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Ferroelectric and pyroelectric properties of Mn-doped lead zirconate titanate ceramics

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Abstract

$PbNb_{0.02}(Zr_{0.95}Ti_{0.05})_{0.98}O_3$ (PNZT95/5) ceramics with Mn doping were prepared and the effects of Mn doping on the phase structure and electrical properties were investigated. It was found that Mn addition did not cause a remarkable change in rhombohedral perovskite structure, but significantly altered ferroelectric and pyroelectric properties of the PNZT95/5 ceramics. PNZT95/5 ceramics usually possessed a normal single hysteresis loop character when no aging process was employed, whereas Mn doped PNZT95/5 (PNMZT95/5) ceramics exhibited a double-hysteresis-like loop character because of the defect dipoles formed by Mn^{2+} and O^{2-} vacancies. Meanwhile, ferroelectric features such as the polarization and coercive field showed a strong frequency and temperature dependence. Furthermore, Mn substitution resulted in the weakened dielectric property and enhanced pyroelectric property of the ceramics. The relevant pyroelectric coefficient (p) and detectivity figure of merit (F_D) increased from 7.90×10^{-8} to 9.15×10^{-8} C cm^{-2} K^{-1} and 8.69×10^{-5} to 16.74×10^{-5} Pa$^{-1/2}$, respectively, which make the PNMZT95/5 ceramics potential application in commercial infrared detectors.

Keywords: B. Defects; C. Dielectric properties; C. Ferroelectric properties; D. PZT

1. Introduction

The Zr-rich $Pb(Zr_{0.95}Ti_{0.05})O_3$ (PZT95/5) ceramics are important ferroelectric materials with excellent dielectric, pyroelectric properties and fast response of infrared radiation. However, PZT95/5 ceramics exhibit poor spontaneous polarization ability and hence the polarization reversal becomes difficult due to the neighboring boundary of ferroelectrics (FE)/antiferroelectric (AFE). Moreover, the sintering temperature of pure PZT95/5 ceramics is usually higher than 1200 °C, which gives rise to the compositional variation and the creation of cation vacancies in ceramics because of the volatility of PbO during annealing process. Therefore, much attention has been focused on the modification of PZT by substitution method [1,2]. Compositional modifications using dopants have attracted more and more interest due to their remarkable effects even only small amounts of dopant are used. Nb_2O_5 additives are most often used for this purpose and an amount of about 1 mol% is the most favorable [3–6]. $PbNb_{0.02}(Zr_{0.95}Ti_{0.05})_{0.98}O_3$ with Mn doping (PNMZT95/5) ceramics exhibit double-hysteresis-like loops when no aging process is employed, which is often observed in the conventional ferroelectrics (e.g., $BaTiO_3$) [7–9]. However, to date, little work about this phenomenon in PZT ceramics is reported.

As a matter of fact, the main parameters for judging the quality of pyroelectric materials are the pyroelectric coefficient and figure of merit (FOM). A good pyroelectric material should possess a large pyroelectric coefficient, small dielectric constant and dielectric loss. In this work, Nb_2O_5 and $MnCO_3$ are selected to stabilize FE phase and reduce dielectric loss [10,11]. The pyroelectric and ferroelectric properties, especially the frequency and temperature dependence of P–E loops in PNMZT95/5 ceramics are investigated. A double-hysteresis

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like loop in PNMZT95/5 ceramics is observed for the first time. The formation mechanism of this abnormal hysteresis loop and the influence of Mn on pyroelectric property are also discussed.

2. Experimental procedure

The PNZT95/5 and PNMZT95/5 ceramics were synthesized by a solid-state reaction method. The reagent-grade materials, Pb_3O_4 (98% purity), ZrO_2 (99% purity), Nb_2O_5 (99.5% purity), TiO_2 (99% purity) and $MnCO_3$ (98% purity) were mixed as starting materials according to the stoichiometric ratio and then milled in distilled water for 16 h. After drying, the powders were calcined at 850 °C for 2 h. Then the calcined powders were ground in distilled water for 6 h and dried. The powders were finally granulated and pressed into pellets with 12 mm in diameter and 1.2 mm in thickness. After burnout of binder at 650 °C, the pellets were sintered at 1230 °C in a sealed Al_2O_3 crucible containing lead-rich atmosphere generated by adding sacrificial calcined powder.

The phase structure was examined by X-ray powder diffraction (XRD, X' Pert PRO MPD, Netherlands) at a scanning rate of 1 °/min with a step size of 0.02°. The microstructure of the fresh fractured surfaces of the samples was examined using a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). Dielectric measurement was performed on multi-frequency precision LCRF mete (HP 4294A, Hewlett Packard, Palo Alto, CA). The ferroelectric hysteresis (*P–E*) loop was measured with a Precision LC ferroelectric test system (Radiant Technologies, Northford, United States) at different temperatures and frequencies. Before measuring the pyroelectric properties, the samples were poled in a silicon oil bath at 110–120 °C by applying a DC electric field of 2–3 kV/mm for 30 min. The samples were short-circuited at room temperature for 24 h to remove any space charges that might have been introduced during the poling process. The pyroelectric coefficient was calculated from: $p=(i_p/A)/(dT/dt)$, where i_p is the pyroelectric current, *A* is the area of electrode, *dT*/*dt* is the increasing ratio of the temperature.

