Dielectric and piezoelectric properties of Fe_2O_3-doped $(Na_{0.5}K_{0.5})_{0.96}Li_{0.04}Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$ lead-free ceramics

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Abstract

The effect of a small amount Fe_2O_3 (0.1–2 mol%) doping on the electrical properties of $(Na_{0.5}K_{0.5})_{0.96}Li_{0.04}Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$ (NKLNTS) ceramics was investigated. It was found that the B-site substitution of Fe^{3+} does not change the crystal structure within the studied doping level and all modified ceramics have a pure tetragonal perovskite structure at room temperature. The addition of Fe_2O_3 can promote the sintering of NKLNTS ceramics, and simultaneously cause the grain growth so that Fe^{3+}-doped NKLNTS compositions show degraded densification at higher doping level. Furthermore, the dielectric properties of the NKLNTS ceramics do not show a significant change by Fe_2O_3 doping. However, the addition of Fe_2O_3 was found to have a significant influence on the electric fatigue resistance and the durability against water. The presence of oxygen vacancies caused by the replacement of Fe^{3+} for B-site ions makes the NKLNTS ceramics harder.
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1. Introduction

Lead-containing piezoelectric ceramics such as $Pb(Zr,Ti)O_3$ (PZT) have been widely used for almost a half century due to their excellent dielectric, piezoelectric and electromechanical properties [1]. However, concerns from lead pollution have been attracting more and more attention in the past few years. These conventional lead-based piezoelectric materials usually contain about 60 wt% lead oxide. Therefore, research on lead-free and/or low-lead-content piezoelectric compositions has become more and more active in recent years. The big obstacle currently is the lack of potential candidate materials with electrical properties comparable to those of PZT systems.

Many lead-free compositions have been studied as alternatives to conventional lead-based piezoelectric materials. Since Saito et al. reported on Li, Ta and Sb-modified

$(Na_{0.5}K_{0.5})NbO_3$ (NKN) compositions, the NKN-based piezoelectric systems have been a focus of this field [2–13]. Compared to $Bi_{0.5}Na_{0.5}TiO_3$-based lead-free systems, which have been considered as another important group of candidate materials [14–16], the NKN systems have merits such as higher Curie temperatures and better piezoelectric properties. Many compositions that possess different Curie temperatures, a broad range of electrical properties and have their own morphotropic phase boundaries (MPB), can be produced by changing the ratio of Li to Ta or Sb within the NKN systems. Particularly, the textured (Li, Ta, Sb)-modified NKN ceramics exhibit piezoelectric properties comparable to those of a hard PZT [5]. However, NKN-based material systems tend to have a few drawbacks, for example, difficulty in processing and poling, short electrical fatigue lifetime, heterogeneous microstructure, low durability against water and stability of piezoelectric properties. Additionally, their electrical properties need to be further improved in order to replace lead-containing PZT materials.

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$(N_{0.5}K_{0.5})_{0.96}Li_{0.04}Nb_{0.86}Ta_{0.1}Sb_{0.04}O_3$ (NKLNTS) is a composition near MPB in the NKN–LiTaO$_3$–LiSbO$_3$–LiNbO$_3$ system, which has a tetragonal structure at room temperature and good piezoelectric properties [5]. However, it is found that the material exhibits low durability against water, complex processing procedures and a relatively high loss tangent, etc.

The purpose of this study is to investigate the influence of a small amount of Fe$_2$O$_3$ doping on the densification, microstructure, dielectric, piezoelectric properties and electric fatigue behavior of the NKLNTS ceramics. Fe^{3+} ions are considered as an acceptor to replace B-site ions. The modification of various properties was correlated with the generation of oxygen vacancies and the change in densification by doping.

