



Proceedings of the Estonian Academy of Sciences,  
2017, **66**, 4, 363–371

<https://doi.org/10.3176/proc.2017.4.09>  
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FUNCTIONAL  
MATERIALS

## Behaviour of thermal expansion of $(1-x)\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ solid solutions

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Received 26 April 2017, revised 8 July 2017, accepted 13 July 2017, available online 26 October 2017

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**Abstract.** The features of the dependence of the bulk coefficient of thermal expansion of the  $(1-x)\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  solid solution studied in the series of  $x = 0-0.8$  in the temperature range from 100 to 750 K are reported. The obtained data and observed anomalies of thermal expansion are compared with dielectric properties, heat capacity, and the phase diagram of concentration. The anomalous and lattice constituents of deformation and of the coefficient of thermal expansion are analysed and the data on deformation are used to estimate the Burns temperature and the mean square polarization of the samples found to decrease with the decrease of the  $\text{PbTiO}_3$  concentration.

**Key words:** ferroelectrics, relaxors, ceramics, solid solutions, thermal expansion, phase diagram.

### 1. INTRODUCTION

Recently growing attention has been paid to multi-component mixed oxide perovskites of odd crystalline structures and unique physical properties such as an enormous dielectric permittivity and large piezoelectric and electrostriction coefficients in particular. The  $(1-x)\text{PNN}-x\text{PT}$  solid solutions of the  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PNN) relaxor and ferroelectric  $\text{PbTiO}_3$  (PT) are a noteworthy example [1–4].

The multiferroic PNN has its place in the family of oxide relaxors such as the simultaneously synthesized well-known  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) [5]. A broad frequency-dependent maximum of the dielectric permittivity  $\varepsilon$  in PNN is observed at the temperature of extremum

$T_m \approx 153$  K, which is much lower than in PMN and is most likely the reason why PNN is less studied. The antiferromagnetic transition in PNN proceeds at the Neel temperature  $T_N \approx 5$  K [6].

Ferroelectric lead titanate known since long ago is still actively studied [7,8]. Transition between the para-electric and ferroelectric phases proceeding in  $\text{PbTiO}_3$  at the Curie temperature  $T_C = 763$  K is characterized as a first-order structural transformation with the symmetry change  $Pm3m \rightarrow P4mm$  occurring close to the tri-critical point.

Structural and electrical studies of the  $(1-x)\text{PNN}-x\text{PT}$  system [1,9–12] have shown the phase transition temperature characteristic to PT to decrease with the decrease of  $x$ . A morphotropic region exists on the  $T-x$  phase diagram around  $x \approx 0.35$  wherein several phases can come about: the cubic, pseudo-cubic, tetragonal, and rhombohedral [9].

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More recent studies of heat capacity [13–15] have revealed additional anomaly of uncertain nature at  $\sim 520$  K apart from the anomalies characteristic of phase transitions (at  $x > 0.35$ ) and relaxor behaviour at  $T_m$  ( $x < 0.35$ ). Presently the crystal structure and its change with the temperature is a subject of discussion. All that stimulates further detailed studies of mixed ferroelectric relaxors.

This paper presents results of a study of thermal expansion of the  $(1-x)\text{PNN}-x\text{PT}$  ( $x = 0-0.8$ ) ceramics in the temperature range from 100 to 750 K. Thermal expansion, which is related to properties such as ferroelectricity, piezoelectricity, and pyro-electricity, is one of the basic characteristics of the material important for design of technological devices, revealing the physical nature of phenomena observed in solid solutions, and the crossover from the usual ferroelectric to relaxor behaviour. Polarization and its transformation with the change of composition have also been determined from the data of thermal expansion since often the use of traditional techniques in the case of ceramic materials is complicated. Deformation, mainly determined by polarization square, can be used for the assessment of the macroscopic spontaneous polarization of ferroelectrics and the mean square of polarization in relaxor ferroelectrics.

## 2. SAMPLES AND METHODS

### 2.1. Samples

The samples were prepared of oxides: 99.5% purity grade PbO, 99.0% purity grade NiO, 99.9% purity grade  $\text{Nb}_2\text{O}_5$ , and 99.9% purity grade  $\text{TiO}_2$  at the Institute of Solid State Physics of the University of Latvia by conventional ceramics technology [13,14].

