

Caloric Characteristics of PbTiO_3 in the Temperature Range of the Ferroelectric Phase Transition

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Abstract—The heat capacity and thermal expansion of the PbTiO_3 ceramic sample have been measured in the temperature range 80–970 K. The electrocaloric and barocaloric efficiencies of lead titanate in the ferroelectric phase transition range have been investigated by analyzing the experimental data in terms of the thermodynamic theory of phase transitions, the electrical equation of state $P(T, E)$, the Pippard equation, and the $S(T, p)$ diagram.

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1. INTRODUCTION

Lead titanate PbTiO_3 belongs to the class of ferroelectrics that have long since been known but still being actively studied [1, 2]. The phase transition between the paraelectric and ferroelectric phases of this compound is characterized as a structural transformation of the first order, which is close to the tricritical point, occurs at a temperature $T_0 = 763$ K, and leads to the change in the symmetry $Pm\text{--}3m \rightarrow P4mm$. A wealth of information on the physical and structural properties of lead titanate seemingly gives strong grounds to consider this compound as a model ferroelectric. However, for a number of reasons, there is no unified point of view on the details of the mechanism of the aforementioned phase transition. For example, on the one hand, the synthesis of well-sintered polycrystalline samples has been hampered because of the volatility of lead oxide at high temperatures, which causes a violation of the stoichiometry of the ratio between the oxides [2]. On the other hand, crystals grown by different methods possess, even at room temperature, a high electrical conductivity in the range from 10^{-8} to 10^{-11} ($\Omega \text{ cm}$)⁻¹, which complicates the investigation of their dielectric properties [3, 4]. This leads, in particular, to a significant ambiguity in the values of the Curie–Weiss constant and the saturation polarization, which according to the data obtained from different investigations vary in the ranges $C_{C\text{--}W} = (1.1\text{--}7.9) \times 10^5$ K and $P_s = (40\text{--}80) \mu\text{C cm}^{-2}$, respectively [3, 4]. For the same reason, there is still no infor-

mation about the piezoelectric parameters of the PbTiO_3 compound [5].

Rather more recently, it was found that, when lead titanate is added to relaxor systems, the materials thus obtained, for example, the solid solutions $x\text{Pb}(Me_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}(1-x)\text{PbTiO}_3$ ($Me = \text{Mg, Zn}$), exhibit a number of remarkable properties. First, it turned out that these solid solutions are characterized by very high values of piezoelectric coefficients [6]. Second, no less remarkable is the fact that these materials undergo ferroelectric phase transitions at temperatures considerably lower than the temperature T_0 in PbTiO_3 . And, third, it was established that the aforementioned solid solutions in the phase transformation regions are characterized by a rather large value of the intensive electrocaloric effect (ECE) $\Delta T_{AD}^{\text{ECE}}$ [7–9]. It can be assumed that the nature of this phenomenon is associated with the high electrocaloric efficiency of lead titanate. However, to the best of our knowledge, until now, reliable information on the electrocaloric effect in PbTiO_3 has been not available in the literature. Quite probably, this circumstance is associated with the difficulties encountered in performing direct experimental investigations due to, first, the aforementioned high electrical conductivity of both ceramic and crystalline samples (which, as was shown earlier in [10], complicates the determination of the intensive electrocaloric effect) and, second, the high temperature of the phase transition. In this case, the approach developed in our recent work [11] might appear to be very fruitful. Using a number of ferroelec-

trics as an example, we have demonstrated the possibility of reliably determining the intensive and extensive electrocaloric effects from an analysis of the calorimetric and dielectric data in terms of the electrical equation of state.

Historically, the ferroelectric phase transition in PbTiO₃ had been assigned to displacive phase transformations [12]. And this assignment had been made despite a rather large value of the corresponding change in the entropy $\Delta S_0 \approx 0.8R > R \ln 2$ (where R is the gas constant), which was found already in the first exploratory calorimetric investigations [13]. It seems likely that a significant role here was played by the approach to the classification of the mechanisms of structural distortions in ferroelectrics according to the values of the Curie–Weiss constants, which proved to be rather close to each other for PbTiO₃ (170000 K) and BaTiO₃ (150000 K) [12]. Structural investigations of barium titanate showed that the emergence of the dipole moment is actually associated with small displacements of titanium and oxygen atoms. Furthermore, the obtained value of the change in the entropy $\Delta S_0 \approx 0.06R \ll R \ln 2$ [12], which was caused by the structural distortions, corresponded to the characterization of the phase transition in BaTiO₃ as a displacive phase transformation. As regards lead titanate, some investigations revealed a positional disorder of lead atoms in the cubic phase, which are partially or completely ordered in the phase $P4mm$ [14, 15]. The values obtained for the change in the entropy of the phase transition $\Delta S_0 \approx (5.8–7.3) \text{ J/mol K} > R \ln 2$ from the calorimetric data confirmed the occurrence of the order–disorder transition in PbTiO₃ [13, 16, 17].

