

Sintering and electrical properties of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics modified with lanthanum and iron oxides

Ruzhong Zuo^{a,*}, Min Wang^a, Bing Ma^a, Jian Fu^a, Tao Li^b

^a School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China

^b Superconducting Materials Research Center, General Research Institute for Non-ferrous Metals, No. 2, Xin Jie Kou Wai Street, Beijing 100088, China

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ABSTRACT

Effects of La^{3+} , Fe^{3+} doping and their co-doping on the sintering, structures and electrical properties of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN) ceramics were investigated. A significant modification of sintering behavior can be obtained by the addition of Fe_2O_3 . On the contrary, the addition of La_2O_3 and La-FeO_3 tends to degrade the densification. Moreover, Fe^{3+} doping does not change the crystal structure, thus leading to an unchanged Curie temperature. Owing to a transition from orthorhombic to pseudo-cubic structures, the Curie temperatures of NKN ceramics were significantly lowered by doping La_2O_3 and La-FeO_3 . NKN ceramics modified with a small amount of Fe_2O_3 and La-FeO_3 (less than 0.5 mol%) exhibit improved ferroelectric, piezoelectric and electromechanical properties.

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1. Introduction

Lead-based piezoelectric ceramics such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ have been widely used in industry for many years as actuator, transducer and sensor materials due to their excellent dielectric, piezoelectric and electromechanical properties [1]. However, lead pollution problems have induced people to search for lead-free piezoelectric compositions. This has been currently a new driving force for the development of piezoelectric ceramics.

In the past few years, many lead-free piezoelectric compositions have been investigated. Most of these researches are concerned with the search for new compositions with a morphotropic phase boundary (MPB) where the material shows enhanced dielectric, piezoelectric and electromechanical properties [2–4]. As far as the category of materials is concerned, there have been generally two systems in the perovskite family, showing potential for lead-free candidates: $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT)- and $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN)-based MPB compositions [5–25]. NKN is a composition with an MPB separating two orthorhombic phases, showing better piezoelectric properties than BNT-based systems. However, this material has great difficulty in sintering, showing poor densification ability by ordinary sintering. The ordinarily sintered NKN ceramics show piezoelectric properties of $d_{33} = 80$ pC/N, $k_p = 36$ –40%, $Q_m = 130$, and $\epsilon_{33}^T/\epsilon_0 = 290$ only. Moreover, NKN shows high moisture sensitivity. Both drawbacks lead to low density, high loss tangent,

difficult poling processing and weak mechanical strength. Although the addition of Li, Ta or Sb cations, even BNT and $\text{Ba}(\text{Zr,Ti})\text{O}_3$, can improve its sintering to a certain degree, poor durability against water and uneven microstructure are still difficult to be completely avoided. Of course, these modified NKN-based systems show much better piezoelectric properties irrespective of their property stability and life time. The addition of the alkaline-earth and transitional metal elements are usually used to improve sintering and electrical properties of piezoelectric ceramics. In this respect, NKN had been improved by adding a small amount of various oxides such as ZnO , BaCO_3 , SrCO_3 , SnO_2 , etc. [10,11,16]. These oxides can dissolve into the lattice of NKN, producing lattice defects such as cation vacancies or oxygen vacancies, which are known to induce different changes in piezoelectric properties [26].

The purpose of this study is to investigate the effect of La_2O_3 and Fe_2O_3 doping or their co-doping on the sintering, microstructure, and various electrical properties of NKN ceramics, respectively. The co-doping of La^{3+} and Fe^{3+} in equal molar proportion is actually that they are added in the form of LaFeO_3 . La^{3+} and Fe^{3+} are also frequently used dopants in Pb-based piezoelectric ceramics, helping generate a broad range of electrical properties. Different valence states and ionic sizes of La^{3+} (Fe^{3+}) relevant to A-site (B-site cations) of NKN perovskite lattices (ABO_3 structure) may cause lattice defects when La^{3+} or Fe^{3+} is solely doped. For comparison, the co-doping of La^{3+} and Fe^{3+} will be also explored because no lattice defects are required from the viewpoint of charge equilibrium. Considering the ionic sizes, La^{3+} and Fe^{3+} are arbitrarily fixed at A-site and B-site of NKN lattices, respectively. Correspondingly, A-site vacancies and oxygen vacancies are applied to keep the charge equilibrium.

