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Effects of Mn-doping on the Piezoelectric and Ferroelectric Properties of $(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO_3$ Ceramics

Jiang Xiangping[1,a], Li Longzhu[1,2], Jiang Fulan[1], Zheng Yanyan[1] and Liu Lihua[1]

[1] Department of Material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen, 333001, Jiangxi, China

[2] Department of Material Science and Engineering, Changzhou Institute of Engineering Technology, Changzhou, 213164, Jiangsu, China

[a] jiangxp@hotmail.com

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Abstract. Lead-free piezoelectric ceramics of $(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO_3$+x wt.% Mn (abbreviated as NBKT-x% Mn, x=0~0.5) were synthesized by solid-state reaction. The grain growth of the ceramics was restrained by Mn-doping at a certain extent. The mechanical quality factor Q_m increases and the dielectric loss $tan\delta$ decreases with the increase of Mn-doping. Best piezoelectric properties were obtained for the composition of NKBT-0.2%Mn: d_{33}=158 pC·N^{-1}, $tan\delta$=2.9% at 1 kHz, Q_m=110 and k_p=30%. The P-E loops show that remnant polarization P_r and coercive field E_c decrease slightly with the amount of the Mn^{2+} increasing up to 0.2wt.% and then increase as the content of Mn^{2+} increases further. NKBT-0.5wt. % Mn exhibits strong ferroelectricity with remnant polarization P_r = 38μC/cm^2.

Introduction

It is well-known that PZT-based piezoelectric ceramics have been widely applied to electronic and micro-electric devices. However, the lead-based ceramics may be prohibited due to the toxicity of lead oxide and the need of environment protection. $Na_{0.5}Bi_{0.5}TiO_3$ (abbreviated as NBT) was considered as one of the promising candidate for the lead-free based ceramics since it was found to be ferroelectric [1]. Many studies have intensively focused on this lead-free ceramic due to its superior ferroelectric properties [2-4]. It has a high Curie temperature (T_c = 320°C) and a relatively large remnant polarization (P_r = 38 μC/cm). However, pure NBT piezoelectric ceramics are difficult to pole adequately because of its high coercive field (E_C = 73 kV/cm). Recently, some modifications of NBT ceramics have proved to be helpful in the poling process by forming solid solution with $BaTiO_3$, $SrTiO_3$, $NaNbO_3$, $BiFeO_3$, La_2O_3, $Ba(W_{1/2}Cu_{1/2})O_3$ or $K_{0.5}Bi_{0.5}TiO_3$(KBT) [5-11]. Among them, the (1-x) $Na_{0.5}Bi_{0.5}TiO_3$-x $K_{0.5}Bi_{0.5}TiO_3$ (NKBT) system reveals relatively superior properties near the rhombohedral-tetragonal morphortropic phase boundary (MPB) when x is between 0.16~0.20 [10-13]. However, NKBT also has drawbacks, such as low piezoelectric constant d_{33} and remnant polarization P_r. Many researches have been done to modify the properties of NKBT system. Wang et al. [14] improved the piezoelectric constant d_{33} by using La_2O_3 as a modifier. Yueming Li et al. [15] reported that incorporation CeO_2 into NKBT can reduce the coercive field E_c. However, the remnant polarization P_r of the system is still too low for practical application. Mn^{2+} is believed to be an effective additive for improving piezoelectric properties based on the researches on $Pb(Zr_{0.52}Ti_{0.48})O_3$(PZT) ceramics[16]. In this paper, effects of Mn-doping on the piezoelectric and ferroelectric properties of NKBT were studied. The addition of Mn^{2+} enhances the piezoelectric constant d_{33} and the remnant polarization P_r, meanwhile reduces the dielectric loss $tan\delta$.

Experimental

$(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO_3$-x wt.%$MnCO_3$ (x=0~0.5) ceramics were prepared by solid-state reaction using analytical-grade metal oxides or carbonate powders as raw materials. The starting materials were weighed according to the stoichiometric composition. The weighed batches were wet mixed in alcohol for 6 h. After drying, the powders were calcined at 880°C for 2 h. The calcined powders were mixed again and pressed into disks. The pellets were sintered at 1100°C for 2h in air. All samples were coated with a silver paste fired at 800°C as electrodes and polarized under a DC field of 5kV/mm at 60~120°C in silicon oil bath for 15 ~ 20min. The crystalline structure of the sintered samples was examined by X-ray diffractometer (XRD), and the microstructure was observed by electron probe microstructure analysis (EPMA). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter. The mechanical quality factor and the electromechanical coupling factor of the samples were measured by resonance and antiresonance frequencies using an impedance analyzer. A standard Sawyer-Tower circuit was used to measure the polarization hysteresis (*P-E*) loops.

