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FERROELECTRICS

Investigation on the composition design and properties study of perovskite lead-free piezoelectric ceramics

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Abstract Lead-free piezoelectric ceramics can be divided into perovskite, tungsten bronze, and bismuth layered structure ceramics. In recent years, the authors' group concentrates the researches on the composition design and the properties study of perovskite lead-free piezoelectric ceramics, especially on the $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)- and $K_{1/2}Na_{1/2}NbO_3$ (KNN)-based ceramics. All the ceramics were prepared by the conventional ceramic technique. In this paper, the main results obtained are reviewed with emphasis on KNN-based ceramics, including (1) the design on new BNT-based ceramics based on the multiple complex in the A-site of ABO_3 compounds; (2) the design of KNN-based ceramics focused on the effects of Ag ion substitution, K/Na ratio, and $LiSbO_3$ on KNN-based ceramics; (3) the effects of doping on the properties of BNT- and KNN-based ceramics; and (4) the temperature stability of BNT- and KNN-based ceramics. And some prospects to be resolved in coming years from the viewpoint of the applications of the perovskite lead-free piezoelectric ceramics are also pointed out.

Introduction

It is well known that lead oxide-based piezoelectric ceramics, such as $Pb(Ti,Zr)O_3$ (PZT) and PZT-based multicomponent ceramics, are now widely used in various devices because of their superior properties. However, the toxicity of lead oxide and its high vapor pressure during material processing may bring serious problems. The demand of the sustainable development of the world and the environment and safety concerns with respect to the utilization, recycling, and disposal of Pb-based piezoelectric ceramics have induced a new surge in developing lead-free piezoelectric ceramics with properties comparable to their lead-based counter.

Lead-free piezoelectric ceramics can be divided into perovskite, tungsten bronze, and bismuth layered structure ceramics. Bismuth layered structure ceramics, such as $Bi_4Ti_3O_{12}$, with their low dielectric constant, high T_c, and high anisotropy in the longitudinal and transverse coupling coefficients are susceptible for high T_c sensors, resonators, and filters applications. Tungsten bronze materials, such as $Sr_xBa_{1-x}Nb_2O_6$, are useful for electro-optic and photorefractive applications. Lead-free piezoelectric ceramics with perovskite structure, such as bismuth sodium titanate $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)-based and $K_{1/2}Na_{1/2}NbO_3$ (KNN)-based ceramics, have shown high-electromechanical properties, and some of the ceramics also show high Curie temperature T_c. These ceramics are good candidates for actuator and high-power applications, and also for invasive ultrasonic applications. In recent years, the researches on lead-free piezoelectric ceramics have got much progress, especially after the progress of grain-oriented KNN-based ceramics has been published [1], the people believe that new piezoelectric ceramics should be "lead-free at last" [2].

The authors' group concentrates the researches on the composition design and the properties study of perovskite lead-free piezoelectric ceramics in recent years, especially on the BNT- and KNN-based ceramics. In present article, the main results obtained, especially on KNN-based

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ceramics, are reviewed. Some prospects to be resolved in coming years from the viewpoint of the applications of the perovskite lead-free piezoelectric ceramics are pointed out.

Design of new BNT-based lead-free piezoelectric ceramics

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) is considered to be an excellent candidate for lead-free piezoelectric ceramics because of its relatively high remnant polarization (38 μC/cm^2). However, BNT ceramics without substitutive ions and/or additives are very difficult to pole because of their relatively large coercive field ($E_c = 73$ kV/cm) and high-electrical conductivity. To improve the piezoelectric properties, BNT-based solid solutions with another perovskite components and the doping with other oxides were widely investigated. However, the piezoelectric properties of these ceramics are not good enough for most practical uses.

In order to further enhance the properties of BNT-based ceramics and meet the requirements for practical uses, the authors' group did the investigation on BNT-based ceramics based on the design of the multiple complex in the A-site of ABO_3 compounds. Considering the primary differences between BNT- and PZT-based ceramics, the $(Bi_{0.5}Na_{0.5})^{2+}$, Bi^{3+} and Na^+ in BNT ceramics with ABO_3 structure are defined as A-site, A_1-site, and A_2-site ions, respectively, and A-, A_1-, and A_2-site ions can be simultaneously or singly substituted partially by alkaline-earth metal ions (Ba^{2+}, Sr^{+2}, Ca^{+2}), metal ions with +3 valence (La^{3+}, Y^{3+}, and so on) and metal ions with +1 valence (K^+, Li^+, and so on), respectively [3, 4]. Under this consideration, some new members of BNT-based group, such as $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$, $[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$, $[Bi_{1-y-z}(Na_{1-x-y-z}Li_x)]_{0.5}Ba_ySr_zTiO_3$, $[Bi_{1-y-z}(Na_{1-x-y-z}K_x)]_{0.5}Ba_ySr_zTiO_3$, $[Bi_{1-y}(Na_{1-x-y}Li_x)]_{0.5}Sr_yTiO_3$, $(Bi_{0.5}Na_{0.5})_{1-x-y-z}Ba_xSr_yCa_zTiO_3$, $[(Bi_{1-x-y}La_x)\ Na_{1-y}]_{0.5}Ba_yTiO_3$, and so on, were proposed and patented, and the piezoelectric and ferroelectric properties of these ceramics were investigated.

The results of the X-ray diffractions of all the samples investigated show that the new ceramics possess a single-phase perovskite structure, and the substitute ions diffuse into the BNT lattices to form solid solutions. The bulk density of the ceramics is higher than 97% of the theoretical one. Table 1 exhibits the piezoelectric and ferroelectric properties of new BNT-based ceramics developed in authors' group. From Table 1, it can be found that these ceramics provide excellent piezoelectric and ferroelectric properties, showing that d_{33} = 190–230 pC/N, k_p = 0.34–0.41, P_r = 34.4–40.4 μC/cm^2, and E_c = 2.47–5.16 kV/mm.

Among the new BNT-based ceramics, $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ (BNKLT–*x*/*y*) ceramics possess excellent electrical properties. Compared with pure BNT ceramics, BNKLT−*x*/*y* ceramics possess simultaneously a very large P_r and a relatively low E_c, which leads to the significant enhancement of the piezoelectric properties.

The depolarization temperature T_d is an important factor for BNT-based ceramics from the viewpoint of device applications. Generally, for some classical BNT-based ceramics, the obvious enhancement of piezoelectric properties is accompanied simultaneously by the significant reduction of T_d. However, BNKLT–*x*/*y* ceramics provide simultaneously good piezoelectric properties, strong ferroelectricity, and higher T_d. Figure 1 shows the *P*–*E* hysteresis loops of BNKLT–0.15/0.075 ceramics at different temperature. It can be found from Fig. 1 that BNKLT–0.15/0.075 ceramics provide simultaneously good piezoelectric properties (d_{33} = 164 pC/N, k_p = 0.36), strong ferroelectricity (P_r = 38.9 μC/cm^2, E_c = 3.7 kV/mm), and higher T_d (about 200 °C).

The BNKLT–*x*/*y* lead-free piezoelectric ceramics have been used for making ceramic middle frequency filters and buzzers by using ordinary techniques as used for PZT-based ceramics. The measured performance of BNKLT–*x*/*y* filter and buzzers can be comparable to that of those made by using PZT counter [4].

