequencies exhibits the possibility of increase in the ac conductivity in the samples, which arises due to the release of space charge and lowering of the potential properties in the samples.³⁸ This phenomenon can be corroborated with the intrinsic response from grain or bulk in the materials. Relaxation frequency shifts toward higher temperature for the samples sintered at 1150°C.

Figure 8 shows the variation of imaginary part of impedance with frequency at different temperatures. Asymmetric broad peaks are observed. In the low temperature region, the value of Z'' becomes maximum, which decreases with increasing frequency. The trend of dielectric relaxations in the sample is characterized by the angular frequency given as $\omega_{\max} = 2\pi f_{\max}$ of the peaks observed at temperatures

>350°C. A dispersive nature with monotonous decrement at lower frequencies and saturation region at higher frequencies is observed in the samples, which clearly indicates the intrinsic contribution from space charge, dipolar and electronic polarizations.

The variation of complex impedance system (Nyquist plot) of the samples at different temperatures is shown in Fig. 9. One semi-circular arc is observed, which suggests the intrinsic contribution from (grains interior) bulk properties of the materials.³⁹ The center of the arc below x -axis suggests the non-Debye-type relaxation phenomenon originated by strain–stress phenomenon, grain size, orientations defects, oxygen vacancies and so on. Arc intercept with x -axis (Z') exhibits that the major contribution to conductivity of the materials is due to bulk resistance (R_b),^{40,41} which decreases

Fig. 8. Variation of the imaginary part (Z'') of impedance of KNNL samples sintered at (a) 1050°C and (b) 1150°C as a function of temperature with different frequencies.

Fig. 9. Variation of real and imaginary parts of impedance (Nyquist plot) of KNNL samples sintered at (a) 1050°C and (b) 1150°C at different temperatures.

with increasing temperature thereby indicating typical semiconductor behavior, i.e., NTCR.

Complex modulus method is a very effective tool mostly employed for the analysis and interpretation of various dynamical aspects of electrical transport phenomenon such as average relaxation times, hopping rate of conduction ions and so on. High resistance contributions are mostly dominating in impedance spectra analysis, whereas capacitance contribution can be determined from complex modulus spectroscopy, even though the resistances are comparable. Electrical modulus is defined as⁴²:

$$M^* = \frac{1}{\epsilon^*}; \quad M^* = M' + M'' = i\omega C_0 Z^*. \quad (1)$$

Real and imaginary parts of electric modulus (M^*) can be given by the following equation as:

$$M' = \epsilon' / \epsilon'^2 + \epsilon''^2; \quad M'' = \epsilon'' / \epsilon'^2 + \epsilon''^2, \quad (2)$$

where M' and M'' are the real and imaginary parts of the complex electric modulus.

Figure 10 shows the variation of real part of modulus curve as a function of frequency at different temperatures. The value of M' decreases with temperature, but the value of M' increases with frequency showing a continuous dispersion arising due to the short range mobility of ions/carriers. The nature of variation suggests that the bulk (intra-grain) is responsible for electrical properties of the materials. However, the tendency of the charge flow to restore back is lost under applied electric field. The value of M' becomes maximum at higher frequency, whereas at lower frequencies, it tends to zero indicating the presence of electrode polarization phenomenon present in the samples.⁴³

Variation of imaginary part of modulus (M'') versus frequency at different temperatures is shown in Fig. 11. The asymmetric nature of the curve is observed till 1000 kHz. Peaks corresponding to lower frequency can be assigned to

Fig. 10. Variation of real part of modulus (M') of KNNL samples sintered at (a) 1050°C and (b) 1150°C at different temperatures.

Fig. 11. Variation of imaginary part of modulus (M'') of KNNL samples sintered at (a) 1050°C and (b) 1150°C at different temperatures.

the transportation of mobile carriers to long distances, whereas higher frequency with peaks maximum can be assigned to the confinement of ion/mobile carriers within short range in their potentials.⁴⁴ Peaks broadening exhibits non-Debye-type relaxation present in the samples. Transition from long- to short-range mobility within the samples can be observed in the frequency range where peaks occur.⁴⁵

Figure 12 shows the variation of M' versus M'' at different temperatures. The nature of curve exhibits asymmetric semi-circular arc whose center lies below x -axis. At temperature $>350^\circ\text{C}$, two semi-circular arcs start appearing, indicating the grain boundary and grain effect together. The center of the arc lying below M' indicates the non-Debye-type relaxation present in the samples. However, the arc intercepts tend to shift toward higher values as the temperature is increased. This phenomenon can be correlated with increase in the capacitance with increase in temperature.

