

# Dielectric and piezoelectric properties of MnO<sub>2</sub>-doped K<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>0.92</sub>Sb<sub>0.08</sub>O<sub>3</sub> lead-free ceramics

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Received: 17 May 2009 / Accepted: 24 August 2009 / Published online: 9 September 2009  
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**Abstract** Lead-free MnO<sub>2</sub>-doped K<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>0.92</sub>Sb<sub>0.08</sub>O<sub>3</sub> ceramics have been fabricated by a conventional ceramic technique and their dielectric and piezoelectric properties have been studied. Our results show that a small amount of MnO<sub>2</sub> (0.5–1.0 mol%) is enough to improve the densification of the ceramics and decrease the sintering temperature of the ceramics. The co-effects of MnO<sub>2</sub> doping and Sb-substitution lead to significant improvements in the ferroelectric and piezoelectric properties. The K<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>0.92</sub>Sb<sub>0.08</sub>O<sub>3</sub> ceramic with 0.5 mol%MnO<sub>2</sub> doping possesses optimum properties:  $d_{33} = 187$  pC/N,  $k_p = 47.2\%$ ,  $\epsilon_r = 980$ ,  $\tan\delta = 2.71\%$  and  $T_c = 287$  °C. Due to high tetragonal-orthorhombic phase transition temperature ( $T_{O-T} \sim 150$  °C), the K<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>0.92</sub>Sb<sub>0.08</sub>O<sub>3</sub> ceramic with 0.5 mol%MnO<sub>2</sub> doping exhibits a good thermal stability of piezoelectric properties.

## 1 Introduction

Lead-containing piezoelectric materials with perovskite structure, such as Pb(Zr,Ti)O<sub>3</sub> and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)-PbTiO<sub>3</sub>, have been widely used in electronic and microelectronic devices because of their excellent piezoelectric and ferroelectric

properties. However, the strong toxicity and high evaporation of lead oxide during sintering have caused a crucial environmental pollution. Therefore, it is necessary to develop lead-free piezoelectric ceramics with good piezoelectric properties for replacing the lead-containing ceramics in various applications.

Alkali niobate K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> (KNN), a solid solution of ferroelectric KNbO<sub>3</sub> and antiferroelectric NaNbO<sub>3</sub>, is considered as a promising candidate for lead-free piezoelectric ceramics because of its high Curie temperature (about 420 °C), good ferroelectric properties ( $P_r = 33$  μC/cm<sup>2</sup>) and large electromechanical coupling factors [1, 2]. However, it is very difficult to obtain dense and well-sintered KNN ceramics using an ordinary sintering process because of the volatility of alkaline elements at high temperature. For a well-sintered KNN ceramic (e.g. prepared by hot-pressing technique), it possesses good piezoelectric properties ( $d_{33} = 160$  pC/N,  $k_p = 45\%$ ) and high density ( $\rho = 4.46$  g/cm<sup>3</sup>). [2] However, there is severe degradation in piezoelectric properties ( $d_{33} = 80$  pC/N,  $k_p = 36\%$ ) and density ( $\rho = 4.25$  g/cm<sup>3</sup>) for an air-fired KNN ceramics. [1, 3] A number of studies have been carried out to improve the sinterability and electrical properties of KNN ceramics, including the formation of solid solutions such as Li- and Ta-modified KNN [4], KNN-LiSbO<sub>3</sub> [5, 6], KNN-BaTiO<sub>3</sub> [7], K<sub>0.475</sub>Na<sub>0.475</sub>Li<sub>0.05</sub>NbO<sub>3</sub>-Bi<sub>0.48</sub>Na<sub>0.48</sub>Ba<sub>0.04</sub>TiO<sub>3</sub> [8], KNN-LiNbO<sub>3</sub> [9], KNN-Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> [10] and KNN-Li(Nb,Ta,Sb)O<sub>3</sub> [11], and the use of sintering aids, e.g. K<sub>5.4</sub>Cu<sub>1.3</sub>Ta<sub>10</sub>O<sub>29</sub> [12] and CuO [13]. It has been known that Sb has a much larger Pauling electronegativity than Nb (2.05 vs. 1.5). Therefore, the partial substitution of Sb<sup>5+</sup> for Nb<sup>5+</sup> induces a strong covalency in the KNN perovskite, which favors the ferroelectricity and piezoelectricity. [11, 14] It is also noted that MnO<sub>2</sub> is an effective dopant in the Pb-containing piezoelectric ceramics to enhance densification and reduce loss tangent  $\tan\delta$ . [15, 16] In the present work, MnO<sub>2</sub>-doped

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$\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  ceramics,  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$ , were prepared by ordinary solid-state sintering, and the effects of  $\text{MnO}_2$  doping on the microstructures, dielectric and piezoelectric properties of  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  ceramics were investigated.

