Physics of the Solid State, 2024, Vol. 66, No. 10

04,06,13

Study of the temperature behavior of the heat capacity of a relaxor ferroelectric $PbNi_{1/3}Nb_{2/3}O_3$

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Received August 21, 2024
Revised August 21, 2024
Accepted August 22, 2024

The behavior of the heat capacity of single crystals of a relaxor ferroelectric $PbNi_{1/3}Nb_{2/3}O_3$ (PNN) in the temperature range from 2 to 400 K is considered. The analysis of the results of measurement of the specific heat C_p did not reveal any structural phase transitions in the studied temperature range. In addition, the temperature dependence C_p/T^3 demonstrates non-Debye behavior in the low temperature region and the absence of a low-temperature maximum $C_p/T^3(T)$ characteristic of many related materials. The results obtained were discussed within the framework of modern concepts of the physics of relaxor ferroelectrics with magnetic ions in one of the perovskite sublattices.

Keywords: lead nickel-niobate, lattice dynamics, specific heat, phase transition.

DOI: 10.61011/PSS.2024.10.59625.222

1. Introduction

Single crystals of $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) belong to the class of composite perovskites. PNN crystallizes in the perovskite structure, which is characterized by the general formula ABO_3, where the positions A are occupied by lead (Pb) atoms, and the positions B are occupied by Ni and Nb atoms in relation to $1:2$. The issue of structural phase transitions, as well as the properties of multiferroics in this compound, is of particular interest in connection with the belonging of PNN to relaxor ferroelectrics (relaxors) with a magnetic ion in the B-sublattice. PNN compounds were first synthesized in the late 1950s by G.A. Smolensky and his colleagues [1,2]. The first studies of the dielectric response of PNN showed the existence of a smeared permittivity anomaly with a maximum in the vicinity of $T_m \approx 150$ K, which allowed G.A.Smolensky et al. attributing this compound to the number of ferroelectrics with a „diffuse phase transition“ [3,4]. Further studies of PNN using dielectric spectroscopy showed the frequency dependence of the dielectric response anomaly with a characteristic shift of the maximum permittivity to the high temperature region with an increase of the frequency at which measurements are carried out [5], which is typical for relaxor ferroelectrics [6]. Paper [5] showed that a significant dispersion in dielectric losses is observed above 400 K, apparently due to the Maxwell-Wagner relaxation. The dielectric hysteresis loops observed below T_m remained unsaturated even at 200 kV/cm, which did not allow for a correct assessment of the polarization behavior in PNN in case of temperature changes [3,4]. Studies of the temperature behavior of the volumetric coefficient of thermal expansion in PNN allowed determining the Burns temperature ($T_d = 390 \pm 40$ K), below which the RMS polarization occurs which is determined by polar nanoregions [7].

The study of the magnetic properties of PNN demonstrated the paramagnetic behavior of magnetic susceptibility up to 5 K, below which the contribution of the antiferromagnetic ordering is possible [8].

PNN crystals have cubic symmetry $Pm\bar{3}m$ at room temperature with $a = 4.03$ Å [5]. Assumptions were made about the rhombohedral symmetry of the crystalline phase below T_m [9], but we could not find any reliable data in the literature on the structural studies of PNN in case of temperature changes. The vibrational spectrum of PNN was studied using Brillouin and Raman scattering of light, as well as calorimetry [10–13]. The behavior of a longitudinal acoustic phonon in the vicinity of the diffuse phase transition had a minimum characteristic of relaxor ferroelectrics in the vicinity of T_m [6.10], below which transverse acoustic phonons were observed in the scattering spectra [10]. This implies the occurrence of a rhombohedral phase in PNN below T_m [10]. It should be noted that although PNN was synthesized simultaneously with the model relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), the dynamics of the crystal lattice of this compound has been studied much worse. The studies mentioned above actually exhaust what we have been able to find in the literature. This encouraged us to study the behavior of the heat capacity of PNN, hoping for evidence of the existence of a structural phase transition into a rhombohedral phase.