Figure 13 shows the normalized curve of $M''/M''_{\max}$ versus $\log(f/f_{\max})$ at different temperatures. The modulus plot can be correlated to the dielectric phenomenon observed in the samples.⁴⁶ $M''/M''_{\max}$ curves are not symmetric, implying a nonexponential behavior of the conductivity relaxation. The FWHM of the $M''/M''_{\max}$ spectra is wider than the breadth of a Debye peak (1.14 decade), which suggests the presence of non-Debye type of relaxation phenomenon.⁴⁷

Figure 14 shows the normalized complex electrical impedance with frequency at different temperatures. The master curve enables us to have insight into the dielectric process occurring within the samples. Overlapping of the curves with minor variation in FWHM in the peak pattern at same temperatures can be expressed by nonexponential Debye-type relaxation process.⁴⁸ This conduction process suggests the possibility that ion migration takes place via hopping mechanism accompanied by consequent

Fig. 12. Variation of real and imaginary parts of modulus of KNNL samples sintered at (a) 1050°C and (b) 1150°C at different temperatures.

Fig. 13. Normalized curve of $M''/M''_{\max}$ versus $\log(f/f_{\max})$ of KNNL samples sintered at (a) 1050°C and (b) 1150°C at different temperatures.

Fig. 14. Normalized curve of $Z''/Z''_{\max}$ versus $\log(f/f_{\max})$ of KNNL samples sintered at (a) 1050°C and (b) 1150°C at different temperatures.

time-dependent mobility of other charge carriers of same type in vicinity.⁴⁹

Figure 15 shows the variation of electrical conductivity as a function of frequency, which is given by Jonscher power law.⁵⁰ This law co-relates the frequency dependence with the conductivity of the materials:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n, \quad (3)$$

where σ_{dc} is the conductivity independent of frequency and n is the frequency exponent and A is the coefficient, which are material properties and are activated thermally. The dispersion phenomenon is characterized by the ac-dependent term $A\omega^n$. The physical meaning of n has been defined by Funke⁵¹ for different values of n , as for $n > 1$ small localized hopping within the neighborhood. $n \leq 1$ represents the translational motion followed by sudden hopping of the charge carriers. The value of n calculated using relation (3) in the curve was

Fig. 15. Variation of ac conductivity with frequency of KNNL samples sintered at (a) 1050°C and (b) 1150°C at RT.

found to be 0.7, thus confirming the mechanism of hopping of charge carriers leading to the ac electrical conductivity in the materials. Dispersive nature which gets narrower at higher frequencies is clearly seen in the plot due to electrode polarization, and the high conductivity observed is due to defects such as oxygen vacancies caused by loss of alkali species. The higher value of σ_{ac} for the sample sintered at 1050°C may be due to tungsten bronze-structured secondary impurity phase, which disturbs the stoichiometry of the sample leading to the increase in the conduction mechanism of the samples.

4. Conclusion

Lead-free ($\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}$) NbO_3 ceramics were successfully fabricated by microwave sintering method at 1050°C and 1150°C, respectively. The density of samples sintered at 1150°C is higher than that of sample sintered at 1050°C and is >95% of the theoretical value. X-ray diffraction measurements suggested the formation of perovskite structure with orthorhombic symmetry, which is confirmed by the Raman analysis of the samples. Detailed studies of dielectric and electrical properties indicate that the material exhibits: shift of Curie temperature toward lower temperature side, increase in dielectric permittivity and decrease in dielectric loss by about 50% for the materials sintered at 1150°C. Non-Debye-type relaxation phenomenon is observed for the samples, which are thermally activated process related to the charge hopping mechanism. Nyquist plot exhibits NTCR behavior.

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