Specific heat of a PIN-PMN-PT single-crystal up to 500 K

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The temperature dependence of the specific heat of the single crystal $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) was obtained at 80–500 K by means of ac-calorimetry, and comparison with the calorimetric data for PMN was made, allowing one to determine absolute values of the specific heat of PIN-PMN-PT. For the high-temperature region ($T > 200$ K), the background heat capacity was calculated, the anomalies of the heat capacity for both compounds were determined, and the hump of the temperature dependence of specific heat PIN-PMN-PT was detected for the first time.

Keywords: Ferroelectricity; perovskites; specific heat; relaxors.

1. Introduction

The thermodynamic properties of relaxors and their solid solutions have attracted significant attention during the last decade. This increasing interest is mainly connected with the unique piezoelectric properties of solid solutions $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT), which find wide practical use.¹ The classical relaxor lead–magnesium niobate (PMN) has a significant dielectric anomaly in the region around 270 K, whose form and peak position depends on the frequency of the measurement field.² While differing from the ferroelectric crystals with perovskite structure, PMN keeps cubic symmetry down to helium temperatures; it was shown that the anomaly of the dielectric permittivity was connected with the evolution of nano-sized polar clusters, which do not form the long-range order.³ By applying the electric field above a certain threshold value, ferroelectric order appears,⁴ verified by calorimetric methods also.^{5,6}

The thermal properties of PMN were investigated in some works beginning in Ref. 7. Here the diffused anomaly of heat capacity was discovered in the region of frequency-dependent peak of the dielectric permittivity (250–280 K) by means of differential scanning calorimetry. However in Ref. 8, these results were not confirmed by adiabatic calorimetry: a monotonic temperature dependence of the specific heat, close

to linear at low temperatures, was observed. The systematic excess of the experimental curve above the background specific heat was observed too. These results were confirmed in Refs. 9 and 10 in which the heat capacity were measured by the methods of adiabatic and relaxation calorimetry.

Ferroelectric order may appear in solid solutions PMN-PT, and at different PT concentrations the phase transition to rhombohedral or tetragonal phase is possible.¹² Compounds with a concentration of PT about 30%, corresponding to morphotropic phase boundary (MPB) separating rhombohedral and tetragonal phases, are of particular interest. At these concentrations, the solid solution has a maximum piezoelectric activity, which is connected with the appearance of an intermediate monoclinic phase and the possible rotation of the polarization vector in the electric field.¹³ Thermal properties (thermal conductivity and heat capacity) of solid solutions with different PT concentrations (in particular near MPB) were investigated in Ref. 14 up to 300 K. The temperature dependence of the heat capacity obtained were described by the combination of a Debye and two Einstein functions with empirically selected characteristic temperatures and oscillators forces. However, the area of the ferroelectric phase transition, which is accurately determined around 400 K from dielectric data in Ref. 14 was not investigated.

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Several researchers have paid attention to the ternary systems $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$, in which the temperatures of phase transitions near MPB are significantly higher (up to $T_c \approx 460$ K and $T_{R-T} \approx 130$ K) and high piezoelectric activity is preserving.^{15,16} These crystals are very promising for practical use but their thermal properties have never been reported. In this work we report the results of the measurements of specific heat of such single crystals at temperatures from 80 to 500 K for the first time.

2. Experiment and Results

The subjects of the study were single crystals of $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) grown by the Bridgman method in Xi'an Jiao tong University. Crystal samples had linear sizes of 4–5 mm and were polished to a thickness of 0.3–0.4 mm. As the single crystals of PIN-PMN-PT are mainly grown by the Bridgman technique, compositional segregation phenomena are inevitable, resulting in inconsistency of electrical properties. PT content increases, PMN content decreases and PIN content is almost stable of the crystal boule along growth direction. In this work, single crystal containing 24 mol% of PIN, 49 mol% of PMN and 27 mol% of PT was chosen.

