

## Piezoelectric and dielectric properties of $\text{Li}_x(\text{K}_{0.46}\text{Na}_{0.54})_{1-x}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$ lead-free ceramics

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**Abstract:** Lead-free piezoelectric ceramics  $\text{Li}_x(\text{K}_{0.46}\text{Na}_{0.54})_{1-x}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$  (with  $x$  ranging from 0 to 0.1) were synthesized by conventional solid state sintering method. The effect of cationic substitution of Li for K and Na in the A sites of perovskite lattice on the structure, phase transition behavior and electrical properties were investigated. Morphotropic phase boundaries(MPB) between orthorhombic and tetragonal phase are found in the composition range of  $0.06 \leq x \leq 0.08$ . Analogous to  $\text{Pb}(\text{Zr,Ti})\text{O}_3$ , the dielectric and piezoelectric properties are enhanced for the composition near the morphotropic phase boundary. The  $\text{Li}_{0.06}(\text{K}_{0.46}\text{Na}_{0.54})_{0.94}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$  ceramics show excellent electrical properties, that is, piezoelectric constant  $d_{33}=215$  pC/N, planar electromechanical coupling factor  $k_p=41\%$ , dielectric constant  $\epsilon_{33}^T/\epsilon_0=1303$ , and dielectric loss  $\tan \delta=2.45\%$ . The results indicate that  $\text{Li}_x(\text{K}_{0.46}\text{Na}_{0.54})_{1-x}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$  ceramic is a promising lead-free piezoelectric material.

**Key words:** lead-free ceramics; piezoelectric ceramics; piezoelectric property; dielectric property

### 1 Introduction

The most widely used piezoelectric ceramics are lead oxide based ferroelectrics, especially  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT). Specifically, compositions are formulated at around  $x=0.47$ , corresponding to a morphotropic phase boundary(MPB) separating ferroelectric rhombohedral and tetragonal phases, whereupon the dielectric and piezoelectric properties are greatly enhanced[1]. However, the toxicity of lead oxide and its high vapor pressure during processing have led to a demand for alternative lead-free piezoelectric materials. The search for alternative piezoelectric materials is now focused on alkali niobates, modified bismuth titanates, and systems in which a MPB occurs[2–5]. Among them,  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  (NKN) has been considered a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity and ferroelectricity. The hot pressed NKN ceramics (about 99% of the theoretical density) have been reported to possess a high Curie

temperatures ( $\approx 420$  °C), a large piezoelectric responses ( $d_{33}\approx 160$  pC/N), and a high planar coupling coefficient ( $k_p\approx 45\%$ )[6–9]. However, NKN ceramics sintered by ordinary sintering show relatively lower electrical properties ( $d_{33}=70$  pC/N,  $k_p=25\%$ ) due to the difficulty in obtaining a high density by conventional preparation and sintering in air[10]. Therefore, various techniques, such as hot pressing[8], cold-isostatic pressing[11], and spark plasma sintering[12–13], have been utilized to improve the electrical properties of NKN ceramics. Since these techniques were found to be unsuitable for use in industrial production, many studies were conducted by several researchers in order to prepare KNN based ceramics by conventional solid state sintering method and without cold-isostatic pressing(CIP) process. And the result showed that NKN based ceramics doped with Li, Ta, and Sb showed excellent piezoelectric and electromechanical properties due to the formation of a MPB between orthorhombic and tetragonal ferroelectric phases[14–15].

The textured  $(\text{K}_{0.44}\text{Na}_{0.52}\text{Li}_{0.04})(\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04})\text{O}_3$

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ceramics reported by SAITO et al[16] show excellent properties ( $d_{33}=416$  pC/N,  $k_p=0.61$ ), and proper Ta substitution for Nb could enhance the properties of  $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.96-x}Ta_xSb_{0.04})O_3$ [17]. For  $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$  perovskite ceramics, Li, Na and K occupy the A sites, while Ta, Sb and Nb occupy the B site[16–17] of  $ABO_3$  perovskite structure. However, there have been few studies on the effects of Li-substitution (A site substitution) on the properties of this system.

In this work,  $Li_x(K_{0.46}Na_{0.54})_{1-x}Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$  piezoelectric ceramics were synthesized by traditional solid state sintering process, without sintering aids, cold-isostatic pressing or special powder handling. The effects of cationic substitution of Li for K and Na in the A sites of perovskite lattice on the structure, phase transition behavior and electrical properties were investigated, to determine the existence of MPB and the enhancement of the properties for  $Li_x(K_{0.46}Na_{0.54})_{1-x}Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$  systems.

