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Original Article

Improved Curie temperature, electromechanical properties and thermal stability in ZnO-modified 0.68Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.32$PbTiO_3$ ceramics with coexisting monoclinic and tetragonal phases

Ji Zhang[a], Rui-Xue Wang[a], Lei Sun[a], Zhen-Lin Luo[b], Y.B. Chen[c], Yun-Fei Chang[d], Zheng-Bin Gu[a], Ming-Hui Lu[a], Bin Yang[d], Shan-Tao Zhang[a,*]

[a] National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, College of Engineering and Applied Science & Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China
[b] National Synchrotron Radiation Laboratory and CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei, Anhui 230026, China
[c] National Laboratory of Solid State Microstructures and Department of Physics & Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China
[d] Condensed Matter Science and Technology Institute, Department of Physics, Harbin Institute of Technology, Harbin 150080, China

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ABSTRACT

Further improving electromechanical properties and overcoming relatively low Curie temperature (T_c) of (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$ (PMN-100xPT) are still two scientific issues. Here, we demonstrate a stable coexistence of monoclinic-tetragonal (M_C-T) phases in ZnO-modified PMN-32PT (PMN-32PT:xZnO) due to the diffusion-induced substitution of Zn^{2+} for Mg^{2+}. The Curie temperature, saturated polarization, remnant polarization, piezoelectric coefficient (T_c, P_s, P_r, d_{33}) are increased from (160 °C, 22.0 μC/cm^2, 13.3 μC/cm^2, 350 pC/N) for x = 0 to (180 °C, 30.3 μC/cm^2, 22.4 μC/cm^2, 470 pC/N) for x = 0.06. Moreover, the thermal stability is improved. After annealing at 150 °C, the x = 0.06 sample shows retrained d_{33} value of 209 pC/N, about 4 times larger than that of x = 0 counterpart. The improved properties are attributed to the substituting increased polar nanoregions and easy domain switching in M_C phase.

1. Introduction

Piezoelectric materials with perovskite structure have been greatly investigated due to their wide application in electronic devices, such as actuators, transducers and sensors, etc. Among the reported piezoelectric materials, the relaxor ferroelectrics have attracted much attention for their excellent dielectric and piezoelectric properties. As a model system of lead-based relaxor ferroelectrics with rhombohedral (R)-tetragonal (T) morphotropic phase boundary (MPB), (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$ (PMN-xPT, $0.35 \ge x \ge 0.30$) shows extra high piezoelectric coefficient (d_{33}) and electromechanical coupling coefficient (k_p) at room temperature [1–4]. However, the MPB composition usually exhibit relatively low Curie temperature (T_c ~ 130–170 °C) and much lower ferroelectric–ferroelectric phase transition temperature (T_{F-F} ~ 60–95 °C), which induce poor thermal stability and restrict their applications in high temperature environments like space explorations, geothermal or oil well drillings and so on [5–7].

Therefore, it is of great importance to develop PMN-xPT based piezoelectric materials with enhanced thermal stability to meet the critical requirements of actual applications. Shifting T_c and/or T_{F-F} to higher temperature by forming ternary or even quaternary systems is one of common approaches to solve this problem. For example, Pb($In_{1/2}Nb_{1/2}$)O_3 or $BiScO_3$ was introduced to PMN-xPT to form ternary systems with higher phase transition temperatures (both T_c and T_{F-F}) and remained comparable piezoelectric properties with PMN-xPT binary systems [8–14]. During the past decades, great achievements in the applications of PMN-PT crystals in medical ultrasonic transducers have been achieved. However, compared with the ceramics, the relatively more complex growth methods or conditions, the higher production cost of single crystals should be concerns for further realizing their wide commercial applications [6,10,11,15,16], which means ceramic counterparts are still interesting in low-cost applications. Additionally, ceramic counterparts have more flexibility for some basic research like developing new compositions. Thus, developing PMN-xPT based ceramics is still an important and meaningful issue for researchers around the world [17,18].

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* Corresponding author.
E-mail address: stzhang@nju.edu.cn (S.-T. Zhang).

