Electrical properties of manganese modified sodium potassium lithium niobate lead-free piezoelectric ceramics

Ruzhong Zuo · Jian Fu · Shi Su · Xusheng Fang · Jiang-Li Cao

Abstract Effects of MnO_2 doping on the microstructure, densification, dielectric, ferroelectric and piezoelectric properties of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ (NKLN) lead-free piezoelectric ceramics were investigated. On the one hand, the addition of a small amount of MnO_2 has little effect on the crystalline structure, however, slightly promotes sintering and grain growth, and improves the uniformity of microstructure to a certain degree. On the other hand, MnO_2 doped NKLN ceramics show hard properties in piezoelectric activities, possessing decreased room-temperature dielectric constant, loss tangent and piezoelectric constants d_{33}, and increased mechanical quality factors Q_m. The 1.2 mol% MnO_2 doped NKLN ceramics have a loss tangent of approximately 1%, a Q_m of ~ 170 and a d_{33} of 150 pC/N. These effects were considered to come from the formation of oxygen vacancies and the multi-valence states of Mn ions.

1 Introduction

Concerns of lead pollution from conventional piezoelectric ceramics, such as $Pb(Zr,Ti)O_3$ (PZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT), have urged people to search for lead-free alternatives, although these traditional piezoelectric materials have superior electrical properties and have been widely applied in industry [1]. It was known that to date there have been two main lead-free candidate systems. Alkaline niobate systems considered as nowadays most promising candidates show obvious advantages over $(Bi_{0.5}Na_{0.5})TiO_3$ based systems mostly investigated in an early stage [2–13]. Particularly, the Li, Ta, and Sb modified $(N_{0.5}K_{0.5})NbO_3$ (NKN) ceramics possess significantly improved piezoelectric and electromechanical properties and their properties are comparable to those of PZT systems [5, 8, 12]. These properties can be further obviously advanced by texturing these ceramics in a certain crystallographic direction. However, some problems have been realized in these materials, such as processing complexity, heterogeneous microstructure, low durability against moisture, high loss tangent and low electric fatigue resistance, except that their properties need further to be improved. Therefore, the improvement or modification of these high-performance lead-free piezoelectric ceramics proves to be definitely essential for the final industry application.

As one important member of alkaline niobate systems, Li doped NKN ceramics show relatively high Curie temperatures (T_c) and good electrical properties [6]. A composition of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ (NKLN) near the morphotropic phase boundary (MPB) has a T_c of 463 °C. It thus can be applied as high-performance lead-free candidate materials. Its T_c can compare with typical material systems for high-temperature application, such as $BiScO_3$-$0.64PbTiO_3$ and modified systems [14]. Moreover, the addition of Li greatly improves the densification of NKN ceramics. However, based on shared problems of these systems, Li-doped NKN ceramics needs to be further modified.

The purpose of this study is to investigate the effect of manganese doping on various electric properties and structures of NKLN ceramics. NKLN ceramics were

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reported to have a tetragonal structure at room temperature. Alkaline niobate systems are usually characteristic of soft properties, owing to a relatively high loss tangent (2–5%) and low mechanical quality factors. Manganese ions have been frequently used as a dopant to improve electrical properties of Pb-based perovskite ceramics and some lead-free compositions [15–17]. The role of manganese in Li-doped NKN ceramics will be explored in this work and hard properties are expected owing to MnO_2 doping.

2 Experimental

A conventional mixed oxide route was applied to make the powder with the composition of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$. The raw materials used were sodium carbonate (Na_2CO_3, 99.8%), potassium carbonate (K_2CO_3, >99.0%), lithium carbonate (Li_2CO_3, 99.9%) and niobium oxide (Nb_2O_5, 99.9%). Firstly, these powders were weighed according to the chemical formula and then ball mixed in a planetary mill in anhydrous ethanol for 18 h. After drying, the powder mixture was calcined in an alumina crucible at 900 °C for 5 h. The calcined powder was then mixed with a small amount of manganese oxide (MnO_2, 99.5%), represented by the formula of $(1 - x)NKLN + xMnO_2$ ($x = 0$, 0.003, 0.006, 0.009, 0.012 and 0.015). The MnO_2 added NKLN powder mixtures were milled in a planetary mill for 24 h to reduce the particle size and to get the dopant homogeneously distributed. The dried power was compacted into disks in a stainless steel die.

