Temperature dependent electrical properties of $0.95[(K_{0.5}Na_{0.5})_{(1-x)}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics

P. Palei · P. Kumar · S. Sonia

Abstract Lead free $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ (KNAN-LS) ceramics with $x=0.02$, 0.04, 0.06 and 0.08 have been synthesized by conventional solid state reaction route (CSSR). XRD analysis confirmed the presence of a mixed structure for $x=0.06$. The orthorhombic–tetragonal polymorphic phase transition (PPT) temperature and the Curie temperature (T_c) decreased with the increase in Ag^+ ion content in KNAN-LS ceramics. The relationship between the PPT of the ceramics and the temperature dependence of electrical properties of KNAN-LS ceramics were discussed in detail. The KNAN-LS ceramics with $x=0.06$ showed better piezoelectric and electromechanical properties ($d_{33}=227pC/N$ and $k_p=42.5$ %).

Keywords Perovskite · Poling temperature · Polymorphic phase transition temperature · Piezoelectric properties

1 Introduction

Lead oxide-based piezoelectrics, such as $(Pb_{0.52}Zr_{0.48})TiO_3$ (PZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT), are widely used for piezoelectric actuators, sensors and transducer applications because of having excellent piezoelectric properties and good thermal stability [1, 2]. The high piezoelectric response in these ceramics is attributed to the presence of a morphotropic phase boundary (MPB) between rhombohedral, tetragonal or monoclinic phases [3, 4]. However,

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lead is considered to be toxic and has been barred from many commercial applications. Therefore, in order to replace the lead-based ceramics it is necessary to develop lead-free piezoelectric materials with good temperature stability and excellent electrical properties [5]. According to previous reports, $K_{0.5}Na_{0.5}NbO_3$-$LiSbO_3$ (KNN-LS) ceramics have been considered good candidates for lead-free piezoelectric applications because of their better piezoelectric and ferroelectric properties compared to other lead free ferroelectrics [6]. The superior properties of KNN-LS ceramics over other lead free ceramics are attributed to the presence of the orthorhombic to tetragonal (T_{O-T}) polymorphic phase transition (PPT) near room temperature (RT) [7–9]. Recently, it has been reported that the so called MPB in KNN based ceramics is an orthorhombic to tetragonal polymorphic phase transition type [10]. The MPB in KNN based ceramics is not similar to the MPB in PZT based ceramics.. The phase boundary between orthorhombic and tetragonal phases in KNN based ceramics is not vertical and it shows strong temperature dependence behavior [10]. Hence, optimization of poling temperature (T_p) in KNN based ceramics is very important for achieving the desired piezoelectric properties. When T_p lies near to orthorhombic–tetragonal PPT temperature, non-180° domains can easily switch and be orientated owing to the coexistence of the orthorhombic and tetragonal phases [10]. Consequently, the higher degree of the domain alignment can be obtained, which results in large piezoelectric properties. Although, these KNN based ceramics shows excellent electrical properties at RT, however these properties are not stable over a temperature range [11, 12]. Therefore, from the viewpoint of high temperature applications, it is very important to improve the temperature stability of the electrical properties of KNN–LS ceramics. . Lei et al. reported that the substitution of Ag^+ ion for $(K_{0.5}Na_{0.5})^+$ ion in KNN ceramics resulted an improvement in the piezoelectric coefficient (d_{33})~186pC/N and

planar mode electromechanical coupling factor (k_p) ~42.5 % [13]. They also reported that the piezoelectric properties exhibit good thermal stability up to high temperature, which is a significant improvement in comparison to other KNN-based piezoceramics. Following this report, in the present work we have made an attempt to study the effect of Ag^+ ion substitution in the KNN-LS ceramics.

In this study, $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics with $x=0.02, 0.04, 0.06$ and 0.08 have been synthesized by CSSR. The effect of Ag^+ ion substitution on the structural and electrical properties of $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ has been investigated. The relationship between the PPT of the KNAN-LS ceramics and the temperature stability of electrical properties is studied in detail.