Specific heat measurements were carried out by the ac-calorimetry technique using a calorimeter Sinku-Riko (ACC-1 M/L). The method is based on the determination of the amplitude of the temperature change of the sample under illumination, for a periodic heat flux. Under certain conditions this change in temperature is inversely proportional to the heat capacity of the sample. The source of thermal radiation in the experimental setup was chopped light from a halogen lamp with a frequency of 3–4 Hz. A basic description of the ac-calorimeter is given in Ref. 17, wherein the scaling procedures are also described. The technique was applied for the determination of critical parameters in hundreds of compounds, as for e.g. ferroic crystals. The resolution of the method is at least two orders of magnitude better than those of conventional calorimeters. This method allows to obtain only relative values of specific heat. The absolute value can be estimated relatively with inaccuracy of 1–2 % but the temperature change of the specific heat (C_p) can be obtained with a precision of about 0.1 %.

The calorimetric experiments were performed by heating of the samples from room temperature to 500 K and cooling back. The rate of temperature change was selected from 20 to 30 K/h. The second set of the measurements was made at low temperatures (from room temperatures down to 80 K and heating back).

The temperature dependence of the specific heat of the PIN-PMN-PT is presented in Fig. 1. The graph also presents the data from Ref. 8, obtained for the high-quality PMN single crystals with perovskite structure (absolute values). We connected our relative values for PIN-PMN-PT to absolute values for PMN. The good agreement allows one to

Fig. 1. The temperature dependence of the specific heat: ● — PIN-PMN-PT; ○ — PMN with perovskite structure after Ref. 8.

obtain a quantitative description of the measured temperature dependence.

It is also necessary to note that in the work in Ref. 8 and certain others, the deviation of the temperature dependence of the specific heat at low temperatures from the Debye law was reported. In particular, in Ref. 11 it was noted that at the temperatures $T < 30$ K in PMN the calculated Debye contribution to the specific heat is negligibly small compared to the experimental values and neither the Debye nor Einstein model can describe the behavior of the specific heat at temperatures $T < 30$ K. The authors concluded that in the temperature range 2–30 K the behavior of the C_p cannot be described by the phonon contribution, and the correct descriptions can be obtained only in the frame of the “fractal” approximation, the reasons for the discrepancy attributed to the additional contribution to the specific heat.

If we consider the regions of the phase transitions, one expects to observe the anomalies of the dielectric permittivity and specific heat. According to the dielectric data, the first peak of the dielectric permittivity appears at the 362–403 K and the second is at 435–473 K (depending on the composition and sample).^{18–20} These temperatures correspond to the tetragonal–rhombohedral and cubic–tetragonal phase transitions. However, we observed no visible anomalies of C_p at these temperatures. It is similar to the case of PMN. The authors of Ref. 8 claimed that the behavior of the specific heat in PMN in that temperature range can be due to the formation of a polar short-range order.

From literature we know that if we try to plot the background specific heat of PMN using the data from helium temperatures it shows non-Debye behavior.^{8–10} However, using data for higher temperatures it is possible to calculate the background as a combination of Einstein and Debye functions. We suppose that one can draw such functions for our interval of temperatures. To do this we use the data on frequencies of lattice vibrations from Ref. 21 which lets one

Table 1. Selected intrinsic frequencies and damping parameters of polar modes of PMN obtained from the fit of the reflectivity spectrum. (after Ref. 21)

Label	ω [cm ⁻¹]	γ [cm ⁻¹]
$E_1(\text{LO}2)$	409.7	15.1
$A_1(\text{TO}1)$	63.8	32.5
$A_1(\text{LO}1)$	166.6	95.1
$A_1(\text{TO}3)$	603.8	117.3

Fig. 2. The temperature dependence of the specific heat: ● — PIN-PMN-PT; ○ — PMN crystal after Ref. 9; □ — PMN powder after Ref. 10; solid line — background specific heat.

