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p, T, E-diagram of $Sn_2P_2S_6$ ferroelectric with high-pressure incommensurate phase

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The investigations on the temperature change in dielectric permeability of $Sn_2P_2S_6$ crystal at different misaligning electric fields and hydrostatic pressures have been carried out to establish the form of p, T, E-diagram for this crystal. Based on the investigations on dielectric permeability anomalies, the E, T-diagrams at different magnitudes of hydrostatic pressure and p, T, E-diagram of $Sn_2P_2S_6$ crystal have been constructed. The magnitudes of coefficients in the thermodynamic potential expansion have been estimated and coordinates of critical points in E, T-diagrams have been defined.

Key words: *ferroelectrics, phase transitions, electric field, hydrostatic pressure*

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It is known that under the action of external hydrostatic pressure an incommensurate (IC) phase and, respectively, Lifshitz point (LP) [1] are induced in the proper $Sn_2P_2S_6$ ferroelectric. To obtain additional information on the character of PT and the peculiarities of a pressure behaviour of the thermodynamic potential expansion coefficients in this crystal it was of great importance to investigate the effect of external electric fields on phase transitions along p,T-diagram. In the given work the results of experimental investigations on the effect of electric field and hydrostatic pressure on temperature dependences of the dielectric permeability of $Sn_2P_2S_6$ crystal are given which were conducted to establish the form of p,T,E-diagram of this crystal.

In figure 1 the E,T-diagrams of $Sn_2P_2S_6$ crystal at different hydrostatic pressures are given. The temperature of phase transition polar-incommensurate phase T_c was defined from the maximum of temperature dependence of the dielectric permeability and the temperature of phase transition symmetric-IC phase T_i was defined from the break in the dependence $\varepsilon^{-1}(T)$. It should be mentioned that in the fields in which

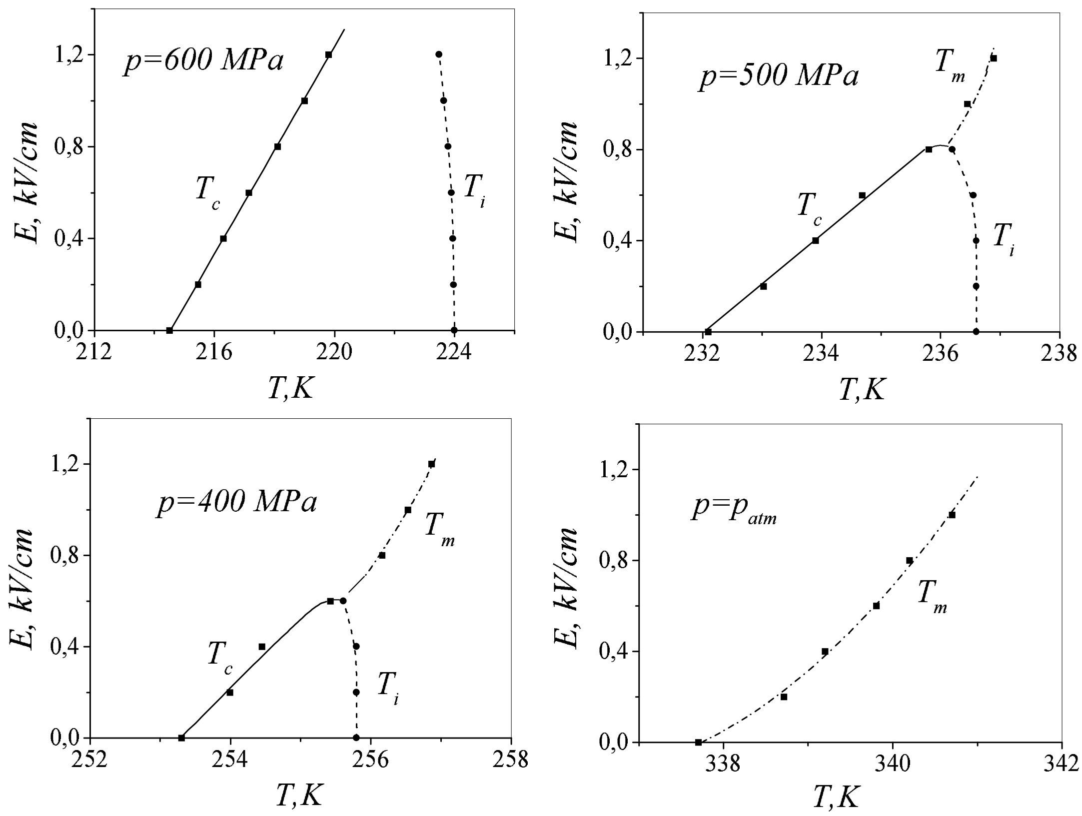

Figure 1. Phase E,T-diagrams of $Sn_2P_2S_6$ crystal at different values of hydrostatic pressure.