2 Experimental procedure

$0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ (KNAN-LS) ceramics with $x=0.02, 0.04, 0.06$ and 0.08 were synthesized by CSSR. Sodium carbonate (Na_2CO_3, 99.9 % purity), potassium carbonate (K_2CO_3), silver oxide (Ag_2O), niobium pentoxide (Nb_2O_5), lithium carbonate (Li_2CO_3) and antimony pentoxide (Sb_2O_5,) (all with 99.99 % purity) were used as starting precursors. Stoichiometric amounts of all the powders were mixed and ball milled with acetone for 8 h, using zirconia balls as the grinding media. The calcination of the powders was carried out at 850 °C for 6 h and single perovskite phase formation was confirmed by X-ray diffraction (XRD) technique. The calcined powders were mixed thoroughly with 2 wt% polyvinyl alcohol (PVA) binder solution and pressed into disks of diameter ~10 mm and a thickness ~1.5 mm under 60 MPa pressure. The sintering of all the ceramics was carried out at 1080 °C for 4 h in air, respectively with a heating rate of 5 °C/min. In order to examine the phases present in the ceramics, XRD analysis of the sintered KNAN-LS ceramics was performed on a PW 3020 Philips diffractometer using Cu Kα (λ=0.15405 nm) radiation. The sintered microstructures were observed using a JEOL JSM-6480LV scanning electron microscope (SEM). Silver paste was applied on both sides of the ceramics and fired at 500 °C for 30 min for good adhesion. Dielectric constant (ε_r) and dielectric loss (tanδ) were measured as a function of temperature using a computer interfaced HIOKI 3532–50 LCR-HITESTER. The ceramics for the piezoelectric property measurements were poled by corona poling in a temperature range of 35 °C–150 °C by applying a dc electric field of 5 kV/mm for 20 min. The d_{33} values of the ceramics were measured by piezo meter (YE2730A d_{33} Meter, APC International Ltd.). The planar mode electromechanical coupling coefficient (k_p) was calculated by resonance and anti-resonance frequencies, measured using HIOKI 3532–50 LCR-HITESTER. The temperature coefficient of k_p and

resonance frequency (f_r) were measured in a temperature range of 35–200 °C, using the equations:

$$\frac{\Delta k_p}{k_{p35°C}} = \frac{k_p - k_{p35°C}}{k_{p35°C}} \tag{1}$$

$$\frac{\Delta f_r}{f_{r35°C}} = \frac{f_r - f_{r35°C}}{f_{r35°C}} \tag{2}$$

3 Results and discussion

Figure 1 shows the XRD patterns of KNAN-LS ceramics, for different values of x, sintered at 1080 °C, respectively. Single perovskite phase peaks without any trace of secondary phase peaks is developed in all the KNAN-LS ceramics. This suggests that Ag^+ ions have completely diffused into the KNN-LS lattice to form homogeneous KNAN-LS solid solutions. It can be seen that the ceramics with $x=0.02$ possess orthorhombic structure. This orthorhombic structure is confirmed by matching the XRD patterns with the JCPDS card no. 71–2171. For $x=0.08$, the KNAN-LS ceramics possesses the tetragonal structure, which is indexed by JCPDS card no.71-0945. Therefore, it can be concluded that coexistence of orthorhombic and tetragonal structure is possible in KNAN-LS ceramics for $0.04 \leq x \leq < 0.08$ [14, 15].

The relative densities (RD) of the KNAN-LS ceramics are given in Table 1. It is found that initially RD increases with the increase in x content up to 0.06 and with the further increase in x content, the RD decreases. The initial increase of RD may be due to the lower decomposition temperature of Ag_2O (~280 °C), which improves the sintering of the ceramics with the formation of liquid phase. The decrease of RD at higher x content may be due to the formation of more amount of liquid phase, which is undesirable [16]. The results shows that the optimum amount of Ag^+ ion content in $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics is $x=0.06$.
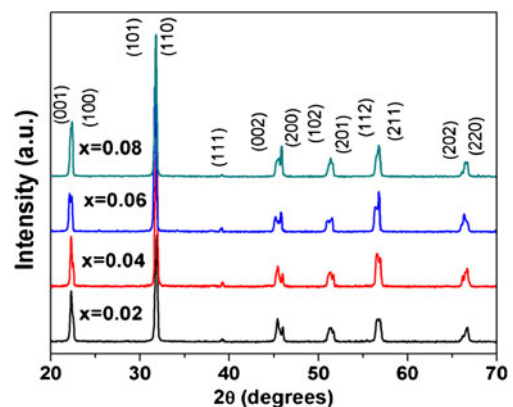
Fig. 1 XRD patterns of $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C
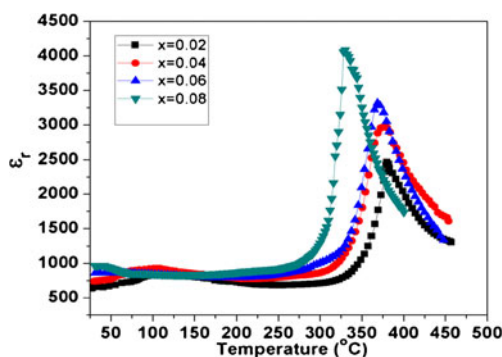
Table 1 Electrical properties, Relative density (RD) and phase transition temperatures of $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ($x=$ 0.02, 0.04, 0.06 and 0.08) ceramics