2. Experimental

Lead-free $[(N_{0.5}K_{0.5})_{0.96}Li_{0.04}][(Nb_{0.86}Ta_{0.1}Sb_{0.04})_{1-x}Fe_x]O_{3-x}$ ($x = 0$, 0.001, 0.0025, 0.005, 0.01, and 0.02) piezoelectric ceramics were synthesized by a traditional mixed oxide route. Oxygen vacancies were considered as a mechanism for the charge equilibrium. The starting powders used in this study were potassium carbonate (K$_2$CO$_3$, 99.0%), sodium carbonate (Na$_2$CO$_3$, 99.8%), lithium carbonate (Li$_2$CO$_3$, 99.9%), tantalum oxide (Ta$_2$O$_5$, 99.9%), antimony oxide (Sb$_2$O$_3$, >99.9%), niobium oxide (Nb$_2$O$_5$, 99.9%) and iron oxide (Fe$_2$O$_3$, 99.5%). The details of powder processing were described previously [9]. The powder mixtures were calcined at 950 °C for 4 h. To improve homogeneity, the powder mixtures were carefully milled and calcined several times under the same conditions. Before compaction, the calcined powder was milled again for 24 h and sieved through 230 meshes. Sintering was carried out in air in the temperature range 1050–1140 °C for 2–4 h. The samples were put on a platinum foil and covered with the powder of the same composition during sintering.

The Archimedes method was used to measure the density of the specimens sintered at different temperatures. The microstructure was observed by a scanning electron microscope (SEM, JEOL6301F, Tokyo, Japan). The crystal structure of the specimens was examined by a powder X-ray diffractometer (XRD, Rigatu, Tokyo, Japan) on crushed pellets using a Cu Kα radiation.

Electrodes were made on two polished sides of the specimens by screen-printing a silver paste and firing it at 500 °C for 30 min. Dielectric property of the samples was measured as a function of temperature and frequency by an LCR meter (HP 4284A, Hewlett-Packard, Palo Alto, CA). Polarization and strain versus electric field hysteresis loops were measured in a silicone oil bath by applying an ac field with a frequency of 300 mHz with a modified Sawyer-Tower bridge and an inductive displacement gauge. The same measurement was performed to record the electric fatigue behavior for 20 cycles on virgin samples. After the samples were poled in a silicone oil bath at 3 kV/mm for

25 min, piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730, Sinocera, Shanghai, China), and the planar electromechanical coupling factor k_p was determined by a resonance–antiresonance method with an impedance analyzer (HP 4192A, Hewlett-Packard, Palo Alto, CA) based on IEEE standards.

3. Results and discussion

Fig. 1 shows the XRD patterns of NKLNTS ceramics with different Fe$_2$O$_3$ doping levels sintered at 1100 °C for 2 h. All compositions have a pure perovskite structure with a tetragonal symmetry, indicating that a small amount of Fe$_2$O$_3$ doping does not have any significant effect on the crystal structure of the NKLNTS ceramics. In addition, the addition of Fe$_2$O$_3$ does not cause any detectable second phases. Therefore, the solubility limit of Fe^{3+} in the perovskite lattice of NKLNTS compositions should be beyond the studied doping levels. The replacement of Fe^{3+} ions for B-site Nb^{5+}(or Sb^{5+}, Ta^{5+}) leads to the formation of oxygen vacancies. As a result, the lattice may have a small shrinkage. However, this can be compensated by the lattice expansion due to different ionic sizes (ionic radii: 0.65, 0.61, 0.64 and 0.64 Å for Fe^{3+}, Sb^{5+}, Ta^{5+} and Nb^{5+}, respectively, CN = 6) [17]. Therefore, no obvious change in the position of diffraction peaks in Fig. 1 can be detected.

