

ELECTRICAL PROPERTIES OF MULTI-VALENT ALTERNATE ABO₃ PEROVSKITE (KNN) MULTI-FUNCTIONAL FERROELECTRIC CERAMICS

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Abstract

Ecological-friendly and unhazardous materials are being prepared by the scientific community in search of novel lead-free ferroelectric materials. K_{0.5}Na_{0.5}NbO₃ belonging to the ABO₃ perovskite was found to be promising ferroelectric lead-free material. A new set of compound, namely, double dopant LKNZN compound was prepared by solid state route. Here, Lithium is partially replaced with Sodium, at A-site, and Zirconium substituted with Niobium, at B-site. The compositional formula of the present investigations is: [(K_{0.5}Na_{0.5})_(1-x)Li_x](Zr_{0.025}Nb_{0.98})O₃, where x=0, and 0.025 9 (labelled as KNN1 and KNN2). In addition we have prepared (K_{0.5}(Na_{0.475}Li_{0.025}))(Zr_{0.025}Nb_{0.98})O₃ (labelled as KNN3). XRD patterns obtained at room temperature have shown maximum intensity peak of (111), confirms the formation of a single-phase. SEM pictures of KNN1 and KNN2 have shown cubical grain with bimodal grain distribution, whereas KNN3 consist of circular bimodal grain distribution. Dielectric measurements were studied on the said above samples. It is observed a hump around 200°C and dielectric transition at 4520°C for all the samples. From this it is evident that: (i) the samples are transforming from orthorhombic phase to tetragonal phase near 200°C (ii) around 420°C, samples transform from tetragonal phase to cubic phase. The results were corroborated to the tolerance factor and lattice distortions.

Keywords: XRD, SEM, Piezoelectric Coefficient (d₃₃), Dielectric constant and Tolerance factor.

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Introduction

Lead-free Piezoelectric elements usages in electronic apparatus has prompted many electronic technological fields such as actuators, sensors, transducer etc. (Shrout and Zhang, 2007; Helke and Lubitz, 2008; Alkoy and Papila, 2010). Since lead-based piezoelectric promising ceramics especially Lead-Titanate (PbTiO_3 ; PT) and Lead Zirconium Titanate (PZT) have shown higher remnant polarisation but on account of Pb- toxic nature, alternative lead-free materials are needed in this direction (Guo *et al.*, 2004; Malic *et al.*, 2005; Pang *et al.*, 2011). As a consequence, it is focused in the area alkali-niobate (KNN) ceramics (Saito *et al.*, 2004; Matsubara *et al.*, 2005) and modified bismuth titanate (BT) (Wada *et al.*, 2001; Wang *et al.*, 2004). Based on the perovskite structure, several investigations are made on lead-free piezoelectric ceramics (Wang *et al.*, 2004; Rubio-Marcos *et al.*, 2007; Rai *et al.*, 2013). Environmentally friendly niobate like $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) based ceramics have shown distinguishable properties like electrical and piezo-electric when the compositional ratio of K/Na is 50/50 (Ramajo *et al.*, 2014). This composition is supposed to show maximum polarization near the morphotropic phase boundary (MPB) because of its inheriting oriented domains. However, as systematic electrical studies on piezoelectric and dielectric properties on pure KNN are limited when compared to those of PZT.

Research has been carried out on aliovalent modified KNN and found to be alternative to PZT in many properties like dielectric, ferroelectric, piezoelectric, etc. Previous works have shown enhanced ferroelectric properties for lower concentrations of Zr at B-site (Ramajo *et al.*, 2014). Li modified at A-site is found to be as sintering aid. It is testified that Li, Ta and Sb doping are efficient for augment in the piezo electric properties of KNN system (Guo *et al.*, 2004; Saito *et al.*, 2004; Li *et al.*, 2008; Chun *et al.*, 2011). They observed high piezoelectric properties near the morphotropic phase boundary (MPB) of Li doped KNN system. In the present work both Lithium and Zirconium ions were added at A- site and B site respectively for $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. Here, Zr and Nb ($x=0$ and 0.025) is added to Sodium, Potassium cation uniformly at A-site. A detailed compositional formula along with its chemical composition is: $(\text{K}_{0.5}\text{Na}_{0.5})(1-x)\text{Li}(x)(\text{Zr}_{0.025}\text{Nb}_{0.98})\text{O}_3$, where $x=0$ & 0.025 ; and $(\text{K}_{0.5}(\text{Na}_{0.475}\text{Li}_{0.025}))(\text{Zr}_{0.025}\text{Nb}_{0.98})\text{O}_3$.