As was shown by the previously performed analysis of the dependences of the total entropy on the temperature and pressure $S(T, p)$ for the case of order–disorder transitions [11], the relatively large values obtained for the entropy of the phase transition suggest that the material also exhibits a significant barocaloric effect (BCE). However, in this case, a noticeable role is also played by the pressure coefficient dT/dp , which characterizes the sensitivity of the phase transition temperature to a variation in the hydrostatic pressure. Information on the latter parameter for PbTiO₃ is rather contradictory. The pressure coefficients dT/dp determined in [18–21] vary over a wide range from -4 to -18 K/kbar . The reliably established fact is only that the pressure coefficient is a nonlinear function of pressure. But, the value of the pressure coefficient under the initial conditions at $p = 0$ remains unknown. However, necessary information can be obtained by comparing the temperature dependences of the heat capacity and thermal expansion coefficient in the temperature range of the phase transformation in terms of the Pippard equation [22].

From the foregoing, it is clear that investigations of the thermal properties, which are not influenced by the electrical conductivity of the sample, make it pos-

sible to perform even though indirect but reliable evaluations of the electrocaloric and barocaloric efficiencies of the material. Undoubtedly, the most reliable information can be obtained by analyzing the data on different properties investigated in the same sample.

In this work, we have performed investigations of the heat capacity and thermal expansion of PbTiO₃ over a wide range of temperatures in order to determine the intensive and extensive parameters of the electrocaloric and barocaloric effects in the temperature range of the ferroelectric phase transition.

2. SYNTHESIS, CHARACTERIZATION OF THE SAMPLES, AND METHODS OF INVESTIGATIONS

Samples of the lead titanate PbTiO₃ were prepared according to the conventional ceramic technology. Lead oxide PbO (special-purity grade) and titanium oxide TiO₂ (special-purity grade) were used as the initial reactants, which were mixed in a stoichiometric ratio of 1 : 1. The homogeneous mixture obtained was pressed into pellets that were used in the solid-phase synthesis performed in an air atmosphere at a temperature of 800°C for 24 h. The synthesized samples were ground in an agate mortar, and the powder thus prepared was investigated using a DRON-2 X-ray powder diffractometer at room temperature. The X-ray diffraction pattern of the powder samples corresponds to the tetragonal symmetry with the unit cell parameters $a = 3.90061(7) \text{ \AA}$ and $c = 4.1522(1) \text{ \AA}$ and the value of the spontaneous deformation $c/a = 1.0645$, which are in satisfactory agreement with the unit cell parameters previously determined for the single-crystal samples [16]: $a = 3.901(1) \text{ \AA}$, $c = 4.153(2) \text{ \AA}$, and $c/a = 1.0646$. No foreign phases in the synthesized sample of PbTiO₃ were found.

The high-temperature measurements of the heat capacity $C_p(T)$ of the PbTiO₃ compound in the range from 360 to 970 K were carried out on an STA 449 C Jupiter synchronous thermal analyzer (NETZSCH, Germany). The experiments were performed in an argon flow at a flow rate of 35 mL/min for several samples weighing from 0.014 to 0.120 g in the heating and cooling modes at a rate $dT/d\tau = 5 \text{ K/min}$. The calorimeter was calibrated using standard reference compounds (In, Ag₂SO₄, BaCO₃, K₂CrO₄, and KClO₄). The accuracy in the determination of the temperature was $\sim(\pm 1 \text{ K})$. The error in the determination of the heat capacity varied within the limits from 4 to 5% over the entire temperature range under investigation.

The measurements of the heat capacity $C_p(T)$ in the low-temperature range (80–300 K) were carried out using an adiabatic calorimeter for a sample with a weight of 0.0926 g in the discrete and continuous heating modes. The error in the determination of the heat capacity did not exceed 0.5%. The methodological

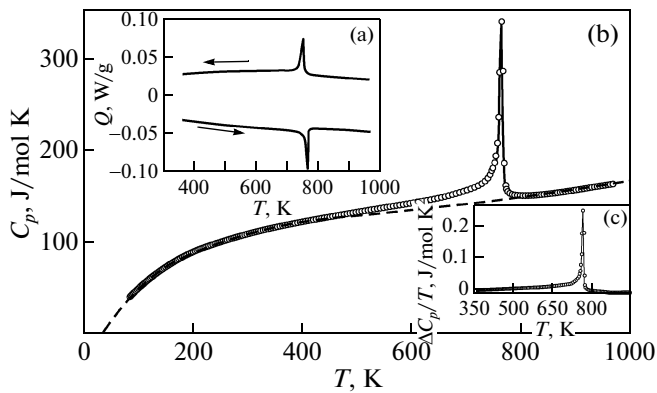


Fig. 1. (a) Dependence of the heat flux Q on the temperature in the heating and cooling modes. (b, c) Temperature dependences of (b) the molar heat capacity and (c) the relative anomalous heat capacity of PbTiO_3 . The dashed line shows the lattice heat capacity.

features of the experiment were described in more details in [23].