The SEM photographs of the NKLNTS ceramics with different Fe$_2$O$_3$ doping levels sintered at 1100 °C for 2 h are shown in Fig. 2. All ceramics exhibit a dense microstructure with a uniform grain size. The grain size increases with increase in Fe$_2$O$_3$ content, from ~1.5 μm for undoped to ~4.2 μm for 1 mol% doped ceramics. The addition of a small amount of Fe$_2$O$_3$ also promoted the densification, as illustrated in Table 1. In addition, it was found that the 0.25 mol% Fe^{3+}-doped NKLNTS ceramics sintered at
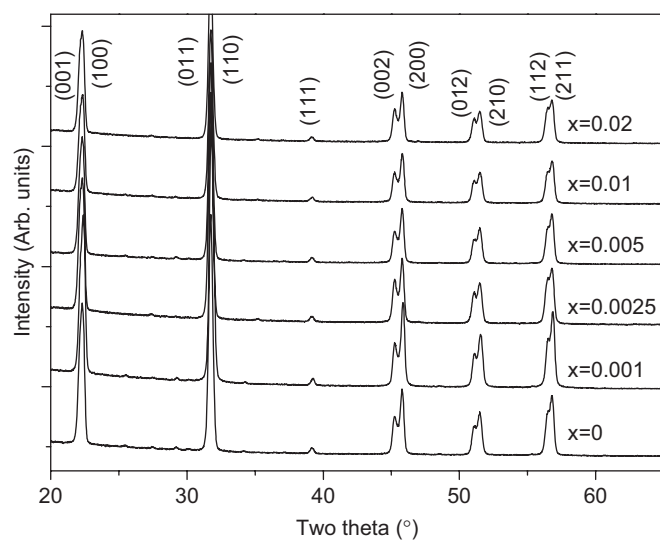

Fig. 1. X-ray diffraction patterns of $[(N_{0.5}K_{0.5})_{0.96}Li_{0.04}][(Nb_{0.86}Ta_{0.1}Sb_{0.04})_{1-x}Fe_x]O_{3-x}$ ceramics.
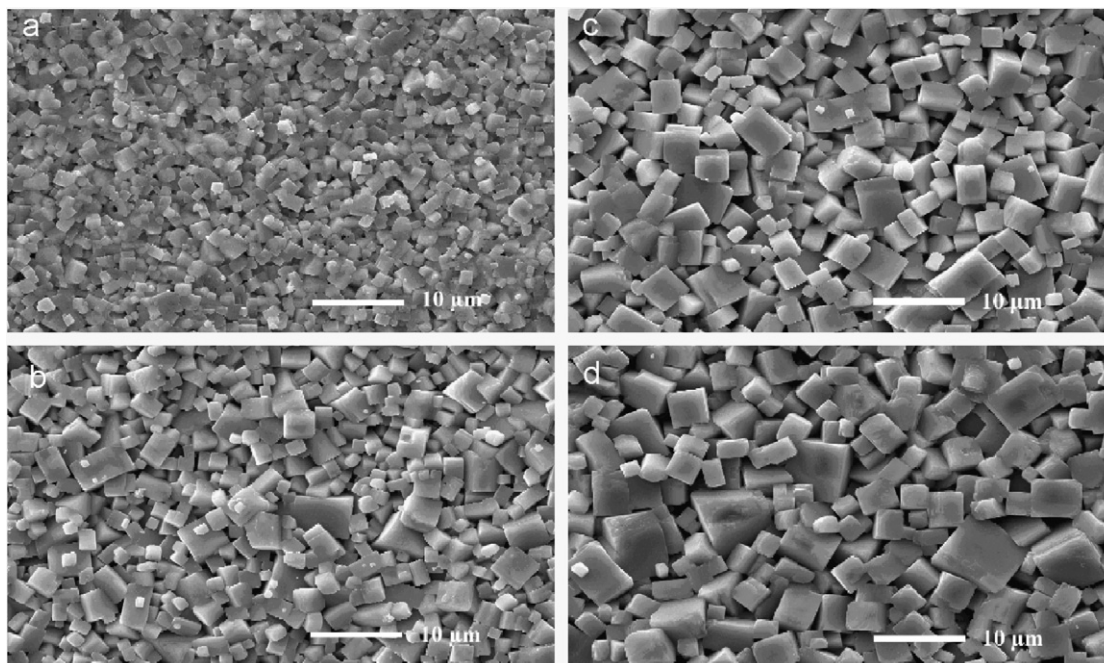
Fig. 2. Surface morphology of $[(N_{0.5}K_{0.5})_{0.96}Li_{0.04}][(Nb_{0.86}Ta_{0.1}Sb_{0.04})_{1-x}Fe_x]O_{3-x}$ ceramics: (a) $x = 0$, (b) $x = 0.0025$, (c) $x = 0.01$ and (d) $x = 0.02$.

