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Synthesis and characterizations of KNN ferroelectric ceramics near 50/50 MPB

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Abstract

Lead free ferroelectric ceramics near the morphotropic phase boundary (MPB) of $K_xNa_{1-x}(NbO_3)$/KNN system (where $x=0.48$, 0.50, 0.52) were synthesized in the single perovskite phase by the partial co-precipitation synthesis route. The compositional dependences of phase, structure and electrical properties were studied in detail. X-ray diffraction (XRD) study revealed the coexistence of orthorhombic and monoclinic structures in $K_{0.50}N_{0.50}NbO_3$. SEM characterization of the sintered KNN ceramics revealed dense and homogeneous packing of grains. Room temperature (RT) dielectric constant (ε_r) ~648, dielectric loss (tan δ) ~0.05 at 100 kHz, a relatively high density (ρ) ~4.49 g/cm^3, remnant polarization (P_r) ~11.76 μC/cm^2, coercive field (E_c) ~9.81 kV/cm, Curie temperature (T_c) ~372 °C and piezoelectric coefficient (d_{33}) ~71 pC/N observed in $K_{0.50}N_{0.50}NbO_3$ suggested that it can be an important lead free ferroelectric material.

Keywords: Perovskite; Dielectric properties; Ferroelectric properties; KNN

1. Introduction

KNN is a solid solution of potassium niobate (KN), a ferroelectric (orthorhombic), and sodium niobate (NN), an anti-ferroelectric (orthorhombic) system. This KNN system possesses an MPB similar to that of the PZT system when the Na/K ratio is ~50/50. As a result of this the piezoelectric, ferroelectric and electromechanical properties of KNN near this MPB are expected to be good and studied in detail [1–9]. KNN near this MPB have been reported to possess high piezoelectric response and good dielectric properties [1,10]. Dense ceramics with a high piezoelectric constant (d_{33}) of ~148 pC/N were achieved by Li et al. using advanced processing methods in $K_{0.50}N_{0.50}NbO_3$ composition [11]. Recently, exceptionally high piezoelectric properties were reported in the $(K,Na)NbO_3$–$LiTaO_3$–$LiSbO_3$ system [12]. This study was based on chemical modifications in the vicinity of the MPB of KNN system by complex simultaneous substitutions in the A (Li) and B (Ta and Sb) sites of the perovskite lattice. In this paper d_{33} values over 400 pC/N were reported for textured ceramics prepared by a complex processing method. The excellent piezoelectric and dielectric properties in the KNN near 50/50 MPB are because of the co-existence of mixed structures [13]. But, this MPB is not clearly marked and the researchers have mainly focused their study on 50/50 MPB. But, a major problem concerning KNN ceramics is to optimize the sintering temperature by the conventional solid state reaction (CSSR) route for several reasons [6]. Therefore, it is a challenge for the researchers to obtain better sintered KNN ceramics. It was also reported that KNN based ceramics were sensitive to moisture and only hot-pressed samples could be sufficiently densified [14]. Recently developed spark plasma sintering is another technique to produce dense bulk samples of KNN ceramics with a relative density higher than 99% [15]. Although these methods can yield high densities and better piezoelectric properties compared to KNN ceramics synthesized by the CSSR route, still it is obvious that normal or pressureless

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sintering of these materials is more suitable for mass production.

Therefore, in the present work, potassium sodium niobate (KNN) systems in the 50/50 MPB region with three different compositions have been synthesized by the partial co-precipitation method. The structural, microstructural, dielectric and ferroelectric properties have been investigated and discussed in detail.