The primary mixture was processed in accordance with the composition and mass of the matching oxides in jasper mills for 12 hours with alcohol, then dried for 6 hours before being pressed into ingot tablets subject to solid phase calcination at 1170 K for 1–3 hours with the technological parameters depending on the batch of the initial ingredients optimized separately for each of the compounds. After subsequent crushing of the tablets and homogenizing the calcinated mass by milling the mass was pressed again into tablets to fire ceramics at 1400–1550 K for one to three hours. After a slow cooling of the synthesized tablets and removal of the surface layer the samples were cut and polished for measurements.

The conditions of the thermal treatment were optimized to improve the structure and to surge the perovskite phase in the material. The quality and the phase composition were studied by X-ray analysis of the synthesized material. The fired ceramics revealed

stoichiometric perfectness of the obtained compounds as well as presence of the undesired pyrochlore phase and other admixtures. The technological parameters used in the study are presented in Table 1.

### 2.2. Thermal expansion

Thermal expansion of the 5–10 mm long samples was studied by a NETZSCH DIL-402C induction dilatometer in a dynamic process within the 100–750 K range at the rate of heating and cooling of 2–3 K/min. The measurements were made in the flow ( $\sim 50$  mL/min) of dry helium (concentration of  $\text{O}_2$  not exceeding 0.05% in bulk) at a load of 30 cN applied to the sample. The calibration of the measuring system was made to comply with the melted quartz standards.

Several series of measurements were conducted with different samples of the same composition. Since, as a rule, the data agreed between the series within the accuracy of the measurements, the series were processed together.

## 3. RESULTS AND DISCUSSION

### 3.1. The data of measured thermal expansion

Dependences of the coefficient of the bulk thermal expansion  $\beta = 3\alpha$  and the bulk deformation  $\Delta V/V$  of the  $(1-x)\text{PNN}-x\text{PT}$  ceramics are presented in Fig. 1 and Fig. 2, respectively, together with the results of thermal expansion of PT from earlier studies [16].

The anomaly of the bulk coefficient of thermal expansion  $\beta(T)$  at the cubic-to-tetragonal phase transition (at the Curie temperature  $T_C$ ) characteristic of pure PT remains distinct enough but it notably decreases in the  $(1-x)\text{PNN}-x\text{PT}$  solid solutions with the decrease of  $x$  down to 0.5. At concentrations of PT below the morphotropic phase boundary at  $x_{\text{MPB}} \approx 0.35-0.38$  the anomaly  $\beta(T)$  broadens becoming characteristic of ferroelectric relaxors (Fig. 1).

#### 3.1.1. Additional anomalies of thermal expansion

In earlier studies [13–15] of heat capacity of the  $(1-x)\text{PNN}-x\text{PT}$  ceramics of  $x = 0.5, 0.4, 0.3$ , the anomalies characteristic of phase transitions of undefined nature were observed at  $\sim 520$  K. We also detected small additional anomalies of thermal expansion in some samples of  $x = 0.2, 0.3, 0.6$ , and 0.8.

Anomalous behaviour of  $\beta(T)$  was observed in some samples of  $x = 0.8$  (0.8B) at  $T \approx 645$  K above  $T_C$  (Fig. 3). The basic anomaly was smaller and shifted to a lower temperature as compared with the sample of the same composition (0.8A) without additional anomalies.

