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Pyroelectric, dielectric, and piezoelectric properties of MnO_2-doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ lead-free ceramics

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Abstract MnO_2 doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ lead-free piezoelectric ceramics were prepared by conventional solid-state reaction process and the effect of MnO_2 addition on the pyroelectric, piezoelectric and dielectric properties were studied. The experiment results showed that the pyroelectric, piezoelectric, and dielectric properties strongly depended on MnO_2 addition in the $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics. Excellent electrical properties were obtained in $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ with 0.8 mol% MnO_2. The large dielectric loss of pure BNT ceramics was significantly reduced, the piezoelectric constant was improved, and it also showed excellent pyroelectric properties when compared with other lead free ceramics, with pyroelectric coefficient $p=17\times10^{-4}$ C/m^2K and figure of merit $F_d=6.56\times10^{-5}$ $Pa^{-0.5}$. With these outstanding pyroelectric properties, the 0.8 mol% MnO_2 doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramic can be a promising material for pyroelectric sensor applications in future.

Keywords Pyroelectric properties · Dielectric properties · Lead-free piezoelectric ceramics · MnO_2 dopants

1 Introduction

Lead-based piezoelectric ceramics such as lead titanate (PT) and lead zirconate titanate (PZT) are widely used in actuators, sensors, resonators, transducers, buzzers and other electronic devices because of their superior ferroelectric, piezoelectric and pyroelectric properties [1]. However, the evaporation of toxic lead during the fabrication of the ceramics will cause environmental problems which are also related to the use and disposal of components. A promising way to solve this problem is to develop lead-free piezoelectric ceramics to replace lead-based piezoelectric ceramics to minimize lead pollution. Recently, there is an increasing interest in developing lead-free piezoelectric ceramics in many countries.

$Bi_{0.5}Na_{0.5}TiO_3$(abbreviated as BNT) is one type of important lead-free ceramics with perovskite structure discovered by Smolenskii et al. in 1960 [2]. For its relatively large remanent polarization (P_r=38 μC/cm^2) at room temperature and high Curie temperature (T_c=320 °C), BNT has been considered to be a good candidate for lead-free piezoelectric ceramics. However, for pure BNT, it is difficult to pole due to high coercive field (E_c=73 kV/cm) and high conductivity, which will make its piezoelectric and pyroelectric properties much lower than PZT ceramics [3]. To improve the piezoelectric and pyroelectric properties of the material, a number of BNT-base solid solutions, such as BNT-$BaTiO_3$, BNT-$Bi_{0.5}K_{0.5}TiO_3$, BNT-$NaNbO_3$, BNT-$KNbO_3$, BNT-$Bi_{0.5}\ K_{0.5}TiO_3$-$Bi_{0.5}Li_{0.5}TiO_3$ and BNT-$Bi_{0.5}\ K_{0.5}TiO_3$-$BaTiO_3$ have been studied extensively [4–9]. They show much better piezoelectric properties and it is easier to handle their poling process compared with pure BNT ceramics.

It is well known that MPB plays a very important role in PZT ceramics because the piezoelectric and dielectric properties show a maximum at around MPB [10]. Among BNT-based solid states, the BNT-BKT system has attracted considerable attention on account of the existence of a rhombohedral-tetragonal morphotropic phase boundary (MPB) in the range of 0.16–0.20 mol BKT [11]. Compared with pure BNT, the BNT-BKT compositions near the MPB show obviously

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decreased coercive field and substantially improved piezoelectric, ferroelectric and pyroelectric properties.