2. Experimental procedure

The MPB compositions of lead free KNN system were synthesized by partial co-precipitation process. Sodium carbonate (Na_2CO_3, 99% purity), potassium carbonate (K_2CO_3, 99% purity) and nobium pentoxide (Nb_2O_5, 99% purity) were used as starting precursors. Initially, the niobium pentoxide powder was ball milled in distilled water separately for 14 h using zirconia balls as the grinding media. The resulting slurry was dried in an oven at 130 °C for 1 h. K_2CO_3 and Na_2CO_3 are hygroscopic in nature therefore during processing of KNN ceramics extra care has been taken. $K_xNa_{1-x}NbO_3$ ($x=0.48$, 0.50, 0.52) MPB compositions were prepared by mixing the stoichiometric amount of K_2CO_3 and Na_2CO_3 powders in the glass beaker containing distilled water and transparent solutions were prepared by stirring. The stoichiometric amount of Nb_2O_5 powder was weighed and added to the transparent solution of K_2CO_3 and Na_2CO_3 followed by continuous stirring and heating. The resulting solution was then dried in an oven for 10 h at 130 °C in order to remove the water. Calcination of the three materials was carried out at 700 °C for 6 h. The calcined powders were mixed with 2 wt% polyvinyl alcohol (PVA) and pressed into disks of ~10 mm diameter and ~1.5 mm thickness using a hydraulic press under a pressure of ~60 MPa. The sintering of the green disks was carried out at 1080 °C for 6 h. The experimental density of the sintered samples was determined using the Archimedes method. The phase and structure were examined by XRD analysis on a PW 3020 Philips diffractometer using CuK_α ($\lambda=1.5405$ Å) radiation. The sintered microstructures were observed using a JEOL T-330 scanning electron microscope (SEM). Silver paste was applied on both sides of the samples and fired at 500 °C for 30 min for the electrical measurements. The dielectric measurements of the samples were carried out in a temperature range from RT to 450 °C by using a computer interfaced HIOKI 3532-50 LCR-HITESTER at 100 kHz frequency. The polarization vs. electric field (P–E) hysteresis loops of the samples were measured by using a computer interfaced conventional Sawyer–Tower circuit. The samples for the piezoelectric property measurements were poled by using a corona poling unit at a temperature of 150 °C (below Curie temperature) by applying a dc electric field of ~3 kV/mm for 30 min. The d_{33} values of the samples were measured by using a d_{33} meter (YE2730A d_{33} Meter, APC International Ltd.).

3. Results and discussion

Fig. 1 shows the XRD patterns of calcined KNN system. with three MPB compositions. XRD peaks confirmed the development of single perovskite phase in all the MPB ceramics of KNN system without any trace of secondary phase peaks. The observed sharp and distinct XRD peaks of MPB ceramics of KNN system suggest good crystallinity and homogeneity of the samples [8,16]. The diffraction lines are indexed in different crystal systems and unit cell configurations using a computer program package 'Powdmult' [17]. Crystal structures were selected with minimum standard deviations, SD, $\sum\Delta d = (d_{obs}-d_{cal})$, where '$d$' is inter-plane spacing. The crystal structures of $K_{0.48}N_{0.52}NbO_3$ and $K_{0.52}N_{0.48}NbO_3$ are monoclinic and orthorhombic, respectively whereas coexistence of orthorhombic and monoclinic structures is found in $K_{0.50}N_{0.50}NbO_3$. The lattice parameters with structures of KNN system with MPB compositions are given in Table 1. The existence of double structures in $K_{0.50}N_{0.50}NbO_3$ confirms the MPB nature at this composition [18].

Fig. 2 shows the variation of experimental density (d_{ex}) of MPB ceramics of KNN system as a function of potassium (K) content. The d_{ex} is found to be ~4.31 g/cm^3, 4.49 g/cm^3 and 4.38 g/cm^3 in $K_{0.48}N_{0.52}NbO_3$, $K_{0.50}N_{0.50}NbO_3$ and $K_{0.52}N_{0.48}NbO_3$ compositions, respectively. The d_{ex} is found to be maximum. for $K_{0.50}N_{0.50}NbO_3$ MPB composition.

