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Anomalous thermal expansion in PMN−PSN solid solutions

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The temperature evolution of the volumetric coefficient of thermal expansion (CTE) in single crystals $(1-x)\mathrm{PbMg}_{1/3}\mathrm{Nb}_{2/3}\mathrm{O}_3 + (x)\mathrm{PbSc}_{1/2}\mathrm{Nb}_{1/2}\mathrm{O}_3$ (PMN−PSN) at $x = 0.35$ (PMN−PSN35), $x = 0.8$ (PMN−PSN80) and pure PSN has been studied. In PSN and PMNPSN80, an abrupt transition from a smooth decrease in CTE with reaching zero in the cubic phase typical for relaxors to a negative CTE in the rhombohedral phase was observed. Negative CTE exists in the temperature range of about 40 K. In the PMN−PSN35 crystal CTE smoothly passes from positive to negative values. At $T \approx 250$ K a phase transition (PT) to a low-symmetry (presumably monoclinic) phase was found. Below this temperature the CTE smoothly returns to positive values.

Keywords: relaxors, antiferroelectrics, phase transitions, negative thermal expansion, solid solutions.

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Material having zero or low coefficient of thermal expansion (CTE) are interesting in terms of application in some areas of instrument engineering, in particular as basis for micropositioners, high-temperature piezoelectric sensors, to ensure alignment of temperature expansion coefficients in multilayer ceramic capacitors, as well as to monitor biaxial elastic stresses in thin films [1].

In ferroelectrics the negative CTE is below Curie temperature T_c was identified in many compounds, in particular in PbTiO_3 and compounds based on it [2] and other ferroelectrics [3], as well as in relaxors $\mathrm{PbMg}_{1/3}\mathrm{Nb}_{2/3}\mathrm{O}_3$ (PMN) [4].

In high temperature paraelectric phase the thermal expansion was determined by anharmonicity of phonon vibrations. But below T_c a ferroelectric order is set, which gives negative contribution to the thermal expansion. Sign of thermal expansion in ferroelectric phase is the result of balance between two competing factors: anharmonicity of lattice vibrations and ferroelectric order.

In lead-containing relaxors with perovskite structure of $\mathrm{Pb}B'_{1-x}B''_x\mathrm{O}_3$ type the effect of zero thermal expansion (ZTE) is frequently observed. Above Burns temperature T_d the relaxor ferroelectrics demonstrate normal positive CTE (positive thermal expansion, PTE) similar to major of perovskites. ZTE is generally observed below temperature T_m, at which the dielectric permittivity reaches maximum [5,6]. At that crossover from PTE to ZTE is observed upon cooling at temperatures close to temperature of diffusion scattering occurrence, associated with the formation of correlated polar shifts (polar nanoregions).

Note that CTE features in the relaxors and normal ferroelectrics (FEs) have principle differences. In FEs and antiferroelectrics (AFEs) [7] the negative CTE occurs in low-symmetry phase. In paraelectric phase PTE is observed. In relaxors the entire temperature region below T_d is anomalous. The analysis of the thermal expansion behaviour in compounds, which combine properties of relaxors and normal ferroelectrics (antiferroelectrics) is very interesting. Such compounds may include $(1-x)\mathrm{PbMg}_{1/3}\mathrm{Nb}_{2/3}\mathrm{O}_3+(x)\mathrm{PbSc}_{1/2}\mathrm{Nb}_{1/2}\mathrm{O}_3$ (PMN−PSN) solid solutions. In region of low values of $x \leq 0.5$ these compounds demonstrate purely relaxor behaviour, but at higher concentrations of PSN the transition to ferroelectric or antiferroelectric phase is observed. Till present time the thermal expansion in these systems was not studied.

Present paper studied the temperature behaviour of the thermal expansion in single-crystals of solid solutions PMN−PSN at concentrations of PSN $x = 0.35$ (PMN−PSN35), $x = 0.8$ (PMN−PSN80) and $x = 1$ (PSN). The crystals were grown in Institute of Physics of SFU [8]. Studies of dielectric response in case of PMN−PSN80 and PSN crystals showed a typical relaxor behaviour at high temperatures and abrupt decreases in curves $\varepsilon(T)$ at ~ 355 K in PSN and 335 K in PMN−PSN80. These decreases were related to expected phase transitions (PTs) from relaxor phase to ferroelectric phase. In PMN−PSN35 crystal in temperature range of 240 to 360 K any features were not observed.

