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Thermal expansion and polarization of (1-x)PNN-xPT solid solutions

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ABSTRACT

The paper presents the results of detailed studies of the thermal expansion of $(1-x)PbNi_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ solid solutions with $x = 0$-0.8. The anomalous and lattice contributions to deformation and the thermal expansion coefficient are analyzed and the mean square polarization P_d is determined. The results obtained are discussed within the framework of the thermodynamic theory and the Landau 2-4-6 coefficients for solid solutions are estimated.

1. Introduction

In recent years, much attention has been paid to the study of oxide multicomponent mixed perovskites, which have a unique crystalline structure and unique physical properties, in particular, a huge dielectric constant, high piezoelectric and electrostriction coefficients, which makes them very promising for applications in various microelectronic devices. One of the most prominent representatives of such systems are $(1-x)$PNN–xPT solid solutions based on the relaxor $PbNi_{1/3}Nb_{2/3}O_3$ (PNN) and the ferroelectric $PbTiO_3$ (PT) [1, 2].

This paper presents the results of studies of the thermal expansion of ceramic samples of $(1-x)$PNN–xPT ($x = 0$–0.8) solid solutions in the temperature range from 100 to 750 K and the determination of polarization from dilatometric data.

2. Experimental

Samples were prepared using conventional ceramic technology from the mixture of oxides: PbO, NiO, Nb_2O_5, and TiO_2 [1]. The heat treatment conditions were optimized to prevent pyrochlore phase formation. The quality of the samples and their phase composition were checked by X-ray diffraction analysis at room temperature using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα radiation).

Thermal expansion was studied on ceramic samples with dimensions $L = 5$–15 mm in the temperature range 100–750 K on the induction dilatometer NETZSCH DIL-402C in

a dynamic mode with heating and cooling rates of 2–3 K/min. The measurements were carried out by purging ($\sim$50 ml/min) with dry helium.

3. Results and discussion

The temperature dependences of the thermal expansion coefficient β and deformation $\Delta V/V$ of (1-x)PNN–xPT compounds are presented in Figure 1. It is found that the anomaly of the thermal expansion coefficient $\beta(T)$ at the transition from the cubic phase to the tetragonal phase (at T_0), characteristic of pure PT, remains rather sharp, but decreases considerably in the amplitude in solid solutions (1-x)PNN–xPT as x decreases down to 0.35. At concentrations of PT smaller than the concentration corresponding to the morphotropic phase boundary $x_{MPB}\approx0.30$–0.35, the anomaly is smeared out and becomes characteristic for ferroelectrics-relaxors with a minimum at T_m. In compositions with $x = 0.80$ and 0.70, as well as in pure PbTiO$_3$, the phase transition remains a first-order transition, which is clearly seen from the results of measurements of the thermal expansion of these samples in the heating and cooling regimes. The hysteresis of the transition temperature was 3.6 K and 3.1 K, respectively.

The anomalous volume deformation in lead titanate and other ferroelectrics with the initial perovskite structure Pm-$3m$ is mainly determined by the square of the spontaneous macroscopic polarization $\Delta V_{an}/V = (Q_{11} + 2Q_{12})P^2$ and, thus, can be used to estimate it. To extract the anomalous contribution to the deformation and to determine the mean-square polarization P_d, a correct description of the non-anomalous contribution to the volume deformation $\Delta V/V$ and the thermal expansion coefficient $\beta(T)$ are necessary.

The traditional method most often used in the literature [3], in which linear or volume deformation at high temperatures is approximated by linear dependences leads to the overestimation of the values of anomalous contribution to deformation, and the mean square polarization. In this paper, we used another method taking into account the relationship between thermal expansion and heat capacity and its temperature dependence in the framework of the Debye model. The data was processed by a dependency $\beta(T) = aT + bC_D(_T,\Theta_D)$, where a, b and the Debye temperature Θ_D are fitting parameters. The results of processing the experimental data for the composition
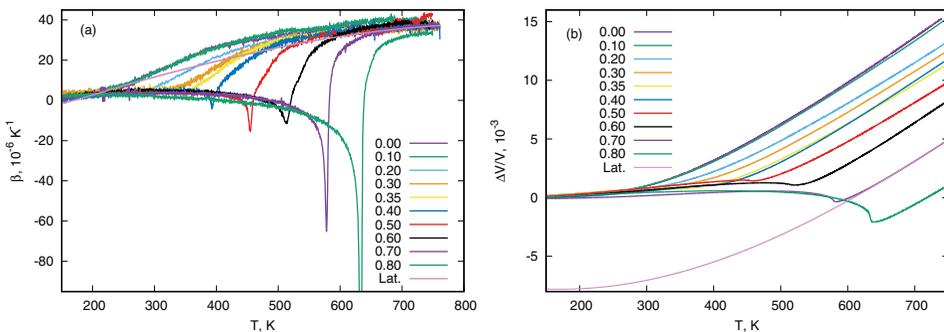

