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Investigation of morphotropic phase boundaries in PIN–PSN–PT relaxor ferroelectric ternary systems with high $T_{r\text{-}t}$ and T_c phase transition temperatures

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ABSTRACT

New morphotropic phase boundary (MPB) compositions with relatively high T_cs were projected in $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Sc_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PIN–PSN–PT) solid solution based on the perovskite tolerance factor, and were experimentally confirmed. The phase structure, dielectric, pyroelectric, piezoelectric and ferroelectric properties of PIN–PSN–PT ceramics were investigated. The rhombohedral–tetragonal phase transition temperatures $T_{r\text{-}t}$ on the order of 189–210 °C, Curie temperatures T_c on the order of 274–285 °C and piezoelectric coefficients d_{33} in the range of 310–360 pC/N, were achieved in xPIN–$(1-x)$PSN–0.37PT (x = 0.15–0.23) ceramics, demonstrating a promising relaxor–$PbTiO_3$ system with high phase transition temperatures. In addition, the maps of T_c, $T_{r\text{-}t}$, d_{33} and ε_r with respect to composition were established, based on which, a clear direction for composition screening in future crystal growth of the PIN–PSN–PT system was given.

1. Introduction

Relaxor–$PbTiO_3$ perovskite ferroelectric materials with morphotropic phase boundary (MPB) compositions, e.g., $Pb(Mg_{1/3}Nb_{2/3})O_3$–$x$$PbTiO_3$ (PMN–xPT, $x \sim 0.3$), have been extensively investigated due to their high electromechanical coupling factors and piezoelectric coefficients [1–10], making those materials promising candidates for ultrasonic transducers [7,8], actuators [9] and piezoelectric sensors [10]. Compared to the $PbZr_{1-x}Ti_xO_3$ ferroelectric systems [11], some relaxor–PT solid solutions can be grown into large size single-crystals, whereupon the electromechanical properties of relaxor–PTs can be benefited from the crystal anisotropy and/or engineered domain configurations [2–5]. Near MPB compositions, the [0 0 1]-oriented PMN–PT single crystals exhibit large piezoelectric coefficients of $d_{33} > 2000$ pC/N and high electromechanical coupling factors of $k_{33} > 90\%$ [2–5]. Currently, PMN–PT crystals can be grown by a modified Bridgman method, with 100 mm in diameter and 200 mm in length [2], which fulfils the size requirement of most piezoelectric devices. However, the Curie temperature T_c (~140 °C) and rhombohedral to tetragonal phase transition temperature $T_{r\text{-}t}$ (–90 °C) are quite low for PMN–PT systems, which restricts their temperature usage range. Thus, searching for new relaxor–PT systems with high T_c and $T_{r\text{-}t}$ are highly desired from application viewpoint.

The phase transition temperature $T_{r\text{-}t}$ is highly associated with the Curie temperature T_c and the shape of the MPB boundary [2,12]. Although some investigations have been performed to predict the shape of the MPB boundary for a relaxor-PT system [12], it is still quite hard to get an accurate shape of MPB phase boundary by theoretical calculation. Thus, enhancing the $T_{r\text{-}t}$ is generally resort to the searching of relaxor–PT systems with high T_c end members. Generally, Curie temperature (T_c) of relaxor–PT with MPB compositions has been ascribed to the tolerance factor (t) of the perovskite structure [13], which can be expressed using the following equation:

$$t = \frac{R_O + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

where R_O is the O ionic radius, R_A and R_B are the average ionic radii of A- and B-site cations, respectively. Low tolerance factor means that the B-site cation prefers a larger volume than the A-

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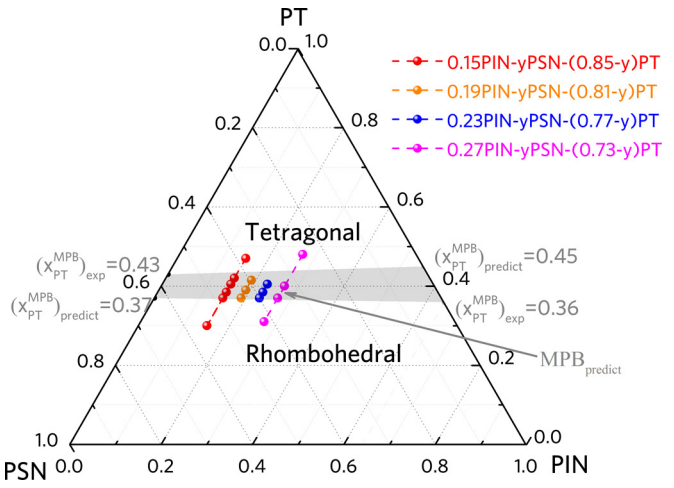

Fig. 1. Predicted MPBs and studied compositions of the PIN–PSN–PT ternary solid solutions.

site cation, leading to a higher T_c. However, when t is lower than 0.9 or higher than 1.1, the perovskite structure will be unstable due to a mismatch between preferred A–O and B–O bond lengths.