3. Results and discussion

Fig. 1a shows the XRD patterns of the synthesized PNZT95/5 and PNMZT95/5 ceramics. Both ceramics possess a typical Zr-rich rhombohedral perovskite structure, no pyrochlore or other phase is observed. From the enlarged XRD patterns in the 2θ angle of 30–32° (Fig. 1b), 43–45° (Fig. 1c) and 54–55° (Fig. 1d), it can be seen that the diffraction peaks shift to a large angle direction, which indicate the distortion of the crystal lattice of the ceramics due to the ionic size effect. It is reported that the distance between O and Mn ions (1.790 Å) is smaller than that between O and Ti ions (1.815 Å) or O and Zr ions (1.937 Å) [12]. Thus, the substitution of Zr^{4+} or Ti^{4+} by Mn^{2+} will cause the shrinkage of crystal cells [13]. For PNZT95/5 and PNMZT95/5 ceramics, *a*, *b* and *c* are 5.824 Å, 5.824 Å, 14.372 Å and 5.813 Å, 5.813 Å 14.350 Å, respectively. This suggests that Mn^{2+} ions enter the lattices of PNZT95/5 and form a normal ferroelectric phase structure.

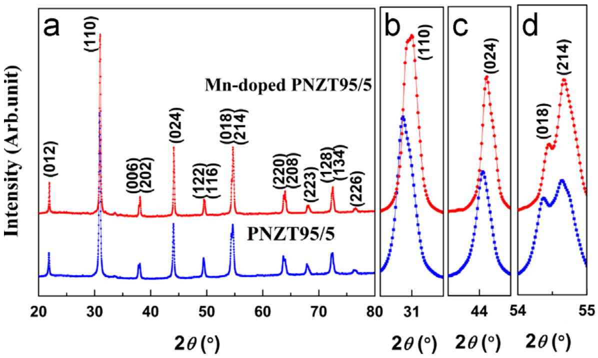

Fig. 1. (a) XRD patterns of PNZT95/5 and Mn-doped PNZT95/5 (PNMZT95/5) ceramics. The corresponding expanded XRD patterns in the 2θ range of (b) 30–32°, (c) 43–45° and (d) 54–55°.

Fig. 2 shows the SEM images of the fractured surfaces of PNZT95/5 and PNMZT95/5 ceramics. It is clearly observed that both ceramics have very similar microstructure after Mn doping. The specimens exhibit a dense and almost void-free intergranular grain structure, the average grain size is about 3.5 μm. It is well known that ferroelectric properties are affected by microstructure (grain size, orientation, uniformity etc.) due to extrinsic contribution from the motion of domain wall. The electric performance difference between these two ceramics, as will be discussed later, should be largely attributed to other factors (e.g., defect dipoles induced by addition of Mn, which may alter the domain wall motion) because there is nearly no microstructure difference between these two ceramics.

Fig. 3 shows the temperature dependences of dielectric constant (ε_r) and dielectric loss (tan δ) of both unpoled ceramics measured at 1 kHz in the temperature range 25–400 °C. The dielectric constant increases gradually when temperature rises and reaches to a maximum value at Curie temperature (T_c), but then decreases with the further increase of temperature. It is also found that the PNZT95/5 ceramics undergoes the ferroelectric–paraelectric transition at about $T_c=233$ °C, while the dielectric peak of PNMZT95/5 shifts to a low temperature with $T_c=224$ °C and the maximum permittivity decreases. These can be ascribed to the stability decrease of ferroelectric domains caused by Mn doping. As a "hard" dopant, Mn doping in PNZT95/5 could lead to the creation of oxygen vacancies due to the valence difference between Zr^{4+} and Ti^{4+} ions, which pins the movement of the ferroelectric domain walls and thus results in a decrease of dielectric constant and dielectric loss. Considering the figure of merit, the room-temperature dielectric constant decreases from 378 to 258 and dielectric loss decreases from 0.0036 to 0.0019 by addition of Mn, this is of great significance for enhancing the performance of pyroelectric devices.

P–E loops are usually used to determine the ferroelectric properties such as remnant polarization (P_r), spontaneous polarization (P_s), hysteresis area (A) and coercive field (E_c). Fig. 4 shows the *P–E* loops at 10 Hz for the unpoled PNZT95/5 and PNMZT95/5 ceramics measured under 3.5 kV/mm at