The thermal expansion was investigated on a DIL-402 C dilatometer (NETZSCH, Germany) at temperatures in the range from 100 to 960 K in the dynamic mode with rates of change in the temperature from 3 to 5 K/min. Corundum reference samples were used to calibrate the dilatometer and to take into account the thermal expansion of the measurement system. The measurements were carried out in the heating and cooling modes, which made it possible to investigate the hysteresis phenomena. For the dilatometric experiments, samples were prepared in the form of pellets with a diameter of 4 mm and a height of ~ 4.8 mm, which were pressed under a pressure of ~ 10 kbar and subjected to sintering in an air atmosphere at a temperature of 800°C for 4 h.

3. RESULTS OF THE INVESTIGATIONS

3.1. Heat Capacity

The results obtained from measurements of the temperature dependences of the heat flux $Q(T)$ through the PbTiO_3 sample with the use of the synchronous thermal analyzer are presented in Fig. 1a. It can be seen from this figure that the anomalies associated with the ferroelectric phase transition are very significant and that the behavior of the heat flux $Q(T)$ is characterized by a large temperature hysteresis of ~ 15 K.

Using the obtained data on the heat flux in the heating mode, we calculated molar isobaric heat capacity of lead titanate. The temperature $T_0 = 763$ K, which corresponds to the maximum value of the heat capacity and is taken as the temperature of the transition between the ferroelectric and paraelectric phases in PbTiO_3 , is in satisfactory agreement with the tem-

peratures previously determined for both crystalline and ceramic samples [13, 16, 17].

The low-temperature investigations of the dependence $C_p(T)$ on the adiabatic calorimeter did not reveal anomalies in the heat capacity. The low-temperature and high-temperature data on the heat capacity were combined with the use of a polynomial function. The combined dependence of the molar heat capacity on the temperature is shown in Fig. 1b.

In order to determine the integral characteristics of the phase transition, we separated the molar heat capacity of PbTiO_3 into the regular component (lattice heat capacity) C_L and the anomalous contribution ΔC_p , which is associated with the emergence of the polarization at temperatures below T_0 . For this purpose, the experimental data on the heat capacity $C_p(T)$ obtained at temperatures significantly different from the temperature T_0 , namely, in the temperature ranges below 300 K and above 850 K, were approximated by the equation containing the Debye and Einstein functions ($T_D = 332$ K and $T_E = 850$ K, respectively) and the second-degree polynomial taking into account the difference $C_p - V_v$. The dependence $C_L(T)$ is shown by the dashed line in Fig. 1b. The anomalous heat capacity, which is determined as the difference $\Delta C_p = C_p - C_L$, is observed over wide temperature ranges in the cubic and tetragonal phases. By integrating the function $\Delta C_p(T)$ over the entire range of its existence (280–850 K), we determined the change in the enthalpy $\Delta H_0 = 5450 \pm 450$ J/mol. This value proved to be closer to the change in the enthalpy $\Delta H_0 = 4900$ J/mol found in [17] and significantly exceeded the value of $\Delta H_0 = 4150$ J/mol obtained in [16]. In the subsequent analysis of the experimental data, we will be interested mainly in the anomalous heat capacity $\Delta C_p/T$; hence, the temperature dependence of this quantity is shown in Fig. 1c. The change in the entropy due to the phase transition was determined to be $\Delta S_0 = \int (\Delta C_p(T)/T) dT = 8.3 \pm 0.6$ J/mol K.

3.2. Thermal Expansion

The temperature dependences of the linear deformation $\Delta L/L_0$ and the coefficient of linear thermal expansion α of the PbTiO_3 compound measured in the heating and cooling modes are shown in Fig. 2. There is a satisfactory agreement between the results obtained in several series of measurements. It can be seen from this figure that both the linear deformation $\Delta L/L_0$ and the coefficient of linear thermal expansion α are characterized by an anomalous behavior over a wide range of temperatures, as is the case with the heat capacity (Fig. 1b). In the tetragonal phase of PbTiO_3 , an increase in the temperature is accompanied by a decrease in the linear size and, correspondingly, in the volume size of the sample. That is why, according to

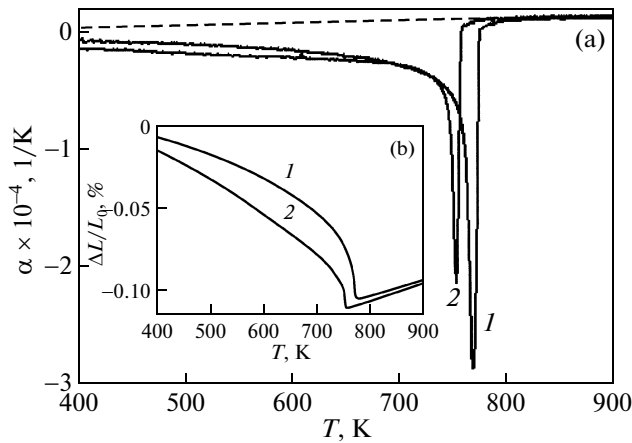


Fig. 2. Temperature dependences of (a) the coefficient of linear thermal expansion α and (b) the linear deformation $\Delta L/L_0$ measured during (1) heating and (2) cooling in the ferroelectric phase transition range. The dashed line shows the lattice contribution.

the Clausius–Clapeyron equation $dT/dp = \delta V/\delta S$, the phase transition temperature of the ferroelectric should decrease with an increase in the pressure, which was actually observed in [18–21]. The temperature corresponding to the minimum of the thermal expansion coefficient $T_{\min} = 767.5$ K, which is taken as the phase transition temperature, and the temperature hysteresis $\delta T_0 = 15$ K are in satisfactory agreement with the parameters determined from the calorimetric measurements. The anomalous contribution to the coefficient of linear thermal expansion $\alpha(T)$ is observed over a wide temperature range of the ferroelectric phase (Fig. 2a).

