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Short communication

Ferroelectric ternary solid solution of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbSnO_3$–$PbTiO_3$ with morphotropic phase boundary

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Abstract

A ternary solid solution of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbSnO_3$–$PbTiO_3$ (PMN–PSn–PT) has been synthesized in the form of ceramics by solid solution reaction and characterized by means of X-ray diffraction, dielectric spectroscopy, and ferroelectric measurements. The study on different oxidation states of tin shows that Sn^{2+} is the dominant valence state, thereby causing an impurity pyrochlore phase of the formula $Sn_2Nb_2O_7$. A morphotropic phase boundary (MPB) region has been determined to exist at room temperature in the solid state ternary system. The compositions within the MPB region show the best piezoelectric properties in the system. For the ceramics of 0.42PMN–0.20PSn–0.38PT which are within the MPB composition range, the Curie temperature T_C, piezoelectric coefficient and coercive field were found to be 165 °C, 345 pC/N and 7.0 kV/cm, respectively. Compared with the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ system, the larger coercive field of PMN–PSn–PT would be attractive in high power sonar applications since it would allow larger bipolar fields to be used at a lower dc bias.

Keywords: A. Solid state reaction; B. Piezoelectric properties; C. Ferroelectric properties; D. Perovskite

1. Introduction

Solid solutions based on lead-based relaxor ferroelectrics with complex perovskite structure have attracted much research attention due to their excellent piezoelectric properties. These kinds of ferroelectric materials have been widely used in the field of electromechanical coupling, including piezoelectric actuators, sensors and acoustic transducers [1–5]. Their excellent piezoelectric properties occur in compositions within the morphotropic phase boundary (MPB) region. This is because the materials with MPB compositions possess a large number of polarization states with similar energy [1] and the instability of the polarization states [6–8], making the materials more electrically active, thereby enhancing the piezoelectric response. It is well known that $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) possesses a large dielectric constant with a broad diffuse maximum of permittivity around −15 °C [9,10]. The material can form a binary solid solution with $PbTiO_3$ displaying relaxor ferroelectric properties and an MPB region, giving rise to enhanced dielectric and piezoelectric properties. However, the low Curie temperature and even lower depolarization temperature of PMN–PT limit its application from being used at high temperatures. In addition, the low coercive field also decreases the thermal stability of piezoelectric properties and reduces the acoustic power. Therefore, many attempts have been made to develop new ferroelectric solid solution systems with high Curie temperature and large coercive field [9,11–13].

$PbTiO_3$ (PT) is a normal ferroelectric compound with a relatively high Curie temperature (T_C) around 490 °C, exhibiting a tetragonal phase below T_C [5]. $PbSnO_3$ (PSn) also belongs to the perovskite structure with monoclinic symmetry [14]. It was reported that PSn can form solid solution with PT (PSn–PT), showing good piezoelectric properties near the MPB region [5–15].

It is expected that PSn can form a ternary solid solution system with PMN–PT to present high piezoelectric properties. This paper reports the synthesis and dielectric,

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piezoelectric, and ferroelectric properties of PMN–PSn–PT ternary ceramics.

2. Experimental procedure

The ceramics of (1–x–y)PMN–xPSn–yPT with the compositions of $x=0$, $y=0.33$; $x=0.10$, $y=0.30$, 0.32, 0.34, 0.36, 0.38, 0.40; $x=0.20$, $y=0.34$, 0.36, 0.38, 0.40, 0.42, 0.44 and $x=0.30$, $y=0.35$, 0.37, 0.39, 0.41, 0.43, 0.45 were prepared by a two-step solid state reaction process using PbO, MgO, Nb_2O_5, SnO_2, and TiO_2 with 99.9% purity as starting materials. First, a columbite precursor $MgNb_2O_6$ (MN) was prepared by mixing MgO and Nb_2O_5 and heating at 1100 °C for 4 h. Second, MN, PbO, SnO_2, TiO_2 were mixed and calcined at 900–950 °C for 4 h with an excess 3 mol% PbO to compensate the volatilization of PbO and form pure PMN–PSn–PT powders. The calcined powders were then thoroughly ground with 2 wt% polyvinyl alcohol (PVA) as a binder. Next, the powders were pressed into pellets, which were heated up to 600 °C for 2 h to eliminate the binder. Finally, the formed pellets were sintered at various temperatures from 1160 °C to 1185 °C for 2 h in a sealed Al_2O_3 crucible to form a series of desired ceramics.