**Table 1.** Technological parameters of the studied (1-*x*)PNN–*x*PT ceramic samples

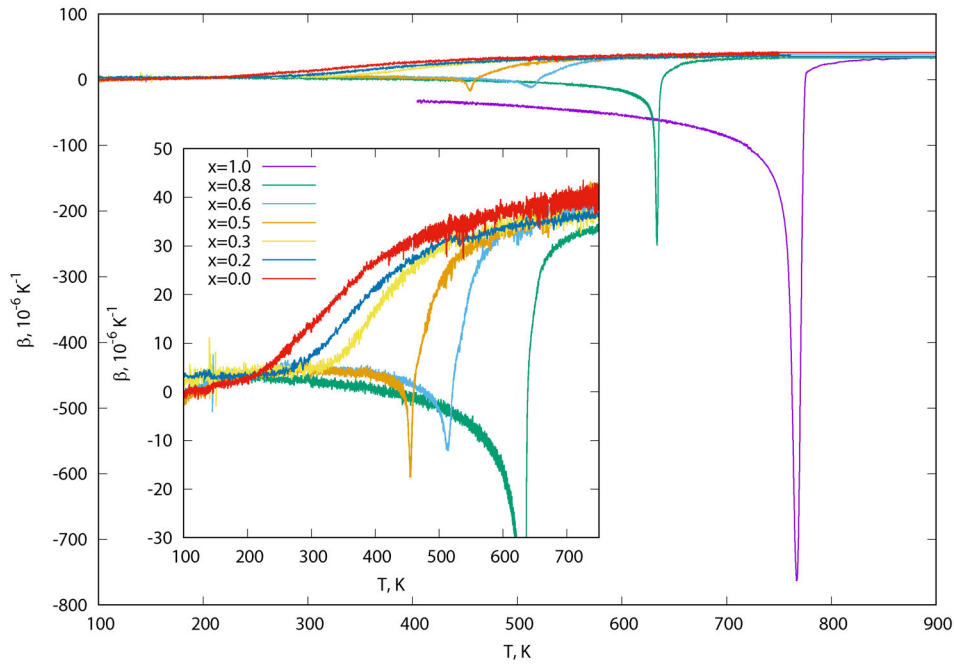
Sample	Composition	Calcination, K/h	Synthesis, K/h	Density, g/cm <sup>3</sup>	Cell Å	Addition
0.0A	PNN		1420/2	7.6176	Cubic, a = 4.03009(7)	
0.1A	0.9PNN–0.1PT	1170/3	1440/3	7.9422		9% pyrochlore
0.1B	0.9PNN–0.1PT	1170/3	1480/1	7.3286	Cubic, a = 4.02434(24)	7% pyrochlore 10% NiO
0.2A	0.8PNN–0.2PT	1170/3	1500/1	–	–	
0.2B	0.8PNN–0.2PT	1170/3	1470/4	–	Tetragonal, close to cubic, a = 4.01430(28) c = 4.02664(46)	5% NiO
0.3A	0.7PNN–0.3PT	1170/3	1470/1	–	–	–
0.3B	0.7PNN–0.3PT	1170/3	1470/1	–	–	–
0.35A	0.65PNN–0.35PT	1170/3	1500/1	8.1153	Tetragonal, a = 3.99796(10) c = 4.01755(13)	3.6% NiO 1% other addition
0.35B	0.65PNN–0.35PT	1170/3	1530/1	–	Tetragonal	–
0.4A	0.6PNN–0.4PT	1170/3	1500/1	8.0734	Tetragonal, a = 3.950202(98) c = 4.05699(15)	1% pyrochlore 1.3% NiO
0.4B	0.6PNN–0.4PT	1170/3	1530/1	–	Tetragonal	
0.5A	0.5PNN–0.5PT	1170/3	1540/1	–	Tetragonal, a = 3.97674(78) c = 4.03261(91)	2% pyrochlore
0.5B	0.5PNN–0.5PT	1170/3	1540/1	7.6021	Tetragonal, a = 3.97674(78) c = 4.03261(91)	2% pyrochlore
0.6A	0.4PNN–0.6PT	1170/3	1520/1	7.8739	Tetragonal, a = 3.96280(49) c = 4.04513(50)	1–2% addition
0.7A	0.3PNN–0.7PT	1170/3	1500/1	7.6739	Tetragonal, a = 3.949457(77) c = 4.05875(12)	1% pyrochlore
0.7B	0.3PNN–0.7PT	1170/3	1530/1	–	–	–
0.8A	0.2PNN–0.8PT	1170/3	1500/1	7.6580	Tetragonal, a = 3.93218(40) c = 4.07805(46)	–
0.8B	0.2PNN–0.8PT	1170/3	1520/1	7.4555	Tetragonal, a = 3.93336(29) c = 4.07845(37)	–

– No data.