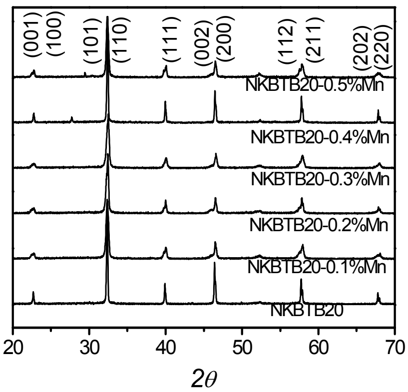

Fig.1. XRD patterns of BNKT–x wt.% Mn ceramics

Results and Discussion

The XRD patterns of the samples are shown in Fig.1. Patterns with x = 0 - 0.3 exhibit a single perovskite structure with no impurity phase, which means Mn^{2+} diffused into the NKBT lattice during sintering. However, non-perovskite structure can be clearly seen in the XRD patterns between 2θ from 25º to 30º when the content of Mn^{2+} is more than 0.3 wt.%.

The cross-section morphological features of NKBT-x wt.% Mn ceramics are shown in Fig. 2. All samples are well crystallized and the crystalline boundaries are clearly observed. It can be clearly seen that the grain growth of the NKBT ceramics is suppressed at a certain extent after the addition of Mn^{2+}. The grain size decreases from about 2 μm to 0.5 μm when the amount of Mn^{2+} increases from 0 to 0.4 wt.%. (Fig.2 a, b and c). However, no significant change is observed in the grain size with the further addition of Mn^{2+} (Fig.2 d).

Fig.3 shows the piezoelectric and dielectric properties measured at 1 kHz as a function of the Mn^{2+} content. It can be seen that addition of Mn^{2+}into the NKBT system reveals a tendency to increase the mechanical quality factor Q_m and reduce the dielectric constant ε^T_{33}. The piezoelectric constant d_{33} increases slightly after the addition of Mn^{2+} within a certain range of amount and then decreases with the more content of the Mn^{2+}. The sample shows the optimal d_{33} of 158pC·N^{-1} at 0.2(wt) % Mn^{2+}. Variation of the electromechanical coupling factor k_p and k_t is almost similar to that of d_{33}, but their maximum value occurs at 0.3% of Mn^{2+}. The mechanism for the effect of the Mn^{2+} is complicated. There are three possible mechanisms. One possible effect is that Mn^{2+}[R(Mn^{2+}) = 67 pm (low spin)] enters into the B-site of the perovskite to substitute for the Ti^{4+}[R(Ti^{4+}) = 60.5 pm], which leads to the creation of the oxygen vacancies. In this case, the oxygen vacancies restrain the movement of domain walls, resulting in the increase of Q_m and the decrease of dielectric constant ε^T_{33}. The second possibility is that Mn^{2+} [R (Mn^{2+})

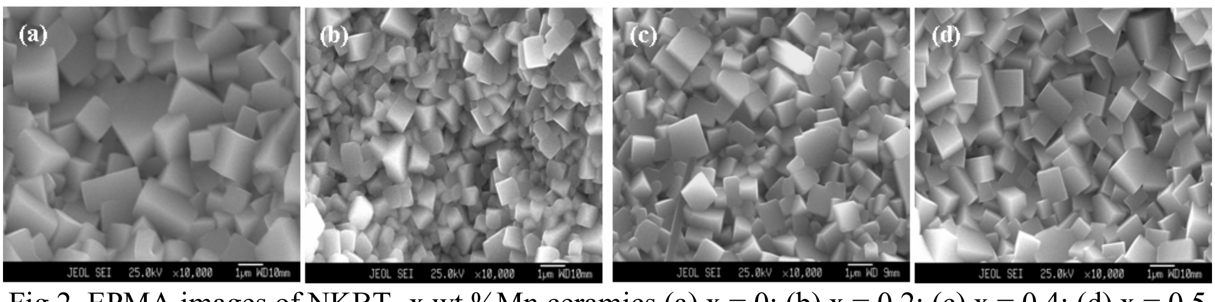

Fig.2. EPMA images of NKBT -x wt.%Mn ceramics (a) x = 0; (b) x = 0.2; (c) x = 0.4; (d) x = 0.5

