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Phase diagram and electrical properties of $Pb(Yb_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ternary ceramics

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ABSTRACT

The ternary ferroelectric ceramics $Pb(Yb_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PYN–PMN–PT), in the vicinity of morphotropic phase boundary (MPB) region, have been prepared by a two-step synthetic process. The ternary phase diagram at room temperature has been established based on the XRD data analysis, which exhibits a curved MPB region. The dielectric, ferroelectric and piezoelectric properties have been characterized, indicating the electrical properties can be adjusted regularly by choosing compositions. The Curie temperature T_C of ternary system varied from 165 to 370 °C. With the increase of PMN content, the piezoelectric coefficients d_{33} increase from 373 to 505 pC/N, and the coercive field E_c decrease from 18 to 6 kV/cm. The results show that the PYN–PMN–PT ternary system can be a potential material for high temperature applications.

1. Introduction

Relaxor-based complex perovskite ferroelectric materials $Pb(B_1,B_2)O_3$–$PbTiO_3$ ($B_1 = Mg^{2+}$, Zn^{2+}, Sc^{3+}, In^{3+}, Yb^{3+}, ..., $B_2 = Nb^{5+}$, Ta^{5+}, W^{6+}, ...) with morphotropic phase boundary (MPB) are widely studied due to excellent dielectric and piezoelectric properties [1–4]. The anomalously high piezoelectric properties near the MPB compositions result from large number of polarization directions available [5] and the instability of the polarization [6–8]. Moreover, a new phase of monoclinic has been discovered near MPB region, which contribute to high piezoelectricity [9–12]. This kind of excellent piezoelectric properties make them promising candidates for the applications as high-performance solid state actuators, multilayer ceramic capacitors, ultrasonic imaging probes and electromechanical transducers [1,5,13–16]. Therefore, the preparation, electrical properties, applications and physics of relaxor-based ferroelectric materials near the MPB regions have been become hot topics in recent years.

As a typical representative of the relaxor-based ferroelectric materials, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMNT) possesses excellent piezoelectric performance, the MPB region of which has been found in the vicinity of 30–35 mol% PT [4,17]. For example, the composition of PMNT (67/33) ceramics exhibit a large piezoelectric constant of $d_{33} = 640$ pC/N and relatively high electromechanical coupling factors of $k_p = 61\%$, $k_t = 43\%$ [18]. Although PMNT ceramics exhibit superior dielectric and piezoelectric performance, the Curie temperature T_C and rhombohedral–tetragonal phase transition temperature T_{RT} are quite low, which restricts the application temperature range [4,15]. Attempts have been made to develop new systems with relatively high T_C and high piezoelectricity [19–21]. In view of this consideration, the $(1-x-y)Pb(Yb_{1/2}Nb_{1/2})O_3$–$xPb(Mg_{1/3}Nb_{2/3})O_3$–$yPbTiO_3$ (PYN–PMN–PT) ternary system appears to be promising materials for high temperature applications. $Pb(Yb_{1/2}Nb_{1/2})O_3$ (PYN) was discovered as an anti-ferroelectric material with T_C around 302 °C, which takes on orthorhombic perovskite structure below T_C [22]. Similar to the PMN, it can be formed a solid solution with normal ferroelectric PT to present an MPB region in the vicinity of 49–50 mol% PT [23,24]. Within the MPB, the PYNT (50/50) ceramics have a relative high Curie temperature T_C (about 371 °C) and the piezoelectric constants d_{33} are in the range of 175–500 pC/N based on different synthetic methods and annealing conditions [25]. Furthermore, PYNT ceramics have a relatively low sintered temperature [25]. It is reasonable to expect that PYNT can form a solid solution with PMNT, in which an MPB is expected to exist, and the piezoelectric properties and T_C of the MPB composition would be enhanced because of high piezoelectric

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performance for PMNT and PYNT ceramics and high T_C for PYNT at MPB compositions. Based on this consideration, the PYN–PMN–PT ternary crystals have been successfully grown by the top-seeded solution method in our group. The Curie temperature T_C, piezoelectric coefficient d_{33} and longitudinal electromechanical coupling factor k_{33} at room temperature reach 205 °C, 1800 pC/N and 90%, respectively, suggesting excellent piezoelectric properties [26]. Therefore, it's necessary to study the PYN–PMN–PT ternary ceramics system in detail including MPB region and electrical properties so as to provide enough information for the growth of PYN–PMN–PT single crystals with higher piezoelectric properties and higher Curie temperature. In this work, the MPB region of the PYN–PMN–PT ternary system has been determined and the electrical properties have been characterized.

2. Experimental procedure

The ceramics of $(1-x-y)$PYN–xPMN–yPT with the compositions of $x = 0$, $y = 0.49$; $x = 0.15$, $y = 0.39$, 0.41, 0.43, 0.45, 0.47; $x = 0.35$, $y = 0.34$, 0.36, 0.38, 0.40, 0.42; $x = 0.55$, $y = 0.31$, 0.33, 0.35, 0.37, 0.39 and $x = 0.67$, $y = 0$ were prepared by a two-step synthetic process using PbO, MgO, Nb_2O_5, Yb_2O_3, TiO_2 with high purity (99.9%) as starting materials. First, the precursors of B-site ions were synthesized by columbite or wolframite methods [3,24,27]. The columbite precursor $MgNb_2O_6$ (MN) was prepared at 1100 °C for 4 h with excess 10 mol% MgO to suppress pyrochlore phase. The wolframite precursor $YbNbO_4$ (YN) was prepared at 1200 °C for 4 h in stoichiometric proportions. Second, MN, YN, PbO, TiO_2 were mixed and calcined at 800 °C for 4 h with excess 3 mol% PbO (to compensate the volatilization of PbO) to form PYN–PMN–PT powders. Third, the calcined powders were thoroughly grinding with 2 wt% polyvinyl alcohol (PVA) as a binder. And then the powders were pressed into pellets, which were heated at 600 °C for 2 h to eliminate the binder. The formed pellets were sintered at various temperatures from 1040 °C to 1160 °C for 2 h in a sealed Al_2O_3 crucible to form the series of desired ceramics.