2. Materials and methods

Single crystals $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) were grown by spontaneous crystallization. The resulting crystals were transparent and had a yellow-green color. The composition and structure of PNN crystals was been confirmed by X-ray fluorescence (XRF) and X-ray diffraction analysis.

The sample weighing 54 mg was selected from grown PNN single crystals, its value ensure the highest accuracy in calorimetric measurements. The specific heat capacity of the PNN sample was measured by relaxation calorimetry using a physical properties measurement system (PPMS, Quantum Design Inc.). Two separate experiments were conducted to cover the temperature range from 2 to 280 K. The heat capacity was measured in the temperature range from 280 to 2 K in the first experiment, and then it was measured in the range from 2 to 180 K. The sample was first cooled to 10 K in the second experiment and then it was kept at this temperature for 5–10 min to ensure thermal equilibrium. The sample was then heated to 125 K at a controlled rate of 5–10 K/min. The heat capacity measurements began after reaching the target temperature, which were carried out in the range from 125 to 280 K. Measurements in the temperature range from 200 to 400 K were conducted continuously, ensuring a smooth temperature change.

3. Results and discussion

Figure 1 shows the temperature dependences of the specific heat and dielectric constant of PNN single crystals. It is clearly seen in Figure 1, *a* that the temperature dependence $C_p(T)$ does not show any anomalies in the studied temperature range that could be associated with a structural phase transition. An insert is shown in Figure 1, *a* for a more detailed consideration of possible anomalies, which is an enlarged image of the specific heat in the range from 100 to 250 K. The existence (in addition to the phase transformation into a relaxation state) of the structural phase transition from the cubic to the rhombohedral phase was assumed in this particular temperature range [9,10]. The temperature dependence $C_p(T)$ in the box to Figure 1, *a* also has no features (jumps, „kinks" etc.). Thus, we can assume that PNN remains structurally stable within the considered temperature range. This behavior $C_p(T)$ is in good agreement with the behavior of the real part of the dielectric response PNN (Figure 1, *b*), shown at four different frequencies: 0.1, 1, 10 and 100 kHz.

The dielectric response demonstrates a broad frequency-dependent anomaly with the maximum T_m at 10 kHz in the vicinity of 150 K, which is characteristic of a relaxor ferroelectric [5,6]. As discussed earlier [5], the maximum dielectric response of PNN shifts towards higher temperatures with an increase in the test (measuring) frequency. This frequency-dependent shift is a distinctive feature of relaxor ferroelectrics and indicates a complex relaxation of local polarization in the crystal structure of PNN. We do not observe additional anomalies in the dielectric response in the temperature range from 100 to 500 K.

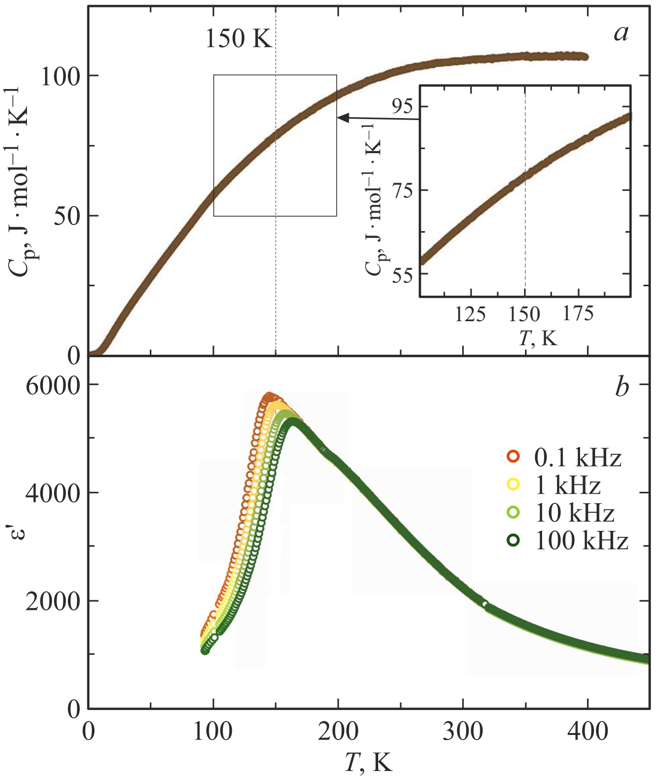

Figure 1. Temperature dependence *a*) heat capacity C_p and *b*) dielectric constant ε' [5] of PNN single crystals (the inset shows on an enlarged scale the dependence $C_p(T)$ in the region of „the smeared phase transition").

