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Processing, structure, and electrical properties of MnO_2-doped $Pb(Yb_{1/2}Nb_{1/2})_{0.10}(Zr_{0.47}Ti_{0.53})_{0.90}O_3$ ceramics

Yixuan Zhang[a], Haiyan Chen[b,*], Dali Mao[a]

[a]State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, 800 Dongchuan Road, 200240 Shanghai, China
[b]Institute of Marine Materials Science and Engineering, Shanghai Maritime University, 201306 Shanghai, China

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Abstract

We prepared $Pb(Yb_{1/2}Nb_{1/2})_{0.10}(Zr_{0.47}Ti_{0.53})_{0.90}O_3$ (PYN–PZT) piezoelectric ceramics of pure perovskite structure using the columbite precursor method with the addition of 0–0.8 wt% MnO_2, and investigated in detail the effects of adding MnO_2 on the sinterability, structure, and electrical properties of PYN–PZT ceramics. With a small addition of MnO_2 (≤ 0.5 wt%), the Mn ions are homogeneously dissolved in the PYN–PZT ceramic, leading to full densification when sintered at 1220 °C. However, further addition of MnO_2 prevents densification, causing a high porosity and small grain size. The doping of MnO_2 transforms the phase structure from tetragonal to rhombohedral. The addition of MnO_2 up to a maximum of 0.5 wt% remarkably improves the mechanical quality factor (Q_m) of PYN–PZT ceramics, simultaneously as well as maintains a high d_{33} and k_p. PYN-PZT with 0.5 wt% MnO_2 exhibits excellent electrical properties with $d_{33}=356$ pC/N, $k_p=0.58$, $Q_m=1215$, $\varepsilon_{33}^T/\varepsilon_0=1232$, $\tan\delta=0.0035$, and $T_C=378$ °C.

Keywords: A. Sintering; B. Composites; C. Piezoelectric properties

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1. Introduction

Recently, high-power piezoelectric ceramics have been intensively investigated for device applications such as piezoelectric transformers and ultrasonic motors. Because piezoelectric devices operate at their resonance frequency in transforming electrical and mechanical energy, it is desirable for piezoelectric ceramics to combine a high mechanical quality factor Q_m with a high piezoelectric constant d_{33} and a high electromechanical coupling factor k_p with a low dielectric dissipation $\tan\delta$ [1–4]. However, the temperature rise of piezoelectric devices is also inevitable when they are operated at a high vibration level, so a high Curie temperature T_C is also desired because this extends their range of operating temperature, reduces their temperature dependence, and enhances the output power [5,6].

Many researchers have reported that Mn ions can serve simultaneously as a "soft" and "hard" additive to improve Q_m, d_{33}, and k_p, while lowering $\tan\delta$ for PZT or PZT-based ternary systems [7–10]. Therefore, Mn-doped PZT systems are excellent candidates for high-power applications. It is well known that typical $xPbZrO_3–(1-x)PbTiO_3$ ($x=0.52$) binary systems offer good piezoelectric properties and have a higher T_C (~402 °C) [11,12]; PZTs with ternary systems are usually limited to $T_C < 330$ °C [5]. Of the relaxor ferroelectric ceramics, $Pb(Yb_{1/2}Nb_{1/2})O_3$ (PYN) is antiferroelectric with a monoclinic perovskite structure and has a relatively high T_C (300 °C) [13], and the $(1-x-y)Pb(Yb_{1/2}Nb_{1/2})–xPbZrO_3–yPbTiO_3$ ($x=0.42$, $y=0.48$) ternary system exhibits a high T_C (395 °C) and a high k_p (0.61) [14]. To date, there have been no reports of investigations into MnO_2-doped PYN–PZT, so it is especially important that the effects of MnO_2 on the electrical properties of PYN–PZT be investigated.

Therefore, in this study, we investigate the sinterability, structure, electrical properties, and Curie temperature of PYN–PZT ternary piezoelectric ceramics by adding MnO_2. The purpose of the investigation is to obtain piezoelectric ceramics with a larger Q_m, a larger d_{33}, a larger k_p, a smaller $\tan\delta$, and a higher T_C.

