Comprehensive investigation of structural, dielectric and local piezoelectric properties of KNN ceramics

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In this research paper, we utilized the traditional high-temperature solid-state reaction method to fabricate the $K_{0.495}Na_{0.520}NbO_3$, $K_{0.480}Na_{0.535}NbO_3$ and $K_{0.475}Na_{0.540}NbO_3$ (abbreviated as KNN-1, KNN-2, and KNN-3, respectively) lead-free ion deficient ceramics for understanding the influence of ionic deficiency on the crystalline structure and dielectric/piezoelectric properties of the samples. X-ray diffraction patterns of these samples exhibited a perovskite tetragonal phase. Dielectric anomalies around 287°C and 471°C were identified as ferroelectric to ferroelectric and ferroelectric to paraelectric-transition temperatures for KNN-2 at 1 kHz. It was found that the composition KNN-2 exhibit relatively high Curie temperature i.e., 471°C. The conductivity plots confirm that the activation energies are frequency-dependent. The impedance behavior in our ceramic samples can be analyzed with the bulk/grain effect. The slope of Z' with temperature shows negative temperature coefficient of resistance (NTCR) type behavior in proposed KNN ceramics material.

Keywords: KNN; dielectric properties; X-ray diffraction (XRD); NTCR; PFM.

1. Introduction

The development of lead-free piezoelectric ceramics has drawn great attention these days due to growing environmental concerns. Currently, the market is dominated by lead-based materials due to their exceptional piezoelectric properties.¹ Unfortunately, the high concentration of toxic lead — over 60 wt.% — causes serious harm to human health and contaminates the environment. Due to the toxicity of lead-based compound, we need to develop high-performance lead-free piezoceramics.² There are different kinds of lead-free piezoelectric materials with a perovskite structure that have been widely investigated. They are barium titanate [$BaTiO_3$, BT], (Ba,Ca)(Zr,Ti) O_3 (BCZT)-based,^{3–7} sodium-bismuth titanate [(Bi,Na)TiO₃, BNT], BiFeO₃-based^{8–10} and potassium-sodium niobate [(K,Na)NbO₃, KNN]. Recently, the structure of a rhombohedral–tetragonal (R–T) phase boundary was reported to effectively improve the piezoelectric

properties of KNN-based ceramics resulting in giant d_{33} values of 490–570 pC/N.³ Zhao *et al.* reported the highest piezoelectric properties of $K_xNa_{1-x}NbO_3$ at the optimum Na/K ratio of 0.535/0.480. Furthermore, in our preliminary work, the highest dielectric properties were observed in the 0.95 (K_xNa_{1-x}) NbO₃-0.05LiTaO₃ system. According to another paper, the Na-rich region exhibited higher piezoelectric properties compare to the K-rich region in KNN ceramics. Luo *et al.* reported the effects of low concentration of Na on the phase structure, dielectric and electrical properties of KNN ceramics.³ These confirm that the electrical properties can be enhanced by KNN ceramics with an excess of Na addition during different steps of synthesis and fabrication.¹¹ The reason for excessive K and Na are added in precursor to compensate their volatilization during the annealing process which creates A-site vacancies. Due to this, the formation of large amounts of oxygen vacancies and electron holes in

KNN increases the dielectric loss. Many researchers reported that a 10 mol.% K and Na excess precursor solution was effective in compensating A-site vacancies and improved the crystallinity and the electrical properties.^{12,13} Therefore, excessive A-site ion on the phase and electrical properties of the KNN ceramic was investigated.

The aim of the present work is to achieve high dielectric constant and Piezo-response force microscopy (PFM) response for device applications. To understand the structural, electrical and ferroelectric domain behavior, these applications were briefly studied by using XRD, Impedance study and PFM. We synthesized all the ionic deficient ceramics of KNN (i.e., KNN-1, KNN-2, and KNN-3, respectively) in a user-friendly fabrication procedure (solid-State Reaction Method) and found good dielectric properties for devices applications.