Interestingly, while the dielectric response indicates the occurrence of a relaxor ferroelectric state in PNN at $T < T_m$, no anomalies are observed in the behavior of the heat capacity in the vicinity of the „diffuse phase transition". Such an absence of anomalies in the temperature dependences of the heat capacity in the vicinity of the „diffuse phase transition" was observed earlier for other relaxors PMN, $PbMg_{1/3}Ta_{2/3}O_3$ (PMT), etc. [14–19].

The low-temperature behavior of the heat capacity can be considered in more detail when analyzing the temperature dependence C_p/T^3. Figure 2 shows the behavior $C_p/T^3(T)$ for PNN crystals and, as a comparison, the temperature dependences $C_p/T^3(T)$ for PMN crystals are presented. Figure 2 and the inserts in this figure clearly show that the dependences $C_p/T^3(T)$ for PNN and PMN differ fundamentally in the low-temperature region (at $T < 15$ K): C_p/T^3 increases up to up to 2 K in the PNN crystal with a decrease of temperature, while the dependence C_p/T^3 forms a maximum in the vicinity of 7 K, with a further decrease of the value of C_p/T^3. It should be noted that the low-temperature maximum is observed in many perovskites, both classical (for example, in $BaTiO_3$ [17]) and complex, such as PMN, PMT and $BaMg_{1/3}Ta_{2/3}O_3$ (BMT) [14–19]. In many cases, this maximum can be described in dielectric

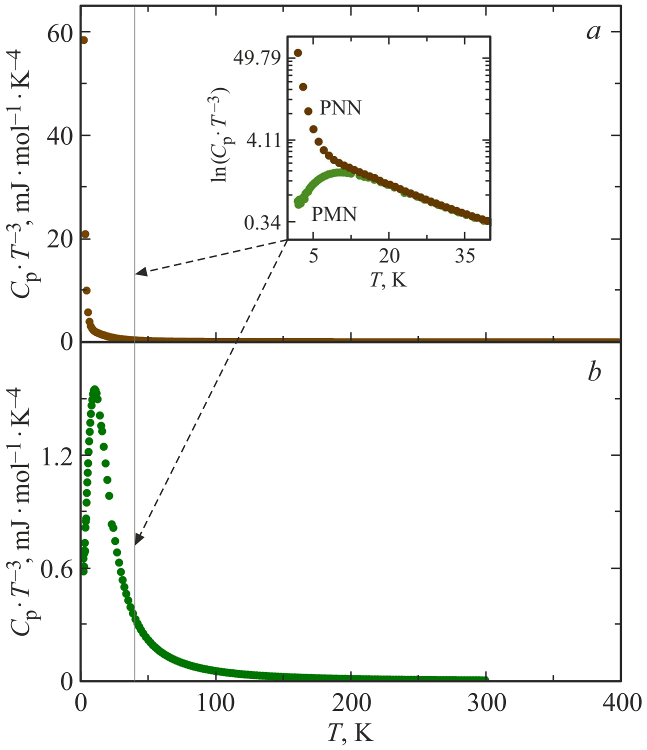

Figure 2. Temperature dependence C_p/T^3 of single crystals *a*) PNN and *b*) PMN (the insert shows the dependencies $C_p/T^3(T)$ of PNN and PMN in the low-temperature region on a semi-logarithmic scale).

compounds using Einstein's formalism:

$$C = 3R\left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{\exp\left(\frac{\hbar\omega_E}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_E}{k_B T}\right) - 1\right)^2}, \qquad (1)$$

where $\omega_E = 2\pi\nu_E$ (ν_E is the frequency of the Einstein mode), and the actual behavior of the heat capacity in the low-temperature region is a combination of contributions from Einstein and Debye:

$$C_D = 9R\left(\frac{T}{\Theta_D}\right)^3 \int\limits_0^{E_D/k_B T} \frac{\exp(x)x^4}{(\exp(x) - 1)^2} dx, \qquad (2)$$

where $R = 8.314$ J/mol/K — universal gas constant, Θ_D — Debye temperature, $E_D = k_B\Theta_D$ — Debye energy.