* Corresponding author. Tel./fax: +86 551 2905285.
E-mail address: piezolab@hfut.edu.cn (R. Zuo).

2. Experimental

Ceramics with the composition of $(\text{Na}_{0.5}\text{K}_{0.5})(\text{Nb}_{1-x}\text{Fe}_x)\text{O}_{3-x}$ ($x = 0, 0.005, 0.01, 0.02, 0.03$ and 0.04), $\text{La}_y(\text{Na}_{0.5}\text{K}_{0.5})_{1-3y}\text{NbO}_3$ ($y = 0.005, 0.01, 0.02, 0.03$ and 0.04) and $(\text{Na}_{0.5}\text{K}_{0.5})_{1-z}\text{La}_z(\text{Nb}_{1-z}\text{Fe}_z)\text{O}_3$ ($z = 0.0025, 0.005, 0.01, 0.015$ and 0.02) were prepared by a traditional solid-state method. The raw materials used in this study were potassium carbonate (K_2CO_3 , 99.0%), sodium carbonate (Na_2CO_3 , 99.5%), niobium oxide (Nb_2O_5 , 99.5%), iron oxide (Fe_2O_3 , 99.7%) and lanthanum oxide (La_2O_3 , 99.5%). After weighing, the powder mixtures were ball mixed in a planetary mill using anhydrous ethanol as the medium in a nylon jar for 20 h. The dried mixtures were calcined at 850°C for 6 h, following a second milling using zirconia balls for 24 h. All calcined powders were then sieved through 200 meshes. Specimens with a diameter of 15 mm and a thickness of 2 mm were prepared in a stainless-steel die under a uniaxial pressure of ~ 50 MPa. Sintering was carried out in air in a programmable oven in the temperature range of 1040 – 1130°C for 4 h. During sintering, the samples were placed in a platinum foil and covered with an inverted alumina crucible.

Densification behavior was characterized by measuring the densities of the sintered samples at different temperatures through the Archimedes method. The microstructure was observed by a scanning electron microscope (SEM, JEOL6301F, Tokyo, Japan). Powder X-ray diffraction (XRD, Rigaku, Tokyo, Japan) patterns of crushed pellets using Cu K α radiation were recorded in the 2θ range of 20 – 60° .

For the electrical measurements, silver electrodes were made on two major surfaces of each disk sample by firing the screen-printed silver paste at 600°C for 30 min. Dielectric properties were measured as a function of temperature ranging from room temperature to 500°C using an LCR meter (HP 4284A, Hewlett-Packard, Palo Alto, CA). Hysteresis loops of polarization versus electric field were measured using a modified Sawyer–Tower bridge driven by an ac field of 50 mHz. A poling treatment was conducted in stirred silicone oil at the temperature of 100°C by applying a dc field of 3 kV/mm, and then the samples were cooled to room temperature by maintaining the electric field. After the poled samples were aged for 24 h, the piezoelectric strain constants d_{33} were measured by a quasi-static Berlincourt-meter (YE2730, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p was obtained by a resonance–antiresonance method by an impedance analyzer (HP 4192A, Hewlett-Packard, Palo Alto, CA).

