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A $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ternary ferroelectric system with high T_C and high piezoelectric properties

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ABSTRACT

$(0.79-x)Pb(In_{1/2}Nb_{1/2})O_3$–$0.21Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ($x = 0.23$–0.35) ternary ferroelectric system in the form of ceramics have been synthesized. Its structure and properties have been studied by X-ray powder diffraction and electric measurements. A morphotropic phase boundary region has been determined in the composition range of $0.28 < x < 0.32$, where the Curie temperature T_C and the rhombohedral–tetragonal phase transition temperature T_{RT} were found to vary from 243 °C to 295 °C and 145 °C to 191 °C, respectively, much higher than PMNT and PZNT systems. The compositions within MPB region exhibit excellent piezoelectric properties such as piezoelectric coefficient $d_{33} > 646$ pC/N, $T_{RT} > 145$ °C, $T_C > 273$ °C and $E_C > 13$ kV/cm for 0.5PIN–0.21PZN–0.29PT and 0.49PIN–0.21PZN–0.30PT, making the ceramics of this system a promising material for high power and high temperature application.

1. Introduction

Relaxor ferroelectric systems of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZNT) with the compositions near the morphotropic phase boundaries (MPB) in the form of single crystals exhibit excellent piezoelectric performances making them promising candidates for medical ultrasonic imaging and medical transducers with high response, broader bandwidth [1–6]. Despite of the excellent properties, the PMNT and PZNT binary systems exhibit a relatively low ferroelectric Curie temperature (T_C) and even lower rhombohedral to tetragonal phase transition temperature (T_{RT}), allowing for depoling at lower temperatures, so as to degrade the piezoelectric properties, thus limiting the use of PMNT and PZNT in many applications. Therefore, numerous studies are focusing on exploring new ferroelectric materials with high Curie temperature such as binary systems of $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$, $Pb(In_{1/2}Nb_{1/2})O_3$–$PbTiO_3$, $BiScO_3$–$PbTiO_3$, etc. [7–9] and the ternary systems of $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, $Pb(Sc_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, $Pb(Yb_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ single crystals or ceramics, etc. [10–14]. Up to now, most of all the ternary systems were focused on PMNT-based systems. Compared with PMNT, the piezoelectric properties, such as T_C, strain and d_{33} of PZNT are higher [1]. Therefore, the PZNT-based ternary system should possess higher piezoelectric properties and high Curie temperature. However, there is less reports about PZNT-based ternary system perhaps due to the difficulty to prepare bulk materials.

With the purpose of developing PZN-based ternary ferroelectric systems with high piezoelectric properties and high T_C, we investigated a $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PIN–PZN–PT) ternary system, which has been rarely reported except the dielectric properties previously [15]. In this work, we report the systematic preparation and dielectric and ferro-/piezoelectric properties of the PIN–PZN–PT ternary ceramics.

2. Experimental procedure

The $(0.79-x)$PIN–0.21PZN–xPT ternary ceramics with compositions of $x = 0.23$–0.35 were prepared by two-step solid state reaction method from the raw materials of PbO, ZnO, Nb_2O_5, In_2O_3, TiO_2 (>99.9%). All compositions were selected in the vicinity of the region which connects the two MPB regions of PZNT and PMNT binary systems with the purpose of establishing the variation of piezoelectric performance with respect to the composition and phase symmetry of the ternary system. First, the precursors of B-site ions were synthesized by columbite or wolframite method [16–18]. The precursors $ZnNb_2O_6$ (ZN) and $InNbO_4$ (IN) were

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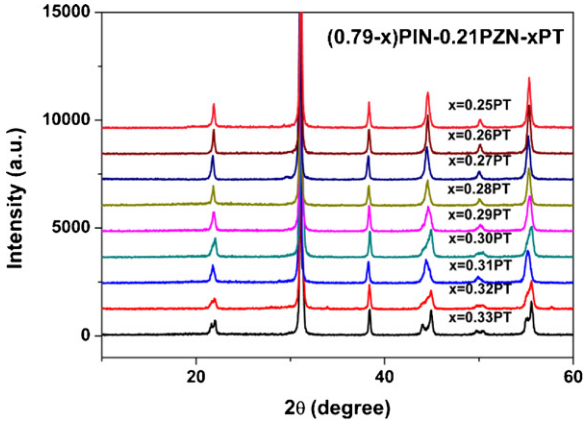

Fig. 1. X-ray diffraction patterns for $(0.79 - x)$PIN–0.21PZN–xPT ceramics, presenting a MPB region from $x = 0.27$ to $x = 0.32$.

synthesized at 1150 °C for 6 h and 10 h, respectively. Here ZnO is in excess of 5 mol% in ZN to suppress pyrochlore phase. Then PbO, TiO_2, $ZnNb_2O_6$ and $InNbO_4$ powders were mixed according to the desired compositions and wet-milled in alcohol for 24 h. After that, the mixed powders were calcined at 800 °C for 6 h and then ground in a mortar for 1.5 h with 5% polyvinyl alcohol binder before they were pressed into pellets, which were heated at 500 °C for 2 h to eliminate the binder, and then buried in calcined powders of the same composition for sintering in a sealed Al_2O_3 crucible at 1150 °C for 2.5 h, where PbO was used as lead source to compensate evaporation.