Nevertheless, in order to meet the stringent requirements for specific applications, the electrical properties need to be improved, for example, by doping of various oxides, among these oxides, MnO_2 is an effective dopant in piezoelectric ceramics to enhance densification and reduce dielectric loss. Recently, H.L.W. Chan reported the effects of MnO_2 addition on dielectric properties of BNKT [12]. They found Mn-doped BNKT restrained the transition of ferroelectric phase to antiferroelectric phase. Xiaojuan Li used MnO_2 as modifier for BNBT lead-free ceramics and found that the electrical properties of BNBT ceramics are significantly influenced by MnO_2 content [13]. However, such kinds of studies have confined to investigate the piezoelectric coefficient and electromechanical coupling factors. So far, there have been few studies on the pyroelectric properties of Mn doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ base lead-free piezoelectric ceramics. In this paper, MnO_2 doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ lead-free piezoelectric ceramics were prepared and the effect of MnO_2 addition on the dielectric, piezoelectric and pyroelectric properties was investigated.

2 Experimental

Conventional ceramics fabrication technique was used to prepare 0.82BNT-0.18BKT + x mol% ($0 \leq x \leq 1.4$). Reagent-grade metal oxides or carbonate powders of Bi_2O_3, Na_2CO_3, TiO_2, K_2CO_3 and MnO_2 with the purity of over 98 % were used as starting materials. The powers were weighed and mixed in the ration of above formula and then thoroughly milled in ethanol for 4 h. The dried slurries were calcined at 850 °C for 6 h, then ball milled again for 4 h. The mixtures were added with PVA as a binder for granulation and pressed to form 15 mm diameter and 1 mm thickness disks. The compacted disks were sintered at 1100–1140 °C for 3 h in air. Silver paste was coated on both sides of the sintered samples and fired at 550 °C to form electrodes. The specimens for measurement of piezoelectric and pyroelectric properties were poled in silicone oil bath with a dc field of 4–5 kV/mm at 60 °C for 30 min.

The bulk density of the sintered sample was measured by the Archimedes method. The piezoelectric strain (d_{33}) was determined using a quasi-static piezoelectric d_{33} meter (ZJ-3A). The planar electromechanical coupling factor (kp) and mechanical quality factor (Qm) were determined by the resonance-anti-resonance technique using an impedance analyzer (HP4192A, Hewlett Packard Ltd.). The dielectric properties with variation of temperature and DC bias field were measured at 1 kHz frequency using a LCR analyzer (HP 4192, Hewlett Packard Ltd.). The pyroelectric coefficient was tested using the Byer-Roundy method [14].

3 Results and discussion

Figure 1 shows the apparent density and the relative density of $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics as a function of MnO_2 addition. From the figure, we can see that all MnO_2-doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics present a rather high relative density, showing its good sintering behavior. For small addition less than 0.8 mol%, the relative density increases further to 99 %. It means that the suitable MnO_2 addition benefits the densification of ceramics during the sintering process. However, excessive addition of MnO_2 to the $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics leads to a decrease in the density of ceramics, which may have resulted from the segregation of impurities at the grain boundary of composition ceramics [15].

Figure 2 shows the variation in the dielectric constant of $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics as a function of temperature and amount of MnO_2. From the figure, it can be seen that the maximum dielectric constant corresponding to the maximum temperature (Tm) decrease with increasing content of Mn, which is ascribed to decrease of stability of ferroelectric domains caused by Mn doping.

The dielectric constants, dielectric loss and mechanical quality factor (Qm) of $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ with the amount of MnO_2 addition at room temperature are shown in Fig. 3. As shown in Fig. 3, the addition of MnO_2 in $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics leads to a decrease of dielectric constants and dielectric loss and the increase of Qm. The lowest dielectric loss of 1.6 % is obtained in the ceramic with 0.8 mol% MnO_2. As a “hard” dopant, Mn doping in $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ would lead to the creation of oxygen vacancies due to the valence different from the Ti^{4+} ion, which pins the movement of the ferroelectric domain walls and results in a decrease of dielectric constants and dielectric loss and the increase of Qm. However, with a