3. Results and discussion

Fig. 1 shows XRD results of NKN ceramics doped with different amounts of Fe_2O_3 , La_2O_3 and La-FeO_3 sintered at 1080°C for 4 h. The results indicate that the addition of a small amount of Fe_2O_3 does not induce any change in the crystal symmetry of NKN compositions. For $0 \leq x \leq 0.04$, all samples possess a pure orthorhombic perovskite structure. No secondary phases are detectable, meaning that all doped Fe^{3+} are dissolved into the lattice. The replacement of Fe^{3+} for Nb^{5+} does not cause any evident change probably because they have similar ionic sizes (ionic radii: 0.64 and 0.65 \AA for Nb^{5+} and Fe^{3+} , respectively; coordination number (CN) = 6) [27]. By comparison, the addition of La^{3+} induces a significant change in the crystal structure. On increasing y , NKN rapidly transits from orthorhombic to pseudocubic phases. The occupation of La^{3+} at A-site tends to shrink the lattice owing to the formation of A-site cation vacancies and a smaller ionic size of La^{3+} than that of K^+ and Na^+ (ionic radii: 1.39 , 1.64 and 1.36 \AA for Na^+ , K^+ and La^{3+} ; respectively, CN = 12) [27].

This may increase the symmetry of a crystal probably by shrinking in the direction of a and c axes of an orthorhombic lattice ($a \approx c > b$) in a pure NKN, as calculated in Fig. 1). The orthorhombic symmetry almost disappears at $y = 0.02$. The effect of La^{3+} – Fe^{3+} co-doping on the crystal structure shows similar tendency to that of only La doping, based on the fact that LaFeO_3 has a rhombohedral perovskite structure at room temperature [28].

Sintering behavior of NKN ceramics modified with dopants is shown in Fig. 2. The data only for two sintering temperatures are provided for clear comparison. Fe_2O_3 -doped NKN ceramics show much better densification than La_2O_3 - and La-FeO_3 -doped ones. A small amount of Fe_2O_3 can significantly improve sintering of NKN ceramics. On further increasing the content of Fe_2O_3 , the improvement of sintering behavior does not further increase. This means that Fe_2O_3 can be an effective modifier for sintering of NKN ceramics. As discussed above, the addition of Fe^{3+} generates oxygen vacancies in the lattice, probably promoting the densification [29]. Moreover, the liquid phase sintering could be another important cause for the improved densification as can be seen in the following SEM pictures. However, these effects can

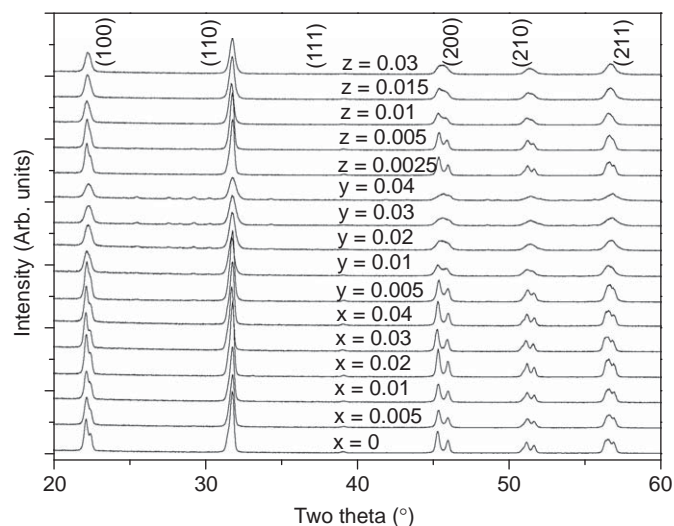


Fig. 1. X-ray diffraction patterns of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics doped with different amounts of Fe_2O_3 (x), La_2O_3 (y) and La-FeO_3 (z) as indicated.