For structural analysis, X-ray diffraction (XRD) was performed at room temperature on an X-ray diffractometer (Rigaku, Japan). The valence states of tin ions were analyzed using X-ray photoelectron spectroscopy (XPS; (VG—Escalab 250). The dielectric permittivity was measured using a computer-controlled Alpha-A broadband dielectric/impedance spectrometer (Novocontrol GmbH), with an AC signal of 0.5 V applied. The piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, model ZJ-4AN). The ferroelectric hysteresis loops were displayed using an aix-ACCT TF2000 analyzer ($f=2$ Hz) at room temperature.

3. Results and discussion

The XRD patterns of the selected samples with the composition of $x=0.20$ are presented in Fig. 1. It can be seen that all the samples exhibit the perovskite structure with a small amount of secondary impurity phase. The main perovskite phase of ceramics samples transfers gradually from rhombohedral phase to tetragonal phase with the increase of PT content. The volume of impurity phase is less than 3% and independent of the composition, which was determined to be $Sn_2Nb_2O_7$. It is known that tin can exist in different oxidation states in solid oxides, such as Sn^{2+} and Sn^{4+} [16]. Fig. 2a shows the spectrum in the binding energy region of 481–502 eV. The dominant features of spectrum are two broad peaks, corresponding to Sn $3d_{3/2}$ and Sn $3d_{5/2}$. The curve-fitting results for the Sn $3d_{5/2}$ peak are shown in the inset of Fig. 2a, which is composed of two peaks, corresponding to two different valence states of Sn^{2+} (486.2 eV) and Sn^{4+} (487.1 eV) [17].

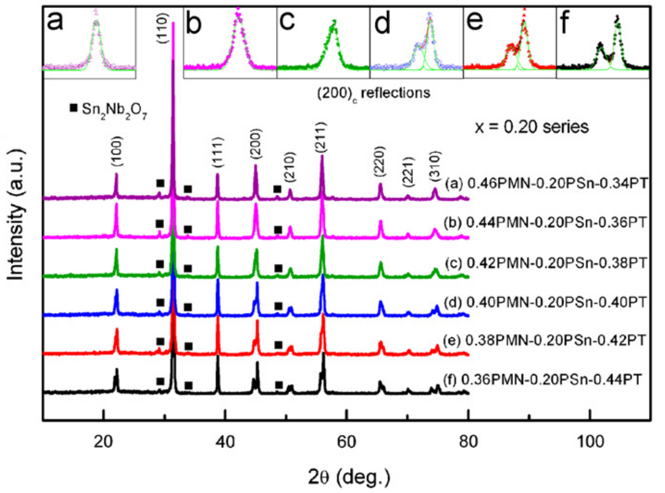

Fig. 1. X-ray diffraction patterns of PMN–PSn–PT ceramics for $x=0.20$, the inset showing $(200)_c$ reflections deconvoluted with different phase components.