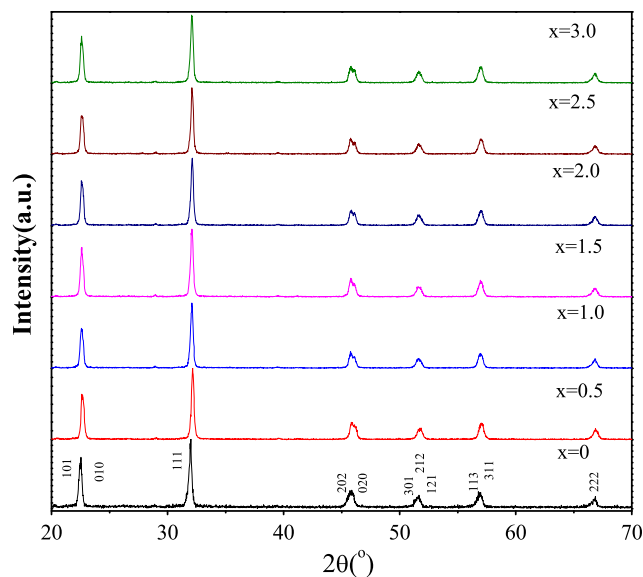
## 2 Experimental

$\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics ( $0 \leq x \leq 3.0$ ) were prepared by an ordinary sintering technique using analytical-grade metal oxides or carbonate powders:  $\text{Na}_2\text{CO}_3$  (99.8%),  $\text{K}_2\text{CO}_3$  (99.9%),  $\text{Nb}_2\text{O}_5$  (99.5%),  $\text{Sb}_2\text{O}_3$  (99%) and  $\text{MnO}_2$  (99%). The stoichiometric  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  powder was first synthesized at 880 °C for 6 h by a solid state reaction. After the calcination,  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  and  $\text{MnO}_2$  powders were weighed according to the formula of  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  and then ball-milled for 8 h. The resulting powders were mixed thoroughly with a PVA binder solution and then pressed into disk samples with the diameter of 15.0 mm and thickness of 1.20 mm. The disk samples were finally sintered at 1,080–1,120 °C for 4 h in air. Silver electrodes were fired on the top and bottom surfaces of the sintered samples. The ceramics were poled under a dc field of 5–6 kV/mm at room temperature in a silicon oil bath for 30 min.

The crystalline structure of the sintered samples was examined using X-ray diffraction (XRD) analysis with  $\text{CuK}_\alpha$  radiation (DX-1000). The bulk density  $\rho$  was measured by the Archimedes' method. The microstructures were observed using scanning electron microscopy (JEOL JSM-5900LV). The relative permittivity  $\epsilon_r$  and loss tangent  $\tan\delta$  of the ceramics at 1, 10 and 100 kHz were measured as functions of temperature using an impedance analyzer (Agilent 4192A). A conventional Sawyer–Tower circuit was used to measure the polarization hysteresis ( $P$ - $E$ ) loop at 100 Hz. The electromechanical coupling factor  $k_p$  and electromechanical quality factor  $Q_m$  were determined by the resonance method according to the IEEE Standard using an impedance analyzer (Agilent 4294A). The piezoelectric coefficient  $d_{33}$  was measured using a piezo- $d_{33}$  meter (ZJ-3A, China).