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*Corresponding author. Tel.: +86 13817567313; fax: +86 2138284804.
E-mail address: hychen@163.com (H. Chen).

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2. Experimental

The compositions of the PYN–PZT systems were $Pb(Yb_{1/2}Nb_{1/2})_{0.10}(Zr_{0.47}Ti_{0.53})_{0.90}O_3 + x$ wt% MnO_2, where $x = 0$–0.8 wt%. $PbTiO_3$ has a higher Curie temperature ($T_C = 490$ °C) than $PbZrO_3$ ($T_C = 230$ °C), so a Ti-rich composition (Zr/Ti = 47/53) was chosen so that PYN–PZT would have a higher T_C. Commercially available PbO, Yb_2O_3, Nb_2O_5, ZrO_2, TiO_2, and MnO_2 were used as raw materials. The samples were prepared by the columbite precursor method to prevent the formation of an undesired pyrochlore phase [15]. Yb_2O_3 and Nb_2O_5 were mixed and calcined at 1100 °C for 4 h, and then the $Yb_2Nb_2O_8$ columbite was synthesized. The PYN–PZT perovskite solid solutions were prepared by reacting the above $Yb_2Nb_2O_8$ with a stoichiometric amount of PbO, ZrO_2, and TiO_2 at 850 °C for 2 h. An excess of 4 wt% PbO was added to compensate the likely loss of Pb during the synthesis. Once synthesized, the PYN–PZT perovskite powders were mixed with 6 wt% polyvinyl alcohol (PVA) solution, and then pressed into 12-mm diameter disks at 100 MPa. The samples were sintered at 20 °C temperature intervals between 1160 and 1240 °C for 3 h in a covered alumina crucible, and the pellets were polished to a thickness of 0.5 mm. Electrodes were made by applying a silver paste on the two major faces of the disks followed by heat treatment at 830 °C for 8 min and subsequent polishing in a dc electric field of 30–40 kV/cm in a Silicon oil bath at 120 °C for 30 min.

The bulk densities of sintered ceramics were determined using the Archimedes method. The sintered samples were ground and polished to remove the surface layer for X-ray diffraction (XRD, D/MAX-RB, Rigaku, Japan; Cu K_α radiation). The quantities k_P and Q_m were calculated via the resonance–antiresonance method using an impedance analyzer (Agilent 4294 A Precision Impedance Analyzer, Japan). We measured d_{33} using a quasi-static piezoelectric d_{33}-meter (Model ZJ-2, China). The capacitance and dielectric dissipation (tan δ) at 1 kHz were measured directly using the impedance analyzer. The capacitance at 1 kHz was measured over a temperature range of 25–450 °C using a computer-controlled measurement system (TH2617, Tonghui Electron, China), then the dielectric constant ε_{33}^T and the relative permittivity $\varepsilon_{33}^T/\varepsilon_0$ were calculated from the capacitance and the dimensions of the samples.

3. Results and discussion

Fig. 1 shows the bulk density of all samples as a function of the sintering temperature. It can be seen that the bulk density of the samples increases with increasing sintering temperature up to 1220 °C. Further increasing the sintering temperature above 1220 °C does not cause any increase in bulk density, so 1220 °C appears to be the most suitable sintering temperature. Adding up to 0.5 wt% MnO_2 results in samples that are well densified at sintering temperatures above 1220 °C. However, it is difficult to sinter the compositions when the MnO_2 content exceeds 0.5 wt%. The best bulk density is 7.85 g/cm^3 for the composition with 0.5 wt% MnO_2 sintered at 1220 °C.

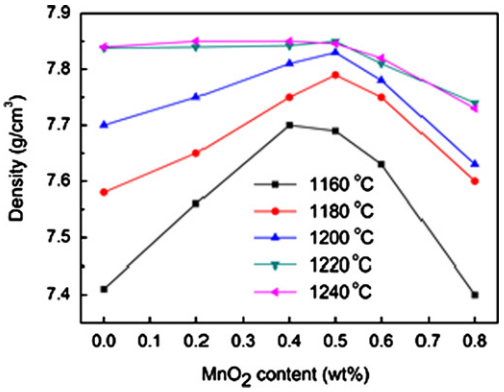

Fig. 1. Density of PYN–PZT as a function of the MnO_2 content for different sintering temperatures.