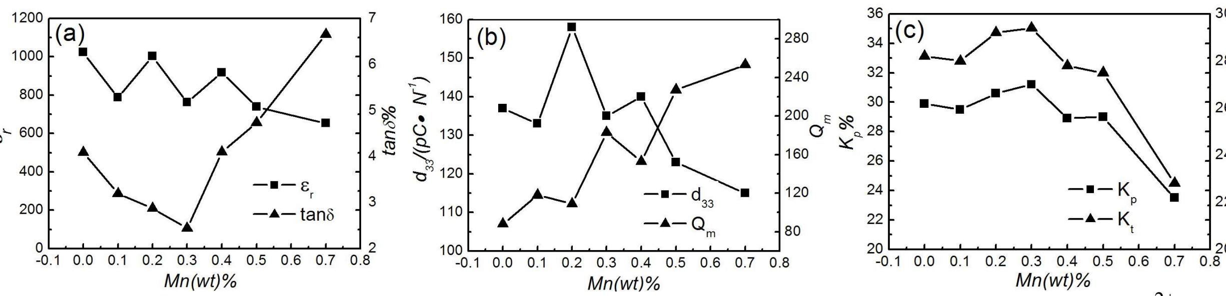

Fig.3. The piezoelectric properties measured at 1 kHz as a function of the amount of Mn^{2+}.

=83pm (high spin)] replaces the Na^+[R (Na^+) = 94pm] in the A-site of system to form vacancies of A-site. This change will improve the piezoelectric properties as the movement of domain walls is facilitated. The last possibility is that excess Mn^{2+} irons remain at grain boundaries, which lead to the deterioration of piezoelectric properties due to the existence of a non-ferroelectric phase at the grain boundaries. All the possibilities may happen simultaneously and give a complex effect on the piezoelectric properties.

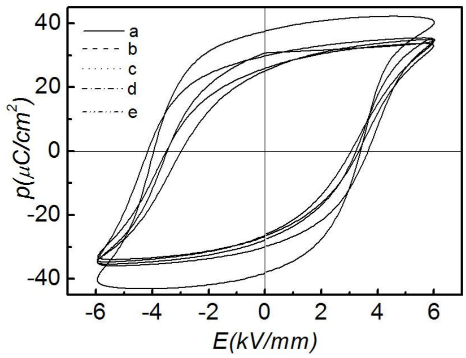

Fig. 4 The *P-E* hysteresis loops of NKBT-x wt.%Mn ceramics at room temperature. (a: x = 0; b: x = 0.1; c: x = 0.2; d: x = 0.4; e: x = 0.5)

The *P-E* hysteresis loops of the NKBT-x wt.%Mn ceramics obtained at room temperature are shown in Fig. 4. The hysteresis loops of the NKBT-x wt.%Mn are well-saturated over a wide range of x with relatively large remnant polarization P_r and low coercive field E_c. It is obvious that the remnant polarization P_r and coercive field E_c decrease slightly with the addition of Mn^{2+} up to 0.2 wt.%, which indicates the facilitation of the domain movement caused by the deformation in lattice. Meanwhile, an increase of the Mn^{2+} leads to an increase of the remnant polarization P_r and coercive field E_c. It can be seen that NKBT-0.5 wt.%Mn has a large remnant polarization of 38μC/cm^2, which is significantly higher than 29.2μC/cm^2 for the pure NKBT. That is to say, the proper amount addition of Mn^{2+} enhances the ferroelectric properties of the NKBT.

Conclusions

The $(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO_3$ + x wt. %Mn (x=0~0.5) were prepared and Mn-doping effects on their piezoelectric properties and dielectric behavior were studied. The XRD patterns show that Mn-doping do not change the crystalline structure of the NKBT ceramics. The microstructures observed by EPMA indicate that the grain growth of the ceramics are restrained by Mn-doping at a certain extent. The piezoelectric properties are improved by doping proper amount of Mn^{2+}. NKBT-0.2 wt.%Mn shows the optimum properties with d_{33}=158 pC·N^{-1}, $tan\delta$=2.9% at 1 kHz, Q_m = 110 and k_P=30%.

Acknowledgments

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