Design of KNN-based lead-free piezoelectric ceramics

In recent years, considerable attention for lead-free piezoelectric ceramics has focused on (K,Na)NbO_3 (KNN)-based ceramics because of their good electrical properties and high Curie temperature [1, 5–21]. The researches on

Table 1 Piezoelectric and ferroelectric properties of new BNT-based ceramics developed in author's group[a]

New BNT-based systems	d_{33} (pC/N)	k_p	k_t	P_r (μC/cm^2)	E_c (kV/mm)
$Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$	230	0.41	0.505	40.4	2.5–4.0
$[Bi_{1-z}(Na_{1-y-z}Li_y)]_{0.5}Ba_zTiO_3$	208	0.37	–	38.5	3.29
$[Bi_{1-z}(Na_{1-x-y-z}K_xLi_y)]_{0.5}Ba_zTiO_3$	202	0.37	–	38.5	2.8–5.16
$[Bi_{1-z-u}(Na_{1-y-z-u}Li_y)]_{0.5}Ba_zSr_uTiO_3$	202	0.34	–	40.4	2.47–4.98
$[Bi_{1-z-u}(Na_{1-x-z-u}K_x)]_{0.5}Ba_zSr_uTiO_3$	191	0.36	–	34.4	2.58

[a] The values of d_{33}, k_p, k_t, and P_r given in Table 1 is the maximum values in this system

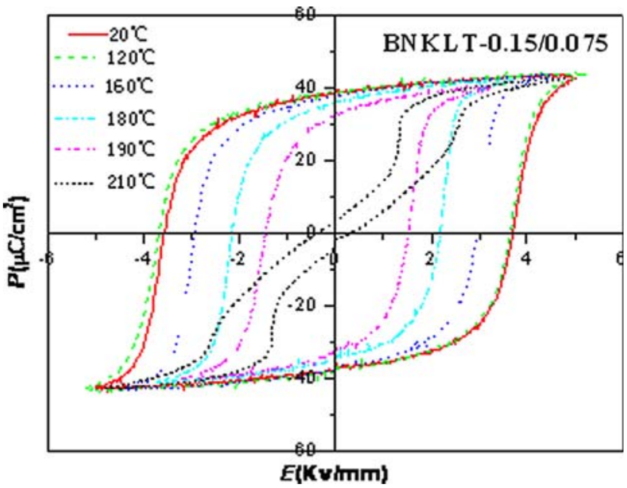

Fig. 1 *P–E* hysteresis loops of BNKLT–0.15/0.075 ceramics at different temperature

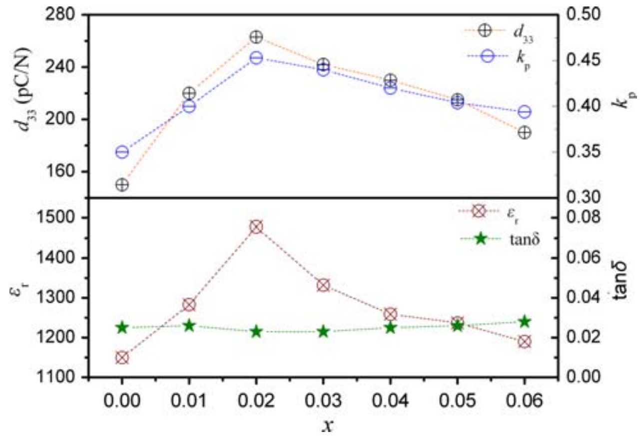

Fig. 2 Piezoelectric d_{33} and dielectric ε_r of KNLNTS–*x*Ag ceramics as a function of *x*

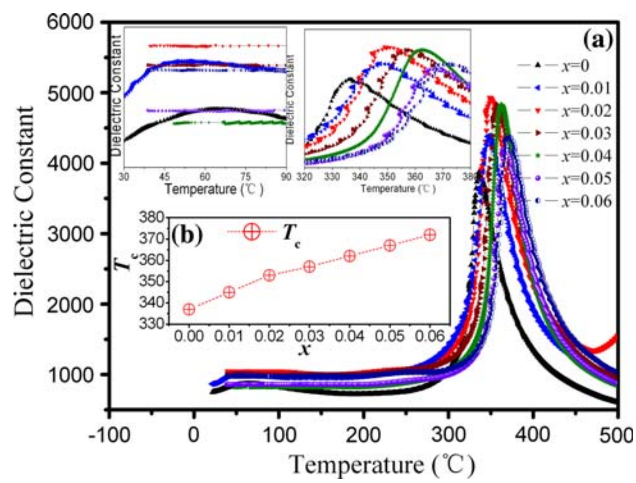

Fig. 3 Temperature dependence of ε_r at 10 kHz (**a**) and T_c (**b**) for KNLNTS–*x*Ag ceramics as function of *x*

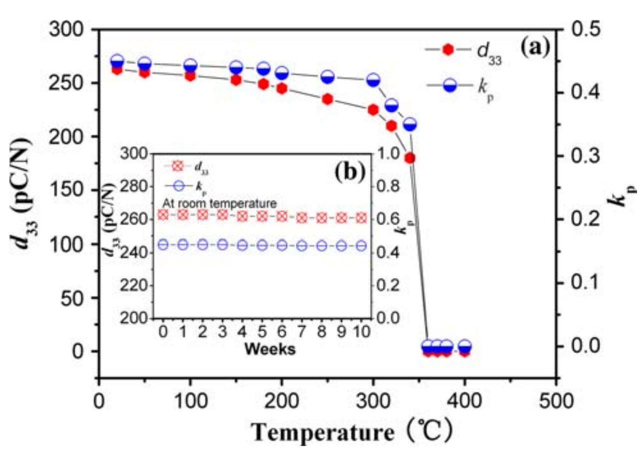

Fig. 4 Thermal-depoling behavior (**a**) and aging characteristic (**b**) of d_{33} and k_p of KNLNTS–*x*Ag ceramics with $x = 0.02$

the design of KNN-based lead-free piezoelectric ceramics in authors' group were mainly focused on three aspects as follows.

Effect of Ag ion substitution on KNN-based ceramics

Many factors may affect the electrical properties of KNN-based ceramics, in which ion substitution plays an important role [20, 21].Previous researches in authors' group showed that Ag^+ could effectively improve the piezoelectric properties of BNT-based ceramics [22]; however, there were few reports on studying the effect of Ag^+ on KNN-based ceramics.

In the study [23], Ag^+ was used to substitute partially for K^+ for the ceramics of $(K_{0.44-x}Na_{0.52}Li_{0.04}Ag_x)(Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ ($x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06) (KNLNTS–*x*Ag), the effect of Ag content on the phase structure and piezoelectric properties of the ceramics, and the thermal-depoling behavior and aging characteristics of the composition with optimized properties were studied. It was found that all ceramics studied possess pure perovskite structure, and the orthorhombic and tetragonal ferroelectric phases of the ceramics coexisted in the composition range of $0.01 < x < 0.03$ at room temperature. Figure 2 gives the piezoelectric and dielectric properties of the ceramics as a function of *x*, Fig. 3(a) shows the temperature dependence of the ε_r for the ceramics at 10 kHz as a function of *x*; (b) the T_c of the ceramics as a function of *x*, and Fig. 4 demonstrates the thermal-depoling behavior (a) and aging characteristic (b) of d_{33} and k_p of the ceramics with $x = 0.02$. From the figures, one can see that d_{33} increases with increasing *x*, reaches maximum (263 pC/N) at $x = 0.02$, and it drops with further increasing *x*. Similarly to d_{33}, the ε_r and k_p also reach a maximum value ($\varepsilon_r \sim 1478$ and $k_p \sim 45.3\%$) at $x = 0.02$. While the tan δ

remains almost unchanged at $x = 0$–0.06. The ceramics possess good aging characteristics as well.

Effects of K/Na ratio on KNN-based ceramics

The electrical properties of KNN-based ceramics depend not only on the composition but also on the temperature, and the coexistence of orthorhombic and tetragonal phases is responsible for the improvement of piezoelectric properties of the ceramics. The researches published show that not the morphotropic phase boundary (MPB), but the polymorphic phase transition (PPT) at room temperature plays an important role on KNN-based materials [12, 24–28]. Therefore, it is necessary to shift the PPT of the KNN-based ceramics to near room temperature in order to obtain good electrical properties.