Sintering was carried out in air in a temperature range of 1,020–1,080 °C for 2–4 h in a high-temperature oven. The samples were buried with the corresponding powder and covered with an inverted alumina crucible. The density of the sintered samples was measured by the Archimedes method. Powder X-ray diffraction (XRD, Rigaku, Tokyo, Japan) patterns of crushed pellets were recorded in the 2θ range of 20–60° with a Cu Ka radiation. The microstructure of the sintered samples from natural surfaces was observed by means of a scanning electron microscope (SEM, JEOL6301F, Tokyo, Japan).

Silver electrodes were made on two major surfaces of each sample for electrical characterization. Dielectric properties were measured as a function of temperature and frequency by a 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 modified Sawyer-Tower bridge and an inductive displacement gauge. For the piezoelectric and electromechanical measurements, samples were firstly poled in a silicone oil bath at 3 kV/mm at 150 °C for 20 min. One day after poling, piezoelectric strain constant d_{33} was then measured by a Belincourt-meter (YE2730,

Sinoceram, Yangzhou, China), and the planar electromechanical coupling factor k_p was determined by a resonance-antiresonance method.

3 Results and discussion

The XRD patterns of the MnO_2 doped NKLN ceramics sintered at 1,050 °C are shown in Fig. 1. The results indicate that NKLN ceramics have a pure tetragonal perovskite structure. The addition of MnO_2 does not change the crystalline structure of NKLN ceramics within the studied doping level. Up to 1.5 mol% MnO_2 can be completely dissolved into the lattice of NKLN ceramics, as no second phase is observed. Mn ions are usually considered to occupy B-site in a perovskite structure. However, it is difficult to decide that A-site cation vacancies or oxygen vacancies will be produced owing to the substitution of Mn ions for Nb^{5+} as Mn ions may have different valences after sintering in air. The role of Mn ions is important as it will have different effects on the electrical properties as an acceptor or donor dopant. However, the lattice constants seem to not clearly change due to the addition of MnO_2 because no shift of the diffraction peaks can be observed. One reason could be that the doping level is still not high enough. In addition, the lattice shrinkage from the atomic vacancies compensates for the lattice expansion from the ionic replacement. (Ionic sizes: 0.67 nm and 0.54 nm for Mn^{2+} and Mn^{4+}, respectively; 0.64 nm for Nb^{5+}) [18].

Figure 2 shows the surface morphology of MnO_2 doped NKLN ceramics sintered at 1,060 °C for 3 h. All samples have cubic grains typical for alkaline niobate ceramics. The grain size increases with MnO_2 doping. Pure NKLN ceramics have an average grain size of 2.7 μm and the
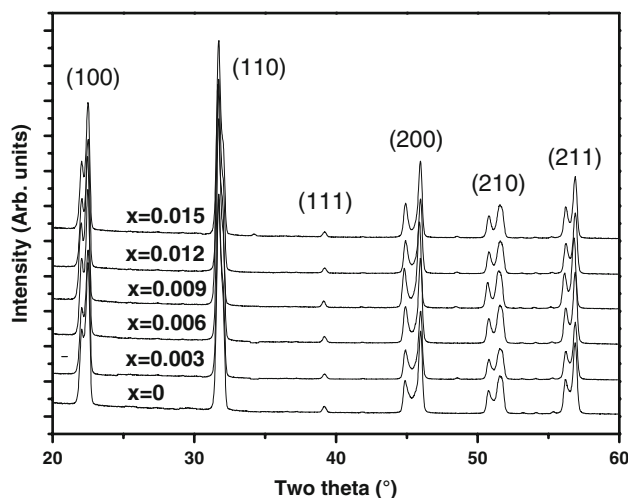