The generally accepted method to describe the low-temperature behavior of heat capacity is the formalism of two-level systems (TLS) for disordered systems [20,21]. In this case, a linear dependence of the heat capacity on temperature is expected at low temperatures (most often at $T < 1.5$ K), i.e. $C = C_D + \alpha T$. In the case of a PMN crystal, the excess (relative to the Debye contribution) heat capacity was best described by combinations of various mechanisms, taking into account the additional, non-phonon contribution [19].

Let us return to the consideration of the low-temperature behavior of C_p/T^3 in a PNN crystal. Unfortunately, we do not have experimental data on the density function of phonon states or the dispersion of phonons in the Brillouin zone. There are also no results of low-temperature acoustic measurements. This does not allow for a correct analysis of the behavior of low-temperature heat capacity in PNN within the framework of the above models.

The dependence C_p/T^3 for PNN demonstrates a pronounced non-Debye behavior in the low temperature region as shown in Figure 2. There is also no maximum determined based on the Einstein contribution to the behavior of the heat capacity. Perhaps this maximum is „masked" by a sharp increase of dependence C_p/T^3, which begins in the vicinity of 10 K (see insert to Figure 2, *a*). Taking into account the possible maximum in the temperature dependence C_p/T^3 still does not allow obtaining a dependence characteristic of the Debye model below 10 K. Thus, the low-temperature behavior of the heat capacity in PNN is not determined by acoustic phonons and suggests the existence of an additional contribution to the dynamics of the crystal lattice. It is possible to see a similar behavior of the dielectric response [5,6], Raman spectra [6,11,12] and a similar structural motif by comparing PMN and PNN crystals, related compounds [6,9]. These two compounds differ only in the substitution of Mg ions for Ni in the crystal structure. The difference in mass cannot lead to such dramatic differences in temperature dependences C_p/T^3. Perhaps the differences observed in Figure 2 are associated with the existence of two types of Ni in the PNN structure: with valence 2+ and 3+, which occur when nickel-containing crystals grow. This situation was observed in the relaxor ferroelectric $PbCo_{1/3}Nb_{2/3}O_3$(PCN), where Co^{2+} and Co^{3+} exist in the crystal volume [22]. A phase charge separation associated with the formation of regions with a predominant content of Co^{2+} or Co^{3+} occurs in the low-temperature region of the PCN crystal [23]. The analysis of the dielectric response and conductivity in PNN, carried out in Ref. [5], suggests the existence of the same features in the low-temperature region of PNN like in PCN, that is, the formation of a state of charge phase separation in PNN. Then the occurrence of a non-Debye contribution to the low-temperature heat capacity of PNN may be associated with the occurrence of low-frequency excitations during phase separation.

4. Conclusion

The paper provides the results of studies of the specific heat capacity of single crystals of $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) in a wide temperature range from 2 to 400 K. The main goal was to study possible structural phase transitions and transformations in this relaxor ferroelectric, taking into account the presence of a magnetic ion in the *B*-sublattice of the perovskite structure.

Our results show no evidence of the existence of structural phase transitions within the studied temperature range, which is consistent with the wide frequency-dependent anomalies observed in the dielectric response of PNN, a behavior characteristic of classical relaxors such as PMN. The low-temperature maximum observed in related materials was not detected in the temperature dependence C_p/T^3. The presence of a non-Debye contribution to the behavior of $C_\mathrm{p}/T^3(T)$ was shown, which may be related to the peculiarities in the distribution of Ni^{2+} and Ni^{3+} ions in the low-temperature phase of PNN.

Further study is required to gain a deeper understanding of the temperature behavior of specific heat and the dynamics of the PNN lattice. The use of inelastic neutron scattering or synchrotron scattering, Raman and acoustic spectroscopy can provide insight into phonon modes and their interactions, offering a more detailed understanding of lattice dynamics.