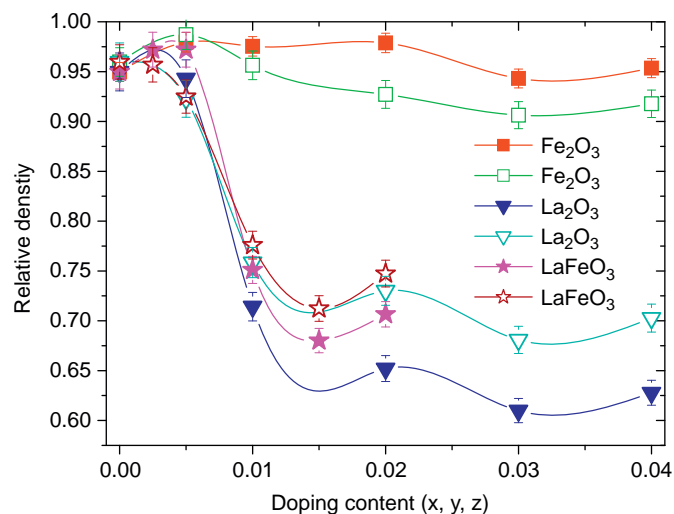


Fig. 2. Sintering profiles of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics sintered at two different temperatures: solid symbols (1080°C) and open symbols (1100°C).

be counteracted by the grain growth simultaneously taking place during heating (see the microstructure *infra*). On the other hand, only a slight improvement can be seen from the case where a little amount of La_2O_3 or La-FeO_3 ($y = 0.005$ and $z = 0.0025$) is added. The addition of more La_2O_3 or La-FeO_3 clearly degrades the densification of NKN ceramics. It seems that the formation of A-site vacancies tends to inhibit the sintering of perovskite systems with volatile A-site elements such as Pb-based perovskite systems. However, the addition of a tiny amount plays a role as an impurity, thereby to a certain degree promoting the densification.

The surface morphology of modified NKN ceramics sintered at 1100°C is shown in Fig. 3. It can be noted that the addition of Fe^{3+} promotes the grain growth, which counteracts the promoting effect of Fe^{3+} doping on sintering. The average grain size is approximately $2.5\ \mu\text{m}$ for undoped NKN ceramics and it changes to about $8.0\ \mu\text{m}$ for 3 mol% Fe^{3+} -doped NKN ceramics, which show a relatively loose microstructure. On the contrary, the addition of La^{3+} clearly inhibits the grain growth. The 0.5 mol% La^{3+} -doped NKN ceramics (Fig. 3d) have a relatively high density, compared to the 2 mol% La^{3+} -doped ones. It seems that the mobility of grain boundary was blocked due to the A-site cation vacancies in these cases. The role of $\text{La}^{3+}\text{-Fe}^{3+}$ co-doping seems to lie between the above two cases (Fe^{3+} and La^{3+}). The addition of 0.5 mol% $\text{La}^{3+}\text{-Fe}^{3+}$ slightly promotes the densification and grain growth

simultaneously; however, more $\text{La}^{3+}\text{-Fe}^{3+}$ co-doped NKN ceramics demonstrate a rather poor density and nearly non-grown grains. It can be thought that a change in crystal structure may make the mass transportation more difficult in compact structures, as NKN ceramics change from an orthorhombic to a pseudo-cubic structure with increasing z or y .

Fig. 4 shows the dielectric properties of doped NKN ceramics sintered in the temperature range of $1060\text{--}1130^\circ\text{C}$ to obtain as high a density as possible. Fe^{3+} , La^{3+} or $\text{La}^{3+}\text{-Fe}^{3+}$ co-doping clearly show different effects on the dielectric constants changing with temperature. A very slight change can be seen for samples doped with Fe_2O_3 . Their Curie temperatures appear the same because of unchanged crystal structures due to the addition of Fe^{3+} . However, the addition of La^{3+} or La-FeO_3 significantly decreases the Curie temperature on increasing the doping content. NKN ceramics become paraelectric phases when the doping content gets higher. These results are consistent with the above XRD results. Generally speaking, donor doping usually results in a lowered Curie temperature as in the case of La^{3+} -doped NKN ceramics [26].