2. Experimental

KNN-1, KNN-2 and KNN-3 ceramics were prepared by the conventional solid-state reaction route. The starting materials were high purity oxide and carbonate powders, K_2CO_3 (> 99.8%), Na_2CO_3 (> 99.8%) and Nb_2O_5 (> 99.9%). The powders were weighed according to the stoichiometric proportion for different required compositions and mixed using mortar pestle in ethanol media for 6 h. The powders were calcined at 900°C for 4 h. After that, the resulting powders were mixed thoroughly with a PVA binder solution. The green pellets were prepared by pressing powders in a 10 mm

diameter die at 100 MPa, then sintered at 950°C for 5 h at heating rate of 3.16°C/min and finally cooled to room temperature at 180°C/h. The phase formation of ceramics was checked with the help of X-ray powder diffractometer (Rigaku Miniflex 600, Japan) with $CuK\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in an extensive range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 60^\circ$) at a scanning rate of 2° min^{-1} at room temperature. The polished surfaces of the sintered samples were electrode with air-drying silver paste. Impedance of the samples was studied using Impedance analyzer (Hioki IM3570, Japan) within the frequency window from 1 kHz to 1 MHz at a temperature interval of 5° from RT to 600°C. Atomic Force Microscopy (AFM) measurements were carried out using a Veeco AFM Multimode Nanoscope (IV) MMAFM-2, Veeco microscopy. Local piezoelectric properties of the fibers were visualized simultaneously by using AFM in contact mode and PFM methods.¹⁴

3. Result and Discussions

Figure 1 shows the Room temperature XRD patterns of KNN-1, KNN-2 and KNN-3 ceramics prepared by solid-state reaction method. It was found that KNN-1 has monoclinic phase whereas in KNN-2 and KNN-3, the existence of (001/100), (101), (002/200), (201/210) and (112/211) which are major lattice planes in the XRD pattern confirms the formation of the orthorhombic structure. In these compositions, there are small amounts of secondary phase $K_2Nb_6O_{16}$ (as shown by $\clubsuit$) which are detectable.¹⁵ The XRD confirmed that

Fig. 1. Room temperature XRD patterns of $K_{0.495}Na_{0.520}NbO_3$ (KNN-1) $K_{0.480}Na_{0.535}NbO_3$ (KNN-2) and $K_{0.475}Na_{0.540}NbO_3$ (KNN-3) compositions calcined at 900°C for 4 h.

Fig. 2. (a) XRD peaks from the (110), (011), (200) and (201) planes of KNN-1, KNN-2 and KNN-3 ceramic fitted to the Gaussian function, and (b) Variations of $\text{FWHM}_{\text{tot}} \cos \theta$ with $4 \sin \theta$ for KNN-1, KNN-2 and KNN-3, respectively.

Fig. 3. The variation of dielectric constant (ϵ') as function of temperature of KNN-1, KNN-2, and KNN-3 ceramics at different frequencies.

the major perovskite phase exists in structure and minor secondary phase ($\text{K}_2\text{Nb}_6\text{O}_{16}$) exists in KNN ceramics. The calculated and observed 'd' values of all diffraction lines (reflections) of the above compounds suggest that there is a change in the basic crystal structure as compositions change due to the more volatile behavior of Na on high temperature. Therefore, at high sintering temperature, the samples are made with K-rich content, and as the radius of K^+ ($1.33 \text{ \AA}$) is larger than that of Na^+ ($0.97 \text{ \AA}$), this gives rise to an eventually increased crystal parameter. In our samples, the intensity increases with the increase in the concentrations of Na. It reflects the decrease in crystallinity with Na concentration.

Figure 2(a) shows the fitting of XRD peak for (101) lattice plane for KNN-1, KNN-2 and KNN-3 ceramics fitted to Gaussian function. The coefficient of determination of fitted peaks to Gaussian function is closer to unity compared to other functions. This coefficient is also symbolized by R^2 which is interpreted as the goodness of fit of a regression.

