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Phase transitions in $Sn_2P_2S_6$ ferroelectric under high pressures

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We have made dilatometric studies of phase transitions in $Sn_2P_2S_6$ ferroelectric under high hydrostatic pressures. We investigated the pressure dependence of the coefficients in an expansion of the thermodynamic potential in the order parameter in the vicinity of the Lifshitz point.

Key words: *pressure, ferroelectrics, compressibility*

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The $Sn_2P_2S_6$ monoclinic crystals are proper ferroelectrics, whose unit cell parameters under standard conditions are a=9.378Å, b=7.488Å, c=6.513Å and β=91.150° [1]. Under atmospheric pressure $p = p_{\mathrm{atm}}$ a temperature increase induces a phase transition (PT) $T_0 = 337K$ into a nonpolar phase with a change of symmetry from P_c to $P2_1/c$. By means of a uniform compression ($p = 180\mathrm{MPa}$) we can also realize the $Sn_2P_2S_6$ crystal transition from the ferroelectric state into the paraelectric state at temperature T=296K.

The investigation of the p,T-diagram of the $Sn_2P_2S_6$ ferroelectric showed that an external hydrostatic pressure induces a high pressure incommensurate phase in this crystal. The multicritical point of p,T-diagram, where a splitting of the commensurate p,T-line $T_0(p)$ into a line $T_i(p)$ and a line $T_c(p)$ bordering the incommensurate phase region occurs, is the Lifshitz point.

For the purpose of further PT and critical behaviour investigation of $Sn_2P_2S_6$ crystal in the vicinity of Lifshitz point, induced by external pressure, we have made pressure behaviour studies and analysis of pressure dependencies for linear and volume compressibilities in the present paper.

The linear compressibilities under uniform compression were determined by the experimental pressure dependencies of the linear deformations, which were obtained by means of optical interference technique [3] proposed previously. In this case, the directions of measurements coincided with crystallographic directions [100], [010], and [001]. The test specimens for experiments were prepared from $Sn_2P_2S_6$ crystals grown by Bridgeman method. The studies were performed in an optical pres-

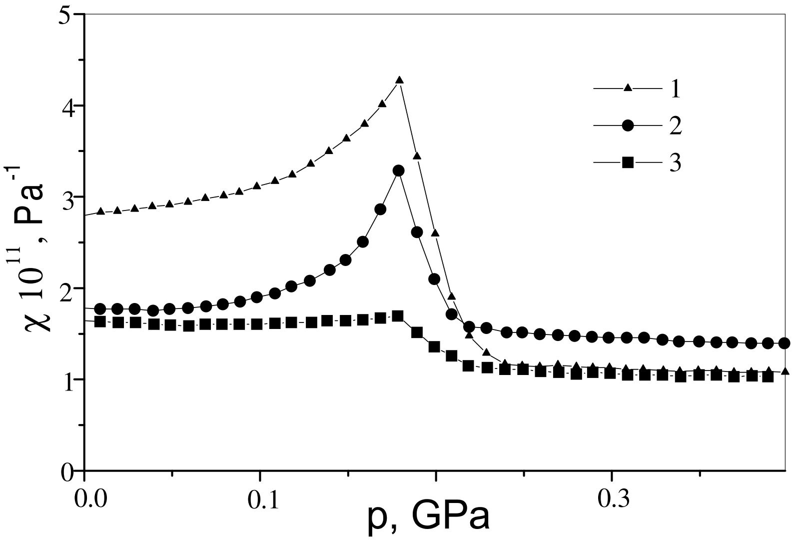

Figure 1. The pressure dependencies of linear compressibility of the $Sn_2P_2S_6$ crystal for crystallographic axes : 1 — [100]; 2 — [010]; 3 — [001].

sure chamber. The pressure measurement was taken by mechanical and manganin manometers with an accuracy of $\pm$5MPa and temperature was taken by a copper-constantan thermocouple with an accuracy of $\pm$0.1K.

In figure 1 the pressure dependencies for linear compressibilities of $Sn_2P_2S_6$ crystal are shown in various crystallographic directions. It can be seen, that in the vicinity of the PT (p=180Mpa) an anomalous behaviour of linear compressibility occurs for all three directions. The change of the $\chi_{[100]}$ and $\chi_{[010]}$ values at the PT is more significant, than $\chi_{[100]}$ change. This is in agreement with the results of a dilatometric investigation of the temperature expansion coefficient of $Sn_2P_2S_6$ crystals [4] and points to the fact; that the basic structural changes at the PT take place along the crystallographic directions [100] and [010]. This PT may be connected with synphase and antisynphase shifts of Sn^{+2} ferroactive cation. In the paraelectric phase further away from the PT the $\chi_{[100]}$ value is closer to the $\chi_{[001]}$ value than the $\chi_{[010]}$ value. For the [010] direction one observes the smallest value of the thermal conductivity coefficient [5] and the linear thermal expansion coefficient [4]. The anomalous part of the compressibility in the ferroelectric phase $\chi^{\mathrm{an}} = \chi - \chi^{\mathrm{reg}}$ (χ^{reg} is the χ value in paraelectric phase) reveals that at $p = p_{\mathrm{atm}}$ the values obey $\chi^{\mathrm{an}}_{[100]} > \chi^{\mathrm{an}}_{[100]} \neq 0$ and $\chi^{\mathrm{an}}_{[010]} = 0$.