## 3 Results and discussions

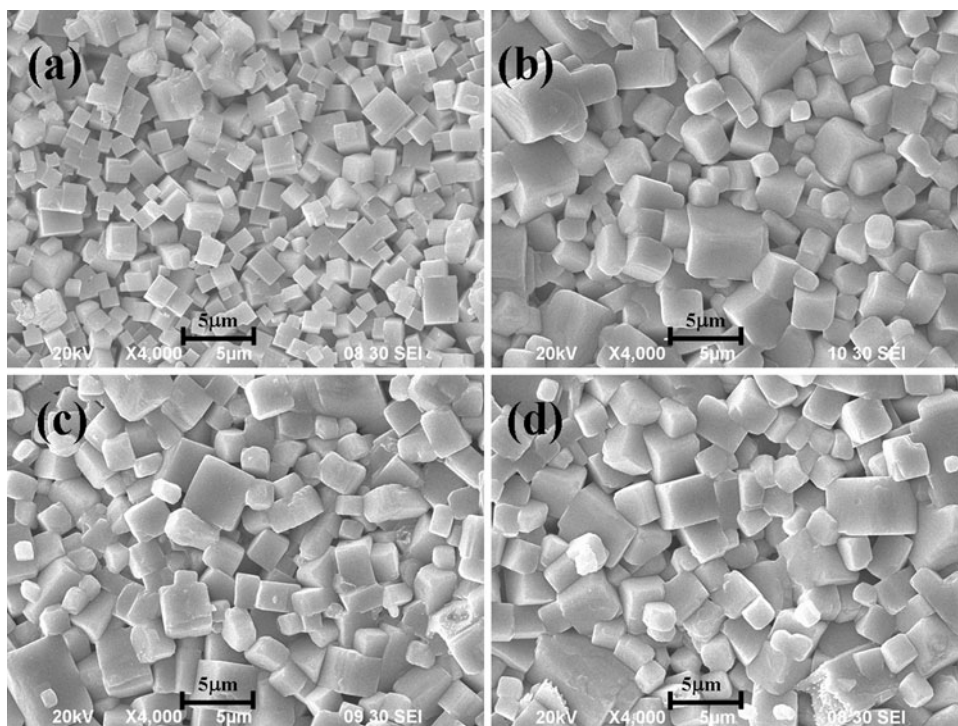
Figure 1 shows the XRD patterns of  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics. From Fig. 1, all the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics possess a pure perovskite structure with orthorhombic symmetry and no second phase can be detected. The XRD patterns of the ceramics have been indexed by JCPDF card 71-2171.



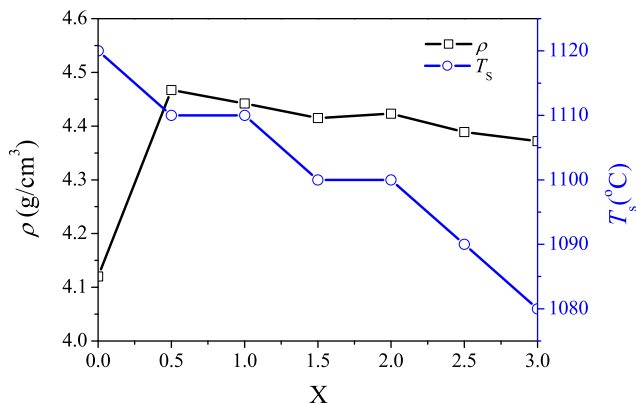
**Fig. 1** XRD pattern of  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics

The addition of  $\text{MnO}_2$  to  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  does not cause any significant change to the crystalline structure.

The SEM micrographs of the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics with  $x = 0, 1.0, 2.0$  and  $3.0$  are shown in Fig. 2, while Fig. 3 shows the variations of the bulk density  $\rho$  and optimum sintering temperature  $T_s$  with  $x$ . As shown in Fig. 2a, although the sintering temperature is high (1,120 °C), the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramic with  $x = 0$  (i.e., without  $\text{MnO}_2$  doping) has a very loose structure and a large amount of pores can be found. For the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  ceramic (i.e.  $x = 0$ ), the grains have a diameter of about 1.2  $\mu\text{m}$ . However, after the doping of a small amount of  $\text{MnO}_2$  ( $\geq 0.5$  mol%), the grain size increases significantly to about 2.5  $\mu\text{m}$ , the ceramics can be well sintered at 1,080–1,110 °C and become considerably dense, and there is almost no pore on the surface of the ceramics (Fig. 2b–d). As shown in Fig. 3, the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  ceramic without  $\text{MnO}_2$ -doping has a low bulk density of 4.12  $\text{g}/\text{cm}^3$ . On the basis of the XRD results, the relative density of the ceramic with  $x = 0$  is about 90%. However, after the doping of 0.5–1.0 mol%  $\text{MnO}_2$ , the ceramics give a high density of 4.44–4.48  $\text{g}/\text{cm}^3$  (relative density > 97%). As  $x$  further increase to 3.0, the bulk density decreases slightly to 4.37  $\text{g}/\text{cm}^3$  (relative density  $\sim 95\%$ ). For each composition, the ceramics were sintered at different temperatures and their density was measured. The optimum sintering temperature was determined as the sintering temperature by which the ceramic has the largest density. From Fig. 3, as  $x$  increases, the optimum sintering temperature for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics decreases. It can be clearly seen that the addition of a