An R^2 close to unity indicates that a regression line fits the data well, whereas an R^2 closer to zero indicates a poor fit.

Stripping the instrumental, strain and size broadening factors depend on the shape of the peaks. For Gaussian peaks, the relation is defined as follows:

$$\text{FWHM}_{\text{obs.}} = \text{FWHM}_{\text{size}} + \text{FWHM}_{\text{strain}} + \text{FWHM}_{\text{inst.}} \quad (1)$$

Estimation of the instrumental broadening ($\text{FWHM}_{\text{inst.}}$) is desirable to correct the width of different peaks. $\text{FWHM}_{\text{inst.}}$ was determined by fitting the XRD profiles to a Gaussian function. FWHM_{tot} involving both $\text{FWHM}_{\text{size}}$ and $\text{FWHM}_{\text{strain}}$ can be expressed as

$$\text{FWHM}_{\text{tot.}} = \text{FWHM}_{\text{size}} + \text{FWHM}_{\text{strain}}, \quad (2)$$

where

$$\text{FWHM}_{\text{size}} = \frac{K}{D \cos \theta}; \quad \text{FWHM}_{\text{strain}} = C \varepsilon_0 \tan \theta. \quad (3)$$

Fig. 4. The variation of real part impedance (Z') with frequency at different temperature for KNN-1, KNN-2 and KNN-3 ceramics.

Fig. 5. The variation of imaginary part impedance (Z'') with frequency at different temperature for KNN-1, KNN-2 and KNN-3 ceramics.

Rewriting the equation for lattice strain and particle size effects:

$$\text{FWHM}_{\text{tot}} = (\text{FWHM}_{\text{obs}}^2 - \text{FWHM}_{\text{inst}}^2)^{1/2}. \quad (4)$$

Here, FWHM_{obs} and $\text{FWHM}_{\text{inst}}$ are the measured peak broadening and instrumental broadening in radian, respectively.

On solving Eq. (3), we have

$$\text{FWHM}_{\text{tot}} \cos \theta = \frac{K}{D} + C\varepsilon_0 \tan \theta. \quad (5)$$

Here, D is the grain diameter, $k = 0.9$ – 1.0 depending upon grain shape and $C\varepsilon_0$ is the strain in material

$$Y = mx + C. \quad (6)$$

On comparing (5) and (6), $m = C\varepsilon_0 = \text{slope} = \text{strain of sample}$.

Figure 2(b) shows the variation of $\text{FWHM}_{\text{tot}} \cos \theta$ with $\sin \theta$ and the slope of this plot is used to calculate the strain of

the materials as explained in the above equation and the strain in our materials are $\sim (0.57 \pm 0.043\%)$, $(1.357 \pm 0.24\%)$ and $(1.045 \pm 0.151\%)$. All the reflection lines in XRD pattern were used for obtaining the average crystalline size using the Debye–Scherrer equation.¹⁶

$$D = 0.9\lambda / \text{FWHM}_{\text{tot}} \cos \theta. \quad (7)$$

Here, D is the diameter of the particle, λ is the x-ray wavelength (0.154 nm), and θ is the Bragg angle of the reflection. The calculated average crystalline sizes from Eq. (7) are ~ 30.86 , 40.50 and 64.87 nm, respectively.

Figure 3 shows the variation of dielectric constant (ε') as a function of the temperature of KNN-1, KNN-2, and KNN-3 ceramics at different frequencies. KNN-2 and KNN-3 ceramics have a two sharp-phase transitions at 287°C and 471°C , each respectively representing the orthorhombic to tetragonal (at T^1) and tetragonal to paraelectric cubic (at T^2 or T_c) phase transitions. It is also observed that with an increase of Na, the dielectric constant decreases corresponding to the

Fig. 6. The Cole-Cole plot of KNN-1, KNN-2 and KNN-3 samples at different temperature.

ferroelectric–paraelectric phase transition, but the T^1 phase transition peaks shifted to a little lower temperature from 454°C to 422°C.

