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The exploration on the origin of enhanced piezoelectric properties in metal ion doping (K, Na)NbO_3 based lead-free ceramics

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Abstract

In this work, we studied the effects of Ni_2O_3 and Co_2O_3 contents on the crystal structure, microstructure, orthorhombic-tetragonal phase transition temperature ($T_{o\text{-}t}$), and electrical properties of $[(K_{0.43}Na_{0.57})_{0.94}Li_{0.06}][(Nb_{0.94}Sb_{0.06})_{0.95}Ta_{0.05}]O_3$(KNLNST) lead-free ceramics. It was found that the Ni_2O_3 addition with appropriate amount could shift the $T_{o\text{-}t}$ downwards to the room temperature, and thus obviously increased the room temperature piezoelectric coefficient (d_{33}), planar electromechanical coupling coefficient (k_P), dielectric coefficient ($\sum_r$) and the remnant polarization (P_r). These were consistent with experimental results observed in Fe_2O_3 doping KNLNST ceramics. On the contrary, Co^{3+} doping shifted continuously the $T_{o\text{-}t}$ upward and deteriorated obviously piezoelectric properties of KNLNST ceramics. Fe, Co and Ni have similar ion radii and thus they play the same doping role (accept or donor doping) during sintering process. All these mean that the coexistence of orthorhombic and tetragonal phase at room temperature, rather than ion doping was the main reason for enhanced room-temperature piezoelectric properties in metal ion doping KNLNST lead-free ceramics. This work provides a new way for designing and developing new lead-free material with high piezoelectric properties at room temperature.

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I. Introduction

Recently, lead-free piezoelectric ceramics have received increasing attention because of their environmental friendliness [1-3]. Among lead-free ceramics, $(K_{0.5}Na_{0.5})NbO_3$ (KNN), the solid solution of ferroelectric KNO_3 and antiferroelectric $NaNO_3$, is considered one of the most promising candidates for developing lead-free piezoelectric devices because of its high Curie temperature (T_c=420 °C), good ferroelectric properties (P_r =33 μC/cm^2) and large electromechanical coupling factors (k_p=46%) [4-6]. However, single orthorhombic phase structure at room temperature makes this material exhibiting a low room temperature piezoelectric coefficient (80 pC/N) [7], which severely restricts its commercial applications. In order to improve piezoelectric properties of KNN materials, $LiNbO_3$ (LN), $LiSbO_3$ (LS), $LiTaO_3$ (LT), $BaTiO_3$, $SrTiO_3$ and $Bi_{0.5}Na_{0.5}TiO_3$, etc., are introduced into KNN forming solid solution [8-15]. The enhanced electrical properties in these systems are attributed to chemical substitutions shifting the polymorphic orthorhombic-tetragonal phase transition temperature ($T_{o\text{-}t}$) downward and thus forming coexistence of orthorhombic and tetragonal phase at room temperature [16,17]. On the other hand, oxides such as CuO [18], MnO_2 [19,20], CeO_2 [21] and Fe_2O_3 [22] with low melting point have been also usually added into KNN-based materials as sintering aids to improve their microstructural and electrical properties. It is reported that CuO addition can lead to liquid phase sintering in the ceramics [18], and thus improving the densities and the electrical properties; the introduction of MnO_2 could be used to reduce leakage current and dielectric loss [19,20]; doping CeO_2 can promote grain growth and improve piezoelectric properties [21]; Fe_2O_3 with low doping amount is considered to be a “soft” addition for alkali niobate ceramics and the addition of Fe_2O_3 can increase obviously piezoelectric coefficient of the ceramics [22].

In our previous study, we found that by adding sintering aid (Fe_2O_3) with proper amount, $[(K_{0.43}Na_{0.57})_{0.94}Li_{0.06}][(Nb_{0.94}Sb_{0.06})_{0.95}Ta_{0.05}]O_3$ (KNLNST) lead free ceramics exhibited very good piezoelectric and dielectric properties (d_{33} = 306pC/N, kp = 47.0%, $\sum_r$=1483, tanδ=0.023) [23]. However, the internal mechanism of enhanced electrical properties in Fe_2O_3 doping KNLNST ceramics has not been known clearly. It may originate in the decrease of $T_{o\text{-}t}$ or is due to the "soft" doping effect. It is well known that Ni^{3+}, Co^{3+} has similar valence, ionic radius, and chemical properties with Fe^{3+}, and thus in order to investigate the origin of superior electrical properties in metal ion doped KNLNST materials, it is of great interest and importance to explore doping influences of Ni^{3+} and Co^{3+} ions on electrical properties of KNLNST materials.