**Fig. 2** SEM micrographs of the  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + x\text{mol}\%MnO_2$  ceramics: **a**  $x = 0$ , sintered at  $1,120\text{ }^\circ\text{C}$  for 4 h; **b**  $x = 1.00$ , sintered at  $1,110\text{ }^\circ\text{C}$  for 4 h; **c**  $x = 2.00$ , sintered at  $1,090\text{ }^\circ\text{C}$  for 4 h; and **d**  $x = 3.00$ , sintered at  $1,080\text{ }^\circ\text{C}$  for 4 h



**Fig. 3** Variations of the bulk density  $\rho$  and optimum sintering temperatures  $T_s$  with  $x$  for the  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + x\text{mol}\%MnO_2$  ceramics

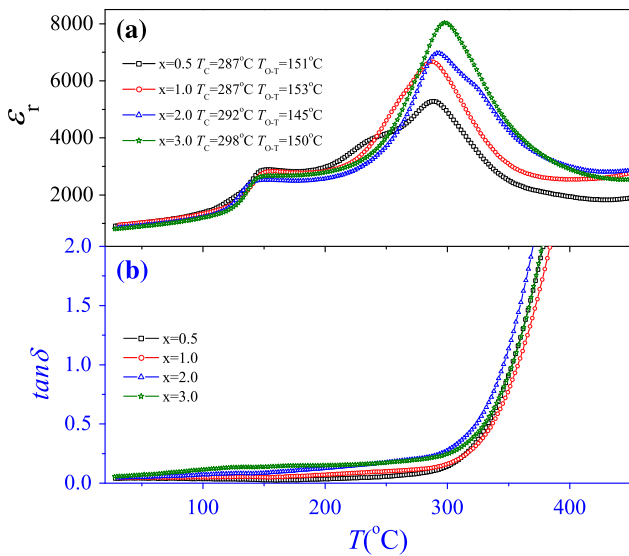
small amount of  $MnO_2$  to the  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3$  ceramics results in the significant improvement in densification and a decrease in sintering temperature.

The temperature dependences of  $\epsilon_r$  and  $\tan\delta$  for  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + x\text{mol}\%MnO_2$  ceramics at 1 kHz are shown in Fig. 4. Similar to the pure KNN [1, 2], two transition peaks are observed: one is associated with the paraelectric cubic-ferroelectric tetragonal phase transition at  $T_c$  and the other is the ferroelectric tetragonal-ferroelectric orthorhombic phase transition at  $T_{O-T}$ . As shown in Fig. 4a, the observed  $T_{O-T}$  for  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + x\text{mol}\%MnO_2$  ceramics is insensitive to the doping level  $x$  of  $MnO_2$ .

For the ceramics with  $x = 0.5\text{--}3.0$ , the observed  $T_{O-T}$  is about  $150\text{ }^\circ\text{C}$ . Unlike  $T_{O-T}$ , the observed  $T_c$  increases from  $287$  to  $298\text{ }^\circ\text{C}$  with  $x$  increasing from  $0.5$  to  $3.0$ . It can be also seen that as  $x$  increases, the value of the dielectric peak at  $T_c$  increases significantly. From Fig. 4b, for the ceramics with  $x = 0.5, 1.0, 2.0$  and  $3.0$ , the observed  $\tan\delta$  has a very weak dependence on temperature below  $T_c$  and retain almost unchangeable with temperature increasing. However, as temperature increases above  $T_c$ , a sharp increase in  $\tan\delta$  is observed in the ceramics with  $x = 0.5, 1.0, 2.0$  and  $3.0$ , which should be attributed to a decrease in electrical resistivity of the ceramics at higher temperatures, at which the ceramics become electrically conductive.