Fig. 5 compares the ferroelectricity of doped NKN ceramics sintered at 1080°C for 4 h. It can be seen that the addition of a small amount of Fe_2O_3 or La-FeO_3 can improve ferroelectric properties of NKN ceramics. The remanent polarization is $15.1\ \mu\text{C}/\text{cm}^2$ for undoped NKN ceramics, changing to $21.5\ \mu\text{C}/\text{cm}^2$ for the 0.5 mol%

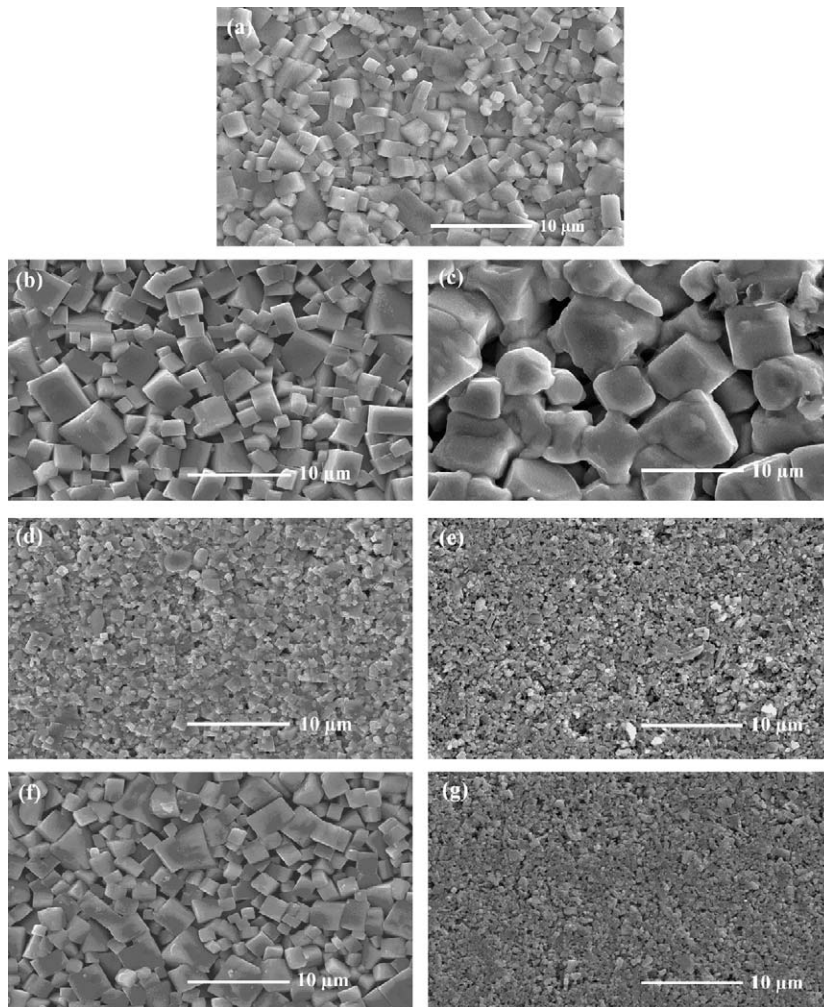


Fig. 3. Surface grain morphology of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics doped with different amounts of Fe_2O_3 (x), La_2O_3 (y) and La-FeO_3 (z): (a) $x = 0$ or $y = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $y = 0.005$, (e) $y = 0.02$, (f) $z = 0.005$ and (g) $z = 0.015$.