The experiments were carried out using the universal diffractometer PILATUS@SNBL of Swiss-Norwegian beamline of synchrotron source ESRF [9] and the diffuse scattering diffractometer in beamline ID28 ESRF [10]. The single-crystal was secured to a quartz tube secured on goniometer. The scattered radiation was registered using a position sensitive detector PILATUS 2M [9]. The wavelength of the incident radi-

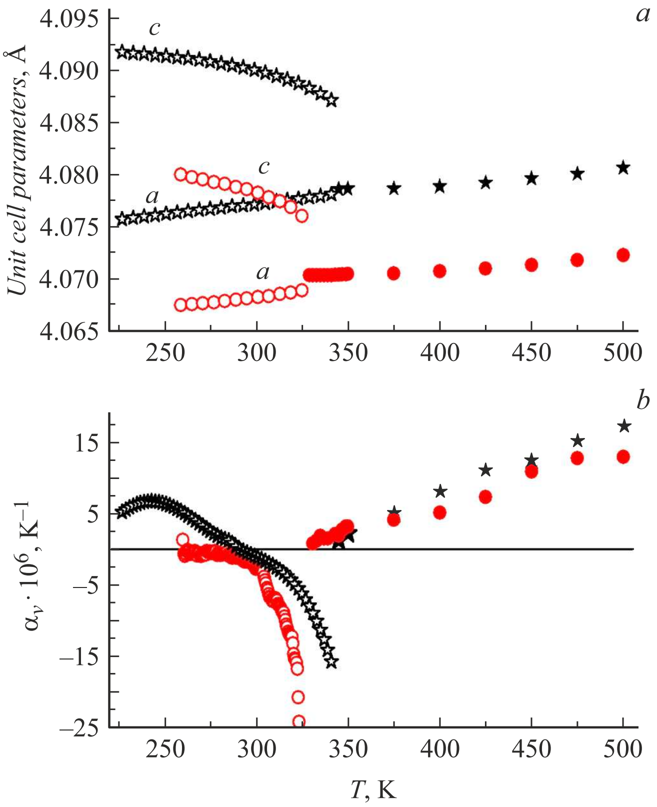

Figure 1. Temperature dependences of cell parameters (*a*) and bulk CTE (*b*) of PSN single-crystals (asterisks) and PMN–PSN80 (circles) above (filled symbols) and below (clear symbols) of transition temperature.

ation was 0.69 Å. The sample temperature was controlled by blowing with nitrogen jet at set temperature.

The cell parameters were calculated based on diffraction pattern obtained from the initial single-crystal data using package CrysAlisPro software [11], they were processed in program FULLPROF [12] in Profile-matching mode.

The data obtained were indexed in a simple cubic cell with space group $Pm\bar{3}m$. For all three compositions the superstructural reflections were observed ($h{+}1/2\ k{+}1/2\ l{+}1/2$), indicating the existence of chemical ordering of $\mathrm{Pb}B'_{1/2}B''_{1/2}\mathrm{O}_3$ type, where $B' = \mathrm{Nb}$, and B'' contains a mixture of all other cations. Degree of order can be characterized by a parameter $S = 2g_b - 1$, where g_b — „correct" occupancy of appropriate positions. Value S was determined based on the comparison of experimental intensities and intensities calculated for ideal ordering of diffraction reflections, and turned out to be close to 1 for all three crystals, but the superstructure peaks were significantly widened. Form and size of ordered regions were determined based on dimensions of diffraction ellipsoid; as a result it was identified that we can say about ordering in scale of about 30 nm.

The temperature dependences of cell parameters were tracked (Fig. 1, *a*), and based on them the coefficients of thermal expansion of samples were calculated (Fig. 1, *b*). At the temperature $T_{tr} \approx 347$ K for PSN crystal and $T_{tr} \approx 325$ K for PMN–PSN80 crystal the peaks splitting occurs corresponding to PT of first kind into rhombohedral phase. In high temperature phase during cooling the CTE gradually decreases to values close to zero, near the transition temperature. During transition into the low-temperature phase the lattice cell volume decreases jump-like, and below T_{tr} the negative CTE is observed it is kept in range about 40 K wide.

For PMN–PSN35 the dependence $a(T)$ is observed, it fundamentally differs from those described above.

Fig. 2, *a* shows the temperature dependence of the cell parameter obtained based on data measured in the diffractometer PILATUS@SNBL, which did not identify PT resulted in the symmetry decreasing. Upon the temperature decreasing to $T \approx 315$ K the relaxor behaviour of the dependence $a(T)$ is observed with gradual gradient decreasing, but in contrast to clean PMN [5] below 315 K (Fig. 2, *b*) CTE continues decreasing and reaches minimum at $T \approx 245$ K, after which it gradually returns to positive values. The same form of dependence $a(T)$ was described for the case of disordered PSN [6], where a abrupt transition into the low temperature phase was identified. Study of the beamline form of remote reflections made in beamline ID28 ESRF showed that at 225 K there is peaks splitting (see insert in Fig. 2, *a*), which presumably can be related to monoclinic distortions of the cell. The transition turns out to be rather „long" and ends at $T \approx 150$ K.