Figure 4 shows the variation of the real part of impedance (Z') with frequency at different temperatures. The pattern shows a sigmoidal variation as a function of frequency in the low-frequency region followed by a saturation region in the high-frequency region (above 1 kHz) and suggests the presence of mixed nature of polarization behavior in the material. The impedance value is observed to increase first in the low-frequency region with the rise in temperature followed by a relative decrease at subsequently higher temperatures. The result may be related to a change in the charge-ordering pattern with temperature; the effect showing a clearly perceptible change in its behavior in the low-frequency region. A decreasing trend of Z' with the rising in temperature suggests the presence of negative temperature

coefficient of resistance (NTCR) in the material in the low-frequency region but tends to merge in the high-frequency region at almost all temperatures. There is a possibility of increase in ac conductivity with the rise in temperature in the high frequency region (possibly) due to the release of space charge. This space charge comes from mobile ions which in the present case could be the oxygen vacancies.^{17,18}

Figure 5 exhibits frequency and temperature dependence of imaginary part of impedance (Z'') for KNN solid-solutions. In low-temperature/frequency range, Z'' has very high value for all the compositions which decreases with the rise in frequency and attains low values. This is an interesting (unusual) trend in the variation of Z'' with frequency/temperature for KNN ceramic samples. The appearance and nature of peaks at a characteristic angular frequency $\omega_{\max}$ ($= 2\pi f_{\max}$) provides information on the type and strength of the dielectric relaxation phenomenon occurring in the material. At different

Fig. 7. Variation of imaginary part modulus (M'') with frequency at different temperatures of KNN-1, KNN-2 and KNN-3 ceramics.

temperatures, the spectrum shows a monotonous decrease having dispersive nature of pattern in the low-frequency region followed by a plateau at the higher frequencies. This observation clearly suggests the presence of electronic, dipolar and space charge polarizations in these materials.

The relaxation frequencies can also be obtained from a Z'' - Z' Cole-Cole plot (Nyquist diagram). Figure 6 shows a set of impedance data taken over by a wide range of frequencies at temperatures of 400°C, 450°C and 500°C, respectively. The slopes of the lines of KNN ceramics decreased in the range of 400–500°C and bend towards the real axis. The appearance of semi-arc at maximum temperature indicates that only the bulk grain effect can represent this behavior. Further, the radii decrease with the increase of temperature, thereby indicating the NTCR nature of the KNN ceramics. Another interesting result for the KNN ceramics is that the

Cole-Cole plots could not be represented by full semicircles until the highest temperature (shown with blue lined color in Fig. 6 (inset)). The semi-circular arc was depressed and the center of the arc was below the x -axis. This behavior indicates that this sample has a poly-dispersive non-Debye behavior. A parallel RC equivalent circuit has fitted very well with high-frequency data.¹⁹

Figure 7 shows the variation of imaginary part of the modulus (M'') with frequency at different temperatures for KNN compound with different Na content. M'' shows the strong peaks and the position of the peak, i.e., $M''_{\max}$, shifted to higher frequencies as the temperature was increased. The frequency region below peak maximum M'' determines the range in which charge carriers are mobile on long distances. At frequency above peak maximum, the carriers are confined to potential wells, being mobile on short distances. The peaks are asymmetric and broader than the

Fig. 8. Variation of real (M') and imaginary part (M'') of modulus of different temperature of KNN-1, KNN-2 and KNN-3 ceramics.

ideal Debye curve. The frequency range where the peaks occur is indicative of the transition from long range to short range mobility.²⁰

The complex electric modulus spectrum M' versus M'' is shown in Fig. 8 for $K_{1-x}Na_xNbO_3$ ceramics at different temperatures. The patterns are characterized by the presence of little asymmetric and depressed semicircular arcs whose center does not lie on M' axis. The behavior of the electric modulus spectrum is suggestive of the temperature-dependent hopping type of mechanism for electric conduction (charge transport) in the system and non-Debye type dielectric relaxation.