Fig. 3 shows the SEM micrographs of the KNN ceramics sintered at 1080 °C. The SEM micrographs reveal clear grain boundary with regular shaped grains. Inhomogeneous distribution of grains can be seen in $K_{0.48}N_{0.52}NbO_3$ and $K_{0.52}N_{0.58}NbO_3$ ceramics. Less porosity and relatively better homogeneity of grains in the $K_{0.50}N_{0.50}NbO_3$ ceramic suggest that the presence of mixed structure increases the

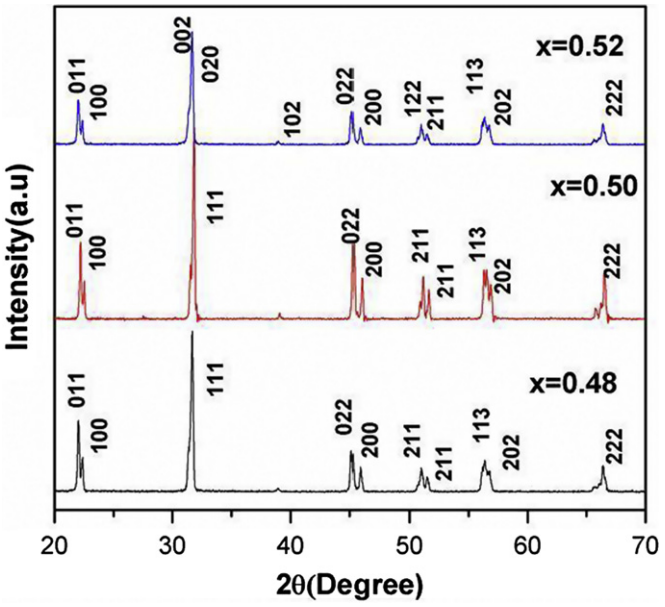

Fig. 1. XRD patterns of MPB compositions of $K_xNa_{1-x}NbO_3$ system ($x=0.48$, 0.50, 0.52) calcined at 700 °C.

Table 1
Structure, lattice parameter, grain size, remnant polarization and coercive field at MPB compositions of the $K_XNa_{1-X}NbO_3$ system (x=0.48, 0.50, 0.52).

Compositions	Structure	Lattice parameters	P_r (μC/cm^2)	E_c (KV/cm)
$K_{0.48}Na_{0.52}NbO_3$	Monoclinic	a=4.1321 Å, b=4.0341 Å c=7.3538 Å	6.3	5.1
$K_{0.50}Na_{0.50}NbO_3$	Monoclinic + Orthorhombic	a=5.6729 Å, b=5.6424 Å, c=3.9447 Å, a=5.6423 Å, b=5.6732 Å, c=3.9445 Å	9.84	10.93
$K_{0.52}Na_{0.48}NbO_3$	Orthorhombic	a=39.2630 Å, b=8.1183 Å, c=6.0457 Å	9.8	11.77

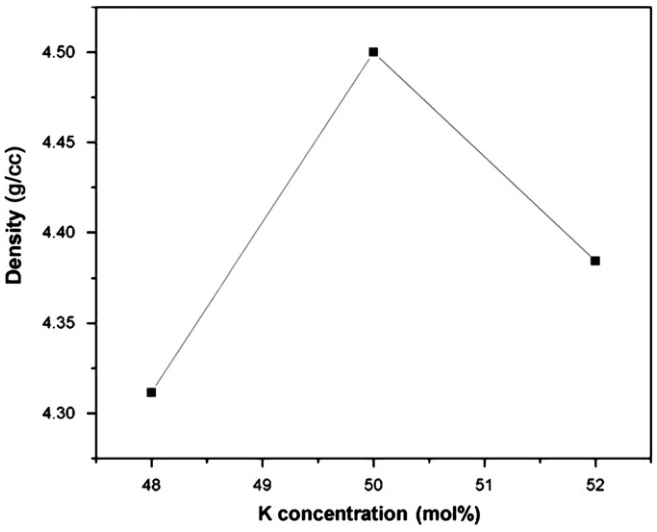

Fig. 2. Density at MPB compositions of $K_XNa_{1-X}NbO_3$ system (x=0.48, 0.50, 0.52).