Based on above considerations, in this work, effects of Ni_2O_3 and Co_2O_3 addition on the crystal structure, microstructure, orthorhombic-tetragonal phase transition behavior and resulting electrical properties of $[(K_{0.43}Na_{0.57})_{0.94}Li_{0.06}][(Nb_{0.94}Sb_{0.06})_{0.95}Ta_{0.05}]O_3$ ceramics were investigated. Combined with our previous work, we hope to find the origin of high piezoelectric properties in metal ion doped KNN-based lead-free ceramics.

II. Experimental procedure

$[(K_{0.43}Na_{0.57})_{0.94}Li_{0.06}][(Nb_{0.94}Sb_{0.06})_{0.95}Ta_{0.05}]O_3$ + x mol% Ni_2O_3 (Co_2O_3) ceramics were synthesized by conventional solid state reaction method. High-purity oxides and carbonates, namely, Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Li_2CO_3 (99.99%), Nb_2O_5 (99.99%), Ta_2O_5 (99.99%), Sb_2O_3 (99%), Ni_2O_3 (99.99%) and Co_2O_3 (99.99%) were used as raw materials and weighed according to the nominal compositions. After mixing and drying, the powder mixtures were calcined at 900 °C for 3.5 h, followed by a ball milling for 4 h. The dried powders were pressed into disk samples with 10 mm

diameter and then sintered in air at 1090~1120 °C for 4 h in 5 ml enclosed alumina copple by adding powder with the same chemical composition of disks as sintering atmosphere. Silver paste was fired on both surfaces of the ceramics at 750 °C for 10 min as electrodes for the measurement of electrical properties. In order to measure piezoelectric properties, the ceramics were poled at 80 °C in silicone oil by applying a DC electric field of 4 kV/mm for 10 min.

The crystal structure was examined by an X-ray diffractometer (XRD, D8 discover, Bruker, Germany). The microstructure of natural free surfaces was observed by a scanning electron microscope (SEM, JSM-6510LV, Jeol, Tokyo, Japan). Piezoelectric coefficient (d_{33}) was measured using a quasistatic piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). Planar electromechanical coupling factor (k_p) was determined by a resonance/ anti-resonance method according to the institute of electrical and electronic engineers (IEEE) Standard on Piezoelectricity with an low frequency impedance analyzer (HP4192A, Agilent, Palo Alto, CA). Room-temperature dielectric properties of the ceramics were measured at 1kHz by the above analyzer. The temperature dependence of dielectric properties was analyzed by using an LCR meter (Wayne Kerr 6500B, UK) attached to a specially designed furnace with computerized control and data acquisition.

III. Results and discussion

2.1 Crystal structure, microstructure and electrical properties of Ni_2O_3 doping KNLNST ceramics

Fig. 1(a) and 1(b) show respectively room-temperature XRD patterns of KNLNST ceramics with different Ni_2O_3 contents in the 2θ ranges of 20° to 60° and 44° to 47°. As can be seen from the figures, all ceramics possess pure perovskite structures without

any detectable secondary phase. This suggests that Ni^{3+} has completely diffused into the KNLNST lattices to form solid solutions. According to the discussion in our previous work [24,25], the intensity ratio of I(202)/I(020) represents the volume ratio between the orthorhombic and tetragonal phases. For pure orthorhombic and tetragonal phase it is about 2 and 1/2, respectively. If the intensity ratio of the two split peaks is between 2 and 1/2, it is concluded that the orthorhombic and tetragonal phases are co-existing in the ceramics. Table 1 lists the integral intensity ratios of I(202)/I(020) for KNLNST ceramics with different Ni_2O_3 contents, which are estimated from XRD patterns shown in Fig. 1(b). As seen, with increasing Ni_2O_3 content from x=0 to x=0.17, orthorhombic and tetragonal phases coexist in all compositions at room temperature and the ratio of I(202)/I(020) first decreases and then increases. At x=0.05, the orthorhombic and tetragonal phases show the best coexistence ratio (1.26), where good room-temperature electrical properties may be obtained.

Fig. 2 presents SEM micrographs of KNLNST + x mol% Ni_2O_3 ceramics. As seen, all ceramics are well sintered, and it is obvious that with the increase of Ni_2O_3 content, the grains of the ceramics gradually become large, as shown in Fig.2(c) and 2(d), which indicate Ni_2O_3 is a good sintering aid, such as CuO [29], MnO_2 [27], and Fe_2O_3 [23]. However, as shown in Fig.2(e) and 2(f), further increasing x to 0.13 and 0.17, the ceramics show irregular grains morphologies. When the content of Ni^{3+} is high, besides occupying the vacancies at the A-site formed by Na^+ and K^+ ions volatilization during sintering process, redundant Ni^{3+} ions may enter into interstitial positions and/or partly replace B-site cations in the crystal lattice, just like the dual occupation behavior found for CuO [26], MnO_2 27], and Fe_2O_3 [23], doping in the perovskite ABO_3-type lattice. The interstitial Ni^{3+} ions can easily cause electrical charge imbalance in local zones. This generates cation vacancies and lattice distortion and thus resulting in strong stress

in the grains. As a result, irregular grains are observed.