In the low-temperature range, the dependences $\Delta L/L_0(T)$ and $\alpha(T)$ exhibit anomalies observed at temperatures of ~ 250 and ~ 380 K, respectively (Fig. 3a). These anomalies are associated with the increase and decrease in the volume of the sample, respectively. However, the X-ray diffraction investigations did not reveal any anomalous behavior in the temperature dependences of the lattice parameters of the samples at these temperatures (Fig. 3b). Furthermore, no anomalies were found in the investigation of the permittivity of the samples.

4. ANALYSIS AND DISCUSSION OF THE RESULTS

The problem of low-temperature phase transitions in PbTiO₃ has been discussed by many researchers. However, there is still no consensus of opinion among them regarding the possibility of their existence. In the tetragonal phase of PbTiO₃, the anomalous behavior was observed in the temperature dependences of the polarization and permittivity [24], birefringence [25], and thermal expansion [2]. However, the correspond-

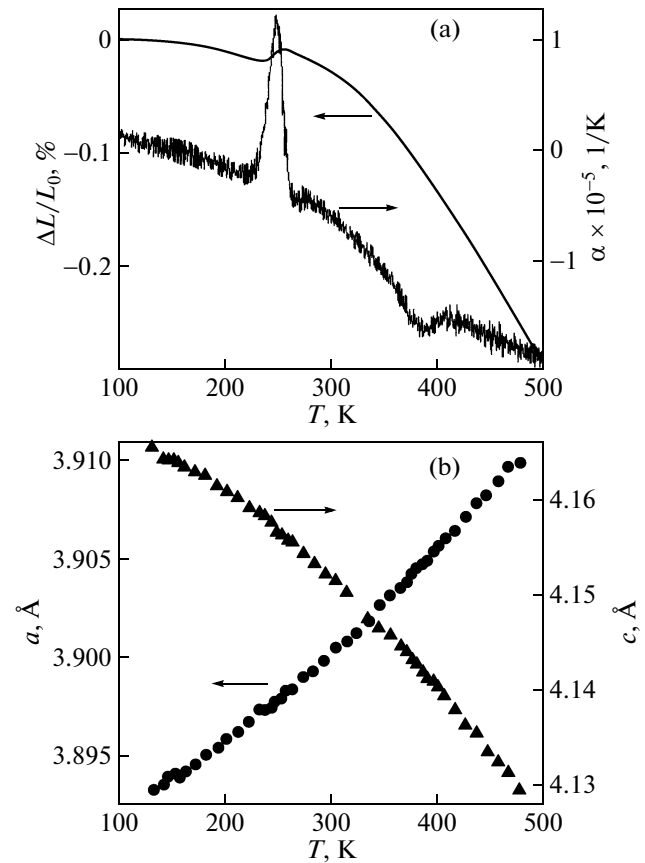


Fig. 3. Results of low-temperature measurements of (a) $\Delta L/L_0(T)$ and $\alpha(T)$ and (b) tetragonal unit cell parameters a and c .

ing temperatures of these anomalies differ significantly. This suggests that there is a relation between the observed phenomena and the individual characteristics of the samples. However, according to our data obtained for the same sample, there are anomalies in the behavior of the dependences $\Delta L/L_0(T)$ and $\alpha(T)$, but no anomalies are observed in the dependences $C_p(T)$, $a(T)$, and $c(T)$.

4.1. On the Mechanism of the Phase Transition $Pm\bar{3}m \rightarrow P4mm$

The entropy $\Delta S_0 = 8.3$ J/mol K determined in our study for the phase transition in PbTiO₃ is in satisfactory agreement with the values of $\Delta S_0 = (7.7\text{--}8.6)$ J/mol K obtained in [17, 26]. It is obvious that such large values of $\Delta S_0 \approx R(\ln 2.5 - \ln 2.8)$ do not correspond to displacive phase transitions in perovskite-type crystals, for which rather small changes in the entropy $\Delta S_0 \leq 0.2R$ were established experimentally [27]. It is known that the entropy is proportional to the anharmonicity parameter of the atomic vibrations $\delta \approx \langle x^2 \rangle / a_0^2$ (where $\langle x^2 \rangle$ is the amplitude of the mean-square displace-