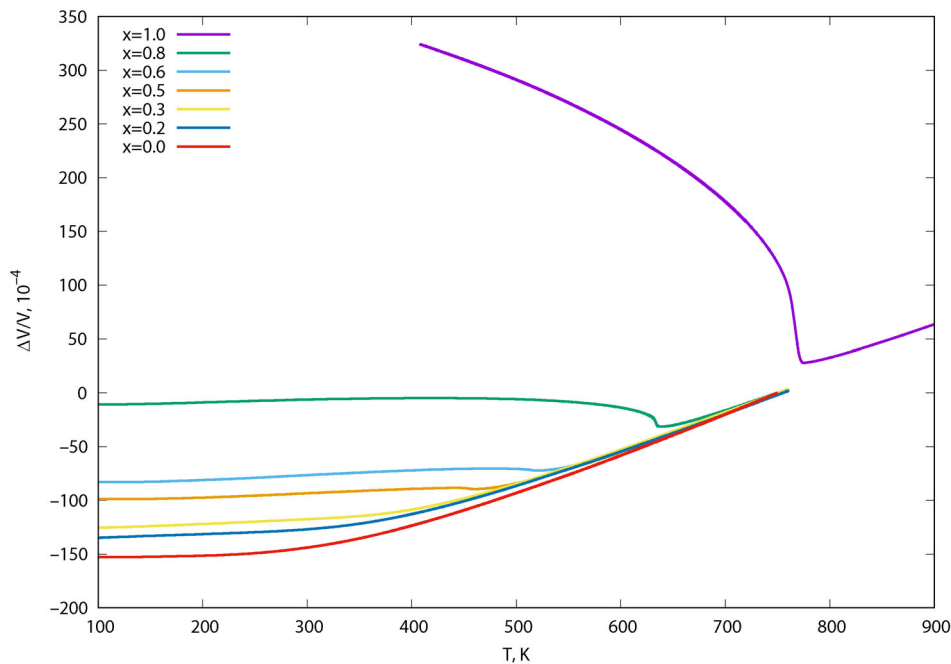
The same is most likely observed in sample 0.6A of  $x = 0.6$  in which the anomaly is somewhat smaller than what would be expected from the trend of  $\beta$  at decreasing  $x$  (Fig. 1). In compounds of  $x = 0.2$  and  $x = 0.3$  an anomaly observed in heat capacity [13] is seen at  $T \approx 520$  K. A strongly different behaviour of the coefficient of thermal expansion is observed in two samples of  $x = 0.3$  (0.3A and 0.3B). While in sample 0.3B the  $\beta(T)$  is consistent with that of other compositions ( $x = 0$  and  $x = 0.2$ ), the broad minimum of the  $\beta(T)$  characteristic of relaxors is practically not observed in sample 0.3A exhibiting the most pronounced additional anomaly.

The reason of such behaviour is most likely related to conditions under which the samples are prepared, to thermal history, and to possible presence of foreign phases. The main problem with studies and applications of the PNN and PNN–PT ceramics [17], as well as PMN and PMN–PT ceramics [18], is obtaining a single-phase perovskite material. The problem of the synthesis consists in avoiding the formation of the undesired pyrochlore phases –  $\text{Pb}_{1.45}\text{Nb}_2\text{O}_{6.26}$  or  $\text{Ti}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_4$  [19].

Results obtained on samples without or with the smallest additional anomalies (Figs 1 and 2) are used for further analysis.



**Fig. 1.** Bulk coefficient of thermal expansion of  $(1-x)\text{PNN}-x\text{PT}$  ceramics as a function of temperature. The data on pure PT from [16].



**Fig. 2.** Bulk deformation  $\Delta V/V$  of  $(1-x)\text{PNN}-x\text{PT}$  ceramics as a function of temperature. The data on pure PT from [16].