x	0.02	0.04	0.06	0.08
d_{33}(pC/N)	143	157	227	186
k_p	0.35	0.36	0.425	0.38
ε_r(10 kHz)	633	740	858	941
T_c(°C)	380	376	368	331
$T_{o\text{-}t}$(°C)	120	101	65	Below RT
RD (%)	95 %	95.5 %	96.5 %	95.7 %

The temperature dependent behavior of dielectric constant (ε_r) at 10 kHz frequency of KNAN-LS ceramics is shown in Fig. 2. Similar to pure KNN ceramics, above RT two phase transitions are observed in all the KNAN-LS ceramics except for $x=0.08$. The first phase transition temperature corresponds to orthorhombic-tetragonal transition ($T_{o\text{-}t}$) and the second one is ferroelectric-paraelectric (the Curie temperature, T_c). With the increase in x content, there is a decrement in both these phase transition temperatures. It is found that for the KNAN-LS ceramics with $x=0.02$, the $T_{o\text{-}t}$ and T_c occurs at $\sim$120 °C and $\sim$380 °C, whereas for $x=0.06$ the $T_{o\text{-}t}$ and T_c occurs at$\sim$65 °C and $\sim$368 °C, respectively. For the KNAN-LS ceramics with $x=0.08$, the $T_{o\text{-}t}$ goes below RT. The T_c of the ferroelectric samples with a perovskite structure is generally proportional to the tolerance factor "t", which is estimated by the following formula:

$$t = (r_A + r_O)/\sqrt{2}\ r_B + r_O$$

where r_A, r_B, and r_O represent ionic radii of A-site cation, B-site cation, and oxygen ion, respectively [4]. In KNAN-LS ceramics, Ag^+ ions occupy the A-site. Since the ionic radius of Ag^+ ions is slightly lower than that of K^+ and Na^+ ions, the Ag^+ ions doping is expected to lower the tolerance factor t, and hence the T_c of the sample decreases with increase in Ag^+ ions content in KNAN-LS ceramics. Also, the decrease of $T_{o\text{-}t}$ and T_c implies that stability of orthorhombic phase and tetragonality in the ceramic is decreasing and the fraction of orthorhombic phase at RT in the KNAN-LS samples is decreasing with the increase in x content. The values of ε_r, $T_{o\text{-}t}$ and T_c of different KNAN-LS ceramics are given in Table 1.

The temperature dependence of dielectric loss (tanδ) at 10 kHz frequency of KNAN-LS ceramics is shown in Fig. 3. It can be seen that with the increase in x content tanδ values at RT decreases, which may be due to the increase in bulk density in the ceramics with the increase in x content. The values of tanδ in case of the KNAN-LS ceramics with $x=0.06$ remain very low in a wide temperature range.

Figure 4 shows the effect of poling temperature on the d_{33} and k_p piezoelectric coefficients. As shown in Fig. 4, the T_p has an obvious effect on the piezoelectric properties of the KNAN-LS ceramics and the piezoelectric properties reach maximum values when $T_p \rightarrow T_{o\text{-}t}$. Maximum values of piezoelectric coefficient (d_{33})$\sim$227 pC/N and planar mode coupling coefficient (k_p)$\sim$0.425 are obtained in case of KNAN-LS ceramics (with $x=0.06$) when T_p is near PPT, which are better than the pure KNN-LS ceramics, reported in our earlier work [17]. The improvement of the piezoelectric properties of KNAN-LS (with x=0.06) ceramics, poled at optimum T_p (near RT), is due to the fact that at PPT simultaneously orthorhombic and tetragonal phases coexist, which increases the number of available polarization directions.