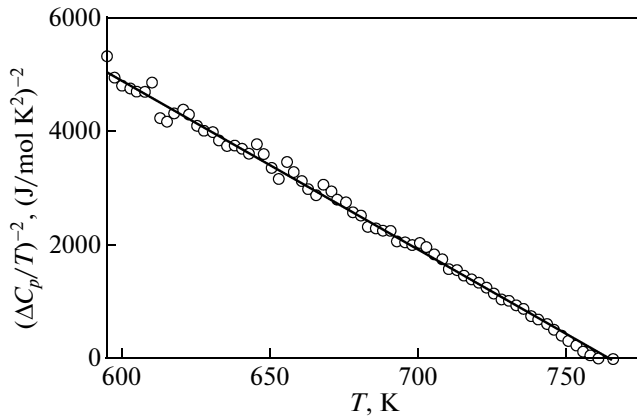


Fig. 4. Behavior of the anomalous heat capacity of PbTiO_3 in the phase $P4mm$ in accordance with relationship (2).

ment of the atoms) [12]. The limiting case of anharmonicity corresponds to a positional (orientational) disorder of atoms (ionic groups) over several equivalent crystallographic positions N_0 . The ordering of structural elements as a result of the reduction of the symmetry due to the phase transition leads to a decrease in the number of equivalent positions N_1 . The corresponding change in the entropy should be equal to $\Delta S = R \ln N_0/N_1$.

A structural model of PbTiO_3 was proposed using the results obtained from the neutron and X-ray diffraction experiments. According to this model, the lead atoms are disordered in the phase $Pm-3m$ and, with an equal probability, occupy one of the six positions associated with the displacement of the atoms from the $(0, 0, 0)$ position by $\sim 0.2 \text{ \AA}$ in the $\langle 001 \rangle$ direction [14, 15]. In the phase $P4mm$, an ordering of the lead atoms occurs in one position. The change in the entropy in this case should be equal to $\Delta S = R \ln 6$. The change in the entropy experimentally determined in our study has a lower value: $\Delta S_0 = R \ln 2.8$. Thus, it can be assumed that the lead atoms at temperatures $T < T_0$ remain disordered.

4.2. Electrocaloric Effect

As was already mentioned above, the electrocaloric effect can be fairly reliably determined using the electrical equation of state. The obtained data on the anomalous heat capacity of PbTiO_3 (Fig. 1b) allow us to verify the applicability of the phenomenological theory to the description of the phase transition $Pm-3m \rightarrow P4mm$ by analyzing the thermodynamic potential [28]

$$\Delta\Phi = A_T(T - T_c)P^2 + BP^4 + CP^6. \quad (1)$$

In accordance with one of the consequences of the theory [29], the ratios between the coefficients in the equation for the thermodynamic potential (1) can be

determined from data on the excess heat capacity at $T < T_0$:

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \left(\frac{2\sqrt{B^2 - 3A_T C}}{A_T^2}\right)^2 + \frac{12C}{A_T^3}(T_0 - T). \quad (2)$$

The applicability of relationship (2) to the description of the data presented in Fig. 1c was analyzed by varying the considered ranges of temperatures within wide limits. The optimum results of the approximation are presented in Fig. 4. It turned out that the square of the inverse relative excess heat capacity is a linear function of temperature over a very wide temperature range $\Delta T_L = (600-750) \text{ K}$. As the temperature T_0 is approached, the obtained values deviate from dependence (2) due to the smearing of the latent heat of the phase transition, which in the ceramic sample is inevitable.

From the dependence $(\Delta C_p/T)^{-2}(T)$, we obtained data on the following ratios between the coefficients in the equation for the thermodynamic potential (1): $B/(A_T)^2 = -9 \text{ (J/mol K}^2\text{)}^{-1}$ and $C/(A_T)^3 = 2.5 \text{ (J/mol K}^{3/2}\text{)}^{-2}$. In order to determine directly the values of these coefficients, there are not enough data on the temperature dependence of the permittivity, which is used for calculating the Curie–Weiss constant C_{C-W} and the related coefficient $A_T = 2\pi/C_{C-W}$. As was noted above, according to the data obtained by different investigators, the values of C_{C-W} for PbTiO_3 vary over very wide ranges [3, 4]. This circumstance, of course, to a large extent, is determined by the temperature range included in the analysis. For example, in [16], it was demonstrated that, for the same sample, the chosen values of the Curie–Weiss constant C_{C-W} can differ by a factor of almost two. At the same time, the Curie–Weiss constant C_{C-W} is a dimensional characteristic that indicates the closeness of the phase transition to the tricritical point, because it is associated with the difference between the temperature of the first-order phase transition T_0 and the Curie–Weiss temperature T_C . Using the obtained ratios of the coefficients of the thermodynamic potential (1) and the equation $T_0 - T_C = B^2/4A_T C$ [29], we determined the desired difference $T_0 - T_C = 8.1 \text{ K}$. In accordance with this value, we chose the Curie–Weiss constant $C_{C-W} = 5.7 \times 10^5 \text{ K}$. As a result, we obtained the following values of the desired coefficients: $A_T = 1.1 \times 10^{-5} \text{ K}^{-1}$, $B = -2.9 \times 10^{-8} \text{ (J/mol)}^{-1}$, and $C = 4.6 \times 10^{-13} \text{ (J/mol)}^{-2}$.