The nomenclature of the samples is as follows:

- 1) $(\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3) \rightarrow \text{KNN}$
- 2) $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Zr}_{0.025}\text{Nb}_{0.98})\text{O}_3 \rightarrow \text{KNN1}$

- 3) $(\text{K}_{0.5}(\text{Na}_{0.475}\text{Li}_{0.025}))(\text{Zr}_{0.025}\text{Nb}_{0.98})\text{O}_3 \rightarrow \text{KNN2}$
- 4) $(\text{K}_{0.5}\text{Na}_{0.5})_{0.975}\text{Li}_{0.025})(\text{Zr}_{0.025}\text{Nb}_{0.98})\text{O}_3 \rightarrow \text{KNN3}$

Materials and Methods

All the samples KNN, KNN1, KNN2 and KNN3 were synthesized by using the conventional solid state reaction method. Reactant samples were calcined at 200°C for 2 hours before grinding and mixing. The reactant oxide powders were high purity with 99.99% (AR grade) made. The reactant powders K_2CO_3 , Na_2CO_3 , Nb_2O_5 , ZrO_2 , Li_2CO_3 were taken in the stoichiometric ratio and mixed thoroughly. The powder was ground for 8 hours. The mixed powders were calcined at 850°C for 2 hours, for KNN1, at 1000°C for 4 hours and for KNN2 & KNN3 at 980°C for 4 hours respectively using a programmable furnace. Since Zirconium is known to be a non-reactive refractory and hard material, therefore the calcination temperature of KNN1 is found to be more, compared to the rest of compounds. Further Li is known to be sintering aid, therefore calcination temperature for KNN2 and KNN3 is less when compared to KNN1. Moreover, Zr^{+4} has higher ionic radius ($0.72 \text{ \AA}$), compared to Nb^{+5} ($0.64 \text{ \AA}$), it is expected that KNN1 needs higher sintering temperature during

Sintering reaction process than that of KNN perovskite structure.

The calcined powders were mixed with 2 wt% of binder (polyvinyl alcohol) and pressed uniaxial to prepare circular shaped pellets of 10mm in diameter and 1 to 1.5mm thickness. Pressed pellets were final sintered at the temperatures 1000°C for 4-5 hours, at 1075°C for 3-hours respectively as mentioned above.

X-ray diffraction analysis was obtained by using Phillips expert diffractometer with $\text{Cu-K}\alpha$ radiation. The angle (2θ) and intensity (arbitrary units) was measured between 10 - 80° with the scan step of 2° per minute. The micro structures of various samples were studied by using scanning electron microscope (SEM-Carl Zeiss EVO 18 microscope). The samples were silver-painted on the both sides during the electrical measurements. Dielectric properties were studied by means of HP 4192A impedance analyzer in the frequency range of 1 kHz to 1 MHz. For the measurement of piezoelectric coefficient (d_{33}), the samples were initially poled in a silicon oil bath at 5 kV/cm electric field for 40 minutes at 160°C temperature. Piezometer system PM100 was used to measure d_{33} . It was noticed that d_{33} value of the samples depend on the poling time, temperature and the electric field applied.

