Effect of doped Mn on piezoelectric properties of (Na$_{0.5}$Bi$_{0.5}$)$_{0.92}$Ba$_{0.08}$TiO$_3$ lead-free ceramics

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Abstract: Piezoelectric ceramics (Na$_{0.5}$Bi$_{0.5}$)$_{0.92}$Ba$_{0.08}$TiO$_3$ + x % MnCO$_3$ (BNBT-Mn, x = 0 - 1.6, mass fraction) were synthesized by conventional solid state reaction. The results show that when the addition of MnCO$_3$ is 0 - 1.4 %, BNBT-Mn ceramics exhibit a single-phase perovskite structure. With the increase of content of MnCO$_3$, piezoelectric constant and electromechanical coupling factor increase rapidly when x is lower than 0.3. Then they both decrease when x is in the range of 0.3 and 1.6. When x = 0.3, piezoelectric constant and electromechanical coupling factor reach the maximum value of 160 pC/N and 58.5 % respectively, which can improve the temperature stability of BNBT-Mn.

Key words: lead-free ceramics, Mn, piezoelectric properties

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1 INTRODUCTION

There has been great interest in the studies of the lead-free materials with dielectric, piezoelectric and ferroelectric properties in the field of functional materials for their amiability to environment. (Na$_{1/2}$) TiO$_3$ (NBT) ceramics have been widely studied because of their relatively large remnant polarization ($P_r$) of 38 μC/cm$^2$ and coercive field of 73 kV/cm$^2$. However, NBT can not replace lead zirconate titanate (PZT) based ceramics because the piezoelectric properties of NBT are still not comparable to those of PZT. Recently, many researchers have investigated the effects of small amount of dopant, such as Ba, Pb, Ca, Sr, Se, NaNbO$_3$, on NBT ceramics. Among them, (Na$_{1/2}$Bi$_{1/2}$)$_{1-x}$Ba$_x$TiO$_3$ (BNBT) binary system ceramics has the most satisfactory piezoelectric properties. The piezoelectric constant ($d_{33}$) and electromechanical coupling constant ($k$) are 125 pC/N and 48 %, respectively.

In order to improve the piezoelectric properties of BNBT ceramics, BNBT based piezoelectric ceramics doped with Mn ions were synthesized by conventional solid state reaction. The effects of Mn ions on the microstructure and properties of BNBT ceramics were discussed in this paper.

2 EXPERIMENTAL

(Na$_{1/2}$Bi$_{1/2}$)$_{0.92}$Ba$_{0.08}$TiO$_3$ + x % MnCO$_3$ (x = 0 - 1.6, mass fraction) ceramics were prepared by the conventional ceramic fabrication technique. Stoichiometric amount of Bi$_2$O$_3$ (99.99 %), Na$_2$CO$_3$ (99.8 %), TiO$_2$ (99 %), BaCO$_3$ (99 %), MnCO$_3$ (96 %) powders were thoroughly mixed for 4 h and calcined at 850 °C for 2 h, then, the ball milling and ground ceramic powders were used to make cylindrical pellets with 10 mm diameter and 1 mm thickness. The pellets were sintered for 2 h at 1 100 °C in air.

The phases and microstructures of the sintered ceramics were observed by an X-ray diffractometer (XRD, D/Max3C) and scanning electron microscopy (SEM, JSM-5610LV). The sintered ceramics were pasted with silver on both sides, subsequently poled in silicon oil bath at 70 - 80 °C for 10 min in the poling field of 3 - 6 kV/mm. The electromechanical coupling factor ($k$) was obtained by a resonance-antiresonance method using a low-frequency impedance analyzer (HP4192A). The quasi-static $d_{33}$ meter (ZJ-2) was utilized to measure the piezoelectric constant.

3 RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns for BNBT + x % MnCO$_3$ ceramics. It can be seen that the BNBT + x % MnCO$_3$ ceramics with x = 0, 0.3 and 1.4 have the single-phase perovskite structure. The spectrum for BNBT + 1.6 % MnCO$_3$ ceramics shows broadened peaks and some peaks are separated, which implies that the second phase appears. Besides, the diffraction peaks shift to the higher an-
angles, which indicate the decrease of lattice constant.

Fig. 1 XRD patterns for BNBT$_x$MnCO$_3$ ceramics
1. $x=0$; 2. $x=0.3$; 3. $x=1.4$; 4. $x=1.6$

The SEM images of BNBT$_x$MnCO$_3$ ceramics with $x=0$ and 0.3 are shown in Fig. 2. It shows that the density and homogeneity of ceramics are improved when 0.3 % MnCO$_3$ is added.

Piezoelectric strain constant and electromechanical coupling factor as a function of the amount of MnCO$_3$ are shown in Fig. 3. Fig. 3 shows that with the increase of content of MnCO$_3$, piezoelectric constant and electromechanical coupling factor increase rapidly when $x$ is lower than 0.3, then they decrease slightly when $x$ is in the range of 0.3 and 1.4, and finally decrease rapidly when $x$ is over 1.4. When 0.3 % MnCO$_3$ is added to BNNT ceramic, the maximum value of $d_{33}$ and $k_t$ are 160 pC/N and 58.5%, respectively.

Fig. 3 Effect of MnCO$_3$ on piezoelectric constant of BNNT ceramic

Fig. 4 shows the effect of the poling field ($E_p$) on the electromechanical coupling factors $k_t$. It can be seen that $k_t$ of BNBT + 0.3 % MnCO$_3$ ceramics has the maximum value of 58.5% when the low poling field is 4.5 kV/mm. However, for BNBT ceramics, $k_t$ is not saturated when the poling field is smaller than 5 kV/mm. Additionally, the value of $k_t$ for BNBT ceramics is smaller than that of BNBT + 0.3 % MnCO$_3$ in the same poling field, which indicates that the coercive field of BNBT + 0.3 % MnCO$_3$ is decreased.

Fig. 4 Effect of poling field on $k_t$ of BNBT + $x$% MnCO$_3$ ceramics
1. $x=0$; 2. $x=0.3$

Fig. 5 shows temperature stability of longitudinal extension vibration resonance frequency ($f_r$) for BNBT and BNBT + 0.3 % MnCO$_3$ ceramics. In the temperature range of 20 to 120 °C, longitudinal extension vibration resonance frequency for BNBT + 0.3 % MnCO$_3$ ceramic is almost linearly decreased from 2457 to 2434 kHz, while that of