In figure 2 the pressure dependence of the volume compressibility of the $Sn_2P_2S_6$ crystal at $T = 296$K are given. In the insert the critical index dependence α_{cr} of $\ln(\tau)$ (where $\alpha_{\mathrm{cr}} = (p - p_o)/p_o$) is given which characterizes an anomalous behaviour of the volume compressibility in the vicinity of the PT ($p = p_{\mathrm{atm}}$). For $-2 < \ln(\tau) < 0$ the α_{cr} is close to the value of $0.30 + 0.03$, which is characteristic to the Lifshitz point. With further decreasing τ the α_{cr} value monotonically decreases to 0.20. Such a dependence of the α_{cr} is, probably, connected with the transition from multicritical to critical behaviour.

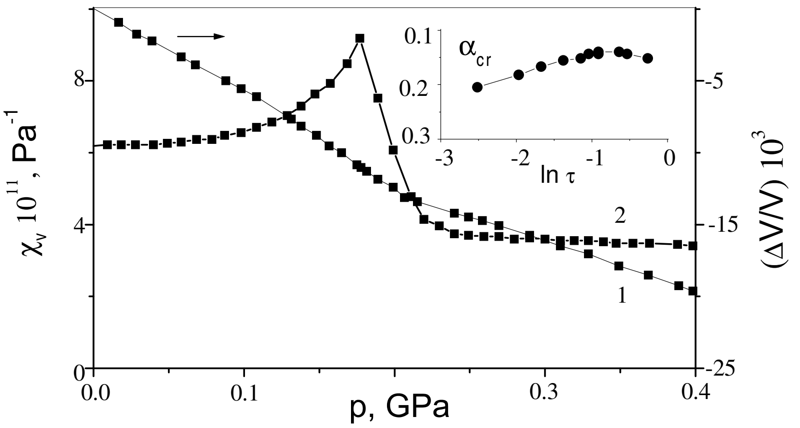

Figure 2. The pressure dependencies of $\Delta V/V$ value (1) and $\chi(p)$ volume compressibility (2) of the $Sn_2P_2S_6$ crystal at $T = 296$K (in the insert — the pressure dependencies of α_{cr} critical compressibility index).

Using the results of investigations obtained for linear compressibilities of $Sn_2P_2S_6$ crystal and s_{11}, s_{22}, s_{33} compliances values [6], the shearing components of s_{11}, s_{22}, s_{33} compliances tensor are defined. The calculated values are $-2.25 \cdot 10^{-11}\text{Pa}^{-1}$, $-0.55 \cdot 10^{-11}\text{Pa}^{-1}$, $-0.15 \cdot 10^{-11}\text{Pa}^{-1}$, respectively. Taking into account these data the components of stiffness tensor: $c_{11} = 2.30 \cdot 10^{10}$Pa, $c_{22} = 3.10 \cdot 10^{10}$Pa, $c_{33} = 4.45 \cdot 10^{10}$Pa and the velocities of a longitudinal elastic wave for different directions: $v_{[100]} = 2.55 \cdot 10^3$m/s,$v_{[010]} = 2.96 \cdot 10^3$m/s, $v_{[001]} = 3.55 \cdot 10^3$m/s are also defined. These results are in good agreement with experimental ones for the ultrasound velocity in $Sn_2P_2S_6$ crystal [7] (which at room temperature are equal to $2.62 \cdot 10^3$m/s, $2.97 \cdot 10^3$m/s and $3.75 \cdot 10^3$m/s, respectively).

In figure 3 the pressure dependencies of the $\chi_{[100]}$ linear compressibility at different temperatures are given. These results enabled us to study the transformation of the $\chi(p)$ dependencies along the p,T-diagram. For temperatures $T < 296$ K the $\chi(p)$ behaviour is different from similar dependencies obtained at $T > 296$ K. Thus, at $T = 272$K the two PT, namely p_c and p_i, with the pressure range of $\Delta p = 11.6$ MPa are revealed which limit the region of the incommensurate phase. With the further temperature decreasing the $p_c - p_i$ pressure width increases (at $T = 274.5$ K $\Delta p = 21.6$ MPa). The values of p_c and p_i pressures at different temperatures are in good agreement with the p,T phase diagram of $Sn_2P_2S_6$ crystal (figure 3) based on the complex optical, dielectric and pyroelectric studies. For curves 4–6 in comparison with curves 1–3 (figure 3) in the pc region (ferroelectric-incommensurate phases) the maximum value of isothermic compressibility $\chi_{\max}$ increases and the pressure width of an anomalous behaviour of the $\chi(p)$ in the vicinity of the PT simultaneously decreases which is explained by the first-order character of this PT.

