Composition design, phase transitions and electrical properties of Sr^{2+}-substituted xPZN–0.1PNN–$(0.9-x)$PZT piezoelectric ceramics

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Abstract

The influences of PZN content and Sr^{2+} substitution on the structure and electrical properties of $Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{0.52}Ti_{0.48})O_3$ (abbreviated as PZN–PNN–PZT) piezoelectric ceramics were studied. All as-prepared PZN–PNN–PZT ceramics presented single phase of perovskite structure, while higher PZN contents favored rhombohedral symmetry and larger grain size. Meanwhile, with the increase in Sr^{2+} content, the phase structure changed from a mix of tetragonal and rhombohedral symmetries to a pure rhombohedral symmetry. Although the ferroelectric Curie temperature (T_C) was decreased with increasing the PZN and Sr^{2+} contents, the piezoelectric constant (d_{33}) exhibited the opposite trend. As a result, optimum comprehensive electrical properties were obtained in the 0.1PZN–0.1PNN–0.8PZT composition with 10 mol% Sr^{2+} substitution: $d_{33} \sim 800$ pC/N, $k_p \sim 0.65$, $\varepsilon_r \sim 4081$, $T_C \sim 176$ °C, $P_r \sim 30.92$ μC/cm². Thus, the 10 mol% Sr^{2+}-substituted 0.1PZN–0.1PNN–0.8PZT ceramic is a promising candidate for high performance applications.
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1. Introduction

In the past few decades, due to the excellent piezoelectric and dielectric properties, the lead-based ceramics have attracted a great deal of attention and have been widely used in various applications, such as energy storage capacitors, piezoelectric actuators and transducers [1,2]. Among them, the perovskite lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) has received especially much concern and is often considered as a model piezoelectric material system [3–6]. In the phase diagram of PZT, there exists a coexistence region of rhombohedral and tetragonal phases, known as morphotropic phase boundary (MPB), where the ratio of Zr and Ti is around 52/48 [7,8]. Near the MPB, the highest electrical properties can be achieved, and most commercial PZT ceramics are chosen in the vicinity of MPB.

$Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) are two important relaxor ferroelectric materials with a partially disordered perovskite structure. The PZN and PNN have the diffuse and frequency-dependent maximum in the variation of the relative permittivity with Curie temperature (T_C) of 140 °C and −120 °C, respectively [9–11]. According to the previous studies, the solid solution PZN–PNN–PZT can exhibit very good electrical properties for use as potential piezoelectric candidates. A large piezoelectric coefficient (d_{33}) of 641pC/N was reported for 0.1PZN–0.2PNN–0.7PZT ceramics prepared by the conventional solid-state reaction method [12]. Vittaya-korn et al. successfully obtained pure perovskite structure and quite high permittivity for $(0.5-x)$PZN–0.5PNN–xPZT ceramics by a columbite precursor method [13]. Nabunmee et al. reported the xPZN–$(0.2-x)$PNN–0.8PZT ceramics with extremely high dielectric constant at T_C ($\varepsilon_r = 49800$ at 10 kHz) [14]. Yuan et al. investigated the region of MPB in PZN–PNN–PZT ceramics, and found that in the MPB, the largest d_{33} of the ceramics was about 540 pC/N [15]. All of these reported data render the PZN–PNN–PZT system a potential candidate for

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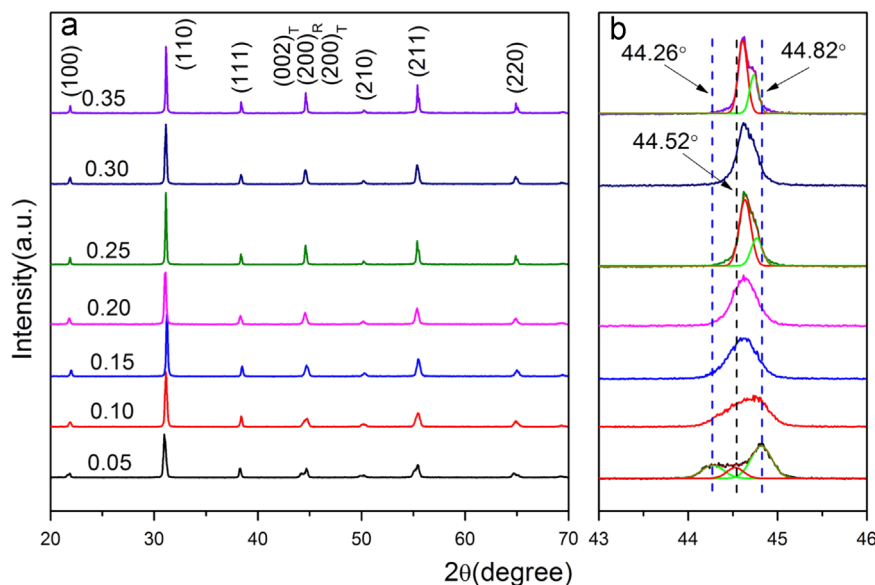*E-mail address:* xhzhu@scu.edu.cn (X. Zhu).