The effect on the densification of adding MnO_2 is clearly seen in the SEM micrographs as shown in Fig. 2. The grain size of pure PYN–PZT is about 2 μm, and when the MnO_2additive is increased to 0.5 wt%, a grain size of approximately 5 μm is observed. The good densification is maintained until the MnO_2 content exceeds 0.5 wt%. Conversely, 0.8 wt% MnO_2 leads to a decrease in grain size to approximately 1 μm, and some pores form at the grain boundary. Therefore, the addition of MnO_2 significantly influences the grain growth and density.

It was reported [16] that when MnO_2 is added to PZT-based ceramics, without exceeding the solubility limit, Mn ions homogeneously dissolve in the perovskite structure and enhance the densification of the material. However, further addition of MnO_2 inhibits grain growth because of the accumulation of Mn ions at the grain boundaries.

Fig. 3 shows the XRD patterns of the sintered PYN–PZT samples as a function of MnO_2 content. In acquiring these XRD patterns, only pure perovskite phase existed and no trace of the pyrochlore structure is detected, which indicates that the addition of MnO_2 changes the phase structure. The pure PYN–PZT without MnO_2 has a tetragonal structure, as evidenced by the splitting of the (002) and (200) peaks. With increasing MnO_2 content, the perovskite structure gradually changes from a tetragonal to a rhombohedral structure across the morphotropic phase boundary (MPB). The change in phase structure is normally considered to be related to the substitution of Mn ions for B-site ions in the perovskite structure of PZT-based ceramics. First, incorporation of Mn ions into B-sites of the perovskite structure near the MPB compositions causes lattice variations, resulting in a small tolerance factor, and stabilizes the rhombohedral structure against the tetragonal structure. Moreover, the addition of MnO_2 shifts the MPB toward the $PbZrO_3$-rich side [17].

Fig. 4 shows d_{33}, k_p, and Q_m as a function of the MnO_2 content. The data indicate that both d_{33} and k_p vary in a similar way with increasing MnO_2 content. When the