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In order to improve the electromechanical properties of PMN-*x*PT ceramics, one needs to know the possible origins of the properties. In general, two contributions should be considered. First, monoclinic (M) phase usually exists in MPB region of PMN-*x*PT relaxor ferroelectrics [9,19–24]. This intermediate phase can bridge the structurally different R and T phases, and make the polarization rotation easier due to that the domains in M phase can be switched continuously in a plane [3,23,24]. Second, for relaxor ferroelectrics, the polar nanoregions embedded in long-range ferroelectric domains can enhance the contribution of domain wall to electromechanical properties [2,4,25,26]. Therefore, it is reasonable to expect that the compositions with M phase and more polar nanoregions shall show significantly improved ferro-/piezoelectric properties [27–30].

On the other hand, it is noted that not only the polar semiconductor ZnO can induce local electric field in $Bi_{0.5}Na_{0.5}TiO_3$-based (BNT) solid solutions, but also the Zn cations can diffuse into the host lattice to act with host cations [30,31]. Thus, it is probable for diffused Zn cations to substitute Mg cations for their close radius [33,34], if ZnO is successfully introduced into PMN-*x*PT. In this way, the expectation that not only the crystal structure of PMN-*x*PT may be changed due to diffusion of Zn cations, but also the remained ZnO can act as both sintering aids and polar semiconductor to improve electromechanical properties may come true [31–34]. In addition, Zn cations are more ferroelectric active than Mg cations resulting from the d^{10} electronic configuration of Zn, which favors covalent bonding between Zn and O, and thus enhances the degree of ferroelectric order [34]. Although there are very few reports on Zn-substituted PMN-*x*PT [33–35], further systematical and deep investigations on the substitution limit, substitution-changed crystal symmetry and properties, etc., are not available in literatures, which are necessary to understand the roles of Zn cations diffusion and ZnO particles.

In this paper, the PMN-0.32PT (PMN-32PT), which is a MPB composition separating R and T phases, is chosen as the research object. The PMN-32PT:*x*ZnO (where *x* represents the mole ratio of ZnO to PMN-32PT) ceramics were prepared, the composition- and temperature-dependent crystal structure and electromechanical properties were investigated systematically. The diffused Zn cations enter into lattice to replace Mg cations to form coexisting phases separating M_c and T phases. And especially, the coexisting phases show greatly improved Curie temperature, electromechanical properties and thermal stability.

2. Materials and methods

PMN-32PT:*x*ZnO ceramics with $x = 0$, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 were prepared using the conventional solid-state reaction method. The dried PbO (99.8%), MgO (99.0%), Nb_2O_5 (99.8%) and TiO_2 (99.0%) were selected as raw materials. To avoid the pyrochlore phase $Pb_3Nb_4O_{13}$, which would degrade the dielectric and electromechanical properties, a two-step columbite precursor method was adopted to synthesize the PMN-32PT powders [36]. First, the stoichiometric MgO and Nb_2O_5 mixture was ball milled in ethanol for 24 h, and calcined at 1100 °C for 4 h to obtain precursor $MgNb_2O_6$. Then, $MgNb_2O_6$, PbO and TiO_2 powders were mixed and ball milled in ethanol for 24 h according to the stoichiometric ratio with an addition of 5 mol% excess PbO to make up for the lead losses in the subsequent high-temperature sintering. After drying process, the mixture was sintered at 900 °C for 2 h to form phase PMN-32PT powders.

After that, both the prepared PMN-32PT powders and the commercial ZnO nano particles (PlasmaChem, Germany, 25 nm) were weighted according to the formula of PMN-32PT:*x*ZnO with $x = 0$, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09. Each mixture was ball milled again in ethanol for 24 h, dried and subsequently pressed into green disks with a diameter of 10 mm under 40 MPa. Sintering was carried out in covered alumina crucibles at 1100 °C for 2 h with increasing and decreasing temperature rate of 5 °C/min. To compensate the volatilization of Pb, the disks were embedded in the corresponding powders during the sintering process.