## 2 Experimental

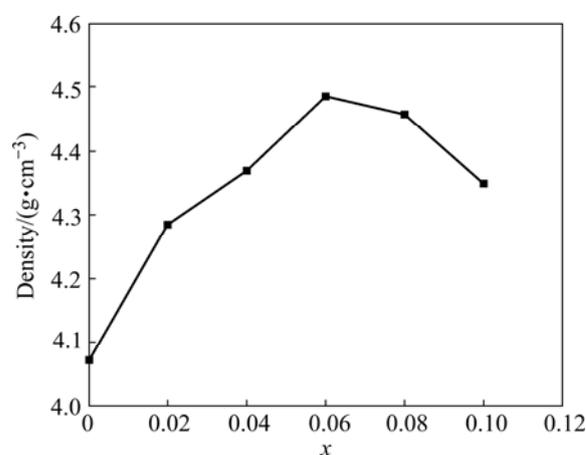
$Li_x(K_{0.46}Na_{0.54})_{1-x}Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$  piezoelectric ceramics (abbreviated as NKNTS- $x$ Li, with  $x$  ranging from 0 to 0.1) were prepared by a conventional mixed-oxide technique using commercially available metal oxides or carbonate powders:  $Na_2CO_3$ ,  $KCO_3$ ,  $LiCO_3$ ,  $Nb_2O_5$ ,  $Ta_2O_5$  and  $Sb_2O_3$ . The powders were weighed and mixed well in alcohol with zirconium balls by ball-milling for 10 h. The calcination was then conducted at  $850$  °C for 4 h. The calcined mixture was ball-milled in alcohol again for 6 h. After drying, it was mixed thoroughly with a PVA binder solution and uniaxially pressed into disk samples with a diameter of 20 mm and a thickness of 2 mm. The disk sample was then sintered at  $1100$  °C for 2 h in air. The crystallite structure of the sintered sample was examined using an X-ray diffractometer (XRD, D/Max-3C, Japan) with  $Cu K_\alpha$  radiation. The lattice parameters were refined by the least-square method. Density was measured by the Archimedes method with distilled water.

Silver paste was applied to the top and bottom surfaces of the samples as electrodes. The ceramic samples were polarized under a dc field of 3 kV/mm at  $100$  °C in a silicon oil bath for 15 min. Piezoelectric constant  $d_{33}$  of the samples was measured by means of quasistatic  $d_{33}$  meter (ZJ-3A) based on Berlincourt method. Dielectric constant  $\epsilon_{33}^T/\epsilon_0$  was obtained by measuring the capacitance at 1 kHz using an impedance analyzer (HP4192A). Resonance measurements were performed using an impedance analyzer (HP 4294A). The electromechanical coupling factors  $k_p$  were calculated from the resonance and the anti-resonance

frequencies according to ONOE'S formula[18].

## 3 Results and discussion

Fig.1 shows the dependence of density ( $\rho$ ) on the chemical composition for the NKNTS- $x$ Li ceramics sintered at  $1100$  °C. The density ( $\rho$ ) of the ceramics bodies increases with increasing  $x$  initially, reaches the maximum at  $x=0.06$  ( $\rho=4.48$  g/cm<sup>3</sup>) and then decreases with further increase in  $x$  value. By adding  $Li_2CO_3$  with the low melting point ( $618$  °C), the liquid formation promotes the sintering of NKNTS- $x$ Li ceramics, hence leading to an increase in the density of ceramics. Further increasing the Li content makes  $1100$  °C too high for sintering NKNTS- $x$ Li ceramics and causes the density to decrease.



**Fig.1** Density as function of composition for NKNTS- $x$ Li system

Fig.2(a) shows the X-ray diffraction(XRD) patterns of NKNTS- $x$ Li ceramics. All the samples are of single perovskite structure and no second phase can be detected, which indicates that Li elements have diffused into the perovskite lattice to form a solid solution. In this case, Li can replace Na and K in the A sites of  $ABO_3$  perovskite structure. Fig.2(b) shows the magnification of Fig.2(a) in the range from  $40^\circ$  to  $55^\circ$ . Fig.3 shows the variations of the lattice parameters as a function of Li content. Combining Fig.2(b) and Fig.3, it can be seen that the NKNTS- $x$ Li ceramics have orthorhombic structures in the case of  $x \leq 0.06$ . With increasing Li content ( $x=0.08, 0.1$ ), however, the structure changes from orthorhombic to tetragonal. The presence of an orthorhombic to tetragonal MPB is indicated in the solid solution range from  $0.06 < x < 0.08$ , as evidenced by the changes of the peaks of XRD patterns shown in Fig.2 and values of lattice parameters shown in Fig.3. The structure of solid solutions transforms from orthorhombic to tetragonal probably due to a distortion of octahedra caused by the

$\text{Li}^+$  ions occupying the A site of NKNTS lattice, which slightly increases the tolerance factor of a  $\text{ABO}_3$  perovskite structure,  $t = (r_A - r_O) / \sqrt{2}(r_B - r_O)$ , where  $r_A$ ,  $r_B$ , and  $r_O$  are the radii of A, B, and O ions, respectively. This somewhat indicates that the orthorhombic and tetragonal structures in NKNTS-xLi have closer energy states.