Figure 5 shows the temperature dependence of planar mode electromechanical coupling coefficient (k_p). It can be seen that in all the KNAN-LS ceramics maximum value of k_p is obtained near PPT. This may be again due to the presence of both orthorhombic and tetragonal structures near PPT. It has been suggested that the domain structure of the KNN-based ceramics near PPT region is the coexistence of orthorhombic (O) and tetragonal (T) polarized domains. There are 12 possible spontaneous polarization (Ps) directions for the O phase and six possible Ps directions for the T phase. The presence of more number of possible polarization states near PPT facilitates better poling and hence improves the piezoelectric properties [18]. However,
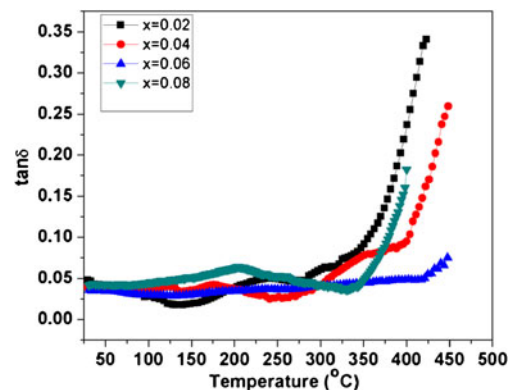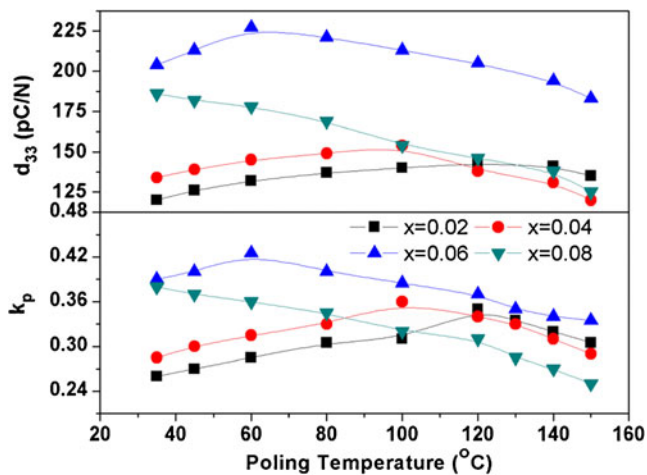

Fig. 2 Temperature dependence of dielectric constant (ε_r) at 10 kHz of $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C

Fig. 3 Temperature dependence of dielectric loss (tanδ) at 10 kHz of $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C

Fig. 4 k_p and d_{33} piezoelectric coefficients as a function of poling temperature for the $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C

near the PPT, the temperature stability of the electromechanical properties of KNAN-LS ceramics becomes worse [19]. In the present case, the thermal stability of k_p of KNAN-LS ceramics with $x=0.08$ is found to be better in comparison to the other ceramics, which may be due to the shifting of PPT below RT. For all the KNAN-LS ceramics, beyond T_{o-t} the value of k_p decreases rapidly and reaches to0 at the T_c. This decrease of k_p at higher temperature is due to the thermal depoling of the KNAN-LS ceramics.. It is known that for a ceramic to be used in high power applications, it should have high frequency constant (N_p).. N_p is calculated by using the equation:

$$N_p = f_r \times L \qquad (3)$$

where L is the diameter and f_r is the resonant frequency of the sample [20]. Figure 6 shows the temperature dependence of frequency constant (N_p) of KNAN-LS ceramics. It can be seen that near PPT, the value of N_p attains a minimum value
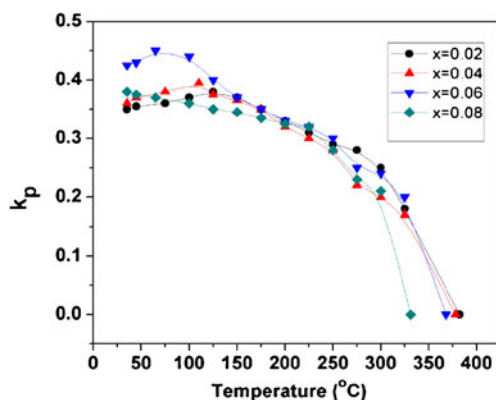