To understand the possible nature of the observed behaviour one shall review the diffused scattering behaviour. Fig. 3, *a* shows the temperature evolution of the diffused scattering in the beamline $\mathbf{Q} = (1{-}q\ \ 1{+}q\ \ 0)$. At high temperature the scattering in the vicinity of $q = 0$ (center of Brillouin zone) prevails. Such pattern of scattering is typical for the relaxors and can be associated with occurrence of correlated cationic (first of all) shifts [13]. Upon cooling below 325 K the decrease in said correlations is observed, which is indicated by decrease in peak intensity of scattering I_Γ and, may be, is due to occurrence of AFE-correlations resulting in the diffused scattering increasing at $q = \pm 0.5$ (I_M) (Fig. 3, *b*).

Summarizing the above, note the following.

We tracked the temperature evolution of lattice cell parameters of PSN, PMN–PSN80 and PMN–PSN35 single-crystals. In PSN, PMN–PSN80 crystals in area of cubic phase existence the CTE behavior characteristic to relaxors was identified. At PT into rhombohedral phase the jump-like decrease in the lattice cell volume occurs. In temperature range of about 40 K below the transition temperature the negative CTE is observed, which is typical for tetragonal lead-containing ferroelectrics, and was not previously

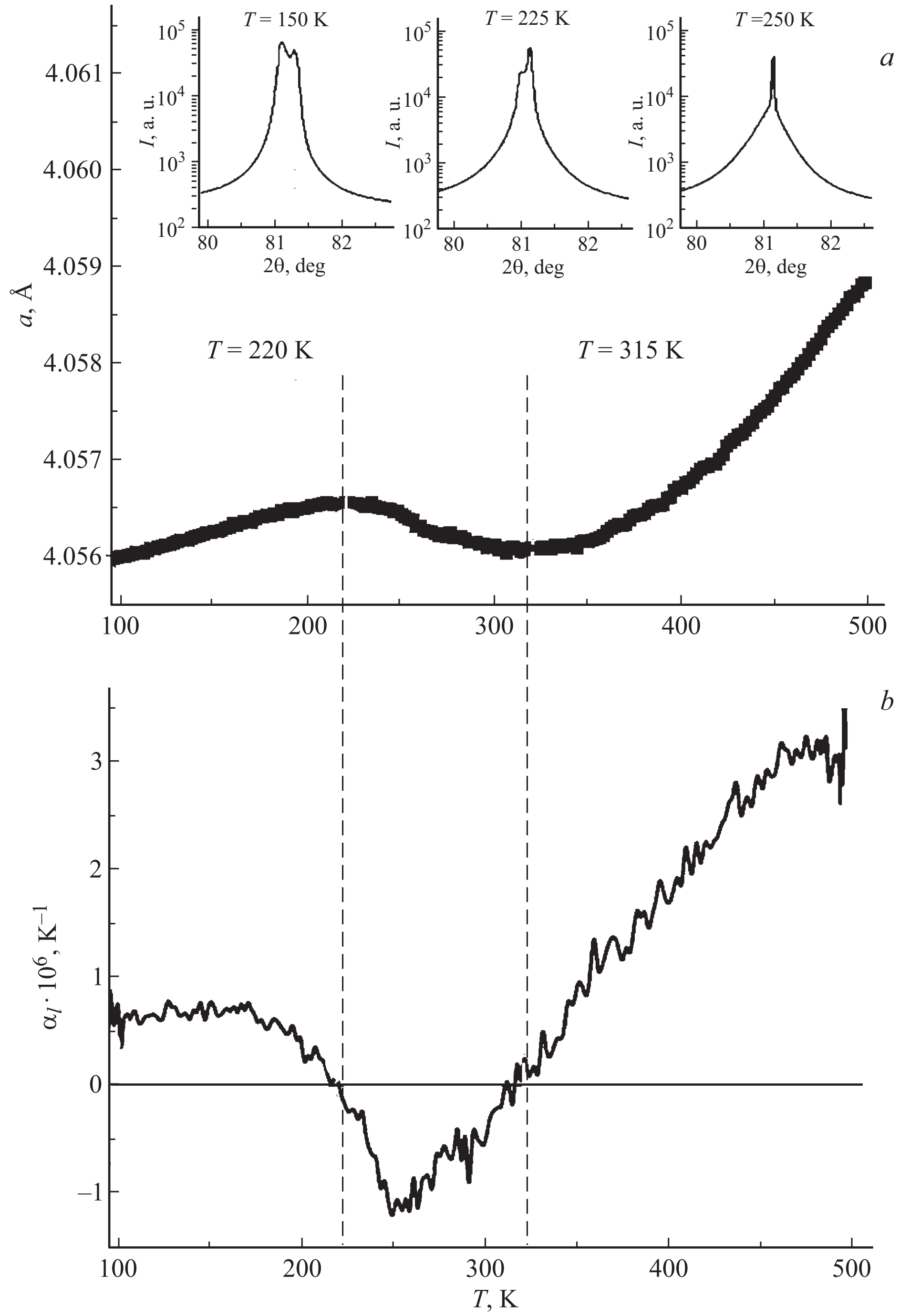

Figure 2. Temperature dependences of cell parameters (*a*) and linear CTE (*b*) for PMN−PSN35 crystal. The inserts show the form of reflection lines (−4 −3 2), measured in high resolution mode (measurements in beamline ID28 ESRF) at different temperatures.