Figure 9 shows the normalized plot of $M''/M''_{\max}$ versus $\log(f/f_{\max})$ at different temperatures for KNN ceramics, respectively. The normalized plot overlaps on a single master curve at different temperatures (i.e., same shape and pattern in the peak position with slight variation in full width at half maximum (FWHM) with the rise in temperature). The value of FWHM evaluated from the normalized spectrum is greater than $\log \frac{2+\sqrt{3}}{2-\sqrt{3}}$, and this indicates the non-Debye

type behavior which is well supported by complex modulus plot.^{21,22}

The ac conductivity (σ_{ac}) of the samples was calculated from the dielectric data using the relation $\sigma = \omega \epsilon \epsilon_0 \tan \delta$ where ϵ_0 is the vacuum permittivity and ω is the angular frequency. The conductivity of all the samples was estimated in the paraelectric temperature range 430–500°C. The variation of $\ln \sigma_{ac}$ with temperature ($K-1$) is shown in Fig. 10. The activation energy (E_a) of the samples (Table 1) was calculated in the high-temperature region (where the tangent loss is relatively low), using the relation $\sigma = \sigma_0 \exp(-E_a/K_B T)$, where K_B is the Boltzmann constant and σ_0 is the pre-exponential factor.

AFM measurements were carried out using a Veeco AFM Multimode Nanoscope (IV) MMAFM-2, Veeco microscopy. Local piezoelectric properties of the fibers were visualized simultaneously by using AFM in contact mode and PFM methods. The PFM technique is based on the converse piezoelectric effect, which is a linear coupling between the electrical and mechanical properties of a material. Since

Fig. 9. Modulus scaling behavior of KNN-1, KNN-2 and KNN-3 ceramics.

Fig. 10. Variation of ac conductivity $\ln \sigma_{ac}$ as a function of inverse of absolute temperature $1/T$ of KNN-1, KNN-2 and KNN-3 ceramics at 1 kHz, 10 kHz and 100 kHz frequencies.

Fig. 10. (Continued)

Table 1. hkl, lattice parameters, and Unit cell Volume of $K_{0.495}Na_{0.520}NbO_3$, (KNN-1) $K_{0.480}Na_{0.535}NbO_3$ (KNN-2) and $K_{0.475}Na_{0.540}NbO_3$ (KNN-3) compositions.

Composition (x)	Crystalline structure	$d_{obs.}$	$d_{cal.}$	Lattice parameters (Å)	Unit cell volume (Å) ³
$K_{0.495}Na_{0.520}NbO_3$ (KNN-1)	Tetragonal	3.9708	3.9708	$a = 11.554$	1590.40
		2.8073	2.8073	$c = 11.91$	
		2.2866	2.2872	$c/a = 1.0310$	
		1.9955	1.9957		
		1.7733	1.7731		
$K_{0.480}Na_{0.535}NbO_3$ (KNN-2)		3.9863	3.9881	$a = 8.4701$	1279.128
		3.4931	3.4937	$c = 18.0825$	
		2.8246	2.8234	$c/a = 2.1349$	
		2.3089	2.3065		
		2.0016	2.0021		
$K_{0.475}Na_{0.540}NbO_3$ (KNN-3)		1.6336	1.6338		1812.09
		4.0123	4.0123	$a = 101873$	
		2.8254	2.8254	$c = 17.4607$	
		2.7720	2.7716	$c/a = 1.7140$	
		2.3016	2.3152		
		2.2634	2.2636		
		2.0056	2.0062		

Table 2. Different physical parameters of $K_{0.495}Na_{0.520}NbO_3$, (KNN-1) $K_{0.480}Na_{0.535}NbO_3$ (KNN-2) and $K_{0.475}Na_{0.540}NbO_3$ (KNN-3) compositions.