Table 1
Room-temperature electric properties of $[(N_{0.5}K_{0.5})_{0.96}Li_{0.04}][(Nb_{0.86}Ta_{0.1}Sb_{0.04})_{1-x}Fe_x]O_{3-x}$ ceramics

Fe_2O_3 content, $100 \times$	0	0.1	0.25	0.5	1	2
Relative density (%)	96.2	97.5	98.1	97.4	96.5	95.6
Dielectric permittivity at 100 kHz	1017	975	971	952	911	910
Loss tangent at 100 kHz	0.044	0.042	0.041	0.039	0.038	0.038
Remanent polarization (P_r)[a] $(\mu C/cm^2)$	21.1	20.0	19.5	19.8	18.5	17.5
Coercive field (E_c) (kV/mm)[a]	1.39	1.39	1.40	1.40	1.42	1.43
Piezoelectric constant, d_{33} (pC/N)	212	228	241	238	210	195
Coupling factor k_p (%)	42	44	46	44	43	39
Mechanical quality factor, Q_m	30	33	37	39	46	57

[a]Determined from the first cycle, at the frequency of 300 mHz.

1060 °C can reach the same density as undoped NKLNTS ceramics sintered at 1100 °C. However, when the doping content of Fe^{3+} is above 1 mol%, the densification was slightly degraded because of a significant grain growth (see Fig. 2d). The influence of Fe_2O_3 doping on the densification behavior is considered to be correlated to the oxygen vacancies caused by doping. The formation of oxygen vacancies may speed up the mass transportation, promoting the densification and grain growth simultaneously. However, grain growth will certainly decrease the sintering potential of the material.

Fig. 3 shows the dielectric properties of the Fe^{3+}-doped NKLNTS ceramics. The dielectric constant versus temperature curves are not apparently influenced by Fe_2O_3 doping. Particularly, the Curie temperature of the Fe^{3+}-doped NKLNTS ceramics shows the same value (~293 °C). The dielectric maxima of the ceramics are slightly reduced when Fe_2O_3 doping is more than 1 mol%, probably due to a relatively low density, which probably also leads to a

slight increase of loss tangent at high temperatures. However, the loss tangent of NKLNTS ceramics between room temperature and ~200 °C was slightly reduced by adding Fe^{3+}. Table 1 also shows a slightly improved mechanical quality factor Q_m with Fe_2O_3 doping. Therefore, Fe^{3+} seems to play a role like an acceptor. However, these values are still high compared to those of a hard PZT.