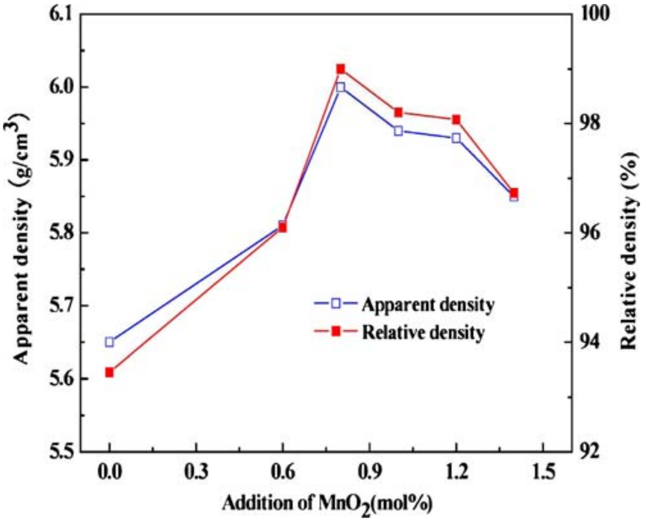

Fig. 1 Dependence of the apparent density and the relative density of $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ with the amount of MnO_2 addition

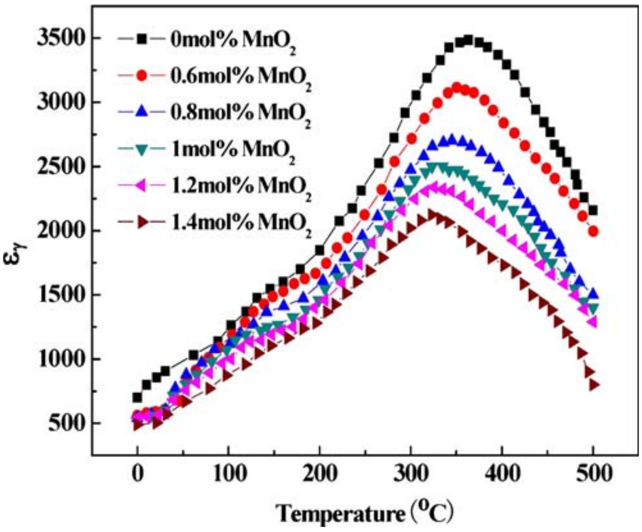

Fig. 2 Temperature dependence of dielectric constant for the $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics with different MnO_2 content

further increase MnO_2 more than 0.8 mol%, the dielectric loss increased rapidly. This may be due to the formation of a chromium oxide layer at this high concentration of Mn, which would cause the increase of electrical conductivity of $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics [16].

The piezoelectric constant d_{33} and the electromechanical coupling factor k_p of $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics as a function of MnO_2 addition are showed in Fig. 4. The d_{33} and k_p first increase and then decrease with increasing MnO_2 concentration, which show the maximum values of 149pC/N and 0.311 at 0.8 mol% MnO_2 addition. Generally, the piezoelectric properties of piezoceramics are determined by the microstructure and the phase structure. When the amount of Mn is lower than 0.8 mol%, the Mn ions will go to B-site and create oxygen vacancies as acceptor dopant, which will harden the material.

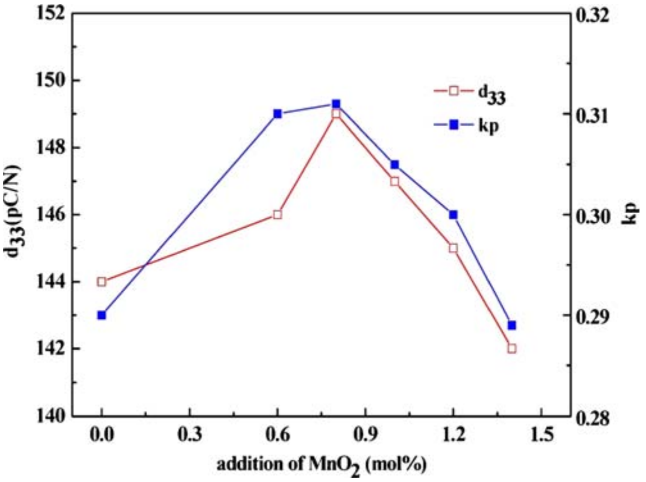

Fig. 4 Piezoelectric constant (d_{33}) and electromechanical coupling factor (kp) of $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ with different MnO_2 addition