Fig. 5 Temperature dependence of the Plannar mode coupling coefficient (k_p) for the $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C
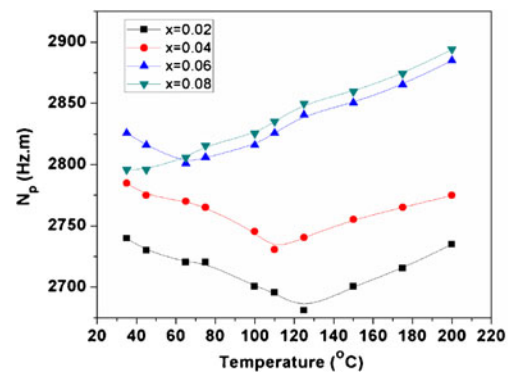
Fig. 6 Temperature dependence of the frequency constant (N_p) for the $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C

and then increases with the further increase in temperature for all the KNAN-LS ceramics except for $x=0.08$. Since the PPT is below RT for KNAN-LS ceramics with $x=0.08$, therefore the minima of N_p near PPT is not observed. It is known that N_p is inversely proportional to elastic compliance. Elastic compliance (s) is defined as the strain produced in a piezoelectric material per unit of stress applied and it is the reciprocal of the modulus of elasticity (Young's modulus, Y). Therefore, the decrease of N_p means the increase of elastic compliance. The reason behind the minimum value of N_p near PPT in KNAN-LS ceramics may be due to the change in mechanical hardness of samples and/or the bonding strength of ionic constituents in NbO_6 octahedral at the phase transition [21]. The variations of $\Delta f_r/f_{r35°C}$ and $\Delta k_p/k_{p35°C}$ in the temperature range of 35 °C to 200 °C for the KNAN-LS ceramics are shown in Fig. 7. It is well known that $\Delta f_r/f_{r35°C}$ and $\Delta k_p/k_{p35°C}$ are two important performance factors of the piezoelectric ceramics. The variation of $\Delta f_r/f_{r35°C}$ is found to be exactly opposite to the variation of $\Delta k_p/k_{p35°C}$. Similar to the variation of N_p, the value of $\Delta f_r/f_{r35°C}$ decreases with the increase in temperature up to PPT in all KNAN-LS
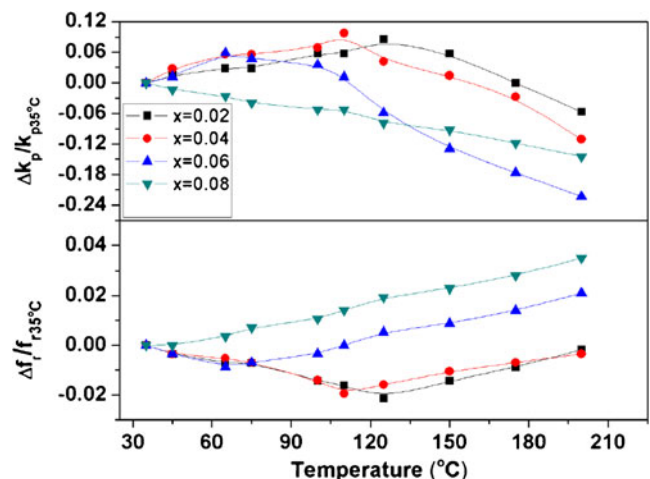
Fig. 7 Variations of $\Delta f_r/f_{r35°C}$ and $\Delta k_p/k_{p35°C}$ with temperature for $0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ ceramics sintered at 1080 °C

ceramics except for $x=0.08$. Whereas the value of $\Delta k_p/k_{p35°C}$ increases with the increase in temperature up to PPT and then decreases with further increase in temperature due to thermal depoling of the KNAN-LS ceramics except for $x=0.08$.

4 Conclusions

$0.95[(K_{0.5}Na_{0.5})_{1-x}Ag_xNbO_3]$-$0.05LiSbO_3$ $(x=0.02–0.08)$ ceramics with good piezoelectric properties were prepared by conventional solid state reaction route. The best piezoelectric properties of $d_{33}\sim227pC/N$ and $k_p\sim42.5$ % were obtained in KNAN-LS ceramics with x=0.06. Mixed phase was found in KNAN-LS ceramics for $0.04\leq x\leq0.08$, which played an important role in the enhancement of the piezoelectric properties. Optimization of T_p was found to be an effective approach to achieve desired piezoelectric properties. The results in this study showed that the KNAN-LS ceramics with x=0.06 can be an effective candidate for lead-free piezoelectric applications.

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