The effects of K/Na ratio on the phase structure and electrical properties of $(K_xNa_{0.96-x}Li_{0.04})(Nb_{0.91}Ta_{0.05}Sb_{0.04})O_3$ (K_xNLNTS, x = 0.32–0.56) ceramics were studied [26]. The polymorphic orthorhombic–tetragonal phase transition temperature was modified by changing the K/Na ratio in the K_xNLNTS ceramics, and the ceramics with a desired PPT near room temperature were obtained. Figure 5 shows the piezoelectric and dielectric properties of K_xNLNTS ceramics as a function of x, and Fig. 6 gives the temperature dependence of the dielectric constant at 10 kHz (a), and T_c and T_{o-t} (b) for K_xNLNTS ceramics as a function of x. From the results, it was found that the PPT temperature plays an important role on the electrical properties of K_xNLNTS ceramics. The ceramics with $x = 0.38$ exhibit enhanced electrical properties (d_{33} ~ 306 pC/N; k_p ~ 48%; k_t ~ 49%; T_c ~ 337 °C; ε_r ~ 1,327; tan δ ~ 2.5%; P_r ~ 34.9 μC/cm^2; E_c ~ 11.3 kV/cm) for a PPT near room temperature. Similar results were also obtained for related KNN-based ceramics [27, 28].

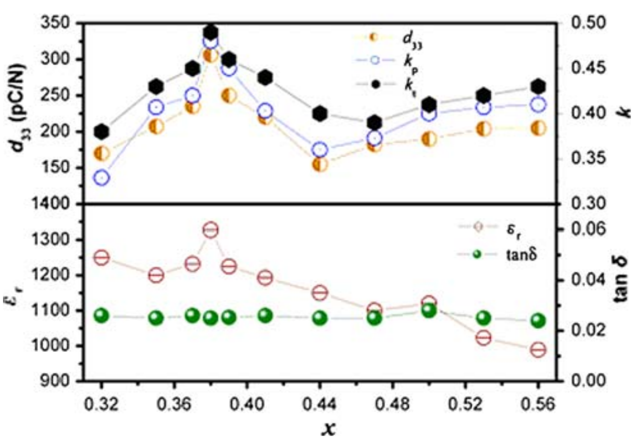

Fig. 5 Piezoelectric and dielectric properties for K_xNLNTS ceramics as a function of x

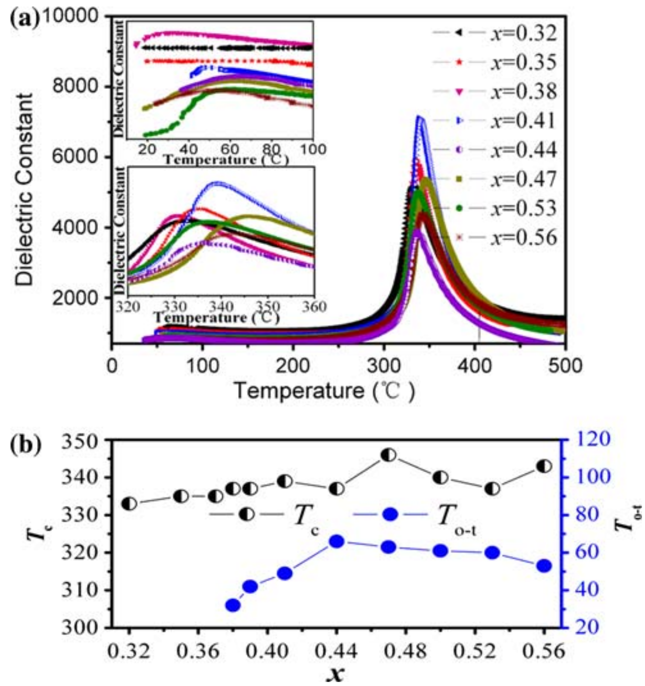

Fig. 6 Temperature dependence of the dielectric constant at 10 kHz (**a**), and T_c and T_{O-T} (**b**) for K_xNLNTS ceramics as a function of x

Effect of $LiSbO_3$ on KNN-based ceramics

There were a few reports about the preparation of (Li, Ta, Sb) modified $(K_{0.48}Na_{0.52})NbO_3$ lead-free ceramics with good piezoelectric properties in the past few years [1, 13]. However, adding Ta to KNN ceramics will limit the applications of these materials because the price of Ta_2O_5 is much more expensive than that of Nb_2O_5. From the view point of applications, $(1-x)(K_{0.48}Na_{0.52})NbO_3$–$x$$LiSbO_3$ [$(1-x)$KNN–xLS] lead-free piezoelectric ceramics were prepared by ordinary sintering, resulting that Ta in the ceramics was completely replaced by Sb [29].

A coexistence between the orthorhombic and tetragonal phases of $(1-x)$KNN–xLS ceramics was identified in the composition range of $0.04 < x < 0.06$. The ceramics near the coexistence exhibit a strong compositional dependence and enhanced piezoelectric properties. The ceramics with 5 mol.% LS exhibit enhanced electrical properties (d_{33} ~ 270 pC/N; k_p ~ 47.2%; T_c ~ 364 °C; T_{o-t} = 35 °C; ε_r ~ 1,412; tan δ ~ 2.8%; P_r ~ 25.7 μC/cm^2; E_c ~ 11.1 kV/cm), and possess low dielectric loss (<2%) at 10 and 100 kHz at high temperature (250–400 °C). The low dielectric loss at high temperature is very important for high-temperature application of the ceramics. Figure 7 gives the piezoelectric constant d_{33} and planar electromechanical coefficient k_p of the $(1-x)$KNN–xLS ceramics as a function of x.

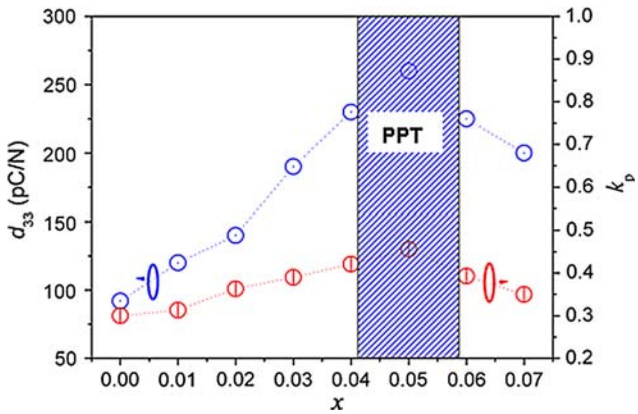

Fig. 7 Piezoelectric constant d_{33} and planar electromechanical coefficient k_p of the $(1-x)$KNN–xLS ceramics as a function of x

The effects of K content on the dielectric, piezoelectric and ferroelectric properties of the $0.95(K_xNa_{1-x})NbO_3$–$0.05LiSbO_3$ ($0.95K_xNN$–0.05LS) ($x = 0.25$–0.75) ceramics were also studied [30]. The experimental results show that the dielectric, piezoelectric, and ferroelectric properties strongly depend on K content in the $0.95K_xNN$–0.05LS ceramics. The $0.95K_xNN$–0.05LS ($x = 0.40$) ceramics exhibit enhanced electrical properties ($d_{33} \sim 280$ pC/N; $k_p \sim 49.4\%$; $T_c \sim 364$ °C; $T_{o-t} = 25$ °C; $\varepsilon_r \sim 1463$; $\tan\delta \sim 2.3\%$; $P_r \sim 30.8$ μC/cm^2; $E_c \sim 14.0$ kV/cm). Figure 8 shows the temperature dependence of dielectric constant at 10 kHz of the $0.95K_xNN$–0.05LS ceramics as a function of x. It was suggested that the enhanced electrical properties of the $0.95K_xNN$–0.05LS ($x = 0.40$) ceramics should be attributed to the polymorphic phase transition near room temperature.