Results and Discussion

Figure 1 shows the XRD pattern of KNN samples (KNN, KNN1, KNN2 and KNN3). The formation of single phase KNN perovskite structure was confirmed with the help of all indexed planes. It can be seen from Figure 1 that all the Li and Zr doped ceramics demonstrate a pure ABO₃ type perovskite structure, without any impurity phase. XRD profiles of all the samples were plotted in the 2θ range of 10-80°. With the help of all indexed planes and based on the parent compound (KNN), the lattice parameters were calculated with the help of POWED4 software. The lattice parameters of all the samples were given in the Table 1.

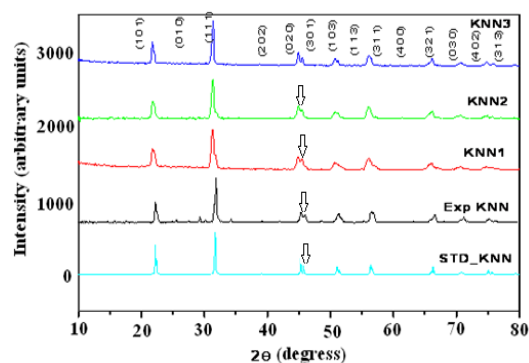


Figure 1. XRD spectra of KNN, KNN1, KNN2, KNN3 samples.

The $k k l$ reflections corresponding to (2 0 2) & (0 2 0) at around 46° of 2-theta and higher intensity of the (2 0 2) peak confirms the orthorhombic structure of all the samples (Chun *et al.*, 2011). It is also observed that maximum diffraction peaks of KNN sample shifted towards left handside of 2θ, which designate the increase in the lattice parameters which clarify the fact that Zr⁴⁺ electronic density is more than the electronic density of Nb⁵⁺ ion. Substituting Zr⁴⁺ in places of Nb⁵⁺ lead to increase the volume of the unit cell (Pontes *et al.*, 2004). The results were constant with the unit cell

volume, depicted in the Table 1. Further, doping of Lithium at A- site resulted in increasing the lattice parameters of KNN2 and KNN3. In addition orthorhombicity and orthorhombic distortion values were found to be high (more than 0.6), clearly confirms the favourable orientation of domain and hence polarisability in these double perovskites.

From the Table 1, it is observed that all the samples have more than 98% of relative density except KNN2 which has 85% of relative density. Among the three samples KNN1 has the maximum density, whereas doping Lithium at A-site, zirconium at B-site decreased its density. Addition of Lithium with Sodium ions at A-site and Zirconium at B-site has changed the density of KNN2 considerably. The radii of the doped ions at A-site and B-site were incompatible with the radii of existing cations. Due to the difference in radii, the A-O and B-O bond length will change and reflect in the parameters. The doped ions may occupy the interstitial sites. Change in lattice parameters also causes the changes in volume and other orthorhombicity values, calculated by using the formula: $\frac{2(a-b)}{(a+b)}$.

The common formula for the tolerance factor in perovskite ABO₃ compounds is given by

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

Here R_A , R_B and R_O are the ionic radii of A, B cations and Oxygen ions correspondingly. In an ideal perovskite structure, A-O distance is $\sqrt{2}$ times B-O distance i.e., the value of t is unity for ideal structure (Ostos *et al.*, 2009).

However, the tolerance factor for the prepared sample ((K_{0.5}Na_{0.5})_(1-x)Li_(x))(Zr_{0.025}Nb_{0.98})O₃ is given by

$$t = \frac{R_O + (0.5)(1-x)(R_K + R_{Nb}) + xR_{Li}}{\sqrt{2}(R_O + 0.025R_{Zr} + 0.98R_{Nb})} \quad (2)$$

Where R_{Zr}^{+4} , R_{Nb}^{+5} , R_O , R_{Li}^{+} , R_K^{+} and R_{Na}^{+} represent the radii of the Zr⁴⁺, Nb⁵⁺, O²⁻, Li⁺, K⁺ and Na⁺ ions correspondingly.