Fig. 3(a) displays the temperature dependence of the dielectric constant ($\sum_r$) under 1KHz from room temperature to 400 °C for KNLNST + x mol% Ni_2O_3 ceramics. Two dielectric peaks can be observed for each dielectric-temperature curve. They are respectively corresponding to the transition from the orthorhombic phase to the tetragonal phase and from the tetragonal phase to the cubic phase. The evolution of the Curie temperature (T_c) and the orthorhombic-tetragonal transition temperature ($T_{o\text{-}t}$) are presented in Fig. 3(b). As shown, with increasing Ni_2O_3 content from x=0 to x=0.17, the variation of the T_c is slight, while, the $T_{o\text{-}t}$ shows a very obvious "V" type evolution. It first shifts downwards and reaches the minimum value of 28.9°C at x=0.05, and then increases continuously, which agrees well with the variation rules of the I(202)/I(020) shown in Table. 1. At high Ni^{3+} content, the existence of strong internal stress in the ceramics, which can stabilize the orthorhombic phase, is responsible to the variation tendencies of the I(202)/I(020) and the $T_{o\text{-}t}$ [23].

Room temperature piezoelectric coefficient (d_{33}), planar electromechanical coupling factor (k_p), dielectric constant ($\sum_r$) and dielectric loss ($tan\delta$) of KNLNST + x mol% Ni_2O_3 ceramics are illustrated in Fig. 4. With the increase of Ni_2O_3 content, d_{33}, k_p and $\sum_r$ first increase and then decrease gradually. Obviously, the room temperature piezoelectric and dielectric properties strongly depend on the ratio of the orthorhombic and tetragonal phase at room temperature. The best electrical properties (d_{33}=295pC/N, k_p=47.2%, $\sum_r$=1412) are obtained in the ceramics with x=0.05, in which the orthorhombic and tetragonal phase can better coexist compared with other compositions.

2.2 Crystal structure, microstructure and electrical properties of Co_2O_3 doping KNLNST ceramics

Fig. 5(a) and 5(b) display respectively room-temperature XRD patterns of KNLNST ceramics with different Co_2O_3 contents in the 2θ ranges of 20° to 60° and 44° to 47°. As shown, Co^{3+} has completely diffused into the KNLNST lattices to form solid solutions. Besides, from the intensity ratio of I(202)/I(020), it can be also seen that both orthorhombic and tetragonal phases coexist in all Co_2O_3 doping KNLNST ceramics, and the orthorhombic phase always dominates.

Surface morphologies of KNLNST + *x* mol% Co_2O_3 ceramics are presented in Fig. 6. As seen, the surfaces of the ceramics with different Co_2O_3 contents are all very dense. With the increase of Co_2O_3 content, the grain size of the ceramics increases obviously. This indicates that Co_2O_3 is also a good sintering aid, just like Ni_2O_3 and Fe_2O_3.

Fig. 7 plots dielectric-temperature curves of KNLNST+ *x* mol% Co_2O_3 ceramics at the frequency of 1kHz. The evolution of the T_c and $T_{o\text{-}t}$ are presented in Fig. 7(b). It is clear that with the increase of Co_2O_3 content, the $T_{o\text{-}t}$ improve continuously, and is far higher than the room temperature. This means that the orthorhombic is the main phase structure of Co_2O_3 doped KNLNST ceramics at room temperature.

Fig. 8 illustrates piezoelectric and dielectric properties of KNLNST+ *x* mol% Co_2O_3 ceramics. As shown in the figure, with increasing Co_2O_3 content, electrical properties of Co_2O_3 doping KNLNST deteriorate continuously.

2.3 The comparison of electrical properties for Fe_2O_3, Co_2O_3 and Ni_2O_3 doping KNLNST ceramics

So far, combined with our previous work, we have prepared Fe_2O_3, Ni_2O_3 and Co_2O_3 doped KNLNST ceramics and studied their piezoelectric and dielectric properties in details. The piezoelectric coefficient of KNLNST ceramics doped with different amounts of Fe2O3 and Ni2O3 can be improved obviously. On the contrary, the introduction of Co_2O_3 deteriorates electrical properties of the ceramics. In the