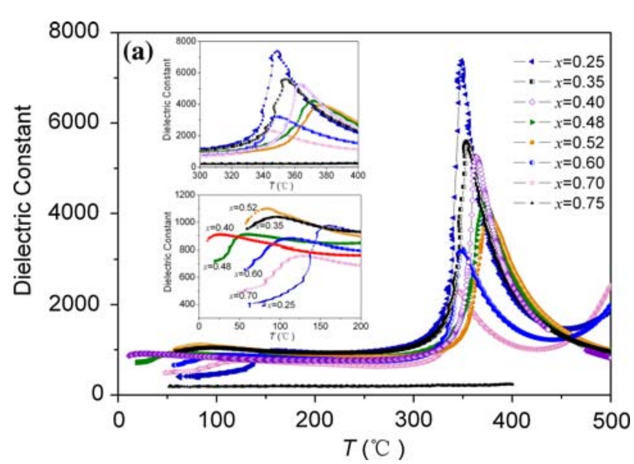

Fig. 8 Temperature dependence of dielectric constant at 10 kHz of the $0.95K_xNN$–0.05LS ceramics as a function of x

Effects of doping on the properties of BNT- and KNN-based lead-free piezoelectric ceramics

Effec of doping on the properties of BNT-based ceramics

In order to investigate the effects of some additives on the electrical properties of the $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ (BNKLT–x/y) ceramics, CeO_2, La_2O_3, Sm_2O_3, $MnCO_3$, MnO_2, Co_2O_3 modified ceramics were synthesized, and the effect of oxide-doping on the piezoelectric and ferroelectric properties of BNKLT–x/y ceramics was investigated [31, 32]. Table 2 shows the electrical properties of the BNKLT–0.175/0.10 ceramics by doping of certain amount of the oxides. For a small amount of La_2O_3 and Sm_2O_3-doping, the piezoelectric properties of the ceramics are enhanced, and the mechanical quality factor Q_m decreases and tan δ increases, which indicate that both the La_2O_3 and Sm_2O_3 only act as donor for BNKLT ceramics. The piezoelectric properties decrease while the Q_m increases and tan δ decreases for the samples doped with certain amount of MnO_2 and Co_2O_3 because of a possible "acceptor doping" effect. The piezoelectric and dielectric properties of BNKLT–0.175/0.10 ceramics have been improved by doping of certain amount of CeO_2 and $MnCO_3$. At room temperature, the ceramics doped with 0.1 wt% CeO_2 show quite good performance with high piezoelectric constant ($d_{33} = 220$ pC/N), high-coupling factor ($k_p = 39.3\%$), enhanced dielectric constant ($\varepsilon_r = 897$), and low dissipation factor (tan $\delta = 2.0\%$) at 1 kHz, which indicates that CeO_2 doping possesses both effects of increasing the piezoelectric properties and decreasing the dissipation factor of the ceramics. The results show that CeO_2 acts as both donor and acceptor in the case with PZT-based ceramics, which may be mainly attributes to the coexistence of Ce^{3+} and Ce^{4+}. Similar to CeO_2 doping, the ceramics doped with 0.05 wt% $MnCO_3$ possess high piezoelectric and ferroelectric properties ($d_{33} = 209$ pC/N, $k_p = 39\%$, tan $\delta = 2.6\%$, $P_r = 39.5$ μC/cm^2). Moreover, the remnant polarization P_r decreases for the ceramics doped with La_2O_3, Sm_2O_3, MnO_2 and Co_2O_3, and the E_c decreases by La_2O_3- and Sm_2O_3-doping and increases after MnO_2- and Co_2O_3-doping.

Figure 9 shows the temperature dependence of ε_r and tan δ of (a) undoped and (b) 0.3 wt % CeO_2-doped BNKLT–0.175/0.10 ceramics at different frequencies (0.1–10 kHz). All the samples show relaxor-like ferroelectric behavior, and the transition temperature from ferroelectric to antiferroelectric phases (T_d) decreases with the addition of CeO_2. Moreover, the platforms of dielectric constant-temperature at T_d are more obscure with an increase in the amount of CeO_2.

Table 2 Electrical properties of BNKLT–0.175/0.10 ceramics doped with different oxides

Amount	$\varepsilon_{33}^{T}/\varepsilon_0$	tan δ	d_{33} (pC/N)	k_p (%)	Q_m	P_r (μC/cm^2)	E_c (kV/mm)
0%	882	0.038	198	37.2	94	38.6	3.60
0.1 wt% CeO_2	915	0.026	220	38.8	104	37.0	2.90
0.5 mol.% La_2O_3	1,248	0.041	178	34.5	81	31.3	3.42
0.3 wt% Sm_2O_3	1,265	0.054	212	35.4	78	33.5	3.12
0.05 wt% $MnCO_3$	931	0.033	209	39.0	102	39.5	3.40
0.1 wt% MnO_2	1,053	0.033	192	33.5	102	36.0	3.59
0.05 wt% Co_2O_3	956	0.036	195	35.9	125	36.2	3.65

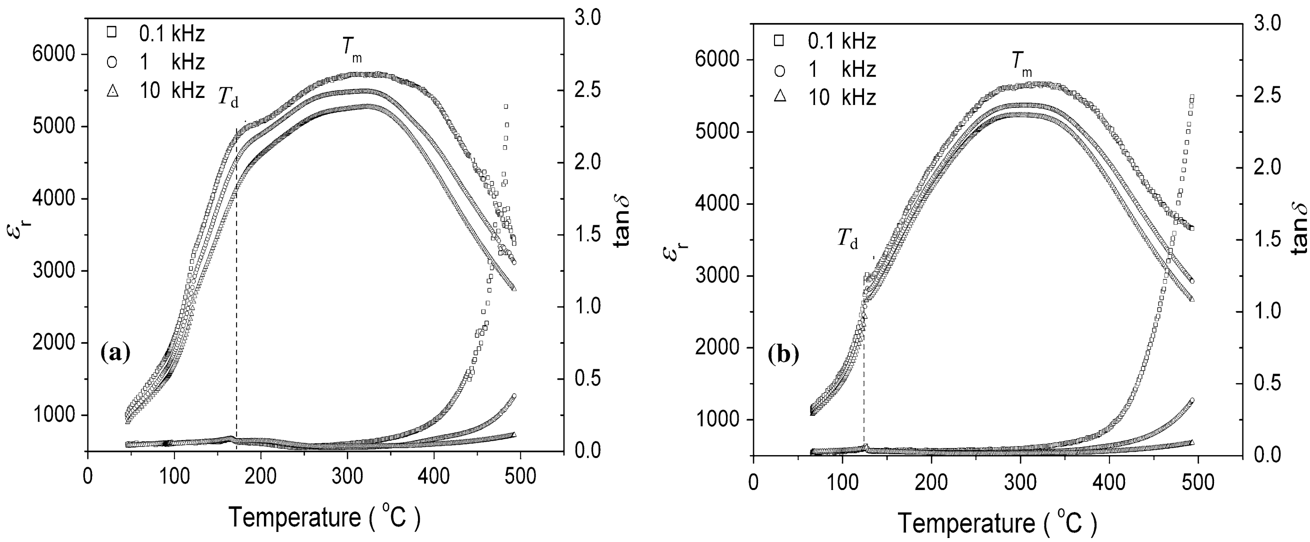

Fig. 9 Temperature dependence of the dielectric properties of **a** undoped and **b** 0.3 wt% CeO_2-doped BNKLT–0.175/0.10 ceramics