The analysis of the electrical equation of state $-E = 2A_T(T - T_c)P + 4BP^3 + 6CP^5$ made it possible to construct the thermodynamic surface $P-E-T$ of the PbTiO_3 ferroelectric (Fig. 5). The calculated value of the polarization $P_s = 46 \text{ \mu C cm}^{-2}$ at room temperature and $E = 0$ fits into the range of values $P_s = (40-80) \text{ \mu C cm}^{-2}$

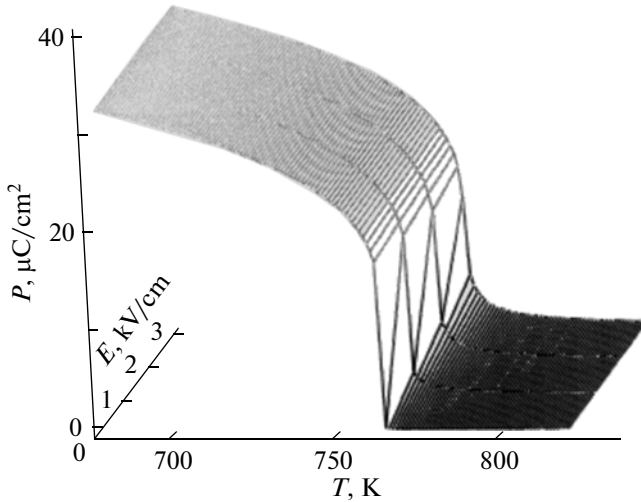


Fig. 5. Thermodynamic surface P – E – T of the PbTiO₃ ferroelectric.

obtained by different authors [3]. In our calculations, we assumed that weak electric fields almost do not affect the coefficients of the thermodynamic potential. This assumption was based on the results obtained from our investigations of the crystals belonging to the ammonium hydrosulfate family [11], which indicate that there is a satisfactory agreement between the experimental and calculated temperature dependences of the electrocaloric effect.

The intensive electrocaloric effect is defined as a change in the temperature of the ferroelectric in response to an external electric field under adiabatic conditions ΔT_{AD}^{ECE} . This parameter can be determined by analyzing the thermodynamic surface P – E – T according to the equation $\Delta T_{AD}^{ECE} = -(T/C_{p,E}) \int (\partial P/\partial T)_{p,E} dE$ [2].

From Fig. 6a, it follows that the intensive electrocaloric effect ΔT_{AD}^{ECE} in PbTiO₃ even in electric fields of ~ 1.5 kV/cm is rather significant and exceeds the corresponding values in the known ferroelectrics [10, 11]. However, the maximum value of $(\Delta T_{AD}^{ECE})_{MAX}$ nonlinearly depends on the electric field strength and tends to saturation (Fig. 6b).

4.3. Barocaloric Effect

In order to evaluate the barocaloric efficiency of PbTiO₃, we used the approach proposed earlier in [11] and based on the analysis of the entropy–temperature–pressure S – T – p diagram. The temperature behavior of the total entropy, which is the sum of the lattice and anomalous contributions $S = S_L + \Delta S_0$, was determined from data on the heat capacity $S =$

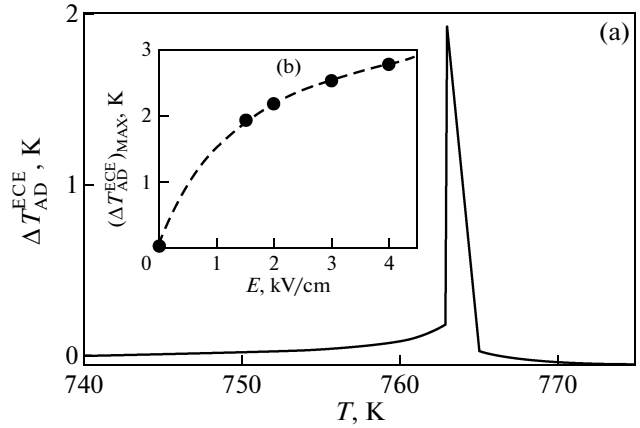


Fig. 6. (a) Temperature dependence of the intensive electrocaloric effect for PbTiO₃ in the electric field $E = 1.5$ kV/cm. (b) Influence of the electric field on $(\Delta T_{AD}^{ECE})_{MAX}$.

$\int (C_p/T) dT$ obtained in our present work. The investigations of the effect exerted by hydrostatic pressure on the permittivity of lead titanate demonstrated [19, 30] that, at pressures $p \leq 1$ kbar, the Curie constant decreases only slightly with an increase in the pressure $dC_{C-w}/dp \approx -4.5 \times 10^3$ K/kbar; i.e., for our sample ($C_{C-w} = 5.7 \times 10^5$ K), this change does not exceed 1%. Therefore, the coefficient A_T in the equation for the thermodynamic potential (1) and, correspondingly, the entropy of the phase transition, which is determined as $\Delta S = A_T P^2$ [29], are not very sensitive to variations in the pressure. The relatively low pressures, of course, will not have a significant effect on the lattice entropy.