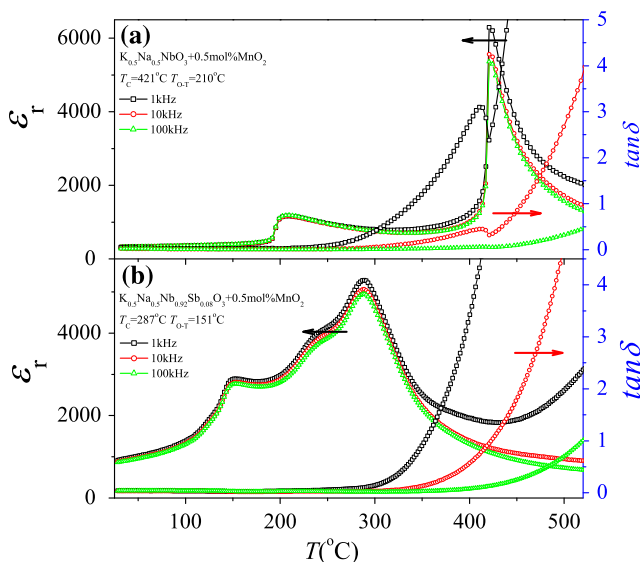
Figure 5 shows the temperature dependences of  $\epsilon_r$  and  $\tan\delta$  for the  $K_{0.5}Na_{0.5}NbO_3 + 0.5\text{ mol}\%MnO_2$  and  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + 0.5\text{ mol}\%MnO_2$  ceramics at 1, 10 and 100 kHz. It can be seen that the  $K_{0.5}Na_{0.5}NbO_3 + 0.5\text{ mol}\%MnO_2$  ceramic (i.e., Sb-free KNN ceramic with 0.5 mol%  $MnO_2$  doping) retains the classic ferroelectric characteristic, and undergoes the cubic-tetragonal phase transition at  $421\text{ }^\circ\text{C}$  ( $T_c$ ) and the tetragonal-orthorhombic phase transition at  $210\text{ }^\circ\text{C}$  ( $T_{O-T}$ ) (Fig. 5a). After the substitution of 8%  $Sb^{5+}$  for  $Nb^{5+}$ , the ceramic (i.e.,  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + 0.5\text{ mol}\%MnO_2$ ) undergoes the same two phase transitions, with both  $T_c$  and  $T_{O-T}$  shifted to lower temperatures ( $287$  and  $151\text{ }^\circ\text{C}$ , respectively) (Fig. 5b).

The  $K_{0.5}Na_{0.5}NbO_3 + 0.5\text{ mol}\%MnO_2$  ceramic is a normal ferroelectric, thus exhibiting a sharp transition peak



**Fig. 4** Relative permittivity  $\epsilon_r$  and loss tangent  $\tan\delta$  of the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics with  $x = 0.5, 1.0, 2.0$  and  $3.0$  at  $1\text{ kHz}$  as a function of temperature

at  $T_c$  in the plot of  $\epsilon_r$  versus temperature as shown in Fig. 5a. However, the substitution of  $8\%$   $\text{Sb}^{5+}$  for  $\text{Nb}^{5+}$  in the  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramic leads to a broadening of the transition peak at  $T_c$ , suggesting the appearance of a diffuse phase transition. A diffuse phase transition has been observed in many  $\text{ABO}_3$ -type perovskites and Bi-layered structure compounds, e.g.  $\text{Ba}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based ceramics [17],  $\text{K}_{0.5}\text{La}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  [18],  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  [19],  $\text{KNN-SrTiO}_3$  [20]. The diffuseness in the phase transition can be determined from the modified Curie–Weiss law  $1/\epsilon_r - 1/\epsilon_m = C^{-1}(T - T_m)^\gamma$  [19], where  $\epsilon_m$  is the

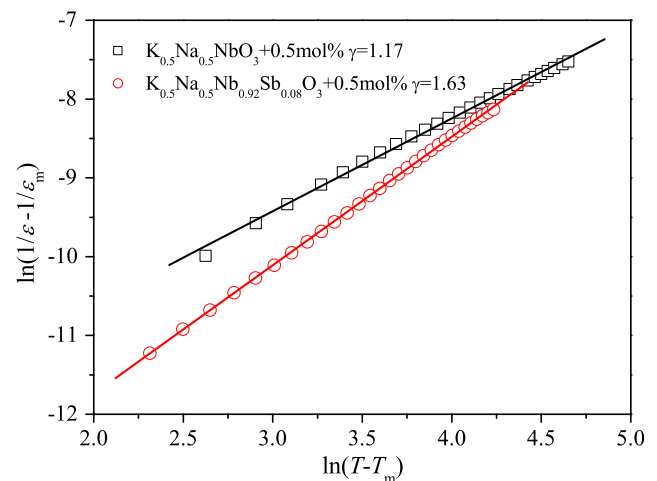


**Fig. 5** Temperature dependences of relative permittivity  $\epsilon_r$  and loss tangent  $\tan\delta$  of **a**  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramics and **b**  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics

maximum value of relative permittivity at the phase transition temperature  $T_m$ ,  $\gamma$  is the degree of diffuseness and  $C$  is the Curie-like constant. The  $\gamma$  can have a value ranging from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric.