Effects of doping on the properties of KNN-based ceramics

In order to investigate the effect of doping on the properties of KNN-based ceramics, $CaTiO_3$-modified $(K_{0.5}Na_{0.5})(Nb_{0.96}Sb_{0.04})O_3$ [(1−*x*)NKNS–*x*CT] ceramics were prepared, their phase structure and piezoelectric properties were studied, and the effect of the poling temperature on the piezoelectric properties of the ceramics was also investigated [33]. The results show that $CaTiO_3$-modified $(K_{0.50}Na_{0.50})(Nb_{0.96}Sb_{0.04})O_3$ ceramics form stable solution with orthorhombic structure, and the Curie temperature and the polymorphic phase transition of the ceramics decreased with increasing *x*. Figure 10 shows the piezoelectric and

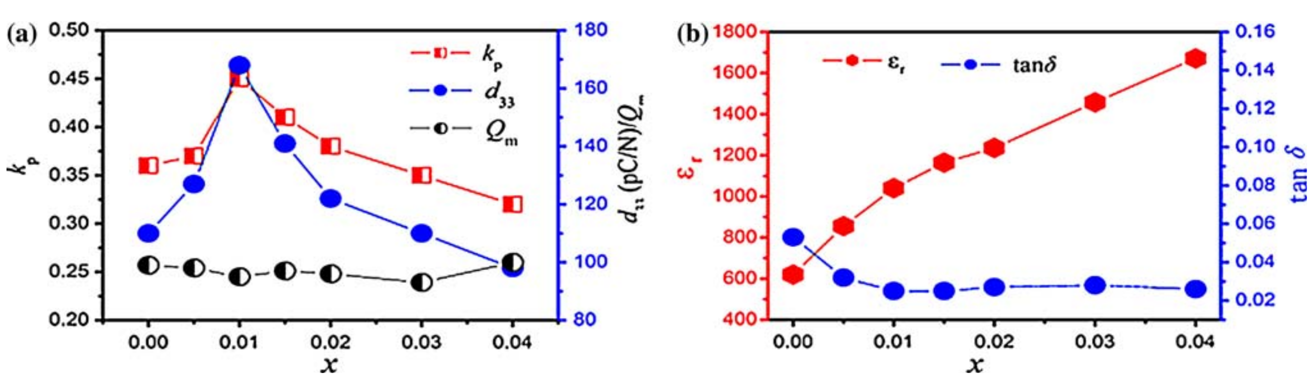

Fig. 10 **a** Piezoelectric, mechanical quality factor, and **b** dielectric properties of the (1−*x*) KNNS–*x*CT ceramics as a function of *x*

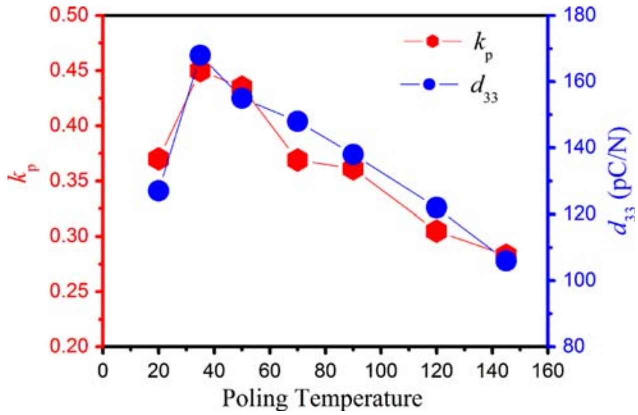

Fig. 11 Piezoelectric constants d_{33} and k_p of the ceramics as a function of the poling temperature

mechanical quality factor (a), and dielectric properties (b) of the (1−*x*)KNNS–*x*CT ceramics as a function of *x*, which indicates that when $x = 0.01$, the piezoelectric properties of d_{33} and k_p of the (1−*x*)KNNS–*x*CT ceramics reach to maximum. Moreover, the polarization temperature (T_p) will affect the piezoelectric properties of the ceramics. When T_p lies near orthorhombic–tetragonal polymorphic phase transition temperatures, non-180° domains can switch and be orientated owing to the coexistence of the orthorhombic and tetragonal phases [34]. Consequently, the higher degree of the domain alignment was obtained resulting in large piezoelectric properties. Figure 11 gives the piezoelectric constants d_{33} and k_p of the ceramics as a function of the poling temperature. The result shows that the piezoelectric properties of the ceramics strongly depend on the T_p. The ceramics with $x = 0.01$ poled at $T_p = 35$ °C possess optimum properties ($d_{33} = 168$ pC/N, $k_p = 45\%$, $T_c = 314$ °C, $T_{o\text{–}t} = 120$ °C, $\varepsilon_r \sim 1186$, and tan $\delta \sim 2.5\%$).

Temperature stability of BNT- and KNN-based lead-free piezoelectric ceramics

Temperature stability of BNT-based ceramics

It is known that the electrical properties of the BNT-based ceramics will change markedly above the depolarization temperature (T_d). Thus, it is very important to study the T_d of BNT-based ceramics from the viewpoint of application. The piezoelectric properties and their temperature dependence of $Bi_{0.5}(Na_{1-x}Ag_x)_{0.5}]_{1-y}Ba_yTiO_3$ (BNBT*y*–*x*Ag, $x = 0$–10 mol.% and $y = 0$–10 mol.%) ceramics were investigated, and the features of the T_d of the ceramics were discussed [22, 35]. The results of the X-ray diffractions investigated show that the MPB in BNBT*y*–*x*Ag system appears to be at $y = 6$–8 mol.%. Figure 12 shows the temperature dependence of the piezoelectric constant d_{33} of (a) BNBT6–*x*Ag and (b) BNBT*y*–4Ag ceramics. It can be found in Fig. 12 that the d_{33} has a sharp fall, and the piezoelectricity almost disappears at T_d for all of the ceramic samples. With increasing amount of Ag up to 6 mol%, the piezoelectric properties are improved while the T_d of the samples is reduced for BNBT6–*x*Ag ceramics. And the T_d of BNBT*y*–4Ag ceramics decreases with increasing amount of Ba up to 6 mol.%, and then increases with further increasing amount of Ba. This result indicates that although the MPB compositions possess the higher piezoelectric properties, the T_d values are much lower than others. It can also be noted in Fig. 12b that the T_d of BNBT10–4Ag ceramics, which possess good piezoelectric and ferroelectric properties ($d_{33} = 137$ pC/N, $k_p = 16.2\%$, and $k_t = 45.0\%$) simultaneously at room temperature, is about 190 °C.

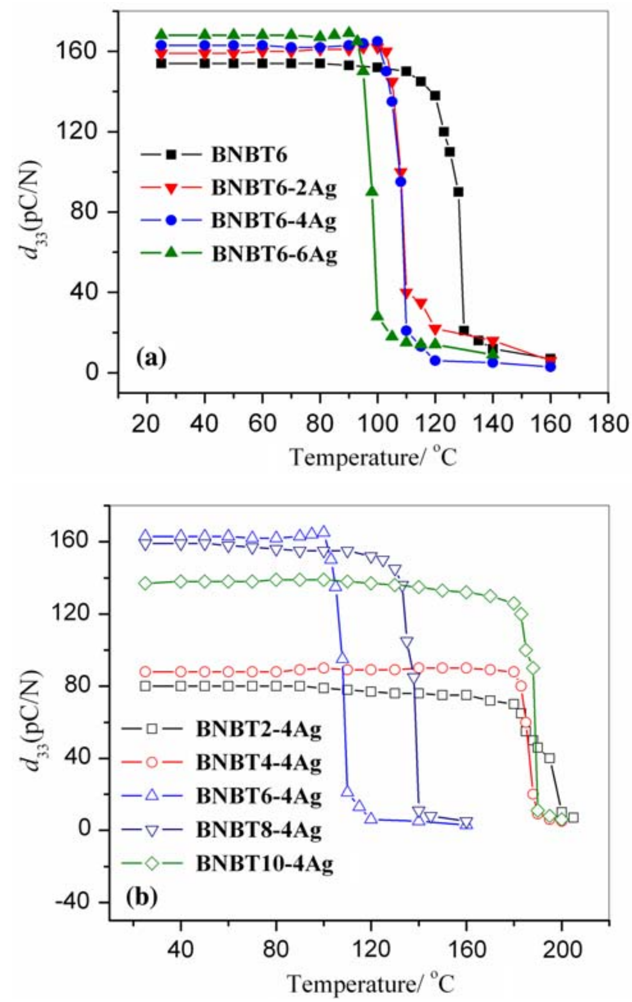

Fig. 12 Temperature dependence of the piezoelectric constant d_{33} of **a** BNBT6–*x*Ag and **b** BNBT*y*–4Ag ceramics