IC phase exists the temperature of dielectric permeability maximum T_m coincides with the temperature of phase transition $T_{\rm c}$.

As it is seen, the temperature of PT $T_{\rm c}$ rises linearly with the increasing field, and the temperature T_i falls non-linearly. So, the temperature interval of IC phase existence decreases with the increasing intensity of electric field and at some value of $E = E_{\rm cr}$ it becomes equal to zero. In the fields $E > E_{\rm cr}$ an incommensurate phase is not realized.

Based on E,T-diagrams of $Sn_2P_2S_6$ crystal obtained at different values of hydrostatic pressures the p,T,E-diagram of this crystal is constructed (figure 2). As the hydrostatic pressure causes considerable changes in PT temperatures (approximately 220 K/GPa [1]), and the electric field changes these temperatures for some degrees, the p,T,E-diagram of $Sn_2P_2S_6$ crystals is constructed in respect to the temperature of PT incommensurate-ferroelectric phase $T_{\rm c}$. The first-order PT from incommensurate into polar phase is shown by solid lines. The second-order PT from symmetric into polar phase is shown by dashed lines. The line of AB critical points smoothly enters Lifshitz point. The lines of the dielectric permeability maximum at $E > E_{\rm cr}$ are shown by dash-dot lines that are not assigned to phase transitions.

Let us estimate the magnitudes of coefficients in the thermodynamic potential expansion

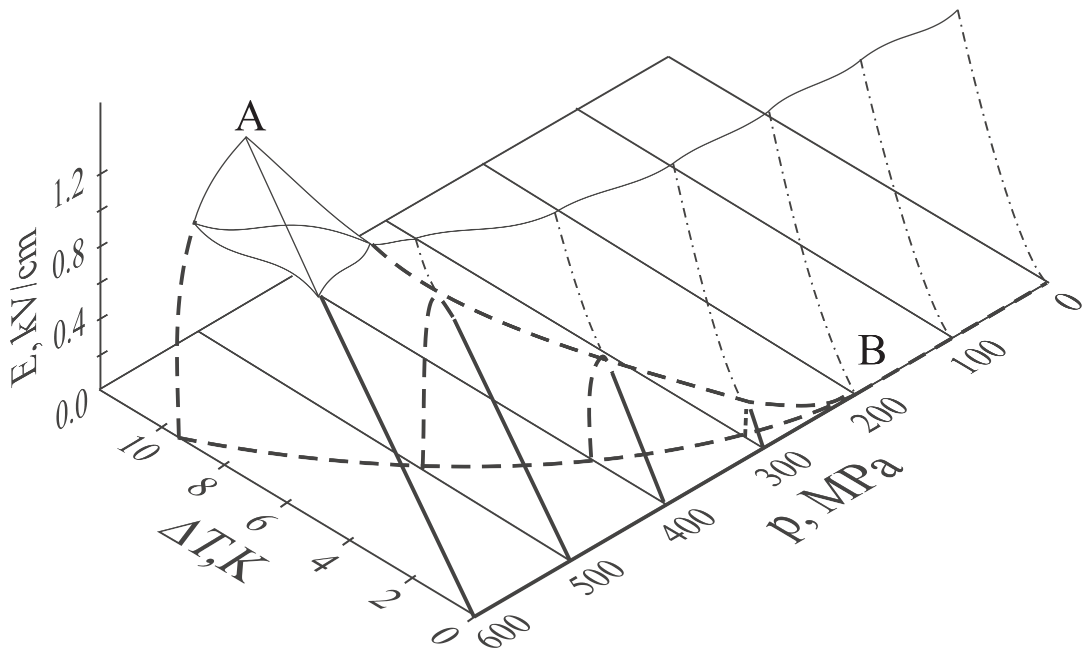

Figure 2. p,T,E-diagram of $Sn_2P_2S_6$ crystal.