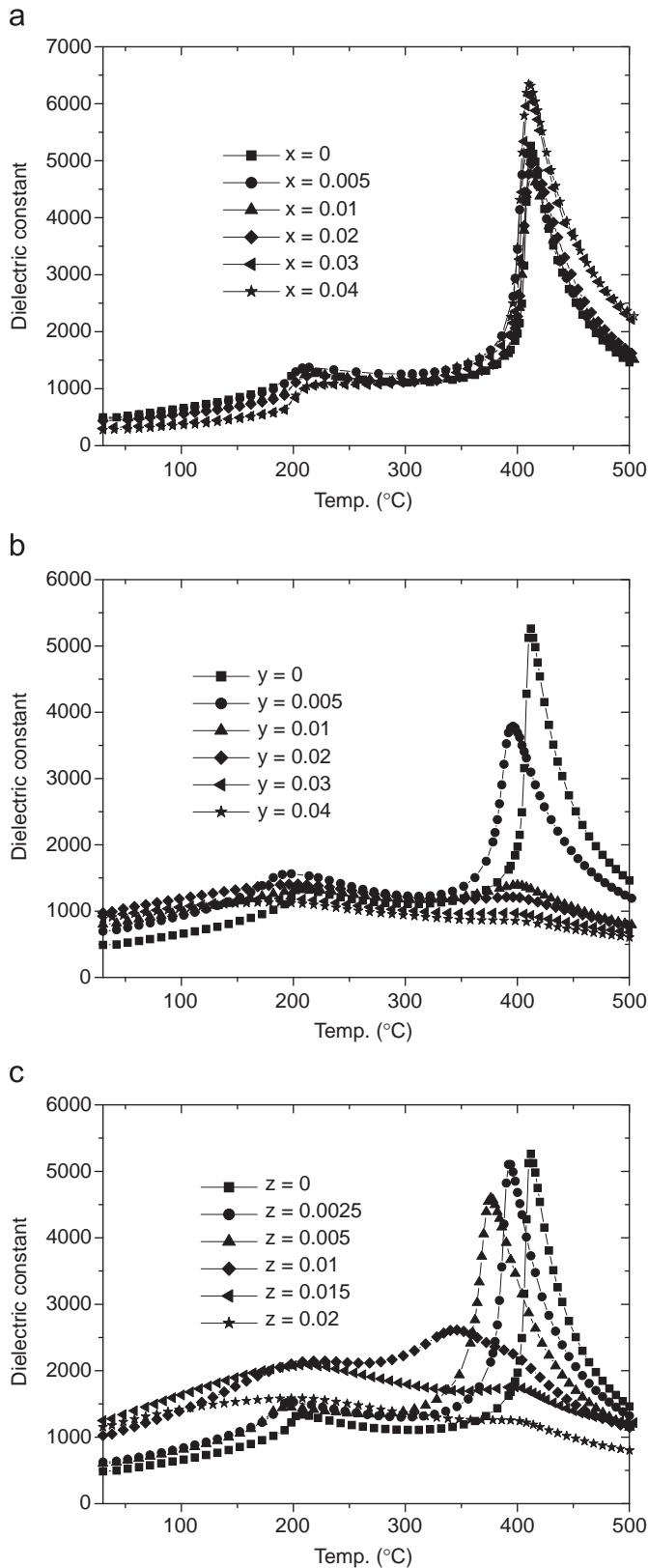


Fig. 4. Dielectric constants at 100 kHz as a function of temperature of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics doped with different amounts of (a) Fe_2O_3 (x), (b) La_2O_3 (y) and (c) La-FeO_3 (z) as indicated.

Fe^{3+} -doped NKN ceramics and further increases to $26.5 \mu\text{C}/\text{cm}^2$ for the 0.25 mol% La-FeO_3 -doped NKN ceramics. Moreover, the coercive fields of the 0.25 mol% La-FeO_3 -doped NKN ceramics are