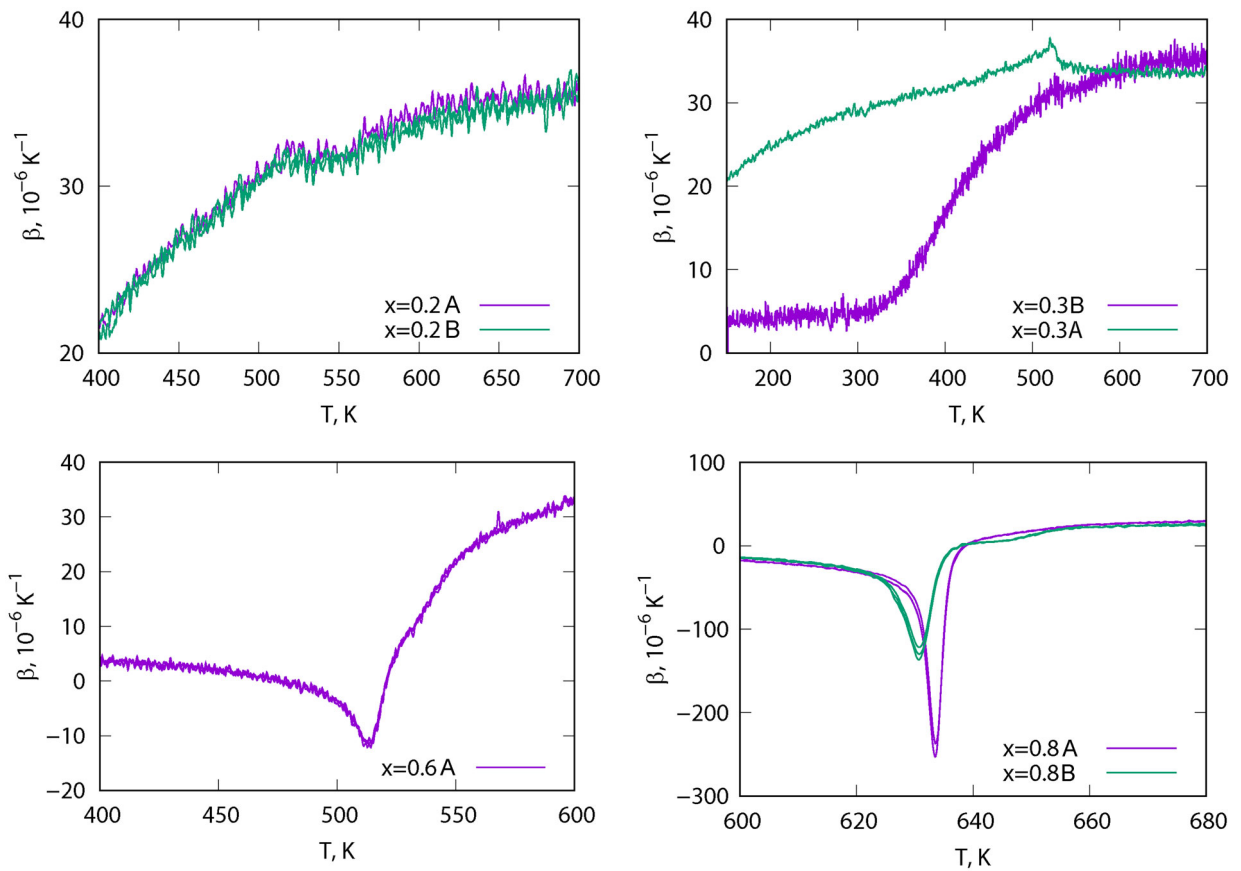
### 3.2. The phase diagram of concentration

A  $T-x$  phase diagram of the  $(1-x)\text{PNN}-x\text{PT}$  system is presented in Fig. 4 together with data from dielectric [9] and thermal capacity [13–15] studies. Within the studied range of concentration and the measurement accuracy, the values of  $T_C$  and  $T_m$  are in good agreement with data published by other authors.

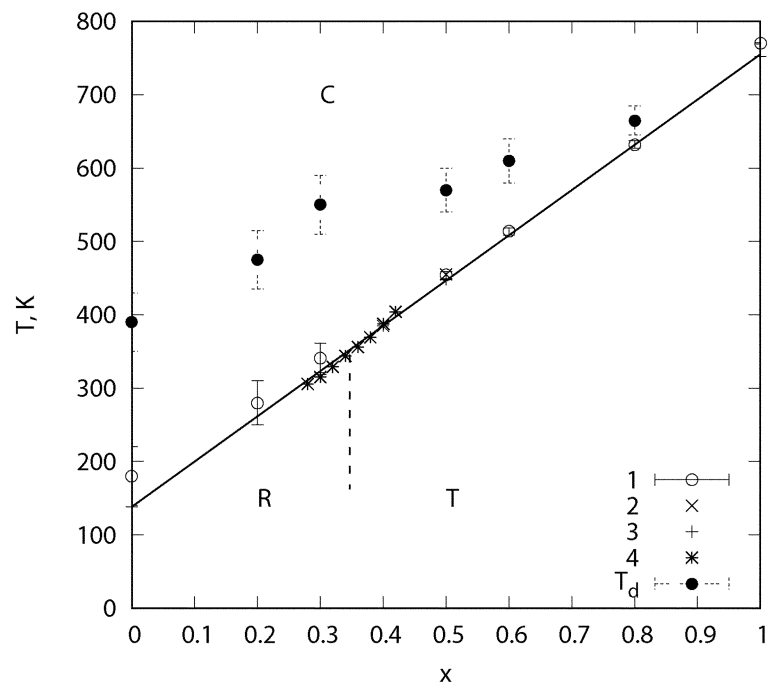
### 3.3. Anomalous contributions to thermal expansion

#### 3.3.1. Thermodynamics

In  $\text{PbTiO}_3$  and its solid solutions, as in other perovskites, the ordering parameter is presented by spontaneous polarization  $\mathbf{P} = (P_1, P_2, P_3)$ . Deformation determined by the square of the macroscopic spontaneous polarization (Eqs 1 and 2) can be used to estimate the latter.