Fig. 1 X-ray diffraction patterns of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ ceramics modified with different MnO_2 doping contents as indicated

1.5 mol% MnO_2 doped NKLN ceramics own an average grain size of 7.1 μm. The densities of all sintered samples are larger than 96% theoretical values. In undoped or less doped NKLN ceramics, grains are not uniform and some grains grow abnormally. The non-uniformity of grains seems to be improved by the addition of MnO_2, as seen from Fig. 2c and d. The exaggerated grain growth was reported to be frequently observed in alkaline niobate tantalate based ceramics. The possible reason is interrelated to the occurrence of lithium which can act as a sintering aid by forming a liquid phase to promote the grain growth and densification simultaneously. This phenomenon has been also observed in Li-doped PMN-PT ceramics [19]. The addition of MnO_2 represses the mobility of grain boundary to a certain degree such that a relatively uniform microstructure is obtained. However, MnO_2 doping does not alter the grain morphology (still cubic) of NKLN ceramics.

The dielectric constant and loss tangent of MnO_2 doped NKLN ceramics as a function of temperature are shown in Fig. 3. The dielectric constant versus temperature curves show that all samples have only one phase transition above room temperature. The Curie temperatures are not changed by the addition of MnO_2. However, it can be noted that loss tangent values slightly decrease with MnO_2 doping below 200 °C. As Mn ions have different valence states which can be readily changed into another, free charges in the ceramics can be absorbed during this process so that the electric resistance can be improved. It was found that MnO_2 dopant can improve the loss values in many materials. MnO_2 was a frequently employed modifier in PZT ceramics. However, at higher temperatures, MnO_2 doped NKLN ceramics exhibit higher losses.
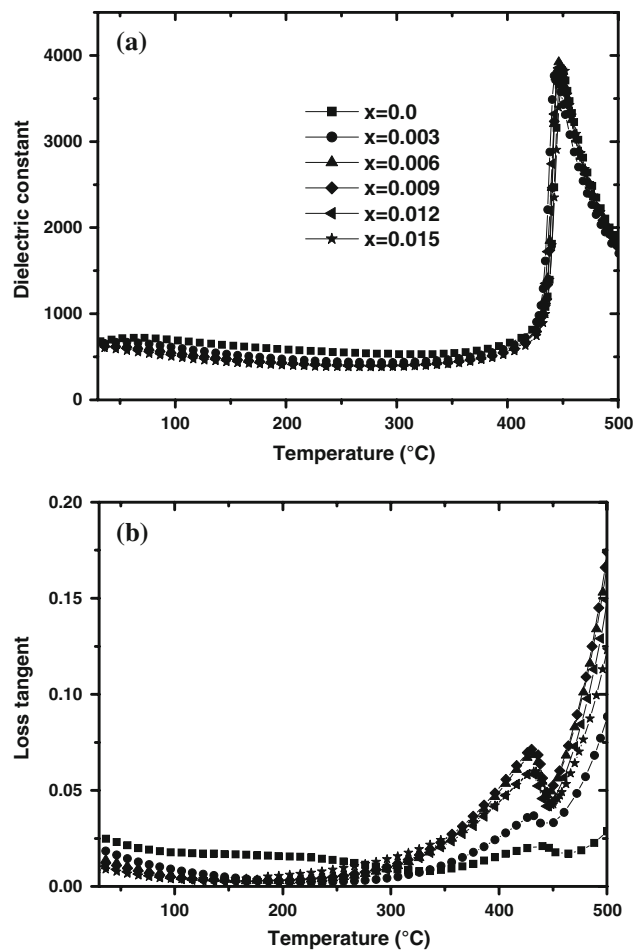

Fig. 3 Dielectric constants (a) and losses (b) at 100 kHz of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ ceramics modified with different MnO_2 doping contents as indicated