Composition	KNN-1			KNN-2			KNN-3		
	1 kHz	10 kHz	100 kHz	1 kHz	10 kHz	100 kHz	1 kHz	10 kHz	100 kHz
T^1 (°C)	—	—	—	287	283	245	234	234	234
T^2 (°C)	454	450	434	471	440	437	426	424	422
ϵ_{max}	2303.4	981.1	456	1704.8	978.2	739.27	1552.8	1169	741.5

Fig. 11. (a) topography, (b) IP, (c) OPP images KNN-1, KNN-2 and KNN-3 ceramics.

Fig. 12. (a) Schematic illustration poling, (b) PFM image. (c) cross-section KNN-3 ceramics.

all ferroelectrics exhibit piezoelectricity, an electric field applied to a ferroelectric sample results in changes to its dimensions. To detect the polarization orientation, the AFM tip is used as a top electrode which is moved over the sample surface.

The OPP and IPP PFM images of the same area of the sample in Fig. 11 show the signal distribution of the piezoelectric response. Figure 11 shows the topography and corresponding d_{33} and d_{15} piezoelectric contrasts. The OPP contrast should contain different signal levels corresponding to 'positive' and 'negative' grains orientations.

RMS = 4.1 nm

Grain size $\sim$ KNN1 - 150 nm.

In order to get a better insight into the polarization switching under an external bias, a dc voltage (+90 V and -90 V) was applied to the bottom electrode while the grounded tip was scanned across the sample surface. Figure 12 displays the OPP piezoresponse image after poling an area of $1 \times 10 \mu\text{m}^2$ inside a larger (un-switched) region of $10 \times 10 \mu\text{m}^2$ (Fig. 12(a)). Since the applied voltage was by far greater than the nucleation bias, one can see additional positive and negative contrast, indicating a full polarization switching in them. Figure 12(c) represents the PFM signal cross-sections taken along the lines marked in the piezoresponse image of the poled sample (Fig. 12(b)).

4. Conclusion

In this study, we utilized the traditional high-temperature solid-state reaction method to fabricate the $\text{K}_{0.495}\text{Na}_{0.520}\text{NbO}_3$, $\text{K}_{0.480}\text{Na}_{0.535}\text{NbO}_3$ and $\text{K}_{0.475}\text{Na}_{0.540}\text{NbO}_3$ lead-free ion deficient ceramics for understanding the influences of ionic deficiency on the crystalline structure, and dielectric/piezoelectric properties of the samples. XRD pattern confirms that KNN-1 has monoclinic phase whereas in KNN-2 and KNN-3, it confirms the existence of the orthorhombic structure. It also confirms that crystallinity decreases with Na concentration. KNN-2 and KNN-3 ceramics have a two phase transitions at 287°C and 471°C . The first phase transitions representing the orthorhombic to tetragonal (at T^1) and second phase transitions representing tetragonal to paraelectric cubic (at T^2 or T_c) transitions. It is also observed that with an increase of Na, the dielectric constant decreases corresponding to the ferroelectric–paraelectric phase transition, but the T^1 phase transition peaks shifted to a little lower temperature from 454°C to 422°C . An impedance study was conducted for the first time to evaluate the effect of the ion deficient in the structure as a secondary grain boundary phase. The semi-circular arc was depressed and the center of the arc was below the x -axis. This behavior indicates that this sample has a poly-dispersive non-Debye behavior. PFM displays the OPP piezoresponse image after poling areas of $1 \times 10 \mu\text{m}^2$ inside a larger (un switched) region of $10 \times 10 \mu\text{m}^2$. Since the applied voltage was by far greater than the nucleation bias, one can see additional positive

and negative contrast indicating a full polarization switching in samples.

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