Figure 1. Temperature dependences of the volume thermal expansion coefficient (a) and bulk deformation (b) on solid solutions (1−x)PNN–xPT. Lat. — lattice (non-anomalous) component of deformation for the composition with $x = 0.70$.
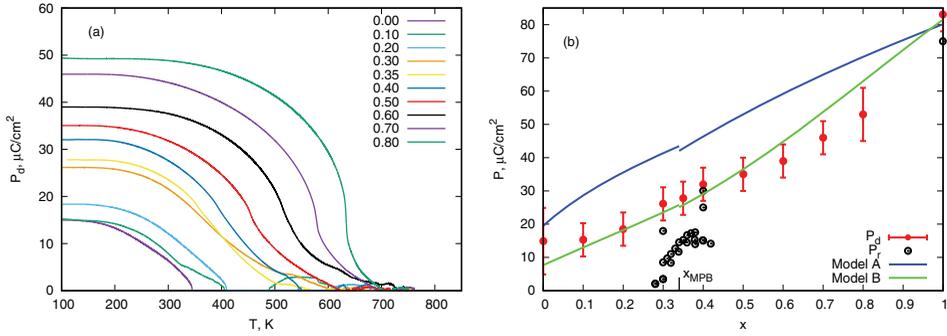
Figure 2. Temperature dependences of mean square polarization, determined from the thermal expansion on $(1-x)$PNN–xPT solid solutions (a). Concentration dependences of the spontaneous polarization (P_r) [2, 4] and mean square polarization P_d, as well as the polarization calculated at $T = 100$ K from two sets of thermodynamic potential PbTiO$_3$ (Model A [5], Model B [6]), for solid solutions $(1-x)$PNN–xPT (b).

with $x = 0.70$ are shown in Figure 1b. The temperature dependences of the mean-square polarization P_d for all the compositions studied are shown in Figure 2a. For solid solutions, we used the same values of electrostriction coefficients as for pure PbTiO$_3$: $Q_{11} = 0.089$ m^4/C^2, $Q_{12} = -0.026$ m^4/C^2 [6].

In mixed perovskites, the paraelectric cubic phase (point symmetry $m3m$) exists at high temperatures. In the traditional phase diagrams $T - x$ of these systems, the cubic phase transforms at low temperatures into ferroelectric rhombohedral (point symmetry $3m$) and ferroelectric tetragonal (point symmetry $4mm$) phases that have an almost vertical boundary (MPB).

A number of authors undertook a thermodynamic analysis of the morphotropic phase diagram using the traditional Ginzburg-Landau-Devonshire theory of phase transitions. Naturally, phenomenological theory requires experimental data, and therefore its predicative power is limited. Nevertheless, the qualitative features of the phase diagrams obtained with such an analysis, and the properties associated with them, may be of interest to researchers. It was shown that, in the first approximation, the appearance of an MPB corresponds to the condition that the symmetry of the free energy density varies from cubic to spherical [5].

Authors [5] considered the expansion of the thermodynamic potential to the sixth degree of polarization and split it into two parts – isotropic, not depending on the polarization direction, and anisotropic, depending on the direction of polarization $F = F_{iso} + F_{aniso}$:

$$F_{iso} = 1/2A_1\left(P_1^2 + P_2^2 + P_3^2\right) + 1/4B_1\left(P_1^2 + P_2^2 + P_3^2\right)^2 + 1/6C_1\left(P_1^2 + P_2^2 + P_3^2\right)^3,$$

$$F_{aniso} = 1/4B_2\left(P_1^4 + P_2^4 + P_3^4\right) + 1/6C_2\left(P_1^6 + P_2^6 + P_3^6\right) + 1/6C_3\left(P_1^2P_2^2P_3^2\right).$$

According to [5], the coefficients for PbTiO$_3$, the parameters of the triple point C-T-R (x'_0, T'_0) and the tricritical point of phase transitions C-T (x^T_{cr}, T^T_{cr}), as well as the temperature T_m in relaxor are needed to determine the coefficients of the thermodynamic potential and to calculate the polarization of solid solutions. We used the approach developed by the authors [5] for a system $(1-x)$PNN–xPT. The values of parameters determined from the two sets of coefficients of the thermodynamic potential

Table 1. Parameters of the thermodynamic potential for PT and $(1-x)$PNN–xPT solid solutions. $B_2(x,T) = b_0(x'_0-x)+b'_2(T-T_C(x))$.

Parameter	PT [5]	PNN-PT (Model A)	PT [6]	PNN-PT (Model B)
$T_C(x)$, K	748	$748x + 153(1-x)$	752	$752x + 153(1-x)$
$A_0(x)$, 10^5 Vm/CK	7.95	$7.95x + 1.85(1-x)$	7.6	$7.60x + 1.99(1-x)$
$B_1(x)$, 10^8 Vm^5/C^3	6.78	$6.78x + 0.37(1-x)$	-2.92	$15x + 14.89(1-x)$
b_0, 10^8 Vm^5/C^3	-9.66	14.63	-17.92	27.15
b'_2, 10^8 Vm^5/C^3	-1.51	-1.51	–	–
C_1, 10^9 Vm^9/C^5	1.39	1.39	1.22	1.22
C_2, 10^9 Vm^9/C^5	1.54	1.54	3.4	3.4
C_3, 10^9 Vm^9/C^5	-4.63	-4.63	-295.2	-295.2
(x'_0, T'_0)	–	(0.34,355)	–	(0.34,355)
(x^T_{cr}, T^T_{cr})	–	(0.65,539.7)	–	(0.65,539.7)

for $PbTiO_3$, and the dependence of polarization on x are presented in Table 1 and Figure 2b, respectively. It can be seen that the model B more adequately describes the experimental data. Therefore, we can assume that in the case of solid solutions $(1-x)$PNN–xPT, the coefficient at the second degree of polarization in comparison with other coefficients is characterized by the strongest temperature dependence.

4. Conclusion

Thus, as a result of the studies, anomalous behavior of the deformation and coefficient of thermal expansion of solid solutions $(1-x)$PNN–xPT was found, and $T-x$ phase diagram was constructed. The results are analyzed in the framework of the thermodynamic theory of phase transitions, and the coefficients of the expansion of the 2-4-6 thermodynamic Landau potential for a system of solid solutions $(1-x)$PNN–xPT are determined. The thermodynamic potential, taking into account the elastic and electrostriction components, makes it possible to calculate other thermodynamic properties, such as deformation, dielectric susceptibility, piezoelectric properties.

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