Funding

This study was financed under the state assignment of the Ministry of Education and Science of the Russian Federation FFUG-2024-0042.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] G.A. Smolensky, A.I. Agranovskaya. ZhTF **28**, *7*, 1491 (1958). (in Russian).

[2] I.E. Mylnikova, V.A. Bokov. Kristallografiya, **4**, *3*, 433 (1959). (in Russian).

[3] V.A. Bokov, I.E. Myl'nikova. FTT **2**, *11*, 2728 (1960). (in Russian).

[4] V.A. Bokov, I.E. Myl'nikova. FTT **3**, *3*, 841 (1961). (in Russian).

[5] A.D. Polushina, E.D. Obozova, V.G. Zalesskii, T.A. Smirnova, S.G. Lushnikov. Phys. Solid State **63**, *10*, 1508 (2021).

[6] R.A. Cowley, S.N. Gvasaliya, S.G. Lushnikov, B. Roessli, G.M. Rotaru. Adv. Phys. **60**, *2*, 229 (2011).

[7] K. Bormanis, M.G. Gorev, I.N. Flerov, A. Sternberg, L. Lace, R. Ignatans, A. Kalvane, M. Antonova. Proceed. Estonian Academ. Sci. **66**, *4*, 363 (2017).

[8] T. Shirakami, M. Mituskawa, T. Imai, K. Urabe. Jpn. J. Appl. Phys. **39**, *7A*, L678 (2000).

[9] K. Kusumoto, T. Sekiya. Ferroelectrics **240**, *1*, 1593 (2000).

[10] H.J. Fan, M.H. Kuok, S.C. Ng, N. Yasuda, H. Ohwa, M. Iwata, H. Orihara, Y. Ishibashi. J. Apl. Phys. **91**, *4*, 2262 (2002).

[11] J. Kano, H. Taniguchi, D. Fu, M. Itoh, S. Kojima. Ferroelectrics **367**, *1 Part 1*, 67 (2008).

[12] T.A. Smirnova, A.I. Fedoseev, S.G. Lushnikov, R.S. Katiyar. Ferroelectrics **532**, *1*, 50 (2018).

[13] K. Bormanis, S.N. Kallaev, Z.V. Omarov, A.R. Bilalov, A. Kalvane. Ferroelectrics **436**, *1*, 49 (2012).

[14] J.J. De Yoreo, R.O. Pohl, G. Burns. Phys. Rev. B **32**, *9*, 5780 (1985).

[15] B.A. Strukov, E.L. Sorkin, V.M. Rizak, N.K. Yushin, L.M. Sapozhnikova. FTT **31**, *10*, 121 (1989). (in Russian).

[16] S.N. Gvasaliya, S.G. Lushnikov, Y. Moriya, H. Kawaji, T. Atake. Physica B **305**, *1*, 90 (2001).

[17] Y. Moriya, H. Kawaji, T. Tojo, T. Atake. Phys. Rev. Lett. **90**, *20*, 205901 (2003). Y. Moriya. PhD Thesis, Tokyo Institute of Technology (2003).

[18] S.N. Gvasaliya, S.G. Lushnikov, I.L. Sashin. Ferroelectrics **285**, *1*, 243 (2003).

[19] S.N. Gvasaliya, S.G. Lushnikov, Y. Moriya, H. Kawaji, T. Atake, M.B. Smirnov, V.Yu. Kazimirov. J. Phys.: Condens. Matter **16**, *49*, 8981 (2004).

[20] W.A. Phillips. J. Low Temp. Phys. **7**, *314*, 351 (1972).

[21] P.W. Anderson, B.I. Halperin, C.M. Varma. Phil. Mag. **25**, *1*, 1 (1972).

[22] A.H. Pandey, V.R. Reddy, A.K. Nigam, S.M. Gupta. Acta Materialia **177**, 160 (2019).

[23] B.Kh. Khannanov, V.G. Zalessky, E.I. Golovenchits, V.A. Sanina, T.A. Smirnova, M.P. Shcheglov, V.A. Bokov, S.G. Lushnikov. JETP **130**, *3*, 439 (2020).

Translated by A.Akhtyamov