Based on the temperature plots of  $\epsilon_r$  at  $10\text{ kHz}$ , the graphs of  $\ln(1/\epsilon_r - 1/\epsilon_m)$  versus  $\ln(T - T_m)$  for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5\text{ mol}\%\text{MnO}_2$  and  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramics were plotted, giving the results shown in Fig. 6. Both the samples exhibit a linear relationship. By least-squared fitting the experimental data to the modified Curie–Weiss law,  $\gamma$  was determined. The calculated  $\gamma$  for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramic is 1.17, revealing the normal ferroelectric characteristic. After the substitution of  $8\text{ mol}\%\text{Sb}^{5+}$ ,  $\gamma$  increases significantly to 1.63, suggesting that the substitution of  $\text{Sb}^{5+}$  makes the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramic become more relaxor, thus exhibiting a broadened transition peak as shown in Fig. 5b. The appearance of the diffuse phase transition may be ascribed to the increase in the disorder degree of B-site ions, resulting from the substitution of  $\text{Sb}^{5+}$  for  $\text{Nb}^{5+}$ .

Except for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  ceramic (i.e., without  $\text{MnO}_2$  doping), all the ceramics can be well sintered at  $1,080\text{--}1,110\text{ }^\circ\text{C}$  and have a dense structure, giving a high relative density ( $>95\%$ ), and so exhibit a well-saturated  $P$ - $E$  hysteresis loop under an electric field of  $5\text{ kV/mm}$ . Figure 7a shows the  $P$ - $E$  hysteresis loops of the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics with  $x = 0.5, 1.5$  and  $2.5$ , while the variations of the remanent polarization  $P_r$  and coercive field  $E_c$  with  $x$  are shown in Fig. 7b. For the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics,  $P_r$  increases slightly and then decreases as  $x$  increases from  $0.5$



**Fig. 6** Plot of  $\ln(1/\epsilon_r - 1/\epsilon_m)$  versus  $\ln(1/T - 1/T_m)$  for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramics and  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5\text{ mol}\%\text{MnO}_2$  ceramics. The symbols denote experimental data while the solid lines denote the least-squared fitting line to the modified Curie–Weiss law

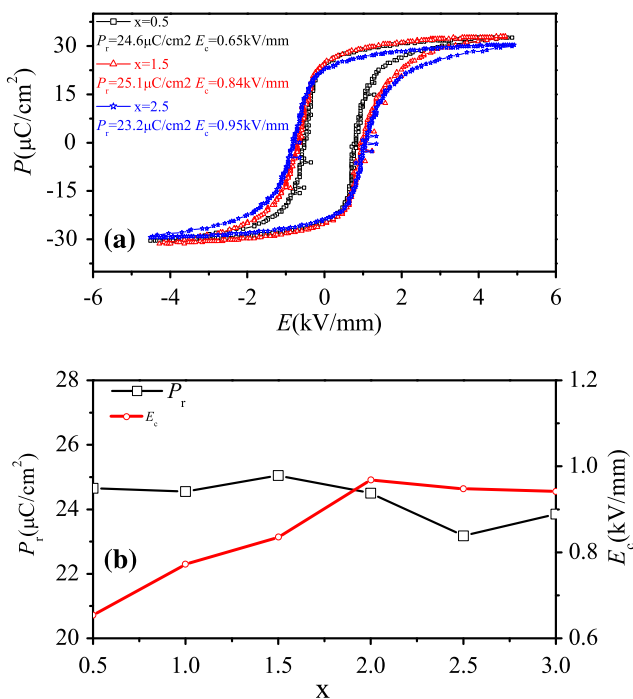
to 3.0, giving a maximum value of 26.8  $\mu\text{C}/\text{cm}^2$  at  $x = 1.5$ , while  $E_c$  increases considerably from 0.65 to 0.97 kV/mm with  $x$  increasing from 0.5 to 2.0 and then decreases slightly to 0.94 kV/mm with  $x$  further increasing to 3.0.

Figure 8 shows the variations of  $d_{33}$ ,  $k_p$ ,  $Q_m$ ,  $\epsilon_r$  and  $\tan\delta$  with  $x$  for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics. After the use of the sintering aid, the density of the ceramics increases significantly from 4.12 to 4.48 (Fig. 3), thus yielding considerable enhancement in  $d_{33}$ ,  $k_p$ , and  $Q_m$  and reduction in  $\tan\delta$ . The optimum content of  $\text{MnO}_2$  is 0.5 mol%. It can be seen that because of the poor densification, the ceramic without  $\text{MnO}_2$  doping exhibits the very high  $\tan\delta$  (65.2%) and relatively poor piezoelectricity ( $d_{33} = 95$  pC/N,  $k_p = 22.6\%$ ,  $Q_m = 6$ ). After the addition of 0.5 mol%  $\text{MnO}_2$ , the  $\tan\delta$  decrease significantly and reaches a minimum value of 2.71%. The great decrease in  $\tan\delta$  should be ascribed to the great enhancement in densification. For the ceramic with  $x = 0.5$ , the good piezoelectric and dielectric properties are obtained:  $d_{33} = 187$  pC/N,  $k_p = 47.2\%$ , and  $Q_m = 123$  (Fig. 8a), while  $\epsilon_r = 980$  and  $\tan\delta = 2.71\%$  (Fig. 8b).