The oxygen vacancies inside the material make the diffusion easier, leading to the good sinteability, increasing the density and improving the poling process. Thus the piezoelectric constant d_{33} and the electromechanical coupling factor k_p gradually increase with the increase of MnO_2 addition. However, a large amount of MnO_2 addition would lead to drastic worsening of the sintering behavior and the formation of cavities in the ceramic bulk. Besides, the excess MnO_2 may precipitate in the grain boundary, which may lead to the accumulation of space charges, thus limiting the movement of the domains. Both of these effects lead to the deterioration of the piezoelectric properties [16, 17].

Figure 5 shows the figure of merits and averaged pyroelectric coefficients of 0.82BNT-0.18BKT as a function of MnO_2 addition in range of 65–80 °C. From the figure it can be seen that with the increase of $MnO_{2,}$ the figure of merit(F_D)and

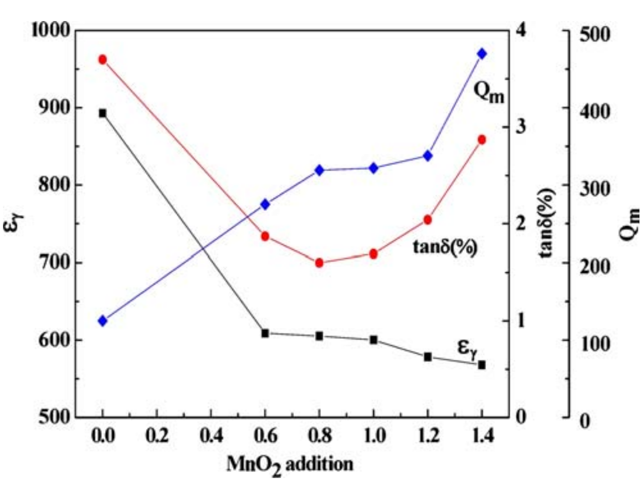

Fig. 3 Dielectric constants, dielectric loss and mechanical quality factor (Qm) of $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ with different MnO_2 addition

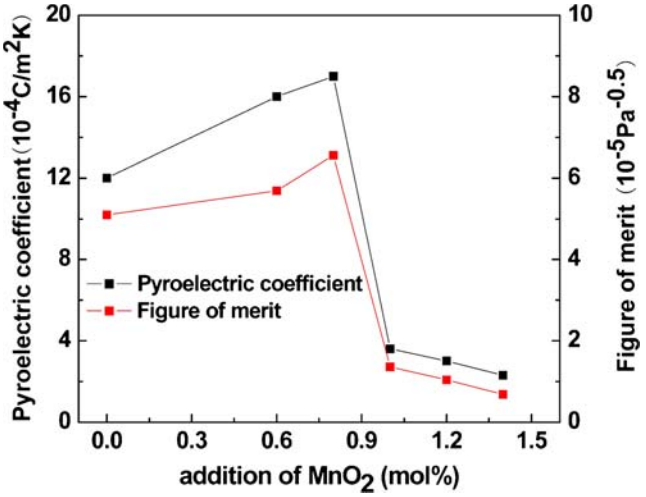

Fig. 5 Pyroelectric coefficients and figure of merits of 0.82BNT-0.18BKT as a function of MnO_2 doping level