sintering process of Fe_2O_3 and Ni_2O_3 doped KNLNST ceramics, with the increase of the content, Fe^{3+} and Ni^{3+} all first occupy Na^+ and K^+ vacancies at A-sites at low doping level and then at B-site and/or interstitials of the ABO_3-type perovskite lattice at higher contents. This indicates that Fe^{3+} and Ni^{3+} can play both roles of donor and acceptor in KNLNST, which seemingly explains well variation trends of dielectric and piezoelectric properties of KNLNST+ *x* mol% Fe_2O_3 and *x* mol% Ni_2O_3. Fe, Co and Ni all belong to fourth period in periodic table, eighth main group elements and their ion radii are very close (ion radii of Fe^{3+}, Co^{3+} and Ni^{3+} are respectively 0.055 nm, 0.061 nm, and 0.060 nm) and thus they play the same doping role during sintering process. Based on different experimental results observed in Fe^{3+}, Ni^{3+} and Co^{3+} doped KNLNST ceramics, it is clear that donor and acceptor dopings are not the main factors that influence electrical properties of KNLNST ceramics. From dielectric-temperature curves of KNLNST ceramics with different contents of Fe_2O_3, Ni_2O_3, and Co_2O_3, it is found that Fe_2O_3 and Ni_2O_3 doping can first shift $T_{o\text{-}t}$ downward to the room temperature, but Co_2O_3 doping shifts continuously $T_{o\text{-}t}$ upward. It is generally thought that there are 12 <110> spontaneous polarization directions for the orthorhombic phase and 6 <001> directions for the tetragonal phase [23]. That is to say, when tetragonal-orthorhombic phase coexist, there are total 18 spontaneous polarization directions [8, 9], which can lead to better electrical properties (e.g., high d_{33},k_p and P_r). All these indicate that for Fe_2O_3, Ni_2O_3, and Co_2O_3 doped KNLNST ceramics, in comparison with donor and acceptor doping, the effect of the variation of the $T_{o\text{-}t}$ on the electrical properties is more obvious. This influence mechanism is different from the morphotropic phase boundary (MPB) that is temperature-independent in lead zirconate titante (PZT). The O and T two phase coexistent zone in KNN-based ceramics is temperature-dependent and generally termed a polymorphic phase boundary (PPB).

IV. Conclusion

In summary, $[(K_{0.43}Na_{0.57})_{0.94}Li_{0.06}][(Nb_{0.94}Sb_{0.06})_{0.95}Ta_{0.05}]O_3$ (KNLNST) + x Ni_2O_3 ceramics with superior electrical properties were achieved by adding Ni^{3+} into the base composition KNLNST. With increasing Ni_2O_3 content from x=0 to x=0.05, the d_{33}, k_P, $\sum_r$, P_r increase from 234pC/N, 42.3%, 1298, and 25.8μC/cm^2 (x=0) to 295 pC/N, 47.2%, 1412, and 32.5μC/cm^2 (x=0.05), respectively. The change patterns of electrical properties were consistent with those reported in our previous work about Fe_2O_3 doped KNLNST ceramics. However, when Co^{3+} with similar ion radius to Fe^{3+}, Ni^{3+} was doped into KNLNST, electric properties of the ceramics were deteriorated seriously. Moreover, it was found that Fe_2O_3 and Ni_2O_3 doping could first shift $T_{o\text{-}t}$ downward to the room temperature, but Co_2O_3 doping shifted continuously $T_{o\text{-}t}$ upward. These results indicate that the decrease of the $T_{o\text{-}t}$ plays a significant role in enhancing electrical properties of KNLNST ceramics in comparison with "doping effects". This work lays a good foundation for developing new lead-free materials with high piezoelectric properties.

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Figure captions

Fig. 1. XRD patterns in the 2θ range of (a) 20-60°and (b) 44-47° for KNLNST + x mol% Ni_2O_3 ceramics.

Fig. 2. (a) Temperature dependence of the $\sum_r$, and (b) $T_{o\text{-}t}$ and T_c for KNLNST + x mol% Ni_2O_3 ceramics at 1 kHz.

Fig. 3. Surface SEM images of KNLNST ceramics with Ni_2O_3 contents of (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.05$, (d) $x = 0.075$, (e) $x = 0.13$, and (f) $x = 0.17$.

Fig. 4. Variations of the d_{33}, k_p, $\sum_r$ and tanδ of KNLNST ceramics with different Ni_2O_3 contents.

Fig. 5. XRD patterns in the 2θ range of (a) 20-60°and (b) 44-47°for KNLNST + x mol% Co_2O_3 ceramics.

Fig. 6. Surface SEM images of KNLNST ceramics with Co_2O_3 contents of (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 1.0$.

Fig. 7. (a) Temperature dependence of the $\sum_r$, and (b) the $T_{o\text{-}t}$, T_c for KNLNST + x mol% Co_2O_3 ceramics at 1 kHz.

Fig. 8. Variations of the d_{33}, k_p, $\sum_r$ and tanδ of KNLNST ceramics with different Co_2O_3 contents.

Table.1. Calculation result of I_{202}/ I_{020} according to XRD patterns of the KNLNST+x Ni_2O_3 ceramics shown in Fig. 1.

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