Fig. 3. The temperature dependence of the excess specific heat: ● — PIN-PMN-PT; ○ — PMN after Ref. 9.

describe the infrared reflectivity spectrum of PMN at room temperature.

We selected parameters shown in Table 1 and used them to calculate characteristic frequencies of Debye and Einstein assuming that the error of the frequencies of lattice vibrations determination is 10 cm⁻¹ (the first mode is used for Debye frequency, others — for Einstein's) and also took into account the data on the thermal expansion of PMN from Ref. 10 for

calculating a linear term in the temperature. As a result we obtained the formula for the background specific heat, which describes well the experimental curves at our disposal:

$$C_p^{\text{bg}} = 3R \cdot \left[2 \cdot \mathcal{D}\left(\frac{575}{T}\right) + \mathcal{E}\left(\frac{105}{T}\right) + \mathcal{E}\left(\frac{234}{T}\right) + \mathcal{E}\left(\frac{880}{T}\right) + 1.7 \times 10^{-4} \cdot T \right],$$

where $\mathcal{D}$ and $\mathcal{E}$ are Debye and Einstein functions respectively, R — the universal gas constant. The data for PMN from Refs. 9 and 10 together with our data for PIN-PMN-PT and the calculated background specific heat are shown in Fig. 2. We observe good coincidence for both compounds at temperatures above 200 K.

In Fig. 3 the excess specific heat for PMN and PIN-PMN-PT are presented. The temperature of the hump is about the temperature of the diffused phase transition obtained by our preliminary dielectric data, and also reported in literature in the similar PIN-PMN-PT compound (24/42/34) 454–469 K.²² One should also note the apparent presence of deviations in behavior of the background specific heat below 100 K for PMN and 200 K for PIN-PMN-PT, which is in accordance with the previous works on specific heat of PMN.^{8–11} Calculation of the background specific heat at these temperatures demands accounting of the consideration stated in Ref. 11.

It is well noted the shift up of 150 K for the temperature maximum PIN-PMN-PT in comparison with PMN. As discussed earlier the addition of PT leads to the increase of the phase transition temperature and it is supposed that the addition of In increases it even more. As we clearly see from calorimetric data, there is a significant shift of transition temperature.

3. Conclusion

The calorimetric data obtained on PIN-PMN-PT showed good coincidence with diffused phase transitions with dielectric measurements for compounds with close concentrations. Having successfully described, the experimental curves by calculating the background specific heat, one finds that the specific heat data is in coincidence with the data of the infrared reflectivity spectrum of PMN.

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References

1. S.-E. Park and T. R. Shrout, Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals, *J. Appl. Phys.* **82**, 1804 (1997).