averaged pyroelectric coefficients(*p*) increase slowly up to a maximum value 17×10^{-4} C/m^{2}K and 6.56×10^{-5} Pa$^{-0.5}$at 0.8 mol% MnO_2 addition and then decrease sharply with further increase of MnO_2. The averaged pyroelectric coefficients are better than other lead-free ceramics (KNLNT: 1.65×10^{-4} C/m^{2}K, KNLNTS: 1.9×10^{-4} C/m^{2}K, BNKBT: 1.65×10^{-4} C/m^{2}K, BNKLBT: 3.6×10^{-4} C/m^{2}K) [18]. The superior F_D and p may be due to the fact that Mn ions will substitute for B-site Ti^{4+} ions with the increasing of MnO_2 content so that oxygen vacancies were created to compensate the charge equilibrium. This gives rise to the local distortion of the oxygen octahedron unit cells. It is easier for dipole to vibrate as a function of temperature, but harder with external electric field. So the pyroelectric properties become better with the increasing of MnO_2 addition until 0.8 %mol. However, when the amount of MnO_2 is over 0.8%mol, Mn ions are supersaturated in the lattice of $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$, and the excess Mn ions accumulate in the grain boundaries, resulting in a pinning effect on a domain which hinders the motion of a domain with the change of temperature. At last the pyroelectric properties become weaker.

4 Conclusions

MnO_2-doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ lead-free ceramics have been fabricated by an ordinary sintering technique. A small amount of MnO_2 improves effectively the densification $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$ ceramics but large additions may drastically deteriorate the sintering performance. The incorporation of a proper amount 0.8 mol % of MnO_2 enhances the dielectric, piezoelectric, pyroelectric properties significantly. Besides, we found MnO_2-doped $(Na_{0.82}\ K_{0.18})_{0.5}Bi_{0.5}TiO_3$-based lead-free ceramics have better pyroelectric properties than other lead-free ceramics. They can be used to fabricate into pyroelectric sensors in future.

References

1. H.C. Yu, Z.G. Ye, Appl. Phys. Lett. **93**, 112902 (2008)
2. G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, Sov. Phys. Solid State **2**, 2651 (1961)
3. Y.R. Zhang, J.F. Li, B.P. Zhang, C.E. Peng, J. Appl. Phys. **103**, 074109 (2008)
4. B.J. Chu, D.R. Chen, G.R. Li, Q.R. Yin, J. Eur. Ceram. Soc. **22**, 2115 (2002)
5. S.C. Zhao, G.R. Li, A.L. Ding, T.B. Wang, Q.R. Yin, J. Phys. D. **39**, 2277 (2006)
6. Y.M. Li, W. Chen, J. Zhou, Q. Xu, H.J. Sun, R.X. Xu, Mater. Sci. Eng. B **112**, 5 (2004)
7. H. Ishii, H. Nagata, T. Takenaka, Jpn. J. Appl. Phys. **40**, 5660 (2001)
8. D.M. Lin, D.Q. Xiao, J.G. Zhu, P. Yu, Appl. Phys. Lett. **88**, 062901 (2006)
9. X.X. Wang, X.G. Tang, H.L.W. Chan, Appl. Phys. Lett. **85**, 91 (2004)
10. G.F. Fan, W.Z. Lu, X.H. Wang, F. Liang, Appl. Phys. Lett. **91**, 202908 (2007)
11. Z.P. Yang, B. Liu, L.L. Wei, Y.T. Hou, Mater. Res. Bull. **43**, 81 (2008)
12. X.P. Jiang, L.Z. Li, M. Zeng, H.L.W. Chan, Mater. Lett. **60**, 1786 (2006)
13. X.J. Li, Q. Wang, Q.L. Li, J. Electroceram. **20**, 89 (2008)
14. G.Z. Zhang, S.L. Jiang, Y.Y. Zhang, T.T. Xie, Curr. Appl. Phys. **9**, 1434 (2009)
15. J. Yoo, J. Hong, H. Lee, Y. Jeong, B. Lee, H. Song, J. Kwon, Sensors Actuators A **126**, 41 (2006)
16. M.K. Zhu, L.Y. Liu, Y.D. Hou, H. Wang, H. Yan, J. Am. Ceram. Soc. **90**, 120 (2007)
17. L.X. He, M. Gao, C.E. Li, W.M. Zhu, H.X. Yan, J. Am. Ceram. Soc. **21**, 703 (2001)
18. S.T. Lau, C.H. Cheng, S.H. Choy, D.M. Lin, K.W. Kwok, H.L.W. Chan, J. Appl. Phys. **103**, 104105 (2008)