Fig. 2 Surface morphology of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ ceramics modified with different MnO_2 doping contents: (a) $x = 0$, (b) $x = 0.003$, (c) $x = 0.009$ and (d) $x = 0.015$
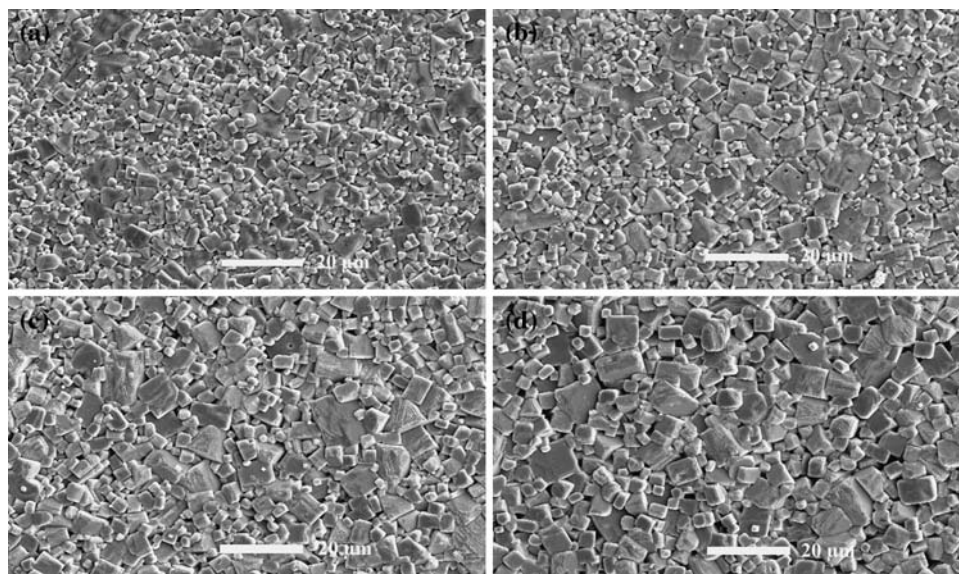
Figure 4 shows the hysteresis loops of polarization and strain versus electric field for MnO_2 doped NKLN ceramics. The remanent polarization P_r and the coercive field E_c are 16.5 $\mu C/cm^2$ and 2.01 kV/mm for undoped NKLN ceramics. As the doping level of MnO_2 is less than 0.9%, P_r decreases rapidly but E_c has a solely slight change with MnO_2 doping. The materials exhibit double hysteresis like
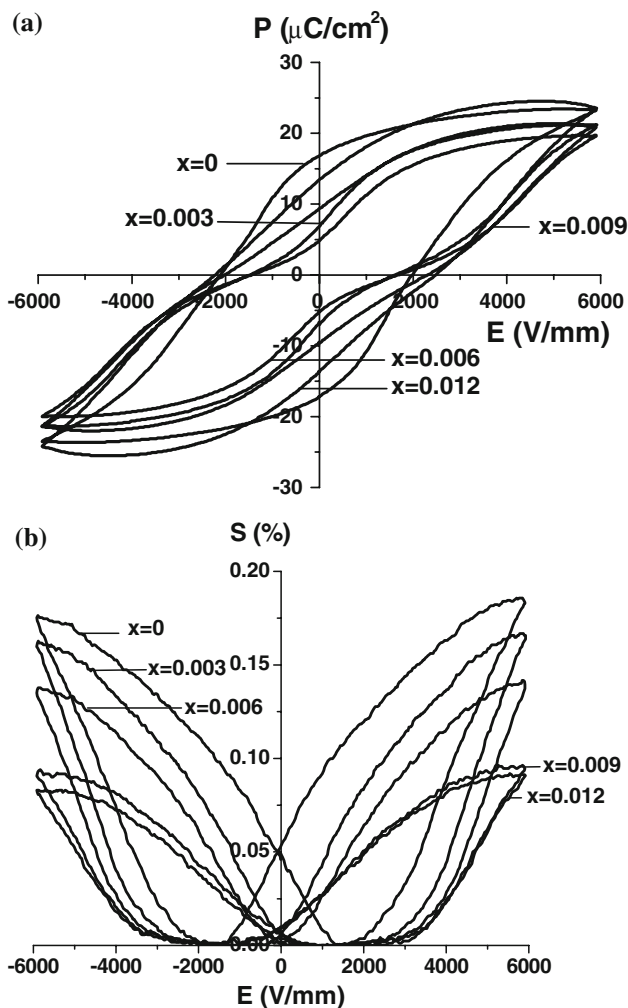