Table 1. Shows Lattice parameters, orthorhombic distortion and orthorhombicity, relative densities and tolerance factors of KNN samples

Sample	Lattice parameters (Å)			Unit cell volume (Å) ³	Orthorhombic distortion = (b/a)	Orthorhombicity = $\frac{2(a-b)}{(a+b)}$	Relative density	Tolerance factor (t)
	a	b	c					
Std KNN	5.653	3.968	0.701	127.11	4.49	0.350	---	1.01
Exp KNN	5.650	3.942	0.697	126.12	4.51	0.3548	99	1.01
KNN1	5.656	3.990	0.705	129.06	4.49	0.3454	99	1.008
KNN2	5.680	3.988	0.702	129.02	4.46	0.3500	85.6	1.007
KNN3	5.690	3.982	0.699	128.24	4.44	0.3531	98.6	1.005

Tolerance factor of the samples were calculate using the above equation. Tolerance factor ‘t’ value is close to unity for stable perovskite structure. It is observed that values for all the doped samples are more than unity. It is also observed, from the table 1, the ‘t’ value decreases slightly for KNN2 and KNN3, compared to KNN1. Li addition to the A -site causes further decrease in this value. This is due to the slight variation in the ionic radii of Zr and Nb ions distortion in the ZrO_6 octahedral. This distortion generally results a change of phase transition behaviour (Sateesh *et al.*, 2015). Keeping this point dielectric measurements were performed on these samples and the results were depicted in the Figure 2.

Figure 2. Shows the variation of dielectric constant with temperature at the different frequencies (10 kHz, 500 kHz and 1.5 MHz) for KNN, KNN1, KNN2 and KNN3 samples respectively. The data was extracted from room temperature to 500°C. Room temperature dielectric loss measured at 10 kHz for all the samples were listed in Table 2. From the Figure 2, it is observed that a hump at 200°C clearly indicates a change in the structure of KNN samples which transforms from orthorhombic phase to tetragonal phase (T_o - T_T). A dielectric peak observed around 420°C clearly confirms a change from tetragonal phase to cubic phase (also known as Curie temperature T_C). At the Curie temperature, the dielectric constant of KNN samples increase and thereafter it decreases. All the dielectric peaks were found to be broad and

found to be diffuse type. More aspect of this would be discussed later.

Figure 3(a-d), shows the Scanning Electron Microscopy (SEM) images of sintered samples KNN, KNN1, KNN2 and KNN3 respectively. The surface morphology of the KNN doped samples were studied by using scanning electron microscope (Carl ZEISS EVO 18 SEM). Incorporation of Zirconium in KNN has shown an increase in the grain size. KNN1, KNN2 have shown cubic grain with bimodal grain distribution. KNN3 has uniform circular bimodal grain distribution. All the samples show good densification and less porosity. The same is confirmed with the density percentage values. The diffusive behaviour of the samples is attributed to Zr^{+4} ions and a considerable uniform grain growth conform the same Ostos *et al.*, (2009). Incorporation of Lithium at A- site along with Zirconium at B- site has slightly changed the shape of the grain of KNN3.

Table 2. Curie temperatures, dielectric constant (at R_T and T_C), dielectric loss at room temperature (RT) for 10 kHz and d_{33}

Sample	$T_C(^{\circ}\text{C})$	Dielectric constant (ϵ)		Tan δ at RT($^{\circ}\text{C}$)	$d_{33}(\text{pC/N})$
		at RT($^{\circ}\text{C}$)	at $T_C(^{\circ}\text{C})$		
KNN	423	283	1247	0.2392	79
KNN1	402	202	1680	0.1206	107
KNN2	433	446	1269	0.6842	79
KNN3	441	233	1661	0.0476	95