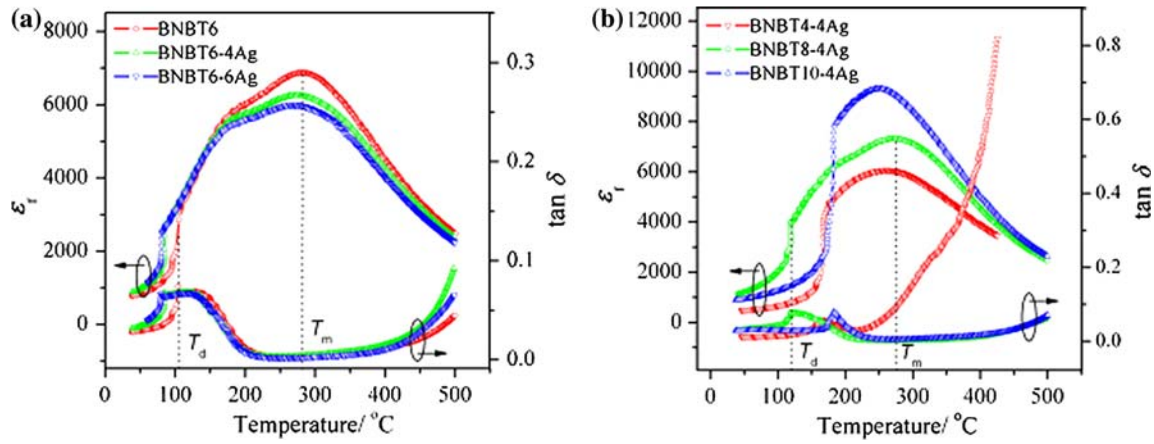

Fig. 13 Temperature dependence of the dielectric properties of **a** BNBT6–*x*Ag and **b** BNBT*y*–4Ag ceramics at 10 kHz

In order to investigate the feature of T_d further, the temperature dependence of dielectric and ferroelectric properties of the BNBT*y*–*x*Ag ceramics were also measured [35, 36]. It can be found in Fig. 13 that two anomalies of dielectric constant corresponding to T_d and T_{max} while only one dielectric loss peak near the T_d are observed. In addition, the characteristic of the diffuse phase transition is more evident for the compositions near the MPB. Figure 14 shows the *P*–*E* hysteresis loops of (a) BNBT6–6Ag and (b) BNBT10–4Ag ceramics at different temperatures. It can be observed in Fig. 14a that the ferroelectricity of the BNBT6–6Ag ceramics is very weak and the loops seem to form double-like *P*–*E* hysteresis loops near the T_d. It indicates that a transition from ferroelectric to antiferroelectric phase may occur between T_d and T_{max} for the BNBT*y*–*x*Ag ceramics. It can also be noted in Fig. 14b that the loop of BNBT10–4Ag ceramics still keeps the typical ferroelectric feature at up to 180 °C. This result is consistent with that obtained from the temperature dependence of the piezoelectric properties (also see Fig. 12).

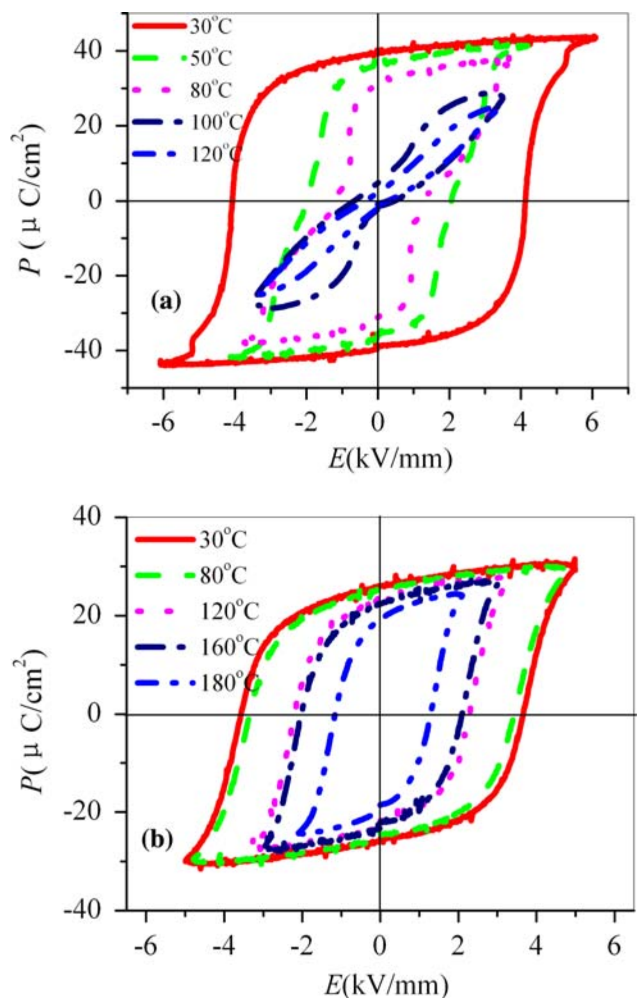

Fig. 14 The *P*–*E* hysteresis loops of **a** BNBT6–6Ag and **b** BNBT10–4Ag ceramics at different temperatures

Temperature stability of KNN-based ceramics

As mentioned above, the enhanced piezoelectric and dielectric properties of the KNN-based ceramics are owing to the presence of the orthorhombic–tetragonal PPT near room temperature [12, 24–26]. Therefore, it is very important to study the temperature stability of the electrical properties of the KNN-based ceramics from the viewpoint of application.

The thermal-depoling behavior, age characteristics, and temperature stability of the $0.98[(K_{0.4725}Na_{0.4725}Li_{0.055})NbO_3]–0.02Ag(Ta_{1-x}Sb_x)O_3$ ceramics were investigated [37]. The experimental results show that Sb strongly affects the microstructure and electrical properties of the ceramics. The partial substitution of Sb slightly decreases the Curie temperature (T_c) and shifts the orthorhombic–tetragonal phase transition temperature ($T_{O–T}$) to below room temperature, as shown in Fig. 15. The ceramics with $x = 0.40$ exhibit optimum properties ($d_{33} = 250$ pC/N, $k_p = 44\%$,