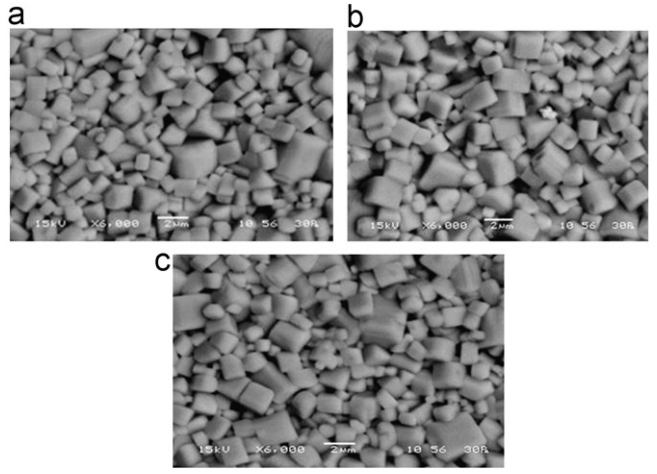

Fig. 3. SEM micrographs at MPB compositions of $K_XNa_{1-X}NbO_3$ system (x=0.48, 0.50, 0.52).

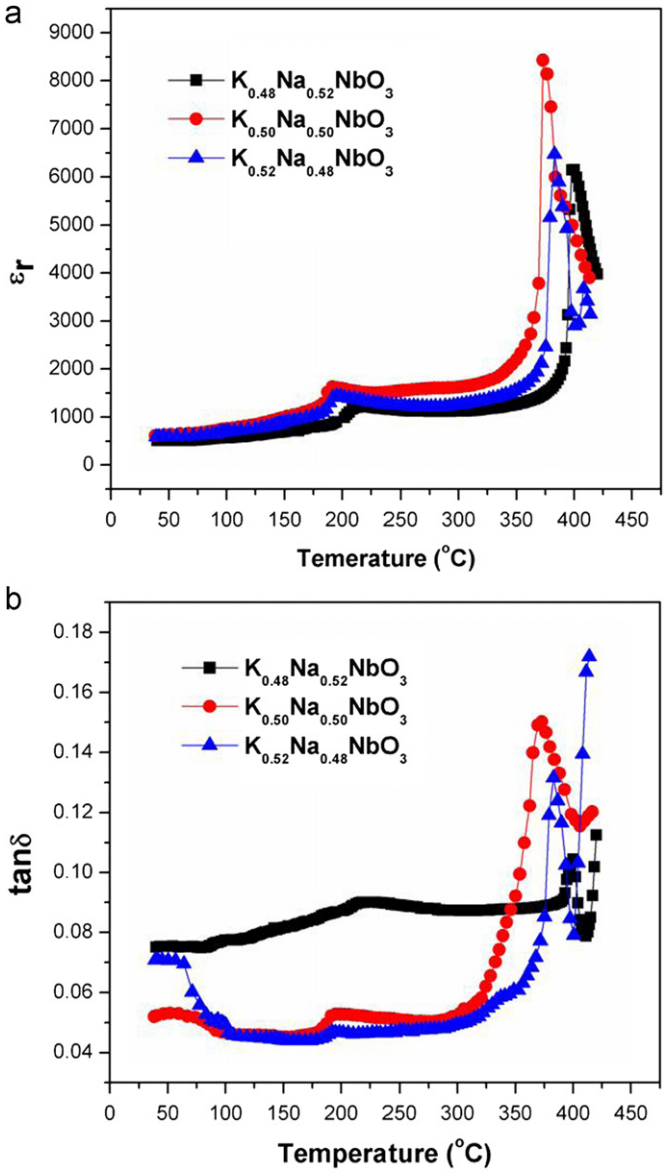

Fig. 4. (a) Variation of ε_r and (b) tan δl vs. temperature at 100 kHz at MPB compositions of $K_XNa_{1-X}NbO_3$ system (x=0.48, 0.50, 0.52).