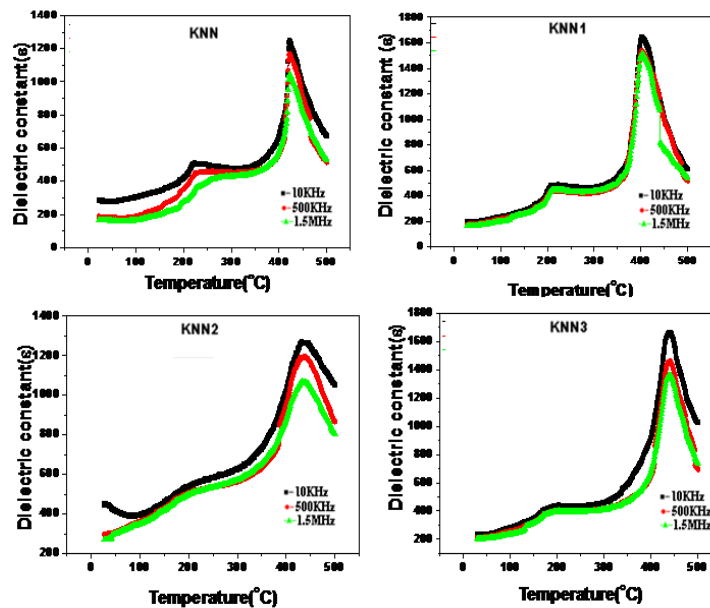


Figure 2. Variation of dielectric constant with temperature at 10 kHz, 500 kHz and 1.5 MHz

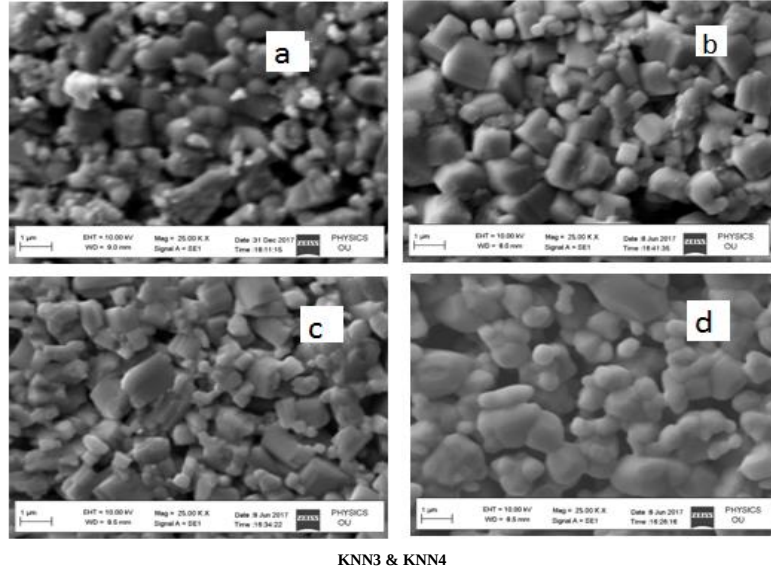


Figure 3. (a-d): SEM micrographs of KNN KNN1 KNN2

From Figure 2, it is noticed that the dielectric constant increases with increasing temperature up to Curie temperature and then decreases. This temperature is noted as Curie temperature. The two transition temperatures are conspicuous in the Figure 2. The dielectric peak height decreases with increasing frequency, and it is attributed to well known that polarization of dipole moment which decreases with increasing the frequency. A slight change in Curie temperature is attributed to ZrO_6 tilt and its distortion. KNN1 transition temperature is found to be less than the Curie temperature of the KNN. Incorporation of larger radius of Zr^{+4} in place of Nb^{+5} site might results in the change in transition temperature (Ostos *et al.*, 2009). Further, it can be explained as substitution of Zr in KNN causes phonon - electron interaction at B-site and finally results into the distortion of BO_6 octahedral structure (Huang *et al.*, 2008; Binhayeeniyi *et al.*, 2010). Thus, shift in ZrO_6 octahedral can be corroborated to the diffuse phase transition (DPT) of the samples (Hennings *et al.*, 1982; Mitic *et al.*, 2010). As mentioned earlier, that the dielectric peaks of all the samples were found to be independent of frequency. This kind of diffuse phase transition (DPT) can be studied with modified Curie-Weiss law, which is different from the following Curie-Weiss law (Merz, 1953).