As was noted previously, the available data on the pressure coefficient $(dT_0/dp)_{p=0}$ for PbTiO₃ are ambiguous and not always reliable enough. For example, Samara [19] obtained the pressure coefficient $= -(8.4 \pm 0.3)$ K/kbar; however, this author, first, did not determine the value of T_0 at $p = 0$ and used the data taken from [30]. And, second, the dependence $T_0(p)$ was investigated at pressures $p > 13$ kbar with the subsequent extrapolation to the pressure range 0–13 kbar.

With knowledge of information on the dependences $C_p(T)$ and $\alpha(T)$, we can estimate the initial slope of the line of the phase transition $Pm-3m \rightarrow P4mm$ in the T – p phase diagram, which is characterized by the pressure coefficient $(dT_0/dp)_{p=0}$, according to the Pippard equation [22]. The relationship between the quantities $C_p(T)$ and $\beta(T)$ is described by a linear dependence

$$C_p = \beta VT_0 / (dT_0/dp)_{p=0} + \text{const.} \quad (3)$$

Here, $\beta = 3\alpha$ is the coefficient of volume thermal expansion.

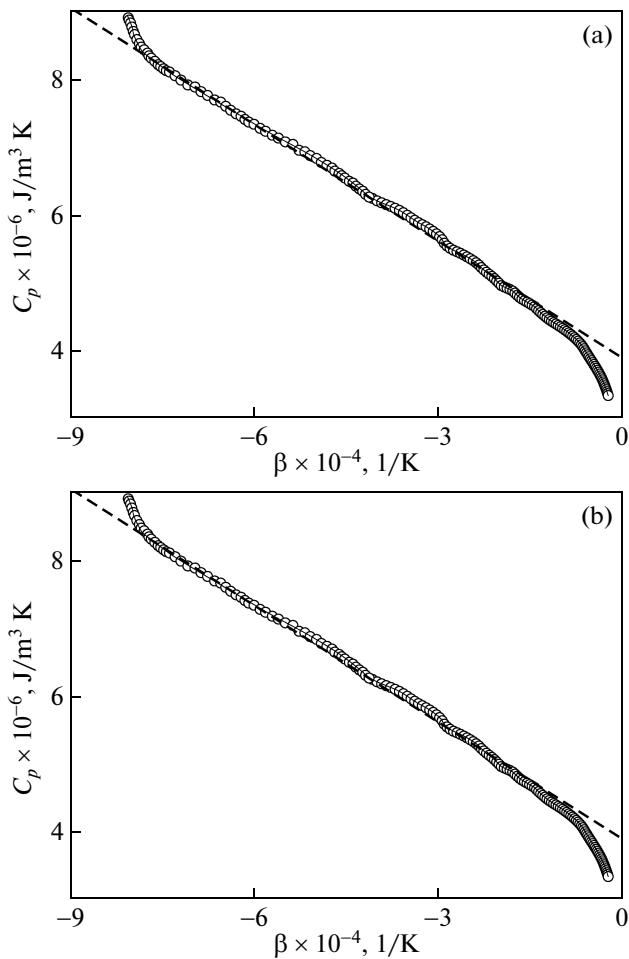


Fig. 7. Relationship between the heat capacity and the coefficient of volume thermal expansion of PbTiO_3 at temperatures (a) $T < T_0$ and (b) $T > T_0$.

Figure 7 presents the experimental data for the ferroelectric and paraelectric phases of PbTiO_3 in accordance with relationship (3). It can be seen from this figure that the expected linear relationship between the heat capacity C_p and the coefficient of volume thermal expansion β holds true at temperatures $T < T_0$ and $T > T_0$ in the ranges 750.6–761.5 and 764.3–767.8 K, respectively. The values of the pressure coefficient $(dT_0/dp)_{p=0}$ for both phases coincide with each other within the limits of the accuracy of their determination $-(14.0 \pm 1.4)$ K/kbar.

The data obtained in this study on the entropy $S(T)$ and the pressure coefficient $(dT_0/dp)_{p=0}$ allow us to estimate the intensive and extensive barocaloric effects, which represent the change in the temperature $\Delta T_{\text{AD}}^{\text{BCE}}$ (at $S = \text{const}$) and the change in the entropy ΔS^{BCE} (at $T = \text{const}$), respectively, under hydrostatic pressure. The position of the anomalous entropy ΔS_0