For structural analysis, X-ray diffraction (XRD) was performed at room temperature on an X-ray diffractometer (Rigaku, Japan) equipped with Cu Kα radiation and a graphite monochromator with an angular range of 10–80°. The data were collected with a scan step of 0.02° (2θ) using a scanning rate of 0.5° min^{-1}. The theoretical density of the sintered samples was calculated based on XRD, while the actual density was measured using Archimedes method. The morphologies of the sintered samples were determined using scanning electron microscopy (SEM, JSM 6700, Japan). The obtained samples were polished and coated with silver paste for electrical measurements. The dielectric properties were measured using a computer-controlled Alpha-A broadband dielectric/impedance spectrometer (Novocontrol GmbH), with an AC signal of 1.0 V (peak-to-peak) applied. The ferroelectric hysteresis loops were displayed using an aix-ACCT TF2000 analyzer (at $f = 2$ Hz) at room temperature. Poling was performed at 120 °C for 15 min at a DC electric field of 15–30 kV/cm. Piezoelectric coefficient was measured using a quasistatic d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, model ZJ-4AN).

3. Results and discussion

The XRD patterns of the selected $x = 0.35$ series are presented in Fig. 1. All the samples exhibit a pure perovskite structure with no secondary phase, indicating that the perovskite structure of the PYN–PMN–PT ceramics is quite stable. Interestingly, it seems that the structure of ceramics samples transfer gradually from rhombohedral to tetragonal phase occurs with increasing PT content.

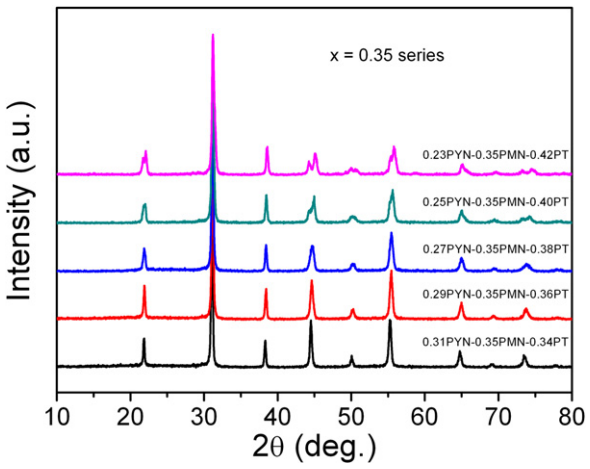

Fig. 1. X-ray powder diffraction patterns of $(1-x-y)$PYN–xPMN–yPT ceramics for the selected series: $x = 0.35$, indicating a phase transition from the rhombohedral to tetragonal phase upon increasing PT.

In order to identify the phase compositions between rhombohedral and tetragonal phases, the special attention was focused on (2 0 0) reflections around $2\theta = 45°$. Fig. 2 presents the experimental XRD data of (2 0 0) reflection peaks profiles for some selected samples, which were deconvoluted with the tetragonal and/or rhombohedral phase components. In general, the XRD profiles of (2 0 0) reflections will show only a single peak R(2 0 0) for the rhombohedral phase due to all the planes of (2 0 0) share the same lattice parameters, whereas it splits into two peaks for the tetragonal phase, the T(2 0 0)/(0 2 0) and T(0 0 2) profiles with an intensity ratio of the T(2 0 0)/(0 2 0) and T(0 0 2) peaks of 2:1. Therefore, the (2 0 0) reflections within the MPB region should be composed of three peaks: one for rhombohedral phase and two for tetragonal phase. As shown in Fig. 2, for each series, strong splitting of (2 0 0) reflections from rhombohedral to tetragonal phase with PT content increasing. Therefore, there is a region, in each series of x, at which the rhombohedral phase and tetragonal phase co-exist, i.e., within MPB region. Based on the above analysis, the MPB are found to be located between 0.42YN–0.15PMN–0.43PT and 0.40PYN–0.15PMN–0.45PT for $x = 0.15$ series; between 0.27YN–0.35PMN–0.38PT and 0.25YN–0.35PMN–0.40PT for $x = 0.35$ series; between 0.10YN–0.55PMN–0.35PT and 0.08YN–0.55PMN–0.37PT for $x = 0.55$ series at room temperature respectively. Thus, the ternary phase diagram of PYN–PMN–PT solid solution at room temperature has been established as shown in Fig. 3, including the reported MPBs for PMNT and PYNT binary system, being 30–35 mol% PT and 49–50 mol% PT [4,17,23,24]. It can be seen that the ternary MPB region is a curved region rather than a linear region. The results are consistent with the result of previous studies [28].

SEM micrographs of the surface for the compositions within the MPB region are shown in Fig. 4. It is clearly can be seen that few pore in the obtained ceramics. The grain size of above samples was listed in Table 1. It is found that with increasing PYN content, the grain size of PYN–PMN–PT within the MPB region change irregularly. The theoretical and actual density of the samples was presented in Table 1. The relative density, listed in Table 1, indicates relative high dense.