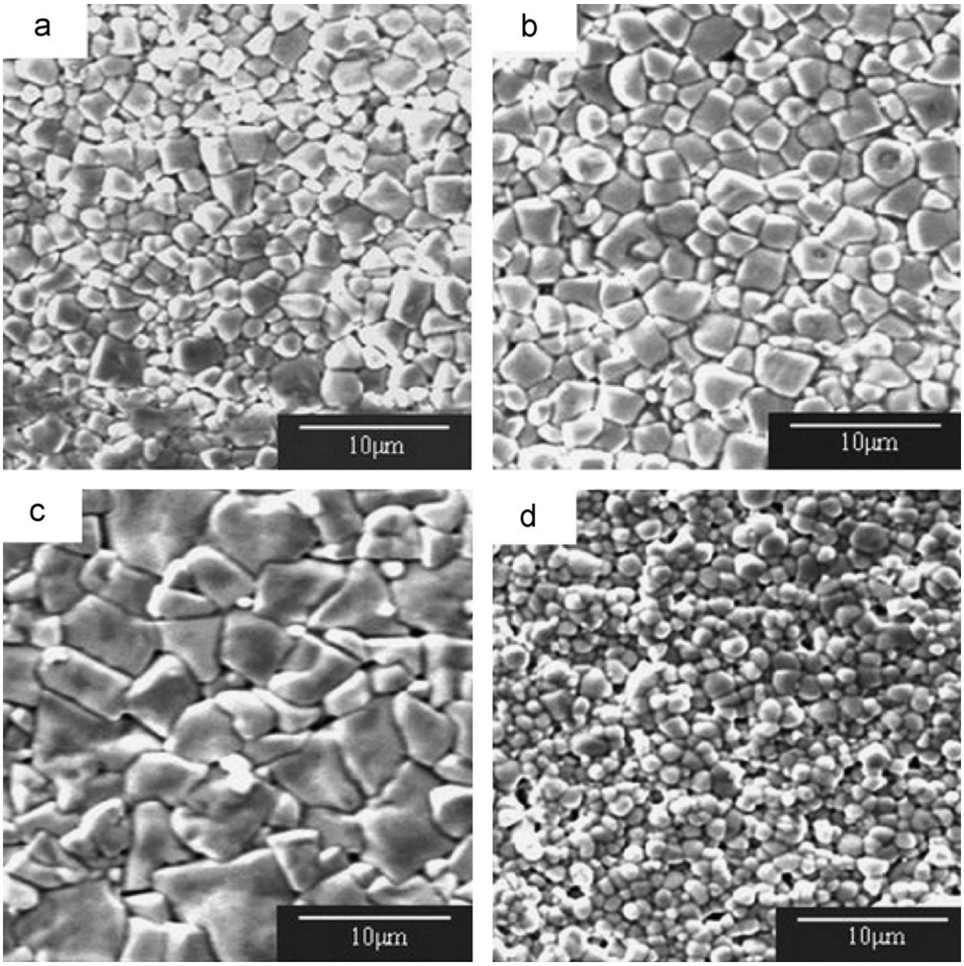

Fig.2. SEM images of the natural surfaces of PYN–PZT doped with MnO_2 by (a) 0, (b) 0.2, (c) 0.5, and (d) 0.8 wt%.

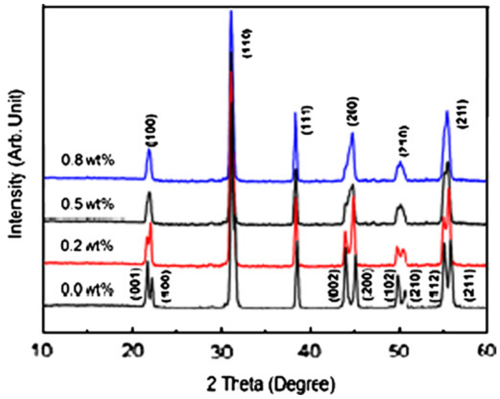

Fig.3. XRD patterns of PYN–PZT with different MnO_2 contents.

MnO_2content is below 0.2 wt%, d_{33} and k_p rapidly decrease with increasing MnO_2 content. The substitutions into B-sites in PYN–PZT by Mn ions leads to the creation of oxygen vacancies, which can restrain the movement of domain walls and result in a decrease in d_{33} and k_p [18]. However, d_{33} and k_p increase with increasing MnO_2 content from 0.2 to 0.5 wt%. The optimum $d_{33}=356$ pC/N and $k_p=0.58$ are obtained at 0.5 wt% MnO_2 content, which corresponds well with the MPB composition and the large grain size [19,20]. As shown in Fig. 4, the acceptor dopants of MnO_2 improve Q_m, and the highest Q_m (=1215) is obtained at 0.5 wt% MnO_2. Further addition of MnO_2 above 0.5 wt% leads to a decrease in Q_m, which may be attributed primarily to nonuniformity of the microstructure and insufficient densification.

The dielectric properties as a function of MnO_2 content at room temperature are plotted in Fig. 5. We see that the functional form of $\varepsilon_{33}^T/\varepsilon_0$ is similar to that of d_{33} and k_p for increasing MnO_2 content, and that $\varepsilon_{33}^T/\varepsilon_0$ attains a larger value (=1232) at 0.5 wt% MnO_2 content, and then decreases significantly as the MnO_2 content increases further. The dielectric dissipation (tan δ) exhibits a contrary tendency compared with Q_m. The acceptor dopants of MnO_2 reduces tan δ, and the smallest value (=0.0035) for tan δ is obtained at 0.5 wt% MnO_2 content.