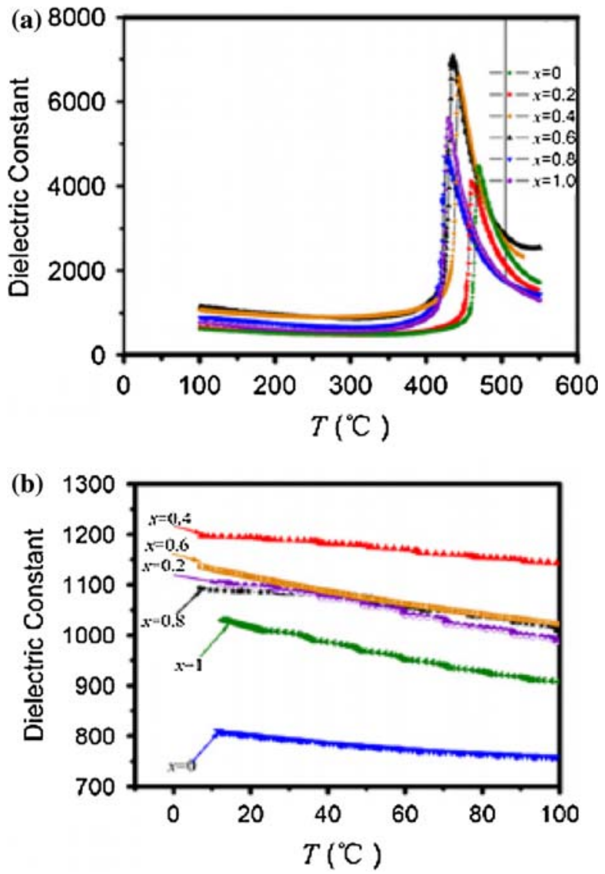

Fig. 15 **a** Temperature dependence of the dielectric constant for the $0.98[(K_{0.4725}Na_{0.4725}Li_{0.055})NbO_3]$–$0.02Ag(Ta_{1-x}Sb_x)O_3$ ceramics at 10 kHz as a function of *x*; **b** the expanded temperature dependences of the dielectric constant for the ceramics from 15 to 100 °C

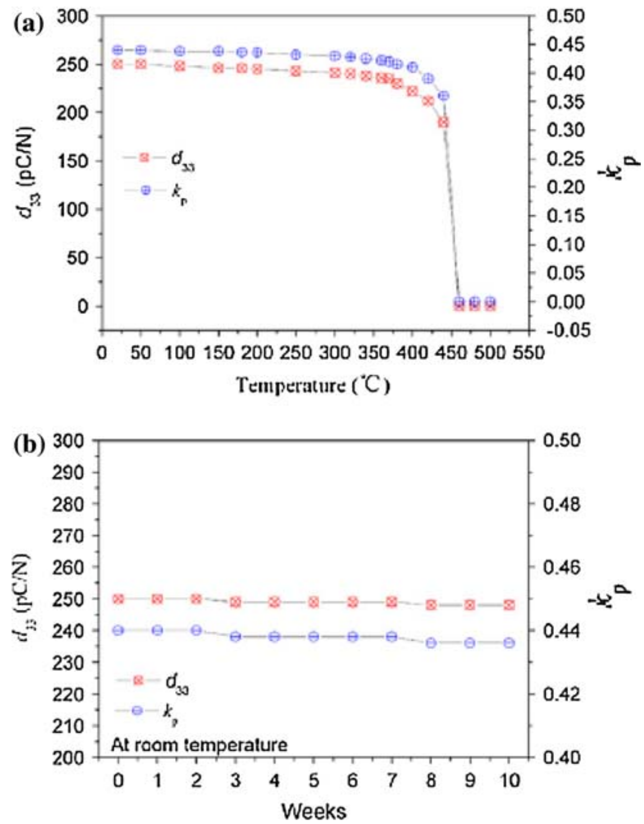

Fig. 16 Thermal-depoling behaviour and aging characteristic of d_{33} and k_p values of the $0.98[(K_{0.4725}Na_{0.4725}Li_{0.055})NbO_3]$–$0.02Ag(Ta_{1-x}Sb_x)O_3$ ceramics with $x = 0.40$. **a** Thermal-depoling behaviour; **b** ageing characteristics

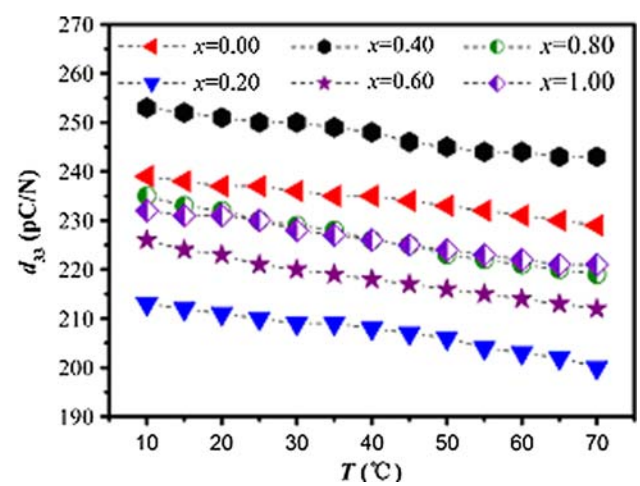

Fig. 17 Temperature dependence of the d_{33} of the $0.98[(K_{0.4725}Na_{0.4725}Li_{0.055})NbO_3]$–$0.02Ag(Ta_{1-x}Sb_x)O_3$ ceramics with *x*

$T_c = 444$ °C, $\varepsilon_r \sim 1186$, $\tan\ \delta \sim 2.7\%$, $P_r \sim 32.0$ μC/cm^2, $E_c \sim 14.8$ kV/cm). The thermal-depoling behaviour of the ceramics with $x = 0.40$ is shown in Fig. 16a. The d_{33} and k_p values were measured at room temperature after annealing for 120 min at each chosen annealing temperature. It can be observed that the d_{33} and k_p values show a slight variation when the annealing temperature is lower than T_c. The d_{33} and k_p values of the ceramics with $x = 0.40$ exhibit almost no change after 10 weeks, as shown in Fig. 16b. These results show that the ceramics with $x = 0.40$ possess good thermal-depoling behaviour and age characteristics. Figure 17 shows the temperature (10–70 °C) dependence of the d_{33} for the $0.98[(K_{0.4725}Na_{0.4725}Li_{0.055})NbO_3]$–$0.02Ag(Ta_{1-x}Sb_x)O_3$ ceramics with *x*. It can be noted that the d_{33} value of the ceramics with $x = 0.40$ was decreased by about 4% with the temperature variation (10–70 °C), exhibiting a flat temperature dependence behaviour. This result indicates that the ceramics with $x = 0.40$, which possesses the optimum piezoelectric properties, also possesses improved temperature stability.

The electrical properties and their temperature stability of the $(K_{0.5-x}Li_x)Na_{0.5}(Nb_{1-y}Sb_y)O_3$ (KLNNS*x*–*y*, $x = 0$–4 mol.% and $y = 0$–8 mol.%) ceramics were also investigated [38]. The KLNNS*x*–*y* ceramics possess better electrical properties, in particular, a high k_p of 49% and a low tan δ of 0.019 were obtained for the

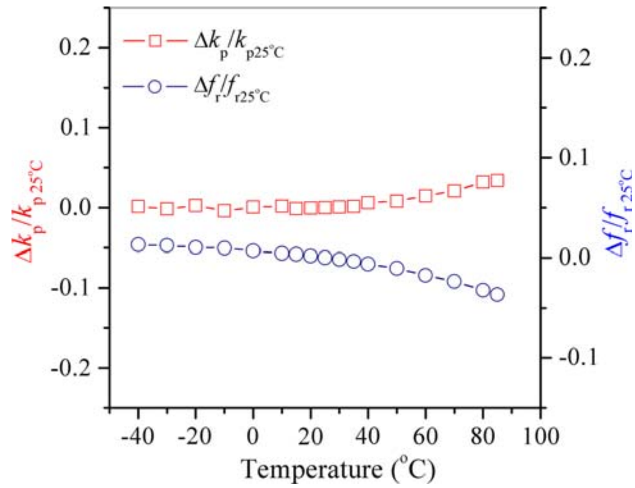

Fig. 18 Variations of $\Delta k_p/k_{p25°C}$ and $\Delta f_r/f_{r25°C}$ in the temperature range of −40 to 85 °C for the KLNNS2.5–5 ceramics