- ²G. A. Smolenskii and A. I. Agranovskaya, Dielectric polarization and losses of some complex compounds, *Sov. Phys. Tech. Phys. Engl. Transl.* **3**, 1380 (1958).
- ³S. Vakhrushev, A. Nabereznov, S. K. Sinha, Y. P. Feng and T. Egami, Synchrotron X-ray scattering study of lead magnoniobate relaxor ferroelectric crystals, *J. Phys. Chem. Solids* **57**, 1517 (1996).
- ⁴E. V. Colla, E. Yu. Koroleva, A. A. Nabereznov and N. M. Okuneva, The lead magnoniobate behavior in applied electric field, *Ferroelectrics* **151**, 337 (1994).
- ⁵M. V. Gorev, V. S. Bondarev and K. S. Aleksandrov, Heat capacity study of PMN near field-induced phase transition, *Ferroelectrics* **360**, 37 (2007).
- ⁶N. Novak, R. Pirc, M. Wencka and Z. Kutnjak, High-resolution calorimetric study of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ single crystal, *Phys. Rev. Lett.* **109**, 037601 (2012).
- ⁷A. Fouskova, V. Kohl, N. N. Krainik and I. E. Mylnikova, Specific heat of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, *Ferroelectrics* **34**, 119 (1981).
- ⁸B. A. Strukov, E. L. Sorkin, V. M. Rizak, N. K. Yushin, L. M. Sapozhnikova, Comparative-study of the heat-capacity of lead magnoniobate with perovskite and pyrochlore structure, *Solid State Phys.* **31**, 121 (1989).
- ⁹Y. Moriya, H. Kawaji, T. Tojo and T. Atake, Specific-heat anomaly caused by ferroelectric nanoregions in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ relaxors, *Phys. Rev. Lett.* **90**, 205901 (2003).
- ¹⁰M. V. Gorev, I. N. Flerov, V. S. Bondarev and Ph. Sciau, Heat capacity study of relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ in a wide temperature range, *J. Exper. Theor. Phys.* **96**, 531 (2003).
- ¹¹S. N. Gvasaliya, S. G. Lushnikov, Y. Moriya, H. Kawaji, T. Atake, M. B. Smirnov and V. Yu. Kazimirov, Specific heat of cubic relaxor ferroelectrics, *J. Phys. Condens. Matter* **16**, 8981 (2004).
- ¹²E. V. Colla, N. K. Yushin and D. Viehland, Dielectric properties of $(\text{PMN})_{(1-x)}(\text{PT})_x$ single crystals for various electrical and thermal histories, *J. Appl. Phys.* **83**, 3298 (1998).
- ¹³M. Davis, Picturing the elephant: Giant piezoelectric activity and the monoclinic phases of relaxor-ferroelectric single crystals, *J. Electroceram.* **19**, 25 (2007).
- ¹⁴M. Tachibana and E. Takayama-Muromachi, Thermal conductivity and heat capacity of the relaxor ferroelectric $[\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3]_{1-x}[\text{PbTiO}_3]_x$, *Phys. Rev. B* **79**, 100104 (2009).
- ¹⁵F. Li, S. Zhang, Z. Xu, X. Wei, J. Luo and T. R. Shrout, Composition and phase dependence of the intrinsic and extrinsic piezoelectric activity of domain engineered $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ crystals, *J. Appl. Phys.* **108**, 034106 (2010).
- ¹⁶S. Zhang, J. Luo, W. Hackenberger and T. R. Shrout, Characterization of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ ferroelectric crystal with enhanced phase transition temperatures, *J. Appl. Phys.* **104**, 064106 (2008).
- ¹⁷I. Hatta and A. J. Ikushima, Studies on phase transitions by ac calorimetry, *Jpn. J. Appl. Phys.* **20**, 1995 (1981).
- ¹⁸X. Li, Z. Wang, C. He, X. Long and Z.-G. Ye, Growth and piezo-/ferroelectric properties of PIN-PMN-PT single crystals, *J. Appl. Phys.* **111**, 034105 (2012).
- ¹⁹Y. Wan, Z. Li, M. Ma, F. Li, Z. Xu, S. Fan and X. Yao, Dielectric behavior and phase transition in [111]-oriented PIN-PMN-PT single crystals under dc bias, *J. Adv. Dielect.* **4**, 1450004 (2014).
- ²⁰L. Li, Z. Xu, S. Xia, Z. Li, X. Ji and S. Long, PIN-PMN-PT single-crystal-based 1–3 piezoelectric composites for ultrasonic transducer applications, *J. Electron. Mater.* **42**, 2564 (2013).
- ²¹J. Hlinka, T. Ostapchuk, D. Noujni, S. Kamba and J. Petzelt, Anisotropic dielectric function in polar nanoregions of relaxor ferroelectrics, *Phys. Rev. Lett.* **96**, 027601 (2006).
- ²²Y. J. Yamashita and Y. Hosono, High Curie temperature piezoelectric single crystals of the $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ ternary materials system, *Handbook of Advanced Dielectric, Piezoelectric and Ferroelectric Materials*, ed. Z.-G. Ye, Woodhead Publishing Series in Electronic and Optical Materials (Woodhead Publishing, UK, 2008), pp. 205–231.