mass transportation, which results in better and homogeneous grain growth [19]. Homogeneous distribution of grains helps in good densification, which is confirmed by the highest experimental density of $K_{0.50}N_{0.50}NbO_3$ ceramic. The melting temperatures of alkali elements and in the KNN system are low and therefore liquid phase sintering takes place in KNN ceramics. Generally this gives rise to the inhomogeneous distribution of grains in KNN based ceramics [20]

Fig. 4(a) and (b) shows the temperature dependence of dielectric constant (ε_r) and dielectric loss (tan δ) at 100 kHz frequency of different MPB compositions of the KNN

system. It is evident from Fig. 4(a) that two sharp phase transitions are observed in ε_r vs. temperature behavior. The value of ε_r increases with the increase in temperature at all MPB compositions. In the high temperature region, the higher value of ε_r may be due to the contributions from space charge polarization, which comes from mobility of ions and imperfections in the material. These combined effects produce a sharp increase in the value of ε_r with the increase in temperature. Further, with the increase of potassium concentration from $x=0.48$ to 0.52 in the KNN system, the ferroelectric–paraelectric phase transition temperature (T_C) decreases. The highest value of ε_r ~8.430 at T_C is observed in $K_{0.50}N_{0.50}NbO_3$ ceramics. The highest value of ε_r in $K_{0.50}N_{0.50}NbO_3$ ceramics can be explained on the basis of the mixed structure nature at this MPB composition. It is well known that the mixed structure nature at a composition increases the non-polar nature which in turn increases the polarization within the material [13]. The larger the polarization within a material, the larger is the value of ε_r.

Fig. 4(b) shows the temperature dependence of dielectric loss (tan δ) at 100 kHz at the different MPB compositions of the KNN system. The behavior of tan δ is very much similar to that of ε_r i.e. two similar kinds of transition peaks are also observed here. It is observed that a higher value of tan δ is obtained with increasing temperature which may be due to the increase in the mobility of ions and imperfections in the material [21]. The temperatures of peak dielectric loss and peak dielectric constant do not coincide. The Kramers–Kronig relation indicates that this can be the consequence of temperature dependent relaxation near the Curie temperature [18]. A modified empirical expression was proposed by Uchino and Nomura to describe the diffuseness of ferroelectric phase transition:

$$1/\varepsilon - 1/\varepsilon_{max} = (T - T_{max})^{\gamma}/C \quad (1)$$

where T_m is the temperature (corresponding to ε_{max}) at which ε value reaches the maximum. γ and C are assumed to be constant, and the γ value is between 1 and 2. The limiting value $\gamma=1$ makes the equation fit the conventional Curie–Weiss law which is valid for the normal ferroelectrics and the limiting value $\gamma=2$ makes the equation fit the materials having diffusive phase transition nature, normally the characteristic of relaxor ferroelectric systems [9,22,23]. γ value between 1 and 2 corresponds to an incomplete diffuse phase transition, where the correlated ferroelectric clusters are hypothesized [22–24]. Fig. 5 shows the graphs between $\log(1/\varepsilon - 1/\varepsilon_{max})$ *vs.* $\log(T - T_{max})$. Diffusiveness factor (γ) is found to be maximum for the $K_{0.50}N_{0.50}NbO_3$ MPB composition. The increase in diffuse phase transition in $K_{0.50}N_{0.50}NbO_3$ suggests that the presence of double structures increases the structural disorder and compositional fluctuations, which leads to increase in the diffusive nature of phase transition.

Fig. 6 shows the *P–E* hysteresis loops at different MPB compositions of the KNN system. The remnant polarization (P_r) increases with the increase in K content in the KNN