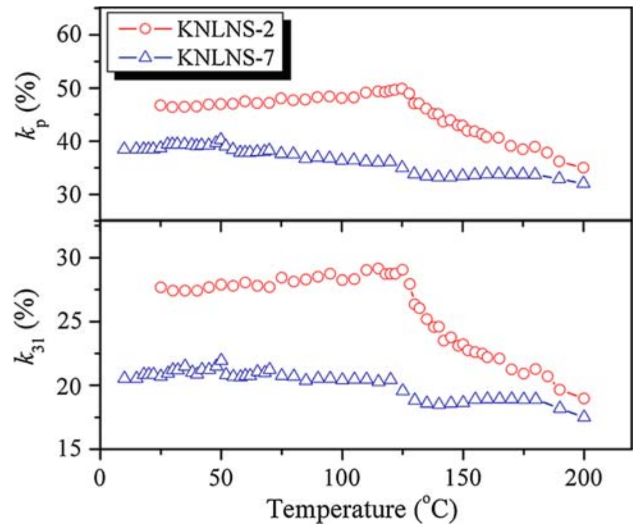

Fig. 19 Temperature dependence of k_p and k_{31} of KNLNS-2 and KNLNS-7 ceramics in the range from room temperature to 200 °C

KLNNS2.5–5 ceramics, while the other electrical properties remains reasonably good: $k_{31} = 30\%$, $d_{33} = 155$ pC/N, $N_p = 3390$, $\varepsilon_{33}^T/\varepsilon_0 = 543$, $T_{O-T} = 140$ °C, and $T_C = 336$ °C. Figure 18 shows the variations of $\Delta k_p/k_{p25°C}$ and $\Delta f_r/f_{r25°C}$ in the temperature range of −40 to 85 °C for the KLNNS2.5–5 ceramics. The $\Delta k_p/k_{p25°C}$ value exhibited a positive maximum of 0.033 at 85 °C. In addition, the $\Delta f_r/f_{r25°C}$ with a positive maximum value of 0.013 was obtained at −40 °C and with a negative maximum value of −0.036 was obtained at 85 °C. The experimental results show that the KLNNS2.5–5 ceramics exhibit good electrical properties, and possess good temperature stability in the temperature range of −40 to 85 °C.

The investigation on the temperature stability of the dielectric, piezoelectric, and ferroelectric properties of the ceramics can be used to study the relationship between the PPT and electrical properties of the KNN-based ceramics. In order to do so, the temperature stability of the dielectric, piezoelectric, and ferroelectric properties of two typical compositions in the $(K_{0.5}Na_{0.5})_{1-x}Li_xNb_{0.95}Sb_{0.05}O_3$ (KNLNS–x, x = 0–10 mol.%) ceramics, i.e., KNLNS-2 ($T_{O-T} \sim 142$ °C) with orthorhombic phase, and KNLNS-7 ($T_{O-T} \sim 58$ °C) with mixed orthorhombic and tetragonal phases, was investigated [39]. The electromechanical factors (k_p and k_{31}) of the ceramics show the maximum values at temperatures close to the PPT, as shown in Fig. 19. In addition, the temperature stability of the resonance frequency is relatively poor near the PPT. After thermal cycling in the temperature range of 20–200 °C, the depoling of the KNLNS-2 ceramics is stronger than that of the KNLNS-7 ceramics. Figure 20 shows the temperature dependence of the P_r and E_c of the KNLNS-2 and KNLNS-7 ceramics in the range from room temperature to 200 °C. It can be found in Fig. 20 that the P_r and E_c exhibit a tendency of reduction with increasing temperature, and a maximum peak in the E_c is observed around the T_{O-T}. These results indicate that the temperature stability of the piezoelectric, dielectric, and ferroelectric properties is relatively poor near the PPT. As thermal cycling between the two different ferroelectric phases can induce the significant degradation of the piezoelectric and ferroelectric properties [40], it is very necessary to shift the PPT away from the application temperature range to improve the temperature stability of the electrical properties of KNN-based ceramics.

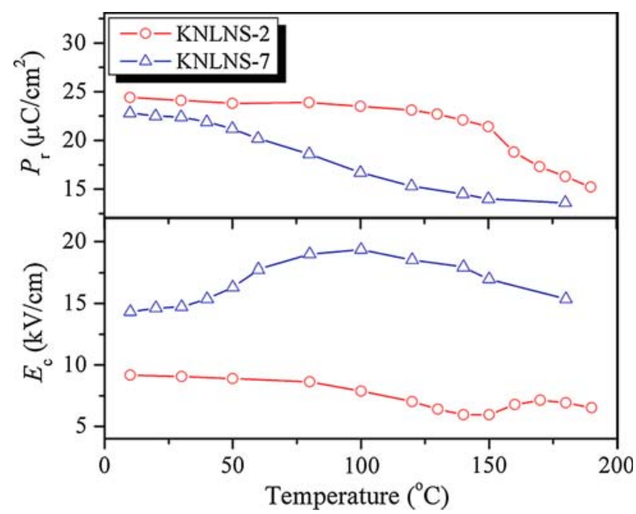

Fig. 20 Temperature dependence of P_r and E_c of KNLNS-2 and KNLNS-7 ceramics in the range from room temperature to 200 °C

In addition, substitution or doping of KNN-based ceramics may change the temperature stability of the materials. For example, the $CaTiO_3$-modified KNN ceramics possess good temperature stability with the polymorphic phase transition of the ceramics being below room temperature, and exhibit high piezoelectric properties when the ceramics were poled at optimum poling temperature [27, 33, 41].

Some prospects to be resolved from the viewpoint of the applications

The research results on the dielectric, ferroelectric, and piezoelectric properties of the perovskite BNT- and KNN-based ceramics published up to now demonstrate that the ceramics are superior candidates for lead-free piezoelectric materials, and these ceramics seem to be suitable for actuator and high-power applications that require a large piezoelectric constant, high Curie temperature, or high depolarization temperature [42]. As an example, the BNT- and KNN-based lead-free piezoelectric ceramics mentioned in this article have much better piezoelectric properties, and also better temperature characterization of the properties. And some of the prototype devices, such as ceramic filters and buzzers, were made by using these materials.

However, compared the researches of lead-free piezoelectric ceramics with those on PZT-based ceramics, there is much more work to be done. From the viewpoint of device applications of the perovskite lead-free piezoelectric ceramics some prospects, which should be resolved at present are mentioned here: understanding deeply the "origin" of the enhanced piezoelectric properties of the ceramics; understanding the loss mechanism of the ceramics and seeking the technique to improve the mechanical quality factor of the materials; seeking various ceramics for different device applications with optimum properties; understanding the properties of the ceramics under different conditions of pressure, frequency, and temperature; understanding the doping mechanism and how various additives affect the properties of the ceramics; understanding the special demand for special device by using lead-free piezoelectric ceramics and developing special ceramics for special device applications; developing new processing technique with low production cost; and so on.

Conclusion

The demand of the sustainable development of the world and the environmental and safety concerns with respect to the utilization, recycling, and disposal of Pb-based piezoelectric materials have induced a new surge in developing lead-free piezoelectric ceramics with properties comparable to their lead-based counter. In recent years, the authors' group concentrates their research work on the composition design and the properties study of perovskite lead-free piezoelectric ceramics, especially on BNT- and KNN-based ceramics. All the ceramics were prepared by the conventional ceramic technique. The main results obtained are reviewed with emphasis on KNN-based ceramics, including (1) the design on new BNT-based ceramics based on the multiple complex in the A-site of ABO_3 compounds; (2) the design of KNN-based ceramics with focused on the effects of Ag ion substitution, K/Na ratio, and $LiSbO_3$ on KNN-based ceramics; (3) the effects of doping on the properties of BNT- and KNN-based ceramics; and (4) the temperature stability of BNT- and KNN-based ceramics. And some prospects which should be resolved in coming years from the viewpoint of the applications are also pointed out. It is believed that lead-free piezoelectric ceramics, especially the perovskite ones, will be put into practical applications in various devices in the very near future.

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