(a)

(b)

Fig. 4 Polarization (**a**) and strain (**b**) versus electric field of $(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$ ceramics modified with different MnO_2 doping contents as indicated

loops, typical of hardened materials [20]. With further increasing the doping content, P_r slightly changes but E_c increases evidently. Both stages indicate that MnO_2 doping makes the material harder. The substitution of Mn ions for B-site Nb^{5+} produces oxygen vacancies. Mn ions and oxygen vacancies may form defect dipoles. Upon being driven by an electric field, defect dipoles tend to distribute along the polarization direction. As a result of low defect migration rates, defect dipoles will provide inner biased field to reverse the switched polarization, causing a low remanent polarization. Moreover, defect dipoles also offer pinning effects on domain switching, making the ceramic become hardened and exhibit a higher coercive field. The corresponding strain driven by an ac field becomes smaller with doping MnO_2, as shown in Fig. 4b. This hardening effect from MnO_2 doping is also reflected by the measurement of dielectric properties where it was seen that both the dielectric constant and loss tangent get lower.

Table 1 summarizes various properties of MnO_2 doped NKLN ceramics. Density is slightly improved when a small amount of MnO_2 is used. However, Room-temperature dielectric properties change with MnO_2 doping. A corresponding change is that the mechanical quality factor Q_m was enhanced by the addition of MnO_2. Piezoelectric constants d_{33} and electromechanical coupling factors k_p become smaller due to pinning effects from defect dipoles, as discussed above. All these changes reflect that MnO_2 doping makes the ceramics harder. Considering that alkaline niobate systems usually have a relatively large loss values and tend to have soft properties, they are not suitable for some high-power or high-voltage applications. Therefore, MnO_2 can be considered as a dopant to decrease the loss values to an acceptable level, and to appropriately improve Q_m as well.

4 Conclusion

MnO_2 doped NKLN lead-free piezoelectric ceramics have been prepared by a conventional solid reaction method. Their structure, density and various electrical properties were investigated. The results show that MnO_2 doping has

Table 1 Room-temperature electric properties of $(1-x)(Na_{0.5}K_{0.5})_{0.935}Li_{0.065}NbO_3$-$xMnO_2$ ceramics

MnO_2 content, $100x$	0	0.3	0.6	0.9	1.2	1.5
Relative density (%)	96.2	97.5	98.1	97.4	96.5	96.1
Dielectric permittivity at 100 kHz	679	645	638	630	619	608
Loss tangent at 100 kHz	0.0248	0.0184	0.0138	0.0122	0.0102	0.009
Piezoelectric constant, d_{33} (pC/N)	210	195	182	165	145	134
Coupling factor k_p (%)	40	38	36	33	30	26
Mechanical quality factor, Q_m	80	85	102	135	169	173

a slight effect on the densification and microstructure of NKLN ceramics. However, the ceramics get harder in piezoelectric activities, exhibiting lower relative permittivity and loss values, higher quality factors, and decreased piezoelectric constants and electromechanical coupling factors. The 1.2 mol% MnO_2 doped NKLN ceramics have a loss tangent of approximately 1%, a Q_m of $\sim$170, a d_{33} of 150 pC/N and a k_p of 30%. The results indicate that MnO_2 can be a usable dopant to make NKLN ceramic possible for some high power applications.

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