The density of the sintered samples was measured using Archimedes method. The structural analysis was carried out by an X-ray diffractometer (Rigaku, MinFlexII, Japan) at room temperature. A scanning electron microscope (JSM-6700F, JEOL) was used to investigate the morphology and microstructure of the ceramics grains. For electric measurements, the samples were polished and coated with silver paste for electrodes. The dielectric properties were measured using a computer-controlled Alpha-A broadband dielectric spectrometer (Novocontrol GmbH) with an AC signal of 1.0 V (peak-to-peak) applied. The ferroelectric hysteresis loops were measured at room temperature using an aix-ACCT TF2000 analyzer at a loop frequency of 2 Hz. The piezoelectric coefficient was measured using a quasistatic d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, model ZJ-4AN).

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the ceramic samples at room temperature. It shows that all samples crystallize in a pure perovskite phase. The (2 0 0) reflection of the ceramic compositions with $x < 0.28$ shows a single peak, exhibiting a rhombohedral symmetry. The compositions with $x > 0.32$ show the splitting of the pseudo-cubic (1 0 0), (2 0 0), indicating a tetragonal symmetry. For $x = 0.28$–0.32, the (1 0 0) and (2 0 0) peaks first become broadened and asymmetrical gradually and then split at $x = 0.33$, suggesting that the symmetry of the phase gradually changes from rhombohedral to tetragonal upon increasing PT content, which is consistent with the further dielectric analysis below. Therefore, a MPB region is indeed present within this composition range.

The SEM images of the fracture surface for 0.49PIN–0.21PZN–0.30PT and 0.50PIN–0.21PZN–0.29PT ceramics sintered at 1150 °C are shown in Fig. 2, exhibiting clear intergranular behavior. The grain size was found to be on the order of 5–8 μm, with minimal porosity. The density of the sintered samples was measured using Archimedes method and their relative density were calculated and listed in Table 1, which is in the range of 95.3–98.8%. It means that sample is highly dense with a tight inter-granular packing, suggesting effective sintering of the ceramics.

As an example, Fig. 3a shows the variations of the dielectric constant (ε') and dielectric loss tangent ($\tan\delta$) as a function of temperature for the poled 0.50PIN–0.21PZN–0.29PT ceramic sample. The plot displays a broad peak with frequency dispersion, the temperature of which shifts to higher temperatures with increasing frequency slightly, suggesting weak relaxor behavior. Fig. 3b shows the real permittivity as a function of temperature at the frequency of 1 kHz for the compositions of $x = 0.24$–0.32. It shows that T_C shifts gradually to higher temperature from 243 °C to 295 °C, and T_{RT} from 191 °C to 145 °C with the changing PT content. The related electric properties for all the compositions are summarized in Table 1.

The measurements of the polarization with different PT contents reveal well developed hysteresis loops. Fig. 4 presents the hysteresis loops displayed at different bipolar electric fields applied. It can be seen that the P_r increases and reaches a maximum of 45 μC/cm^2 at $x = 0.29$ and then decreases upon increasing PT content. Meanwhile, E_C increases along with increasing PT content, indicating that the domain switching becomes harder because of the tetragonal phase. Interestingly,

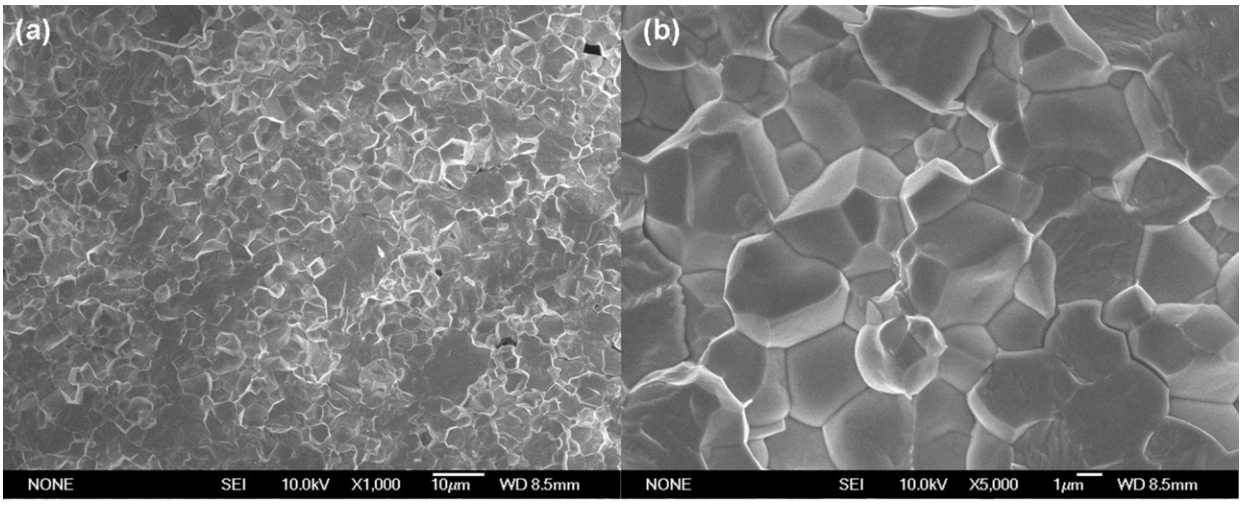

Fig. 2. SEM micrographs of the fracture surface for (a) 0.49PIN–0.21PZN–0.3PT and (b) 0.51PIN–0.21PZN–0.29PT ceramics sintered at 1150 °C.