Many relaxor–PT systems have been explored based on the idea of tolerance factor. For example, $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PIN–PMN–PT) ternary system was prepared [14–21], where the tolerance factor of PIN is 0.964. It was found that the $T_{r\text{-}t}$ could reach 130 °C and the T_c varied from 160 °C to 320 °C by adjusting the composition in PIN–PMN–PT ternary system [17]. However, this $T_{r\text{-}t}$ value does not meet the requirement of high-power transducer applications. Thus it is desirable to develop new relaxor-based material systems with higher $T_{r\text{-}t}$. According to theoretical predictions and experimental results [12,13], the phase transition temperature of $Pb(Sc_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PSN–PT) with MPB composition was found to be higher than that of PMN–PT counterpart, owing to the larger ionic radius of Sc^{3+} (0.75 Å) when compared to Mg^{2+} (0.72 Å). Therefore, it is worthy to investigate a new ternary system by using PSN to substitute PMN end-member in PIN–PMN–PT system.

In this work, we focused on the ternary $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Sc_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PIN–PSN–PT) system for achiving high phase transition temperatures (T_c and $T_{r\text{-}t}$) and good piezoelectric properties. First, the MPB compositions of the selected ternary system are predicted by a linear combination rule and confirmed by X-ray analysis. Second, the phase transition temperatures ($T_{r\text{-}t}$ and T_c) were determined by dielectric and pyroelectric measurements following Choi's work in PMN–PT system [22]. Finally, a phase diagram of the new PIN–PSN–PT system is plotted in contrast with PMN–PT and PIN–PMN–PT systems, meanwhile the values of $T_{r\text{-}t}$, T_c, d_{33} and ε_r at MPB region are mapped out in the new system.

2. Experiments

2.1. MPB design in PIN–PSN–PT ferroelectric system

For a multicomponent ferroelectric system, it is of particular importance to detemine the MPB compositions for achieving high electromechanical properties. For a binary system, the MPB and Curie temperature (T_c) can be predicted by first principles calculations using ionic size (tolerance factor) and ionic displacements of the B cations [13]. The predicted results are consistent with the experimental data as reported in [22,23]. The linear combination rule, which verifies that the MPBs are located around the linear region between the binary MPBs, is used for the MPB prediction in

Table 1
Dielectric, piezoelectric and ferroelectric properties of PIN–PSN–PT polycrystalline ceramis. ρ_r is the relative density, $T_{r\text{-}t}$, rhombohedral to tetragonal phase transition temperature, T_c, Curie temperature, ε_r, relative dielectric permittivity at room temperature, tan δ, dielectric loss, d_{33}, piezoelectric coefficient, k_p, k_t, and k_{33}, electromechanical coupling for planar, thickness and longitudinal modes, P_r, remnant polarization, E_c, coercive field.

xPIN–yPSN–$(1-x-y)$PT	ρ_r (%)	$T_{r\text{-}t}$ (°C)	T_c (°C)	ε_r	tan δ (%)	d_{33} (pC/N)	k_p (%)	k_t (%)	k_{33} (%)	P_r (μC/cm^2)	E_c (kV/cm)
x = 0.15	y = 0.55 95.52	220	247	1000	2.2	300	44	43	59	29.9	7.0
	y = 0.48 95.29	210	274	1100	2.3	360	51	47	65	36.0	7.5
	y = 0.46595.52	167	282	1200	1.8	370	55	54	71	23.4	6.3
	y = 0.44595.52	129	294	2600	1.6	520	61	57	76	25.0	8.4
	y = 0.43 95.39	84	297	3600	1.6	480	59	55	74	33.5	13.3
	y = 0.38 95.36	/	318	1500	0.9	270	45	51	64	28.7	22.2
x = 0.19	y = 0.44 95.18	197	278	1200	2.4	310	50	49	66	26.3	7.2
	y = 0.42 95.17	158	290	1700	1.7	380	54	52	70	24.2	7.1
	y = 0.39595.17	133	303	3100	1.3	480	59	55	74	19.8	10.0
x = 0.23	y = 0.40 95.19	201	280	1400	2.2	310	54	46	66	24.8	7.0
	y = 0.38595.30	172	290	1800	2.0	360	54	50	68	22.2	7.1
	y = 0.36595.18	116	300	2750	1.4	420	54	55	71	20.1	8.7
x = 0.27	y = 0.42 95.17	210	252	1000	2.2	300	51	47	65	30.9	7.8
	y = 0.36 95.17	189	285	1300	2.1	340	54	50	68	34.1	8.2
	y = 0.33 95.29	107	301	2700	1.3	450	58	52	72	30.1	11.6
	y = 0.25 95.29	/	342	1000	0.7	270	50	46	64	19.2	25.4
PMN–0.30PT [37]	\	90	143	4900	2.7	670	\	\	\	25	5.0
PSN–0.43PT [23]	\	120	267	2200	2	570	71	56	\	43	10

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