observed in the compounds with rhombohedral structure.

CTE temperature dependence in PMN−PSN35 is similar to the dependence described in [6] for the case of unordered PSN. Comparison of the obtained dependence $a(T)$ with the behaviour of diffused scattering makes an assumption that two contributions occur resulting to the negative CTE occurrence. In area of $T \geq 325\,\mathrm{K}$ we can expect that definite role is played by correlated shifts characterized by wave vector near the center of Brillouin zone, this is indicated by quick rise of I_Γ upon temperature decreasing. At that CTE reaches zero value similar to case of clean PMN. Upon further cooling we observed I_Γ decreasing, but CTE continues decreasing. At the same time in this temperature region the increase in antiferroelectric fluctuations occurs, which is evident in dependence $I_M(T)$, so we can assume that in range $225 < T < 325\,\mathrm{K}$ just the antiferroelectric short-range order plays a definite role.

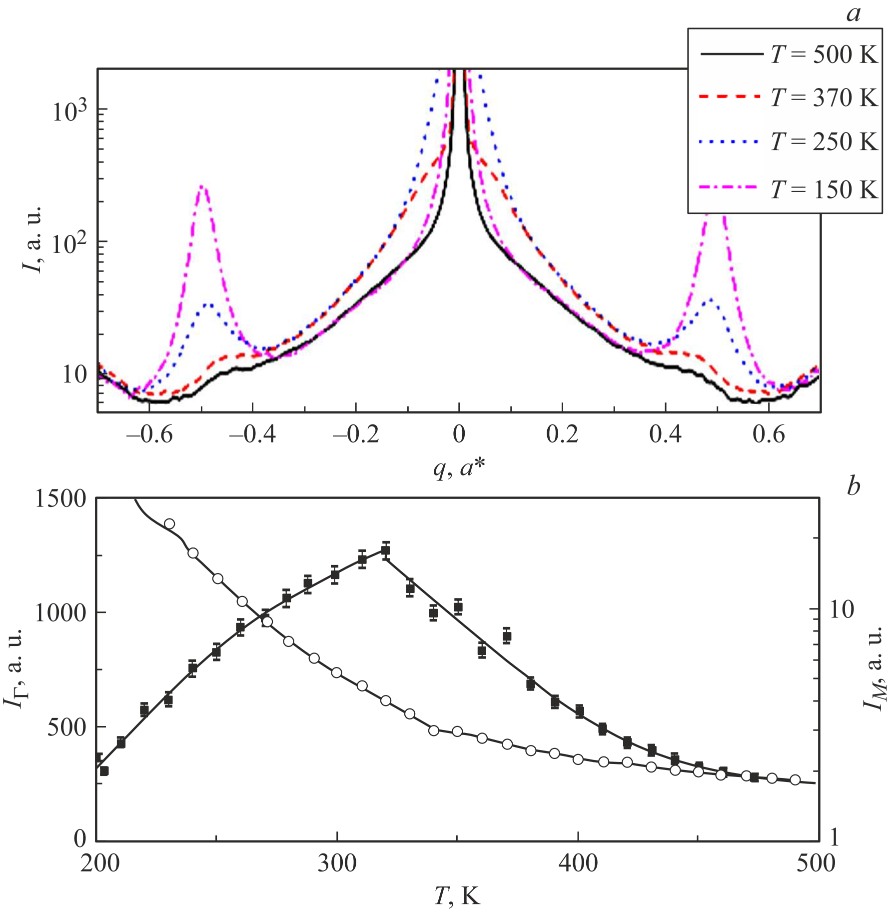

Figure 3. *a* — temperature evolution of diffused scattering in beamline $\mathbf{Q} = (1-q\ \ 1+q\ \ 0)$. *b* — diffused scattering intensity vs. temperature: squares — at $\mathbf{Q} = (1\ \ 1\ \ 0)$ (I_Γ), circles — at $\mathbf{Q} = (1.5\ \ 0.5\ \ 0)$ (I_M).

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Conflict of interest

The authors declare that they have no conflict of interest.

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