$$\Phi = \Phi_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\delta}{2}\left(\frac{\partial P}{\partial z}\right)^2 + \frac{g}{2}\left(\frac{\partial^2 P}{\partial z^2}\right)^2 + \frac{\chi}{2}P^2\left(\frac{\partial P}{\partial z}\right)^2 - PE \ , \quad (1)$$

where $\alpha = \alpha_T(T - T_0)$, $\alpha_T = 1/(\varepsilon_0 C_{\mathrm{w}})$, ε_0 is the electric constant, C_{w} is Curie-Weiss constant. At pressures $p < p_{\mathrm{L}}$ the field dependence of dielectric permeability maximum temperature is given by the expression

$$T_m(E) = T_0 + 1.19\alpha_T^{-1}\beta^{1/3}E^{2/3} \ . \quad (2)$$

From experimental dependences $T_m(E)$ for pressures $p < p_{\mathrm{L}}$, coefficient β in the thermodynamic potential expansion was found. For pressures p_{atm}, 100 MPa, 160 MPa its value was $(8{,}0 \pm 0{,}9) \cdot 10^9$, $(8{,}3 \pm 0{,}9) \cdot 10^9$, $(8{,}4 \pm 0{,}9) \cdot 10^9 \ \mathrm{J \cdot m^5 \cdot C^{-4}}$, respectively. The results of investigations of volume compressibility also testify to the increase of β while approaching LP in p,T-diagram from the side of commensurate PT [2]. However, the values of β defined on the basis of the analysis of experimental dependences $T_m(E)$ are by an order of magnitude greater than the analogous results of dilatometric investigations [2].

In case $\beta > 0$, the superposition of external electric field causes the decrease of the temperature of PT paraelectric-IC phase in accordance with quadratic law [3]

$$T_i(E) = T_i(0) - \frac{48\beta g}{\alpha_T \delta^4}E^2 \ . \quad (3)$$

The temperature of PT ferroelectric-IC phase linearly increases

$$T_{\mathrm{c}}(E) = T_{\mathrm{c}}(0) + \frac{3}{\alpha_T}\left(\frac{\beta g}{2\delta^2}\right)^{1/2} E \ . \quad (4)$$