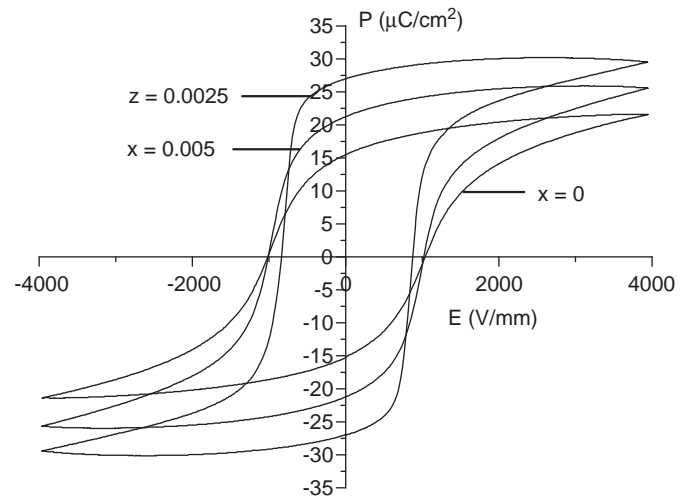


Fig. 5. Hysteresis loops of polarization versus electric field for $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ ceramics doped with different amounts of Fe_2O_3 (x) or La-FeO_3 (z) as indicated.

also slightly reduced. It can be thought that the improvement in ferroelectricity may be due to the adjustment in the crystal symmetry or domain structures, and the enhanced densification behavior. The doping of Fe^{3+} actually should induce hard properties owing to the formation of oxygen vacancies and thus the remanent polarization should not increase. Moreover, the doping of La-FeO_3 does not produce any lattice defect; however, it changes the structure of NKN from orthorhombic to pseudo-cubic symmetry, thereby reducing the ferroelectricity. Therefore, based on the above analysis, the increase of the remanent polarization as a result of doping a small amount of La^{3+} or La-FeO_3 could be predominantly attributed to the change of densification. Unfortunately, La^{3+} -doped NKN ceramics or Fe^{3+} -doped samples at higher doping levels own relatively high conductivities owing to lattice defects (for La^{3+}) and changeable valences (for Fe ions), making the measurement difficult due to a higher leakage current. The higher conductivity of LaFeO_3 itself decreases the resistance of La^{3+} and Fe^{3+} codoped NKN ceramics [28].

The various piezoelectric and electromechanical properties of modified NKN ceramics are shown in Table 1. It should be noted that high loss tangent values were obtained in samples with higher doping contents, also leading to a big dielectric constant value contributed by free charged species at low frequencies. In general, the piezoelectric constant d_{33} and the coupling factor k_p were improved by adding a small amount of Fe^{3+} and La^{3+} - Fe^{3+} . Most improvement caused by Fe^{3+} doping or Fe^{3+} - La^{3+} co-doping can be considered to be a result of the increased densities and a slightly adjusted crystal structure.

4. Conclusions

$\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ lead-free piezoelectric ceramics doped with different contents of Fe_2O_3 , La_2O_3 or La-FeO_3 were prepared by ordinary sintering. Extremely different effects of these dopants on the sintering, structures and electrical properties of NKN ceramics were demonstrated. The addition of a small amount of Fe_2O_3 or La-FeO_3 promotes densification and increases ferroelectric and piezoelectric properties. On the contrary, La^{3+} doping tends to cause poor densities, and thus extremely high loss tangent values. Doped NKN ceramics by ordinary sintering can reach a piezoelectric constant d_{33} of 145 pC/N and a coupling factor k_p of 43%.

Table 1Room-temperature electrical properties of Na_{0.5}K_{0.5}NbO₃ ceramics modified with different amounts of dopants (Fe₂O₃, La₂O₃ and La–FeO₃).

Compositions	Fe ₂ O ₃ (100x)				La ₂ O ₃ (100y)		La–FeO ₃ (100z)		
	0	0.5	1	2	0.5	1	0.25	0.5	1
Relative density (%)	95.1	97.9	97.5	97.6	93.3	75.8	96.7	95.5	78.6
Dielectric constant at 25 °C, 1 kHz	603	593	550	529	815	1357	723	713	1214
Curie temperatures (°C)	412	412	412	412	396	216	392	376	340
Loss tangent at 25 °C, 1 kHz	0.034	0.042	0.043	0.058	0.179	0.315	0.039	0.048	0.091
Coupling factor <i>k_p</i> (%)	32	41	35	29	34	19	43	35	20
Piezoelectric constant <i>d</i> ₃₃ (pC/N)	87	136	106	80	92	28	145	110	35

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