The fatigue behavior of Fe^{3+}-doped NKLNTS ceramics under a number of cycles is shown in Fig. 4. Pure NKLNTS ceramics show rapidly reduced remanent polarization (P_r) and strain (S_r), and asymmetric hysteresis loops, typical of a fast electric fatigue behavior. After 20 cycles, both P_r and S_r averagely decreased from 20.0 $\mu C/cm^2$ and 0.09% to 7.2 $\mu C/cm^2$ and 0.01%, respectively. In addition, the fatigued samples cannot be recovered by a heat treatment. On the other hand, the 0.25 mol% Fe^{3+}-doped NKLNTS ceramics show a significant improvement of the fatigue behavior. After the doped ceramics were cycled for 20 times, both the values of
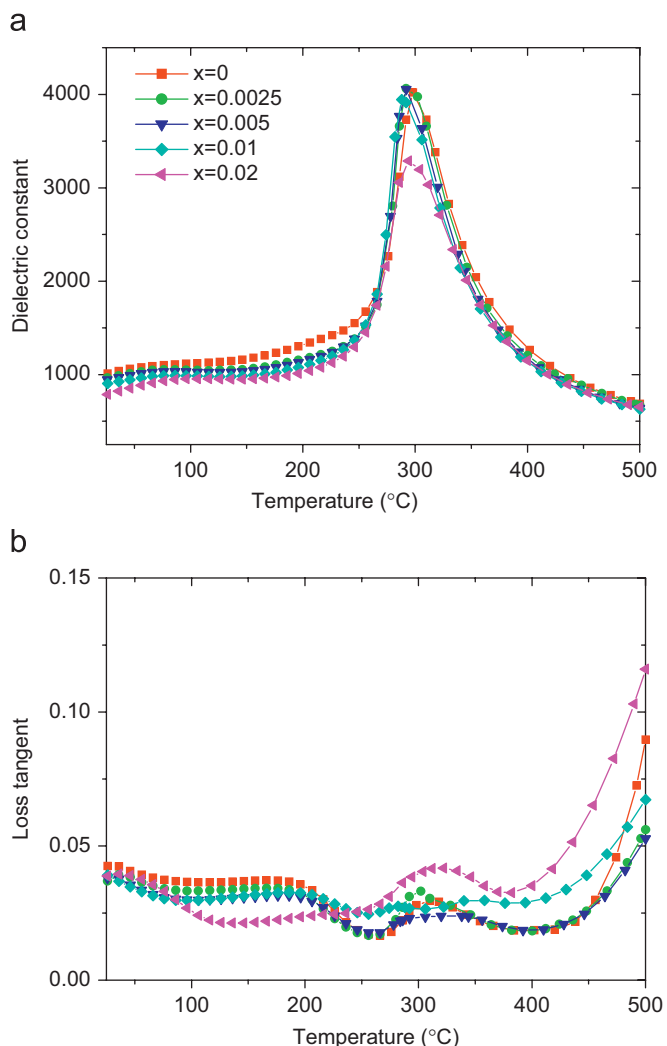
Fig. 3. Dielectric constants (a) and losses (b) at 100 kHz of $[(N_{0.5}K_{0.5})_{0.96}Li_{0.04}][(Nb_{0.86}Ta_{0.1}Sb_{0.04})_{1-x}Fe_x]O_{3-x}$ ceramics.

P_r and S_r and the shape of hysteresis loops did not alter evidently. Therefore, the resistance to the electric fatigue is significantly improved due to a small amount of Fe_2O_3 doping, although the fatigue measurement under more cycles still needs to be done. It is well known that pure alkaline niobate, tantalum and antimonate ceramics usually exhibit a low durability against water or moisture. The reason for this is that secondary phases rich in alkaline elements, which make the grain boundaries rather weak after the water or moisture is absorbed, tend to form during processing [18]. These secondary phases are easily dissolved in water although the amount dissolved might be little. Moreover, the volatilization of A-site alkaline elements causes a deviation from the stoichiometry, generating atomic vacancies. Some kinds of free charges may also stay at the grain boundaries. These charged species are driven to domain walls by electric cycling. Pining of domain walls due to the congregation of the charged species is usually considered as another mechanism of electric fatigue [19,20]. However, this kind of electric

fatigue can be recovered after heat treatment. By comparison, the mechanical weakness in NKLNTS ceramics is considered as the main reason for the failure of ceramics because continuous switching of the domains induces the propagation of micro-cracks [21,22], causing the failure and/or the reduction in P_r and S_r. It was found that another obvious effect of Fe^{3+} doping on NKLNTS ceramics is an increase in their durability against water. The microstructure and loss tangent of the Fe^{3+}-doped NKLNTS ceramics did not show any visible change after the ceramics had been immersed in water for 2 weeks. It seems that the addition of Fe_2O_3 inhibits the formation of unstable second phases. On the contrary, undoped NKLNTS ceramics tend to disintegrate after the same treatment.

Additionally, the ferroelectricity of NKLNTS ceramics is also affected by a small amount of Fe_2O_3 doping. Remanent polarization and coercive field (E_c) measured from the first cycle were used to characterize the ferroelectricity of the materials, irrespective of how their electric fatigue behavior looks like, as seen in Table 1. With increasing the doping content of Fe^{3+}, the NKLNTS ceramics exhibit a slight increase in E_c and a slight decrease in P_r, typical of an acceptor doping. Moreover, both the room-temperature dielectric constant and loss tangent slightly decrease with doping Fe^{3+}. The NKLNTS ceramics become somewhat hard in ferroelectric properties due to the addition of Fe_2O_3. It can be seen from Table 1 that the piezoelectric and electromechanical properties of the NKLNTS ceramics are improved by Fe^{3+} doping except for the 1 and 2 mol% Fe_2O_3-doped ceramics. Piezoelectric constant d_{33} and electromechanical coupling factor k_p firstly increase with Fe^{3+} doping level, which is probably due to an increase in density. As the doping level further increases, both of them slightly decrease due to the hardening effect from an acceptor doping. A small reduction in density at higher doping levels may also contribute to the decrease in piezoelectric and electromechanical properties.