**Fig. 3.** Bulk coefficient of thermal expansion of  $(1-x)\text{PNN}-x\text{PT}$  ceramics of  $x = 0.2$ ;  $x = 0.3$ ;  $x = 0.6$ , and  $x = 0.8$  versus temperature.



**Fig. 4.** Phase diagram of the concentration of the  $(1-x)\text{PNN}-x\text{PT}$  system.

$$\begin{aligned} e_{11} &= Q_{11}P_1^2 + Q_{12}P_2^2 + Q_{12}P_3^2, \\ e_{22} &= Q_{12}P_1^2 + Q_{11}P_2^2 + Q_{12}P_3^2, \\ e_{33} &= Q_{12}P_1^2 + Q_{12}P_2^2 + Q_{11}P_3^2, \end{aligned} \quad (1)$$

$$\begin{aligned} \Delta V/V &= e_{11} + e_{22} + e_{33} = (P_1^2 + P_2^2 + P_3^2)(Q_{11} + 2Q_{12}) \\ &= P^2(Q_{11} + 2Q_{12}), \end{aligned} \quad (2)$$

where  $Q_{11}$  and  $Q_{12}$  are coefficients of electrostriction.

It is necessary to have a correct description of the non-anomalous contributions to deformation and the coefficient of thermal expansion  $\beta_L(T)$  to separate the anomalous contribution of deformation and to determine polarization  $\mathbf{P}$ .

### 3.3.2. Separation of the anomalous contributions

To separate the anomalous contribution to deformation and to assess the mean square of polarization in relaxors, as a rule, deformation linear at high temperatures ( $T > T_C$ ,  $T \gg T_m$ ) is assumed [20–23]. Since  $\Delta V/V(T)$  is obviously nonlinear and the coefficient of thermal expansion  $\beta(T)$  is not constant, such approach does not provide an adequate description of experimental data away from the phase transition to low temperatures. Amounts of the anomalous contributions to deformation and mean square polarization determined this way are, as a rule, overestimated and depend on the range of temperature where the approximation is made.

However, the coefficient of thermal expansion  $\beta(T)$  slightly depends on the temperature above the Debye temperature, and this is the reason of nonlinearity of the deformation. Besides, due to thermo-stimulated defects, there are additional contributions to the deformation

at high temperatures as evidenced by the behaviour of the coefficient of thermal expansion reaching zero with decreasing temperature. At low temperatures, it is necessary to account for the interconnection between temperature dependence of heat capacity and thermal expansion at least within the Debye (or the combined Debye–Einstein) model.

The data on the dependence of the regular (lattice) component of the coefficient of the bulk thermal expansion  $\beta(T)$  were processed by using

$$\beta_L(T) = aT + bC_D(\Theta_D, T) + cC_E(\Theta_E, T), \quad (3)$$

where

$$C_D(\Theta_D, T) = 9R \left( \frac{\Theta_D}{T} \right)^3 \int_0^{\Theta_D/T} t^4 \frac{\exp(t)}{(\exp(t)-1)^2} dt, \quad (4)$$

$$C_E(\Theta_E, T) = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{(\exp(\Theta_E/T)-1)^2}, \quad (5)$$

