The investigations on the temperature change in dielectric permeability of Sn$_2$P$_2$S$_6$ 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$_2$P$_2$S$_6$ 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$_2$P$_2$S$_6$ 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$_2$P$_2$S$_6$ 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$_2$P$_2$S$_6$ 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
IC phase exists the temperature of dielectric permeability maximum $T_m$ coincides with the temperature of phase transition $T_c$.

As it is seen, the temperature of PT $T_c$ 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 $E = E_{cr}$ it becomes equal to zero. In the fields $E > E_{cr}$ an incommensurate phase is not realized.

Based on $E,T$-diagrams of Sn$_2$P$_2$S$_6$ 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$_2$P$_2$S$_6$ crystals is constructed in respect to the temperature of PT incommensurate-ferroelectric phase $T_c$. 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 $E > E_{cr}$ 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

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{diagram.png}
\caption{Phase $E,T$-diagrams of Sn$_2$P$_2$S$_6$ crystal at different values of hydrostatic pressure.}
\end{figure}
\[ \Phi = \Phi_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\delta}{2} \left( \frac{\partial P}{\partial z} \right)^2 + \frac{g}{2} \left( \frac{\partial^2 P}{\partial z^2} \right)^2 + \frac{\chi}{2}P^2 \left( \frac{\partial P}{\partial z} \right)^2 - PE , \]  

(1)

where \( \alpha = \alpha_T(T - T_0) \), \( \alpha_T = 1/(\varepsilon_0 C_w) \), \( \varepsilon_0 \) is the electric constant, \( C_w \) is Curie-Weiss constant. At pressures \( p < p_L \) the field dependence of dielectric permeability maximum temperature is given by the expression

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

(2)

From experimental dependences \( T_m(E) \) for pressures \( p < p_L \), coefficient \( \beta \) in the thermodynamic potential expansion was found. For pressures \( p_{\text{atm}}, \) 100 MPa, 160 MPa its value was \((8,0 \pm 0,9) \cdot 10^9, (8,3 \pm 0,9) \cdot 10^9, (8,4 \pm 0,9) \cdot 10^9 \text{J} \cdot \text{m}^5 \cdot \text{C}^{-4} \), respectively. The results of investigations of volume compressibility also testify to the increase of \( \beta \) while approaching LP in \( p,T \)-diagram from the side of commensurate PT [2]. However, the values of \( \beta \) 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]

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

(3)

The temperature of PT ferroelectric-IC phase linearly increases

\[ T_c(E) = T_c(0) + \frac{3}{\alpha_T} \left( \frac{\beta g}{2\delta^2} \right)^{1/2} E . \]  

(4)
Taking in the first approximation a linear dependence of $\delta$ coefficient of pressure and taking into account that at $p = p_L$ the value $\delta = 0$ we have

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

where $\delta(0) = 1 \cdot 10^{-10} \text{ J} \cdot \text{m}^3 \cdot \text{C}^{-2}$ [4], $\frac{\partial \delta}{\partial p} = -5.55 \cdot 10^{-13} \text{ J} \cdot \text{m}^3 \cdot \text{C}^{-2} \text{ MPa}^{-1}$. The temperature interval of IC phase existence in the absence of the electric field is given by the expression

$$T_i - T_c = \frac{0.375}{\alpha_T g} \left( \frac{\partial \delta}{\partial p} \right)^2 (p - p_L)$$

and from the known values $\partial \delta/\partial p$ and $\alpha_T$ we determine the numerical value of the coefficient $g = (1.3 \pm 0.2) \cdot 10^{-27} \text{ J} \cdot \text{m}^5 \cdot \text{C}^{-2}$.

From expression (3), (4) it is seen that the increase in absolute value $\delta$ 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 $\text{Sn}_2\text{P}_2\text{S}_6$ crystal is not noticed. A similar situation is also observed along $x,T$-diagram of $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ compounds [5]. Probably, this is connected with the supposition that coefficient $g$ at the change of pressure and concentration Se is constant.

Figure 3. Pressure dependence of the value of critical field for $\text{Sn}_2\text{P}_2\text{S}_6$ crystal. On the insert — a pressure dependence of a critical temperature. By solid lines the calculated values are shown, by points — the experimental values.
The coordinates of critical point \((E_{cr}, T_{cr})\) in \(E,T\)-diagram higher of which IC phase is not realized, are found from the condition \(T_i(E) - T_c(E) = 0\). Taking into account (3), (4) we get

\[
E_{cr} = \frac{\delta^3}{16\beta^{1/2}\eta^{3/2}}, \quad T_{cr} = T_0 + \frac{\delta^2}{16\alpha T\eta},
\]

where \(T_0 = \frac{4}{3}(T_i(0) - 2T_c(0))\) [3]. In figure 3 theoretically calculated and experimentally defined values for \(E_{cr}, T_{cr}\) are given. It is seen, that experimental values of \(E_{cr}\) are rather well described by the expression (7), but a pressure change in \(T_{cr}\) about three times exceeds the calculated one that may be caused by the stability of coefficients of field shifts for temperatures \(T_c\) and \(T_i\) along \(p,T\)-diagram.

References

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Проведено дослідження температурної зміни діелектричної проникності кристала $\text{Sn}_2\text{P}_2\text{S}_6$ 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 $\text{Sn}_2\text{P}_2\text{S}_6$. 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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