4. Conclusion

Lead-free NKLNTS piezoelectric ceramics modified with a small amount of Fe_2O_3 were prepared by conventional sintering. It was found that the addition of a small amount of Fe_2O_3 has an obvious effect on densification, microstructure and various electrical properties. Densification is improved by a small amount of Fe_2O_3 doping. Oxygen vacancies generated by substitution of Fe^{3+} ions for B-site cations make the NKLNTS ceramics harder. An important contribution of Fe^{3+} doping is the improvement of electric fatigue behavior of the NKLNTS ceramics studied, which is attributed to the enhancement of mechanical properties, particularly the strengthening of grain boundaries.
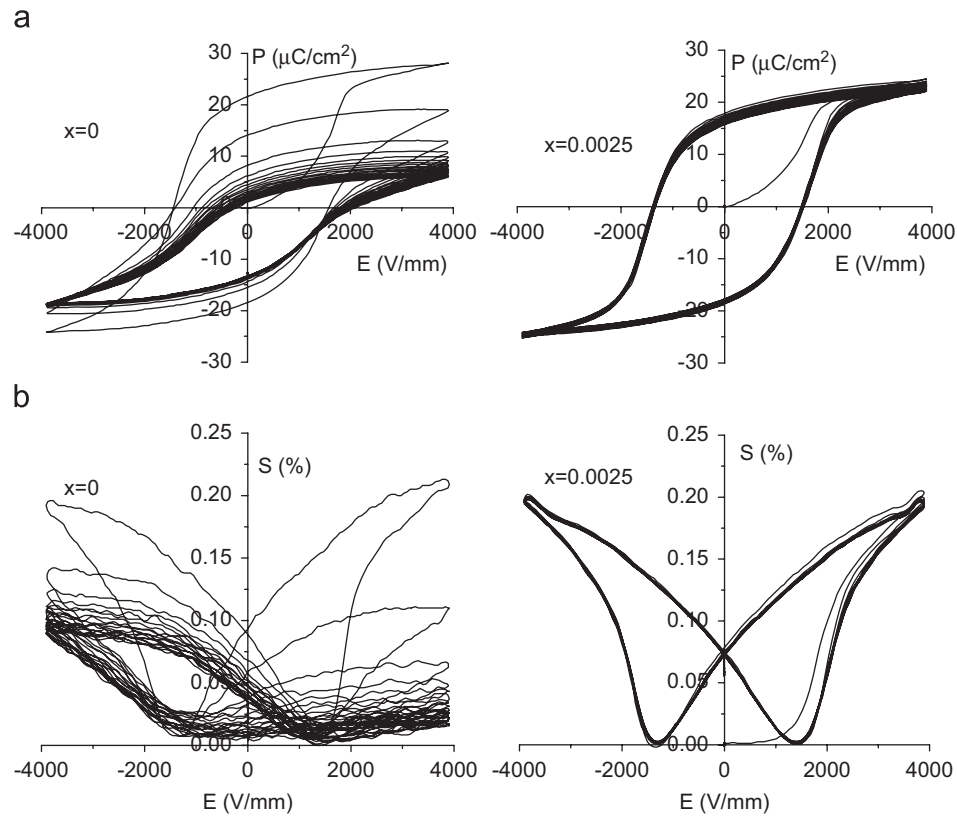
Fig. 4. Polarization (a) and strain (b) of $[(N_{0.5}K_{0.5})_{0.96}Li_{0.04}][(Nb_{0.86}Ta_{0.1}Sb_{0.04})_{1-x}Fe_x]O_{3-x}$ ceramics under an ac field of 300 mHz for the first 20 cycles and at different x.

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Further Reading

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