Fig. 1. XRD patterns of the 1250 °C-sintered xPZN–0.1PNN–(0.9 – x)PZT ceramics with 8 mol% Sr^{2+} doping (a) in the 2θ range of 20–70°, (b) magnified area of (200) peak. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

applications. Until now, however, the d_{33} values of all reported PZN–PNN–PZT ceramics are lower than 800 pC/N, which is still not enough for the top-level applications.

Doping is an important approach to enhance the piezo-electric and dielectric properties of lead-based ceramics. Sm^{3+}, Sr^{2+}, Ba^{2+} and La^{3+} have been studied by doping lead-based ceramics with A-site substitution for Pb^{2+} [16–20]. Zheng et al. reported that Sr-doped PZT ceramics exhibited sharply improved piezoelectric and dielectric properties when compared with pure PZT ceramics [21]. Accordingly, it is believed that A-site Sr^{2+} substitution can improve the electrical properties of PZN–PNN–PZT ceramics similarly.

In this work, the effects of PZN and Sr^{2+} contents on the structure, phase transitions and electrical properties of PZN–PNN–PZT ceramics have been systematically investigated. We focus on improving the piezoelectric coefficient and dielectric constant simultaneously for the top-level applications.

2. Experimental procedure

The PZN–PNN–PZT ceramics with chemical formula of $Pb_{1-y}Sr_y[(Zn_{1/3}Nb_{2/3})_x–(Ni_{1/3}Nb_{2/3})_{0.1}–(Zr_{0.52}Ti_{0.48})_{(0.9-x)}]O_3$ (where $x=0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35$; $y=0.08$ and $x=0.10$; $y=0, 0.04, 0.08, 0.10, 0.12, 0.16$) were prepared by conventional solid state sintering method. The high purity raw materials of PbO (99%), $SrCO_3$ (99%), NiO (98%), Nb_2O_5 (99.5%), ZnO (99%), TiO_2 (99%) and ZrO_2 (99%) were stoichiometrically mixed and ball-milled using ZrO_2 balls in ethanol for 24 h. After a sufficient calcination at 750 °C for 2 h in the air, the calcined mixtures were milled again with the same conditions. Then, the dried powders were mixed with 8% polyvinyl alcohol (PVA) binder solution and pressed into small disks of 10 mm in diameter and 1.0 mm in thickness. Finally, all pellets were sintered around 1250–1300 °C in a lead atmosphere by using the calcined powders. In order to

measure the electrical properties, the sintered ceramics were fired with silver electrodes on both of surfaces at 550 °C for 10 min. All samples were poled in silicon oil bath at ambient temperature for ~5 min under a DC electric field of 2 kV/mm.

The phase structure of the sintered ceramics was recorded by X-ray diffraction (XRD) (DX1000, Dandong, China) at a scan rate of 1.8 ° per min for 2θ varying from 20° to 70°. The surface topography of the ceramics was observed by scanning electron microscopy (SEM, S–3400N, Hitachi, Japan). The dielectric constant and dielectric loss as functions of temperature were measured using an LCR meter (HP 4980 A, Agilent, USA). The piezoelectric coefficient (d_{33}) of the poled ceramics was measured on a quasistatic d_{33} meter (ZJ–3A, Institute of Acoustics, Chinese Academy of Sciences, China), and the planar electromechanical coupling coefficient k_p and the relative dielectric permittivity ε_r at 1 kHz were determined by an impedance analyzer using the IEEE standard. The ferroelectric hysteresis loop (P–E loop) was characterized by using a computer-controlled Radiant Precision Workstation (Radiant Technologies, Inc., USA).

3. Results and discussion

3.1. Effect of PZN content on the electrical properties of PZN–PNN–PZT ceramics

Fig. 1 shows the XRD patterns of xPZN–0.1PNN–(0.9 – x) PZT (8 mol% Sr^{2+}-doped) ceramics with different x ($x=0.05$–0.35) sintered at 1250 °C for 2 h. All the compositions exhibit a single perovskite structure without pyrochlore phase or other second phases. With the increase of x, the splitting peak of (200) nearby $2\theta=45°$ gradually disappeared, demonstrating that there exists a phase transition between tetragonal (T) and rhombohedral (R) in the PZN–PNN–PZT ceramics. In order to analyze the phase structures more clearly, the expended XRD patterns of