Fig.4 shows the dependence of the planar electromechanical coupling factor  $k_p$  and piezoelectric constant  $d_{33}$  on the chemical composition for the synthesized NKNTS-xLi ceramics. Coupling factor  $k_p$

increases with  $x$  up to 0.06 and then decreases with further increase in  $x$  value. At  $x=0.06$ , the sample shows the optimal  $k_p$  of 41%. Variation of the piezoelectric constant  $d_{33}$  with  $x$  is almost similar to that of  $k_p$ . The optimized  $x$  value is also about 0.06, giving maximum  $d_{33}$  value of 215 pC/N. Fig.5 shows the dependence of the dielectric constant  $\epsilon_{33}^T / \epsilon_0$  and dissipation factor  $\tan\delta$  on the chemical composition for NKNTS-xLi. Dielectric constant  $\epsilon_{33}^T / \epsilon_0$  of the samples increases with increasing  $x$  initially, reaches the maximum at  $x=0.06$  ( $\epsilon_{33}^T / \epsilon_0 = 1303$ ) and then shows a slight decrease with further increase in  $x$  value. However, dissipation factor  $\tan\delta$  of the samples decreases with increasing  $x$  initially, reaches the minimum at  $x=0.06$  ( $\tan\delta = 2.45\%$ ) and then increases with further increase in  $x$ . In summary, it can be seen that the optimal electromechanical property occurs in NKNTS-0.06Li composition.

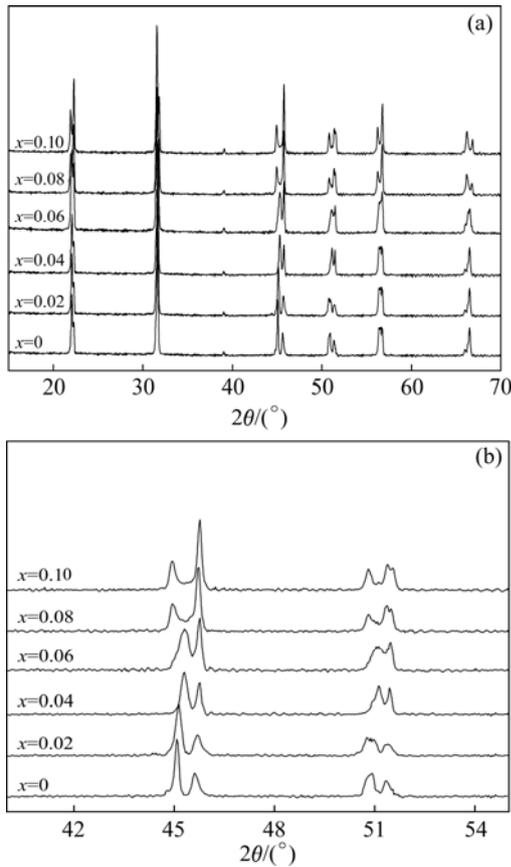


Fig.2 X-ray diffraction patterns of NKNTS-xLi system

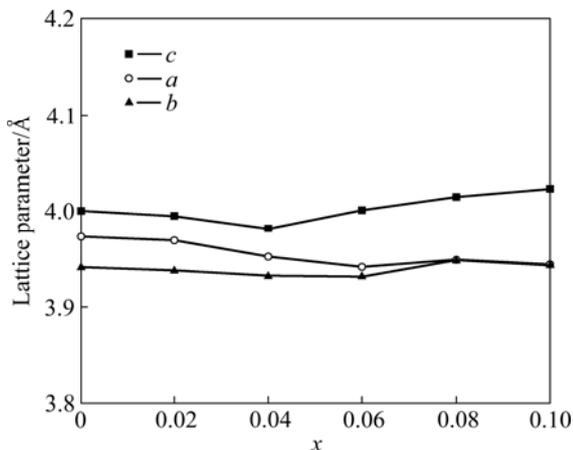


Fig.3 Lattice parameter as function of composition for NKNTS-xLi system

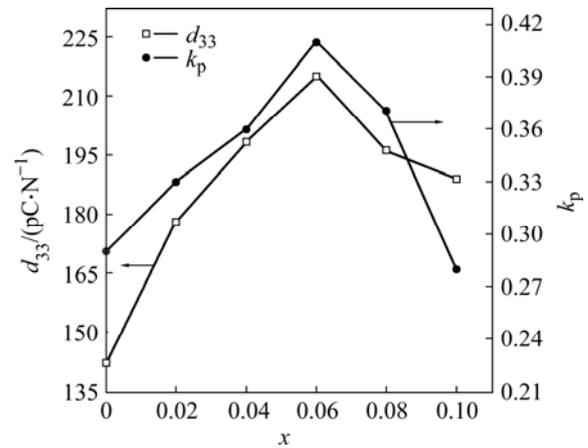


Fig.4 Piezoelectric constant  $d_{33}$  and planar electromechanical coupling factor  $k_p$  as function of composition for NKNTS-xLi system