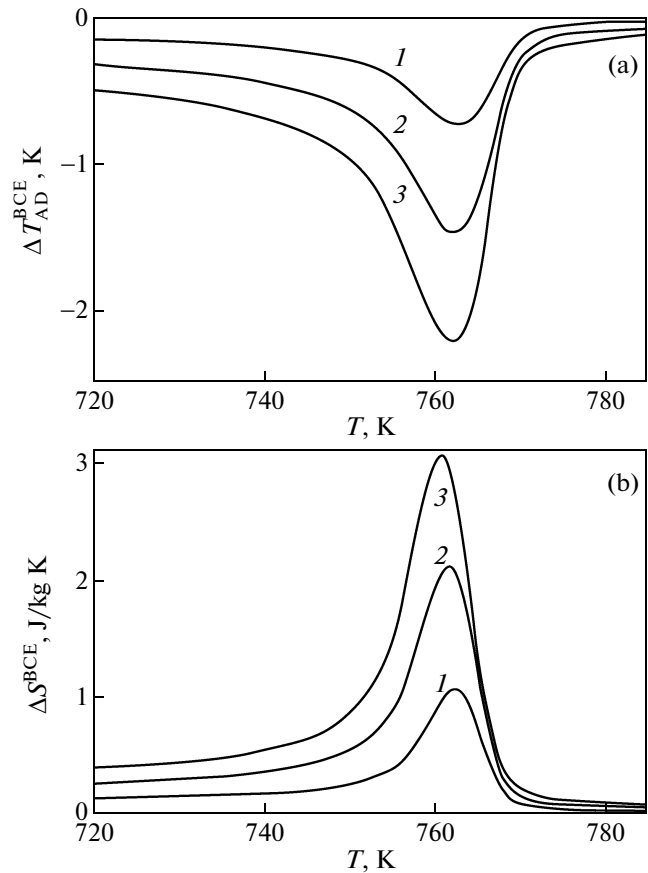


Fig. 8. Temperature dependences of the (a) intensive and (b) extensive barocaloric effects at pressures $p = (1)$ 0.1, (2) 0.2, and (3) 0.3 kbar.

in the dependence $S(T)$ (with respect to the temperature scale) is determined by the pressure coefficient

$$S(T, p) = S_L(T) + \Delta S_0 \left(T + \frac{dT_0}{dp} p \right). \quad (4)$$

The extensive barocaloric effect can be determined as the difference between the total entropies under pressure and without pressure: $\Delta S^{\text{BCE}}(T, p) = S(T, p \neq 0) - S(T, p = 0)$.

The extensive (ΔS^{BCE}) and intensive ($\Delta T_{\text{AD}}^{\text{BCE}}$) barocaloric effects are related by the expression $\Delta T_{\text{AD}}^{\text{BCE}} = -(T/C_p)\Delta S^{\text{BCE}}$ [31]. According to the sign of the pressure coefficient dT_0/dp , the barocaloric effect in PbTiO_3 is reverse; i.e., with an increase in the pressure, the temperature decreases and the entropy increases. The values of the intensive and extensive barocaloric effects, even at relatively low pressures, are very large (Figs. 8a and 8b, respectively).

It is of interest to determine the electric field strength and pressure that are necessary to achieve the same values of ΔT_{AD} and ΔS related to the electroca-

Parameters of the caloric effects in the temperature range of phase transitions in a number of ferroelectrics

Ferroelectric	T_0 , K	E , kV/cm	ΔT_{AD}^{ECE} , K	ΔS^{ECE} , J/kg K	p , kbar	ΔT_{AD}^{BCE} , K	ΔS^{BCE} , J/kg K	References
PbTiO ₃	763	1.5	1.9	-2.2	0.260	-1.9	2.7	
NH ₄ H ₂ SO ₄	160				0.030	1.9	-80	[11]
0.85PMN-0.15PT (ceramics—1 mm)	293	16	1.6					[8]
0.93PMN-0.07PT (film—210 mm)	298	210	2					[9]

loric and barocaloric effects in the same material. For PbTiO₃, the quantities ΔT_{AD}^{ECE} and ΔT_{AD}^{BCE} are equal in magnitude when the electric field strength and hydrostatic pressure are very low (see table). It can also be seen from the table that lead titanate ranks below NH₄H₂SO₄ in barocaloric efficiency due to its giant pressure coefficient $dT/dp = 76.5$ K/kbar [11]. On the other hand, the electrocaloric effect in solid solutions based relaxors is more energy-consuming as compared to PbTiO₃.

5. CONCLUSIONS

The behavior of the anomalous heat capacity of PbTiO₃ over a wide range of temperatures has been satisfactorily described in the framework of the phenomenological theory of phase transitions, which made it possible to reliably determine the coefficients of the thermodynamic potential. The entropy of the phase transition is consistent with the model of disordering of lead atoms in the phase $Pm-3m$, which are ordered in the tetragonal phase. The performed analysis of the electrical equation of state $P(T, E)$ has demonstrated that PbTiO₃ is characterized by large values of the intensive and extensive electrocaloric effects. A relationship between the heat capacity and the thermal expansion in terms of the Pippard equation has been established, and the pressure coefficient $(dT_0/dp)_{p=0}$ has been determined. The barocaloric efficiency has been investigated by analyzing the $S(T, p)$ diagram. It has been shown that the large values of the electrocaloric and barocaloric effects in lead titanate can be achieved at relatively low values of the electric field and hydrostatic pressure.

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