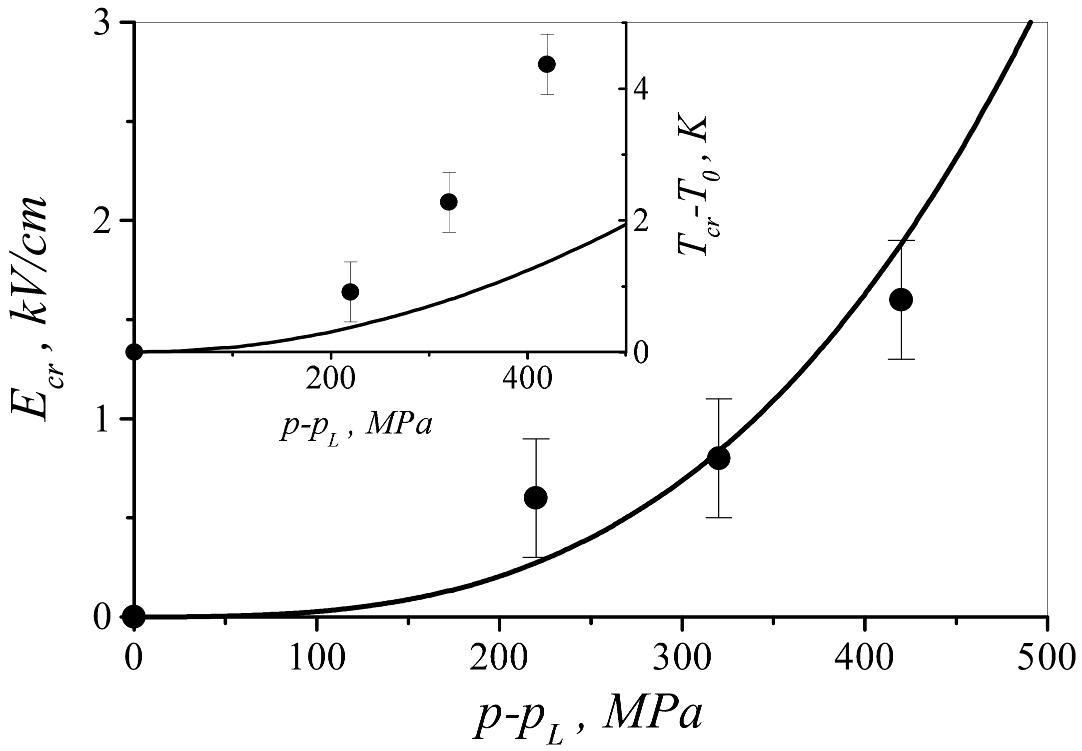

Figure 3. Pressure dependence of the value of critical field for $Sn_2P_2S_6$ crystal. On the insert — a pressure dependence of a critical temperature. By solid lines the calculated values are shown, by points — the experimental values.

Taking in the first approximation a linear dependence of δ coefficient of pressure and taking into account that at $p = p_L$ the value $\delta = 0$ we have

$$\delta(p) = \delta(0) + \frac{\partial\delta}{\partial p}p \quad , \tag{5}$$

where $\delta(0) = 1 \cdot 10^{-10}\,\mathrm{J \cdot m^3 \cdot C^{-2}}$ [4], $(\partial\delta/\partial p) = -5{,}55 \cdot 10^{-13}\,\mathrm{J \cdot m^3 \cdot C^{-2}\ MPa^{-1}}$. The temperature interval of IC phase existence in the absence of the electric field is given by the expression

$$T_i - T_c = \frac{0{,}375}{\alpha_T g}\left(\frac{\partial\delta}{\partial p}\right)^2 (p - p_L) \tag{6}$$

and from the known values $\partial\delta/\partial p$ and α_T we determine the numerical value of the coefficient $g = (1{,}3 \pm 0{,}2) \cdot 10^{-27}\,\mathrm{J \cdot m^5 \cdot C^{-2}}$.

From expression (3), (4) it is seen that the increase in absolute value δ with the increasing pressure has to cause the decrease in coefficients of field shifts of temperatures T_c and T_i while moving away from Lifshitz point. However, within the error of the experiment the change in these coefficients along p,T-diagram of $Sn_2P_2S_6$ crystal is not noticed. A similar situation is also observed along x,T-diagram of $Sn_2P_2(S_{1-x}Se_x)_6$ compounds [5]. Probably, this is connected with the supposition that coefficient g at the change of pressure and concentration Se is constant.

The coordinates of critical point $(E_{\rm cr}, T_{\rm cr})$ in E,T-diagram higher of which IC phase is not realized, are found from the condition $T_i(E) - T_{\rm c}(E) = 0$. Taking into account (3), (4) we get

$$E_{\rm cr} = \frac{\delta^3}{16\beta^{1/2}g^{3/2}} \ , \quad T_{\rm cr} = T_0 + \frac{\delta^2}{16\alpha_T g} \ , \tag{7}$$

where $T_0 = \frac{1}{3}(T_i(0) - 2T_{\rm c}(0))$ [3]. In figure 3 theoretically calculated and experimentally defined values for $E_{\rm cr}$, $T_{\rm cr}$ are given. It is seen, that experimental values of $E_{\rm cr}$ are rather well described by the expression (7), but a pressure change in $T_{\rm cr}$ about three times exceeds the calculated one that may be caused by the stability of coefficients of field shifts for temperatures $T_{\rm c}$ and T_i along p,T-diagram.

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p, T, E-діаграма сегнетоелектрика $Sn_2P_2S_6$ з неспіврозмірною фазою високого тиску

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Проведено дослідження температурної зміни діелектричної проникності кристала $Sn_2P_2S_6$ при різних зміщуючих електричних полях та гідростатичних тисках з метою встановлення виду p, T, E-діаграми цього кристала. На основі досліджень аномалій діелектричної проникності побудовано E, T-діаграми при різних величинах гідростатичного тиску та p, T, E-діаграму кристала $Sn_2P_2S_6$. Проведено оцінку величин коефіцієнтів у розкладі термодинамічного потенціалу та визначено координати критичних точок на E, T-діаграмах.

Ключові слова: *сегнетоелектрики, фазові переходи, електричне поле, гідростатичний тиск*

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