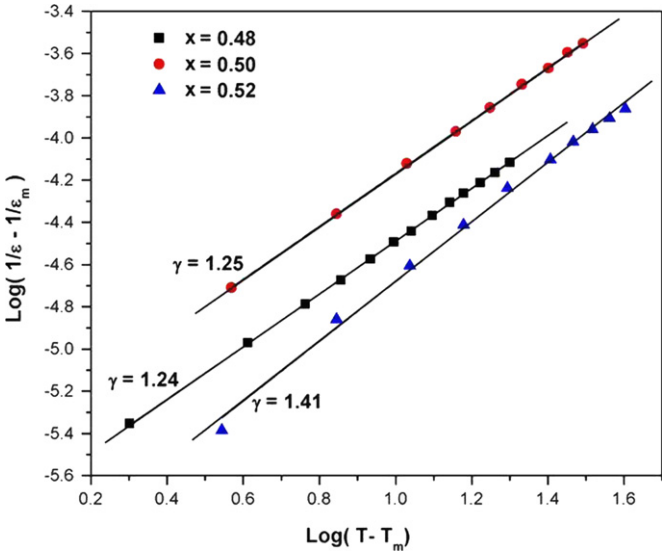

Fig. 5. Variation of $\log(1/\varepsilon - 1/\varepsilon_{max})$ vs. $\log(T - T_{max})$ of MPB compositions of $K_XNa_{1-X}NbO_3$ system ($x=0.48$, 0.50, 0.52).

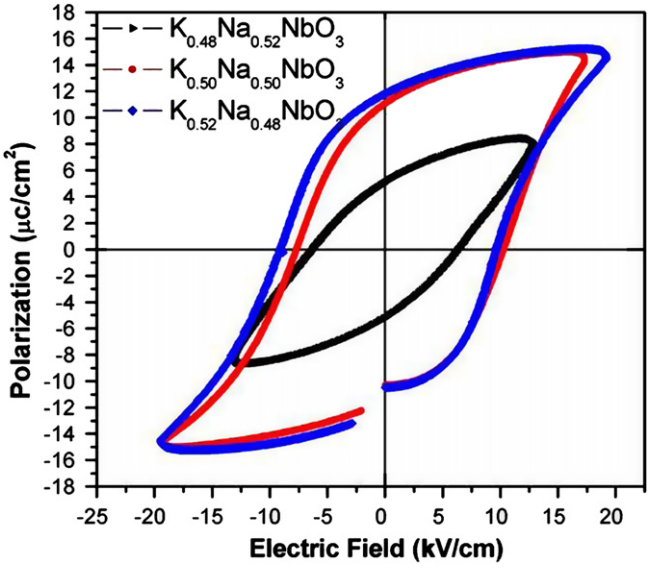

Fig. 6. P–E hysteresis loops of MPB compositions of $K_XNa_{1-X}NbO_3$ system ($x=0.48$, 0.50, 0.52).

system and well saturated hysteresis loops are obtained for $K_{0.50}N_{0.50}NbO_3$–$K_{0.52}N_{0.48}NbO_3$. The remnant polarization (P_r) and the coercive field (E_c) of the MPB compositions are given in Table 1. The piezoelectric constants (d_{33}) are found to be ~52 pC/N, 71 pC/N and 66 pC/N, respectively for $x=0.48$, 0.50, and 0.52 in the $K_xNa_{1-x}(NbO_3)$ system. The maximum value d_{33}~71 pC/N is obtained in case of $K_{0.50}N_{0.50}NbO_3$ ceramics. This can again be explained on the basis of mixed structure nature at this MPB composition. It is well known that the mixed structure nature at a composition increases the non-polar nature, which in turn helps in better poling of the material [13]. Better poling leads to higher value of piezoelectric constant (d_{33}). The present

study shows that the $K_{0.50}N_{0.50}NbO_3$ ceramic can be a good candidate for piezoelectric applications.

4. Conclusions

The $K_xNa_{1-x}(NbO_3)$ (KNN) system at MPB compositions (where $x=0.48$, 0.50, 0.52) was synthesized in the single perovskite phase by partial co-precipitation synthesis route. Coexistence of orthorhombic and monoclinic structures confirmed the MPB nature of $K_{0.5}0N_{0.50}NbO_3$. Maximum values of ε_r and piezoelectric constant (d_{33}) were obtained in $K_{0.5}N_{0.5}NbO_3$. Present study showed that the actual MPB composition of KNN system corresponds to Na/K ratio 50/50 and the ceramics corresponding to this composition can be a good candidate for dielectric and piezoelectric applications.

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