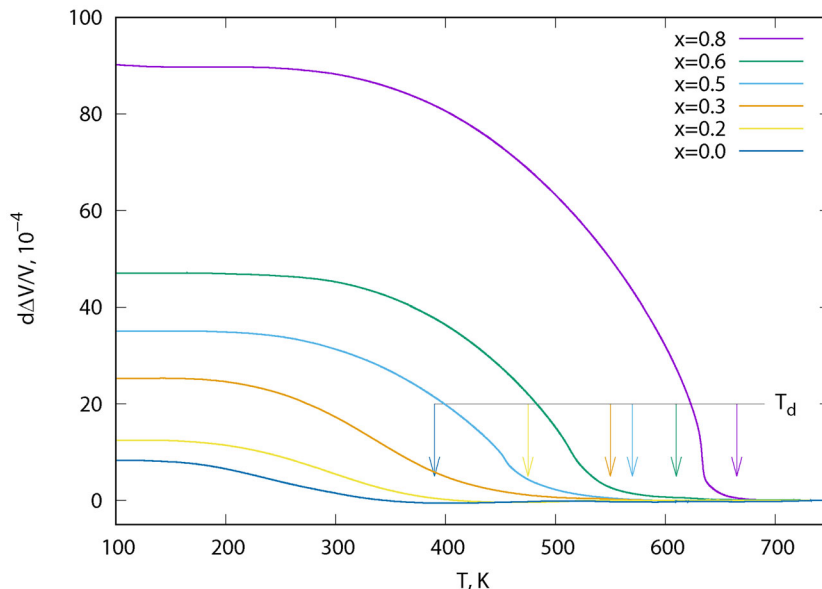
where  $a$ ,  $b$ ,  $c$ ,  $\Theta_D$ ,  $\Theta_E$  denote fitting parameters.

### 3.3.3. Anomalous contribution to deformation and estimation of the Burns temperature

Dependencies of the anomalous contribution to the bulk deformation on the temperature calculated from

$$\Delta V/V - \int \beta_L(T) dT = (Q_{11} + 2Q_{12})P^2 \quad (6)$$

are presented in Fig. 5. A nonzero contribution is observed in all samples above the phase transition temperature  $T_C$

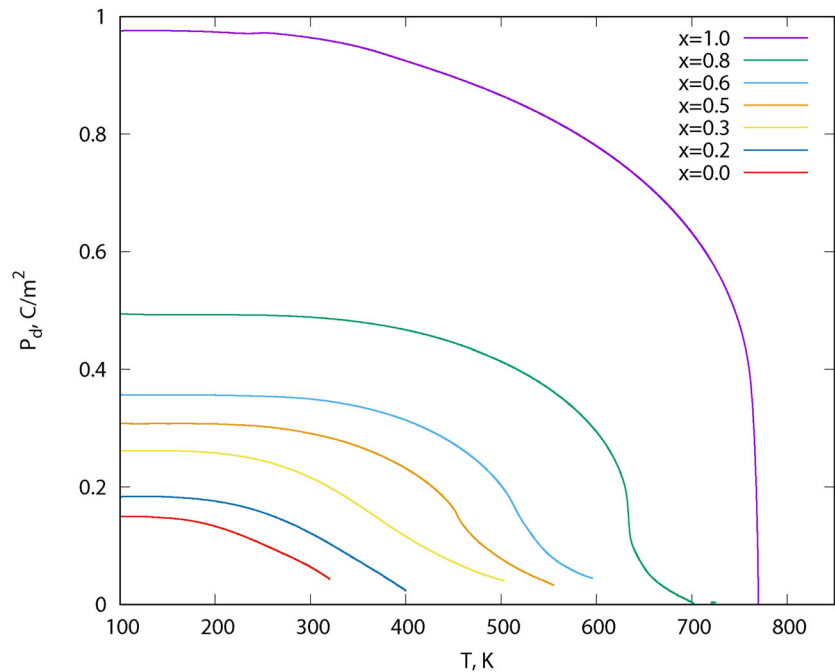


**Fig. 5.** Anomalous contribution to bulk deformation as a function of temperature.

or  $T_m$ , which is related to emerging polar nano-regions of random orientation below the Burns temperature  $T_d$ .

The macroscopic spontaneous polarization  $P_r$  above the temperature of transition to the ferroelectric state is equal to zero while the mean square polarization in the polar nano-regions system is not zero ( $P_d = \langle P^2 \rangle^{1/2} \neq 0$ ). The latter dynamic polarization responsible for a contribution into the anomalous thermal expansion can be found from dilatometric measurements. The calculations of  $P_d$  were made employing the electrostriction coefficients of pure PT ( $Q_{11} = 8.9 \times 10^{-2} \text{ m}^4/\text{C}^2$ ,  $Q_{12} = -2.6 \times 10^{-2} \text{ m}^4/\text{C}^2$ ) assuming they do not change much when PNN is added. Dependence of  $P_d$  on temperature in the studied samples is shown in Fig. 6. The values of saturated  $P_d$  (at 100 K) and other characteristics obtained from thermal expansion data along with the spontaneous macroscopic polarization  $P_r$  from P–E loops of the compounds of  $x = 0.4$  [3,4] are presented in Table 2.