The crystal structure of the ceramics was characterized by powder X-ray diffraction (XRD, Bruker D8, Advance, Germany). Structural refinement was carried out using FULLPROF software [37]. The microstructures were observed by scanning electron microscopy (SEM, FEI Quanta 200). For electrical measurements, the circular surfaces of the ground disks with the diameter of ~ 8.5 mm and the thickness of ~ 0.5 mm were covered with a thin layer of silver paste and fired at 400 °C for 30 min. Temperature dependent dielectric constant (ε_r) and dielectric loss ($\tan\delta$) were measured using an impedance analyzer (HP4294A) at several frequencies on unpoled samples. The piezoelectric coefficient (d_{33}) was measured on poled ceramics (2.5 kV/mm for 30 min) by a Berlincourt-d_{33}-meter (ZJ-6A). The resonant and antiresonant frequencies were measured by the impedance analyzer, and then the planar electromechanical coupling factor k_p were calculated according to IEEE standard. Electromechanical property measurements were carried out in silicone oil with controllable temperature from room temperature (~25 °C) to 150 °C, the polarization-electric field (*P-E*) ferroelectric loops and strain-electric field (*S-E*) curves were measured at 1 Hz by TF analyzer 1000 (AixACCT).

3. Results

Fig. 1(a) shows the room temperature XRD patterns of PMN-32PT powders with different ZnO contents. Clearly, all the prepared samples are crystallized into single-phase perovskite structure, indicating successful suppress of the secondary pyrochlore phase $Pb_3Nb_4O_{13}$. The (200) diffraction peaks ($2\theta = 43.5° \sim 46.5°$) for all samples are enlarged and exhibited in Fig. 1(b). It is well known that the (200) diffraction peak of XRD patterns showing only one single peak correspond to a rhombohedral phase (R), and splitting into two peaks correspond to tetragonal phase (T) [38]. Therefore, the broadening (200) diffraction peaks without splitting observed in sample of $x = 0$ and 0.02 indicates the coexisting of R (dominated) and T phases, confirming the formation of MPB composition. While *x* is increased to 0.04 and 0.05, the (200) diffraction peak begins to split gradually, and split becomes more obvious when $x \geq 0.06$, indicating the appearance of new ferroelectric phases with larger lattice distortion. Further increasing the content of ZnO, the diffraction pattern exhibits no obvious changes (Fig. 1(b), $x \geq 0.06$) suggesting that the newly emerged phase is stable in this composition range.

In order to further clarify the phase structure of PMN-32PT:*x*ZnO ceramics with $x \geq 0.06$, the Rietveld analysis of the XRD data for $x = 0.09$ was performed. The plausible structure models, such as P4 mm, P4mm + R3 m and P4mm + Pm, were considered, and the lowest value of agreement factor was obtained based on the P4mm + Pm model and exhibited in Fig. 1(c). It can be concluded that the doped ZnO has forced the phase of PMN-32PT:*x*ZnO ceramics to transform from the coexistence of R and T phases (R-dominant, $x = 0$, 0.02) to the coexistence state of T and M_C phases with space groups of P4 mm and Pm ($x \geq 0.06$), such phase coexisting state remains relatively stable even when the ZnO content reaches 0.09.

The typical microstructural morphologies of PMN-32PT:*x*ZnO ceramics are shown in Fig. 2(a–h). It is evident that the introduction of ZnO has a significant influence on the microstructure evolution of the samples. (1) For $x = 0$ and 0.02, a few voids can be seen between the boundary of grains, and they vanish when $x > 0.02$. (2) The grain size of the samples increases with the increasing ZnO content from $x = 0$ to 0.09, depicted in Fig. 2(i), the average grain size of the prepared ceramics in this work is about 1.8 μm, 1.8 μm, 5.3 μm, 5.8 μm, 6.7 μm, 8.5 μm, 8.8 μm, 6.9 μm, respectively. (3) The grain morphology evolved from mixture of polyhedra and irregular shapes to polyhedra with increased ZnO content. Since ZnO is widely used as a well-known sintering aid in many dielectric and piezoelectric ceramics [34,39], it is reasonable that ZnO can enlarger the grain size and density of ceramics, and decrease the sintering temperature. (4) As shown in Fig. 2(i), the