With increasing MnO_2 content, the Curie temperature of PYN–PZT decreases and consequently the peak in the dielectric spectrum corresponding to the Curie temperature moves toward room temperature, as shown in Fig. 6. In spite of this result, we also find that T_C for all samples remains high enough to allow the use of these materials in high-power devices. The highest dielectric constant peak is

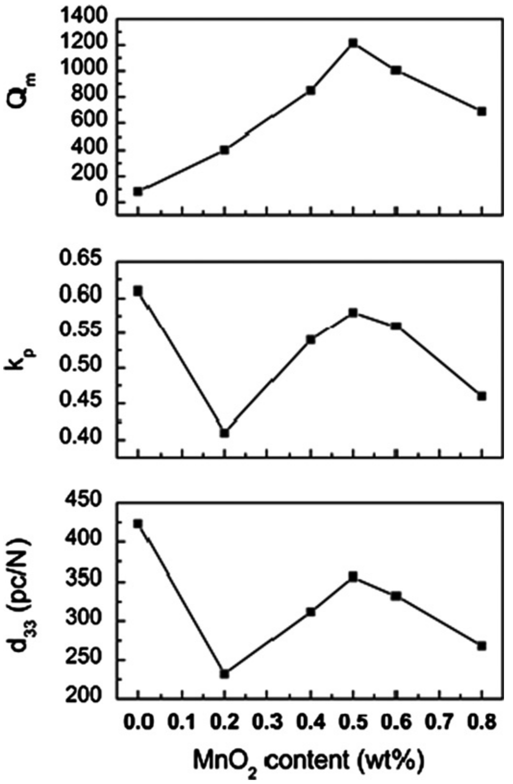

Fig. 4. Quantities d_{33}, k_P, and Q_m for PYN–PZT plotted as a function of MnO_2 content.

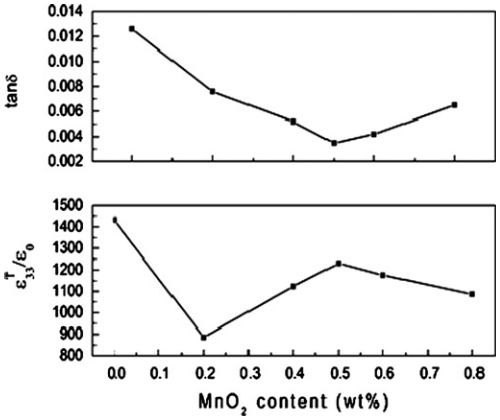

Fig. 5. Quantity $\varepsilon_{33}^T/\varepsilon_0$ of PYN–PZT plotted as a function of MnO_2 content (f=1 kHz).

achieved in the sample at 0.5 wt% MnO_2 content, which gives $T_C = 378$ °C.

4. Conclusions

We investigated the sinterability, structure and electrical properties of MnO_2-doped $Pb(Yb_{1/2}Nb_{1/2})_{0.10}(Zr_{0.47}Ti_{0.53})_{0.90}O_3$ ceramics. With the addition of no more than 0.5 wt% MnO_2, the Mn ions are homogeneously dissolved in the PYN–PZT ceramics, leading to full densification at temperatures as low as 1200 °C. The largest grain size is obtained at 0.5 wt% MnO_2 content. However, further addition of MnO_2 prevents densification, causing a high porosity and a small grain size. The addition of MnO_2 transforms the phase structure from tetragonal to rhombohedral. The optimized electrical properties of PYN–PZT ceramics are $d_{33} = 356$ pC/N, $k_p = 0.58$, $Q_m = 1215$, $\varepsilon_{33}^T/\varepsilon_0 = 1232$, tan $\delta = 0.0035$, and $T_C = 378$ °C, which is attained at 0.5 wt% MnO_2 content.

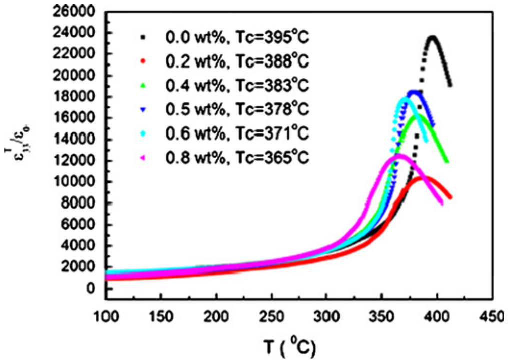

Fig. 6. Temperature dependence of $\varepsilon_{33}^T/\varepsilon_0$ for PYN–PZT as a function of MnO_2 content (f=1 kHz).

Acknowledgments

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