Figure 9 shows the temperature dependence of  $k_p$  for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5$  mol%  $\text{MnO}_2$  ceramic. It can be seen that for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5$  mol%  $\text{MnO}_2$  ceramic, there has no depolarization below 120 °C. Because the  $T_{O-T}$  is relatively high (151 °C), the  $\text{K}_{0.5}\text{Na}_{0.5}$

$\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5$  mol%  $\text{MnO}_2$  ceramic exhibits a very good thermal characteristic. It can be seen that as temperature increases above  $T_{O-T}$ , the piezoelectricity of the ceramic become weak gradually.

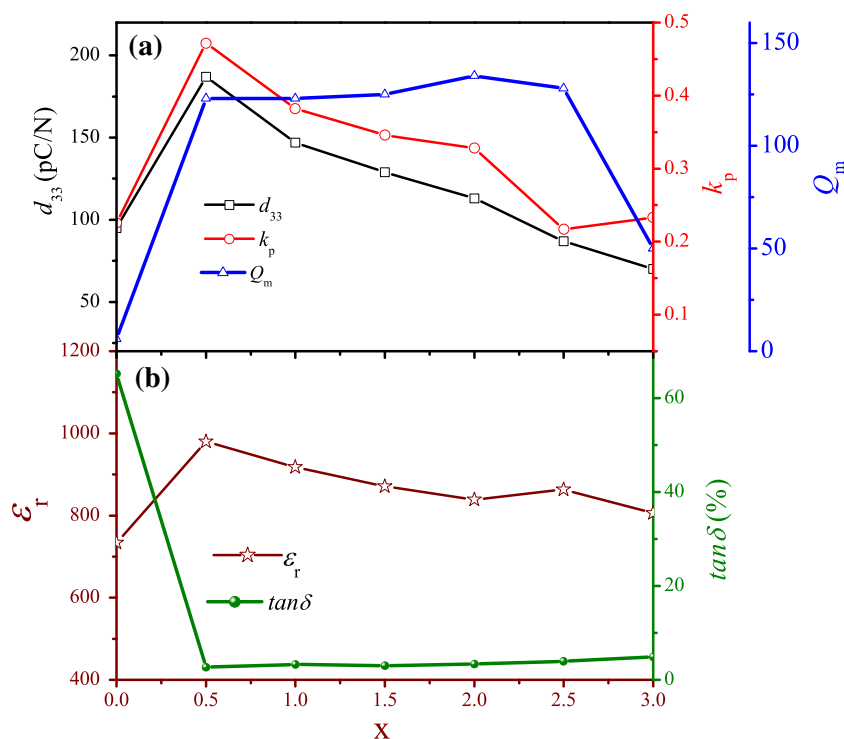
Table 1 shows the electrical properties of  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5$  mol%  $\text{MnO}_2$ ,  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5$  mol%  $\text{MnO}_2$  and  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  (i.e., without  $\text{MnO}_2$  doping) ceramics. It can be seen that compared with the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5$  mol%  $\text{MnO}_2$  ceramic, the  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 + 0.5$  mol%  $\text{MnO}_2$  ceramic exhibits typical “hardened” electrical characteristics (low  $d_{33}$ ,  $k_p$ ,  $\epsilon_r$ ,  $\tan\delta$  and  $P_r$ ; high  $Q_m$  and  $E_c$ ). After the substitution of 8%  $\text{Sb}^{5+}$  for  $\text{Nb}^{5+}$ , the observed  $d_{33}$ ,  $k_p$ ,  $\epsilon_r$ ,  $\tan\delta$  and  $P_r$  increase by about 68, 8, 200, 145 and 13%, respectively, while the observed  $Q_m$  and  $E_c$  decrease by about 63 and 13%, respectively. This suggests that after the substitution of 8%  $\text{Sb}^{5+}$  for  $\text{Nb}^{5+}$ , the ceramics become “softened”, thus giving rise to significant improvements in  $d_{33}$ ,  $k_p$  and  $\epsilon_r$ . The improvement of piezoelectric properties of the ceramics should be attributed to the strong covalency of Sb. For the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + 0.5$  mol%  $\text{MnO}_2$  ceramic, the partial substitution of  $\text{Sb}^{5+}$  for  $\text{Nb}^{5+}$  induces a much stronger covalency in the KNN-based perovskite, which favors the ferroelectricity and piezoelectricity. It can be also noted that because of the poor densification, the  $\text{MnO}_2$ -undoped  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3$  ceramic possesses the very poor piezoelectricity, indicating the effectiveness of  $\text{MnO}_2$  as a sintering aid for improving the sintering performance and electrical properties.