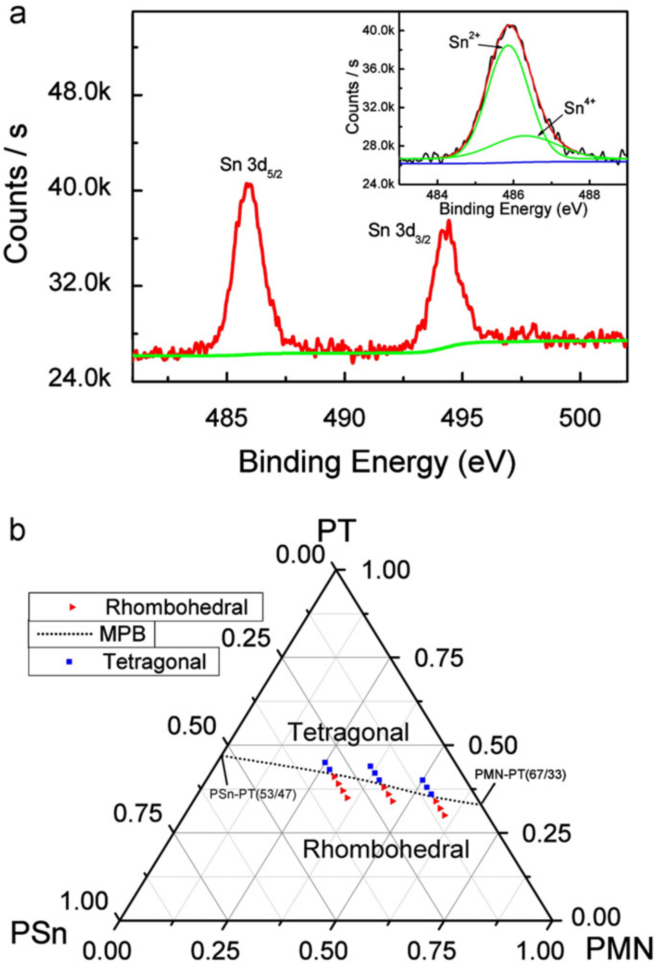

Fig. 2. (a) XPS spectrum of the PMN–PSn–PT ceramic samples, the inset showing the Sn $3d_{5/2}$ binding energy region deconvoluted with Sn^{2+} and Sn^{4+} valence states. (b) Ternary phase diagram of PMN–PSn–PT at room temperature, presenting a morphotropic phase boundary region.

It can be seen that the main valence state is Sn^{2+}, making it easy to form the $Sn_2Nb_2O_7$ pyrochlore phase with Nb^{5+} ions. Therefore, it will be expected to suppress the pyrochlore phase by means of sintering under an oxidizing atmosphere.

Generally, the (200) reflection of perovskite structure show only a single peak R(200) in the rhombohedral symmetry because all the planes of (200) share the same lattice parameters, whereas in the tetragonal phase the (200) reflection splits into two peaks, the T(200)/T(020) and T(002) profiles. In order to study the detailed structural transformation, the (200) reflection peaks of the selected samples with $x=0.20$, as an example, are deconvoluted with different phase components as shown in the inset of Fig. 1. For $y<0.38$, the (200) reflection is composed of only one peak, indicating rhombohedral symmetry. For $y=0.42$ and higher, the (200) reflection splits into two peaks, indicating tetragonal phase. For $0.38<y<0.42$, the (200) reflection is composed of three peaks, indicating the coexistence of rhombohedral and tetragonal phases i.e. within the MPB region. Therefore, the structural transformation from rhombohedral phase, to coexistence of rhombohedral and tetragonal phases and to tetragonal phase with the increase of PT content has been observed in this solid solution system. The MPB region at room temperature for $x=0.10$, 0.20, and 0.30 are found to be around 0.55PMN–0.10PSn–0.35PT, 0.41PMN–0.20PSn–0.39T, and 0.28PMN–0.30PSn–0.42PT respectively, considering that the MPB regions are around 0.67PMN–0.33PT for PMN–PT [18] and around 0.53PSn–0.47PT for PSn–PT [19]. The morphotropic phase diagram of PMN–PSn–PT solid solution at room temperature has been established as shown in Fig. 2b.

As an example, Fig. 3a shows the temperature dependences of the real permittivity (ε') and loss tangent ($\tan\delta$) measured at 100 Hz–100 kHz for the poled sample of 0.42PMN–0.20PSn–0.38PT. It can be seen that the real permittivity shows a sharp peak at 165 °C (1 kHz), indicating the paraelectric–ferroelectric phase transition, i.e. the Curie temperature T_C. The real permittivity shows a broad maximum around the Curie temperature with frequency dispersion, the temperature of which (T_{max}) shifts to higher temperatures with increasing frequency, indicating a typical relaxor behavior. The inset of Fig. 3a shows the loss tangent ($\tan\delta$) as a function of temperature. The room temperature value of ε' and $\tan\delta$ at 1 kHz are 2400 and 0.0135, respectively. The $\tan\delta$ increases significantly at the temperature above T_C due to the increase in conductivity upon further heating.

The Curie temperature and piezoelectric coefficient for the $x=0.20$ ceramics as a function of y (PT) are shown in Fig. 3b. It can be seen that the T_C values increase gradually from 145 °C to 210 °C with the increase of PT content. However the piezoelectric coefficient d_{33} varies in the range 170–345 pC/N, which first increases and reaches its maximum of 345 pC/N at $y=0.38$ and then decreases, indicating that the best piezoelectric properties occur in the MPB region.