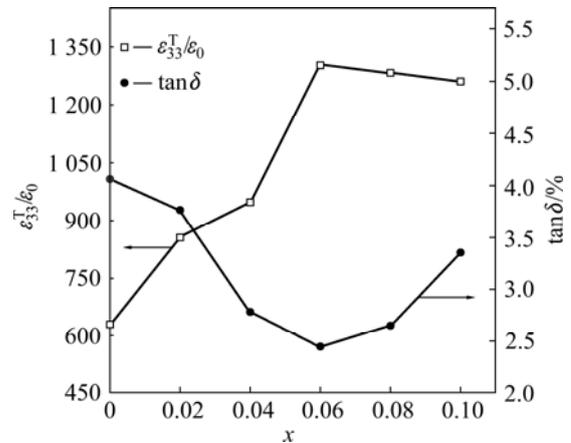


Fig.5 Dielectric constant  $\epsilon_{33}^T / \epsilon_0$  and dissipation factor  $\tan\delta$  as function of composition for NKNTS-xLi system

The content-dependent effect of Li-substitution on the properties of NKNTS-xLi ceramics can be potentially attributed to two factors: chemical modification and

microstructure influence of the material. When the amount of Li-substitution is relatively low, chemical modification caused by dissolution of  $\text{Li}^+$  into the perovskite lattice plays a major role on the properties of NKNTS- $x$ Li ceramics. It is supposed that NKNTS- $x$ Li has  $\text{ABO}_3$  perovskite structure, and in this case, Li can replace Na and K in A sites of  $\text{ABO}_3$  perovskite structure. Due to the difference of ionic radius among  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Na}^+$  ions, this substitution will result in an aberrance of crystal structure, which benefits the reorientation of domains during the polarization process. That may be the explanation for the increase of piezoelectric properties. So, analogous to  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , NKNTS- $x$ Li ceramics with good piezoelectric properties can be obtained by partial substitution of A-site ions  $\text{K}^+$  and  $\text{Na}^+$  by  $\text{Li}^+$ . When the amounts of Li-substitution are increased enough to cause change in microstructure of the ceramics, the influence of microstructure on the properties of NKNTS- $x$ Li ceramics may become dominant. At the MPB composition (near the NKNTS-0.06Li composition), the crystal structure of ceramics is considered to be a coexistence of orthorhombic and tetragonal phase[1]. As the free energy of orthorhombic phase is close to that of tetragonal phase, when applying an electric field, these two phases are easy to change each other. It is helpful to promoting the movement and polarization of ferroelectric active ion at this case, leading to the increase of dielectric constant  $\varepsilon_{33}^T/\varepsilon_0$  and electromechanical coupling factor  $k_p$ . The increase in piezoelectric constant  $d_{33}$  at MPB composition may be attributed to an increased flexibility in domain wall[1]. At higher amount of Li-substitution ( $x > 0.06$ ), chemical modification plays a major role on the properties of NKNTS- $x$ Li ceramics again. While at this moment, the decrease in piezoelectric property of the ceramics may be attributed to the high Li-substitution amount[1].

## 4 Conclusions

1)  $\text{Li}_x(\text{K}_{0.46}\text{Na}_{0.54})_{1-x}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$  lead-free piezoelectric ceramics with  $x$  varying from 0 to 0.1 were prepared and their crystalline structure, dielectric and piezoelectric properties were studied. Results of X-ray diffraction(XRD) show that the ceramics exhibit pure perovskite structure. With the increase of Li-substitution, the crystal structure of the samples changes from orthorhombic to tetragonal symmetry.

2) The measurements of electrical properties reveal that  $\text{Li}_{0.06}(\text{K}_{0.46}\text{Na}_{0.54})_{0.94}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$  ceramic provides relatively high piezoelectric constant  $d_{33}$  (up to 215 pC/N) and high electromechanical coupling factor  $k_p$  (up to 41%). The results show that  $\text{Li}_x(\text{K}_{0.46}\text{Na}_{0.54})_{1-x}\text{Nb}_{0.86}\text{Ta}_{0.1}\text{Sb}_{0.04}\text{O}_3$  ceramic is a

promising lead-free piezoelectric material.

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