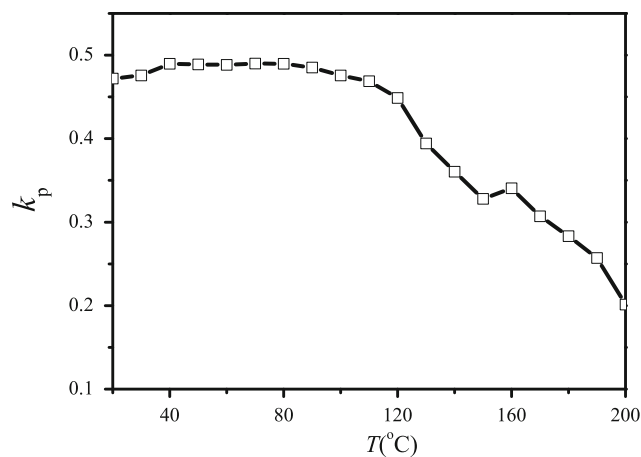
**Fig. 7** **a**  $P$ - $E$  hysteresis loops of the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics with  $x = 0.5, 1.5$  and  $2.5$ ; **b** Variations of  $P_r$  and  $E_c$  with  $x$  for the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics

### 4 Conclusions

$\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  lead-free ceramics have been fabricated by an ordinary sintering technique. Our results show that  $\text{MnO}_2$  is an excellent sintering aid for improving the sintering performance. A small amount of  $\text{MnO}_2$  (0.5–1.0 mol%) improves effectively the densification. The high densification and strong covalence of Sb lead to the significant improvement in the ferroelectricity and piezoelectricity of the ceramics. The ceramic with  $x = 0.5$  exhibits excellent ferroelectric and piezoelectric properties:  $d_{33} = 187$  pC/N,  $k_p = 47.2\%$ ,  $\epsilon_r = 980$ ,  $\tan\delta = 2.71\%$ ,  $P_r = 24.7 \mu\text{C}/\text{cm}^2$ ,  $E_c = 0.65$  kV/mm and  $T_C = 287$  °C. Because of high  $T_{O-T}$ , the ceramic with  $x = 0.5$  exhibits a very good temperature stability of piezoelectric properties. Our results also show that the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ceramics exhibit relaxor characteristic, which may be ascribed to the increase in the disorder degree of B-site ions resulting from the partial substitutions of  $\text{Sb}^{5+}$  for  $\text{Nb}^{5+}$ . It is suggested that the  $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{0.92}\text{Sb}_{0.08}\text{O}_3 + x\text{mol}\%\text{MnO}_2$  ( $x = 0.5$ –1.0) ceramics are an attractive candidate for lead-free ceramics.



**Fig. 8** Variations of  $d_{33}$ ,  $k_p$ ,  $Q_m$ ,  $\epsilon_r$  and  $\tan\delta$  with  $x$  for the  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + x\text{mol}\%MnO_2$  ceramics



**Fig. 9** Variation of  $k_p$  with temperature for the  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + 0.5\text{mol}\%MnO_2$  ceramic

**Table 1** Electrical properties of (a)  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3 + 0.5\text{mol}\%MnO_2$ , (b)  $K_{0.5}Na_{0.5}NbO_3 + 0.5\text{mol}\%MnO_2$  and (c)  $K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O_3$  ceramics

	$d_{33}$ (pC/N)	$k_p$ (%)	$Q_m$	$\epsilon_r$	$\tan\delta$ (%)	$P_r$ ( $\mu\text{m}^2/\text{cm}^2$ )	$E_c$ (kV/mm)
a	187	47.2	123	980	2.71	24.7	0.65
b	111	43.8	330	322	1.10	21.8	0.75
c	95	22.6	6	734	65.2	–	–

**Acknowledgment** This work was supported by the project of Education Department of Sichuan Province (08ZA047), and Science and Technology Bureau of Sichuan Province (09ZQ026-059)

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