Fig. 4 displays the ferroelectric hysteresis loops for $x=0.20$ samples. All samples exhibit saturated loops under a drive of an electric field of ±25 kV/cm. The coercive field E_c increase gradually from 6.0 kV/cm to 11.5 kV/cm with increasing PT content, however, similar to the change trend of piezoelectric coefficient, the P_r values first

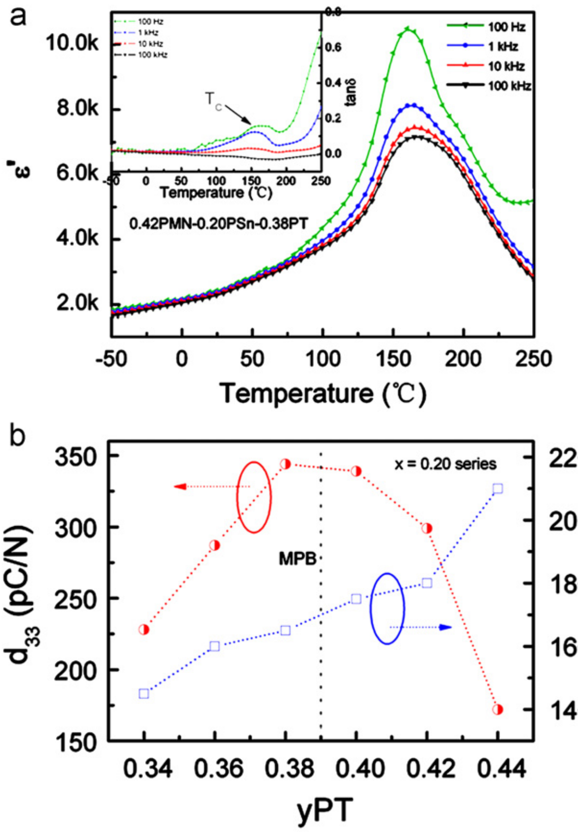

Fig. 3. (a) Temperature dependence of the real permittivity (ε') and loss tangent ($\tan\delta$) for poled 0.42PMN–0.20PSn–0.38PT ceramics sample at various frequencies of 100 Hz, 1, 10 and 100 kHz. (b) Curie temperature T_C and piezoelectric coefficient d_{33} as a function of y (PT) for the composition $x=0.20$.

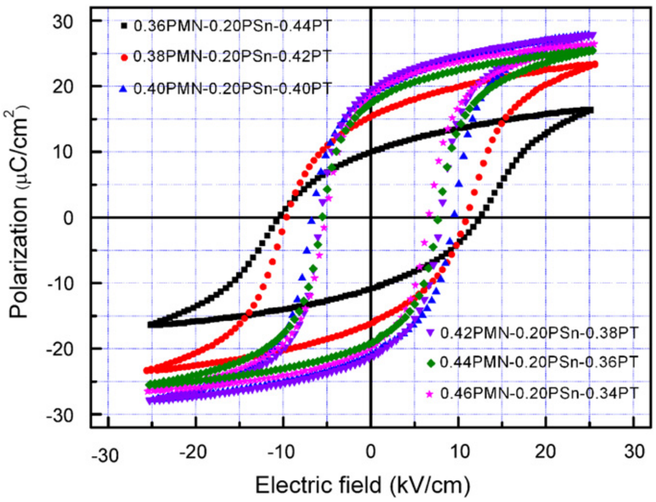

Fig. 4. Polarization vs electric field hysteresis loops of PMN–PSn–PT ceramics with composition $x=0.20$.

increases gradually and reaches a maximum of 20 μC/cm^2 at $x=0.38$ before it decreases.

4. Conclusions

A ternary solid solution of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbSnO_3$–$PbTiO_3$ (PMN–PSn–PT) has been synthesized in the form of ceramics by solid state reaction and characterized by means of X-ray diffraction, dielectric spectroscopy, and ferroelectric measurements. The study on different oxidation states of tin shows that Sn^{2+} is the dominant valence state, which easily causes the pyrochlore phase of $Sn_2Nb_2O_7$ to form. A morphotropic phase boundary (MPB) region has been determined in the solid state ternary phase diagram at room temperature. The compositions within MPB region show the best piezoelectric properties in the system. For the composition $x=0.20$, the T_C varies in the range 145–210 °C and the d_{33} varies in the range 170–345 pC/N. For the ceramics of 0.42PMN–0.20PSn–0.38PT within the MPB region, the Curie temperature T_C, piezoelectric coefficient and coercive field were found to be 165 °C, 345 pC/N and 7.0 kV/cm, respectively. Compared with the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ system, the larger coercive field of PMN–PSn–PT makes it a promising material for use in high power acoustic systems.

Acknowledgments

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