Pure lead titanate has been studied for a long time and scrupulously. Abundance of diverse information on physical and structural properties allegedly allows regarding it as a model ferroelectric material. However, for a number of reasons it is problematic to agree on the details of the phase transition mechanism. For instance, obtaining well-sintered polycrystalline samples presents a severe problem because of stoichiometry being defied by volatility of lead oxide at high temperatures [7]. Crystals grown by various techniques have considerable conductivity even at room temperature intervening with studies of dielectric properties [24,25] and evidently cause substantial ambiguity in the values of saturated polarization over the range of  $P_r = (40\text{--}90) \mu\text{C}/\text{cm}^2$  measured by different authors [24,25]. The value of polarization of PT estimated from the data on thermal expansion in the present study is in good agreement with the data published by other authors [22,24,25].



**Fig. 6.** Mean square polarization  $P_d$  of the studied  $(1-x)\text{PNN}-x\text{PT}$  compounds.

**Table 2.** Characteristics of the  $(1-x)\text{PNN}-x\text{PT}$  ceramics system obtained from the data of thermal expansion

Compound	$T_C$ , K	$T_m$ , K	$T_d$ , K	$P_d$ , $\mu\text{C}/\text{cm}^2$	$P_r$ , $\mu\text{C}/\text{cm}^2$
PNN		$180 \pm 30$	$390 \pm 40$	15	
0.8PNN–0.2PT		$280 \pm 30$	$475 \pm 40$	18	
0.7PNN–0.3PT		$340 \pm 20$	$550 \pm 40$	25	
0.6PNN–0.4PT	400				30 [4]; 18 [3]
0.5PNN–0.5PT	$454 \pm 5$		$570 \pm 30$	32	
0.4PNN–0.6PT	$514 \pm 5$		$610 \pm 30$	36	
0.2PNN–0.8PT	$632 \pm 5$		$665 \pm 20$	47	
PT	$770 \pm 1$			96; 86 [19]	40–90 [21,22]

The data available on polarization in the (1-x)PNN-xPT solid solutions [3,4] and in pure PT are of the order of magnitude consistent with the present results. This confirms reliability of the employed method.

#### 4. CONCLUSIONS

The anomaly of the bulk coefficient of thermal expansion at the transition from the cubic to the tetragonal phase was found to remain distinct enough while its intensity is decreasing with the decrease of  $x$ . At PT concentrations below the morphotropic boundary the anomaly broadens acquiring the pattern specific to relaxor ferroelectrics.

The Burns temperature  $T_d$  at which the polar nano-regions emerge was determined along with  $T_C$  and  $T_m$  from the data of thermal expansion of the (1-x)PNN-xPT solid solution series studied in samples of  $x = 0, 0.2, 0.3, 0.5, 0.6, \text{ and } 0.8$ .

The interval between  $T_d$  and  $T_m$  reaching  $\sim 200$  K in compounds of  $x < x_{MPB}$  decreases with the growth of the PT concentration. The possibility of separating the regular and anomalous contributions to deformation and estimating reliably the mean polarization square  $P_d$  was confirmed by the analysis of the obtained results.

The local mean square polarization present in (1-x)PNN-xPT compounds decreases with the decrease of the PT concentration.

#### ACKNOWLEDGEMENTS

The publication costs of this article were covered by the Estonian Academy of Sciences and the University of Tartu.

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### **(1-x)Pb(Ni<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-xPbTiO<sub>3</sub> tahke lahuse soojuspaisumine**

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On esitatud (1-x)Pb(Ni<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-xPbTiO<sub>3</sub> tahke lahuse soojuspaisumise koefitsiendi temperatuurisõltuvus temperatuurivahemikus 100 kuni 750 K ja PbTiO<sub>3</sub> kontsentratsioonide vahemikus  $x = 0-0,8$ . Saadud andmeid ja vaadeldud soojuspaisumise anomaaliaid on võrreldud dielektriliste omaduste, soojusmahtuvuse ning kontsentratsiooni faasidiagrammiga.

On näidatud, et on võimalik eraldada anomaalsest ja regulaarsest soojuspaisumisest tingitud deformatsiooni komponendid. Deformatsiooni andmeid on kasutatud Burnsi temperatuuri hindamiseks ja näidatud, et ruutkeskmine polarisatsioon kahaneb koos PbTiO<sub>3</sub> kontsentratsiooni kahanemisega.