$$\epsilon = \frac{C}{T - T_C} \quad (3)$$

Diffuse nature or broadening of the peak indicates a transformation of ferroelectric phase to

paraelectric phase of the sample. However, DPT behaviour of a sample is better understood by modified Curie-Weiss law given by.

$$\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}} = \frac{(T - T_{\tau\max})^\gamma}{C_1} \quad (4)$$

In the above Equation (4) the terms γ is the critical exponent of non-linearity and C_1 is Curie like constant. γ was calculated from the best curve fit or slope of the graph.

Figure 4 shows the variation of $\ln\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}}\right)$ with $\ln(T - T_m)$. Here γ represents the slope of the curve. If $\gamma = 1$, it stands for sharp phase transition where as 2 explains for relaxer type.

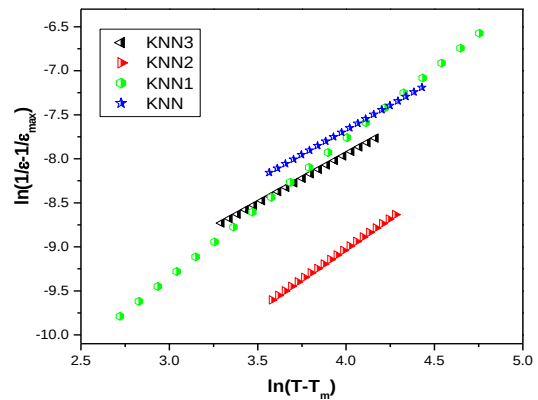


Figure 4. Modified Curie-Weiss fittings for all the KNN samples at 10 kHz

Figure 4 shows the best curve fit for γ of all the samples. The exponent γ is found to be in the range of 1.06 to 1.38. Lithium-ion radius is smaller when compared to the radii of other A- site ions (Sodium and Potassium cations). A known fact is that the Curie temperature can be effected by many factors such as stress, change in chemical composition, particle size, grain size and concentration of oxygen vacancies (Uchino *et al.*, (1981); Uchino *et al.*, 1989; Begg *et al.*, 1994; Albertson, 1998; Jung *et al.*, 2002; Lee, 2007; Dian *et al.*, 2017).

The diffusive phase transition can be described by an empirical parameter ΔT_{diff} , defined by Equation 4 (Uchino *et al.*, 1981).

$$\Delta T_{\text{diff}} = T_{0.9\epsilon_{\text{max}}(10\text{kHz})} - T_{\epsilon_{\text{max}}(10\text{kHz})} \quad (5)$$

The variation observed between the temperature corresponding to 90% of maximum of dielectric constant and maximum dielectric constant at high temperature side ($T_{0.9\epsilon_{\text{max}}}$). Both the values were extracted at a particular frequency, say 10 kHz. Piezoelectric values of KNN, KNN1, KNN2 and KNN3 are listed in Table 2. Among all the samples KNN1 has the maximum d_{33} value, compared to the rest of the samples. The piezoelectric coefficient of KNN is found to be the same as that of KNN2. Based on the above results it is concluded that changes in the transition temperature and other lattice parameters are attributed to different ionic radii of ions occupied at A- and B- sites.

Conclusions

The Zirconium, Lithium doped KNN ceramic samples were prepared by solid state reaction method. The single phase was confirmed by the XRD spectra. All the samples have shown higher densities. A slight changes observed in the lattice parameters were attributed to lattice stain, developed during the multiple ionic substitutions at A= ad B-sites. Substitution of Zr^{4+} into B site has increased the piezoelectric coefficient d_{33} and also high dielectric constant at Curie temperature. There are two peaks corresponding to phase transitions. First one corresponds to Orthorhombic to tetragonal and the second one represents tetragonal to cubic phase transition. This study shows that KNN1 and KNN3 are better compositions compared to pure KNN or KNN2.

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