The PT in proper $Sn_2P_2S_6$ ferroelectric in the liquid-like crystal model approximation at one-dimensional modulation in the incommensurate phase may be described by the density expansion of the thermodynamic potential Φ in the order

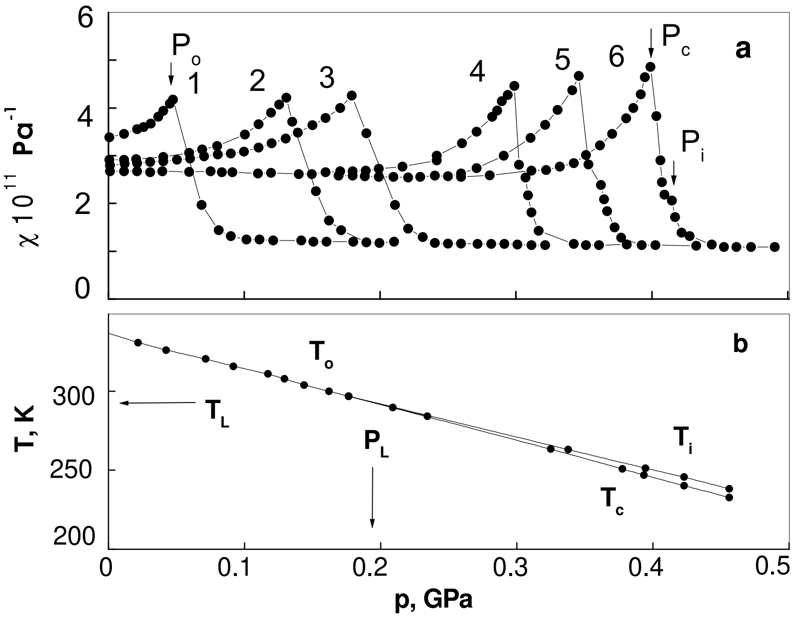

Figure 3. a) The pressure dependencies of $\chi_{[100]}$ linear compressibility of the $Sn_2P_2S_6$ crystal : 1 – T = 327K; 2 – 307; 3 – 296; 4 – 272; 5 – 260; 6 – 247.5. b) The phase p,T-diagram of the $Sn_2P_2S_6$ crystal.

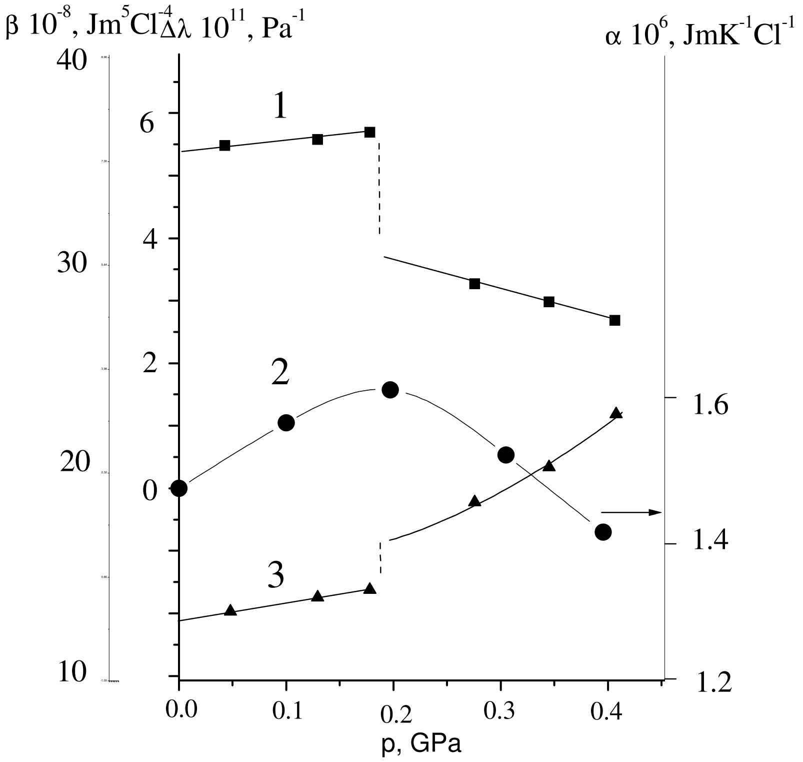

Figure 4. The pressure dependencies of $\Delta\chi_V$ (1), α_0 (2), β (3) values of the $Sn_2P_2S_6$ crystal.

parameter $\eta = P_s$ with the account of its spacious derivatives:

$$\Phi = \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\gamma}{6}\eta^6 + \frac{\delta}{2}(\frac{\partial\eta}{\partial z})^2 + \frac{g}{2}(\frac{\partial^2\eta}{\partial z^2})^2 + \dots\ , \tag{1}$$

where $\alpha = \alpha_0(T - T_0)$, β, γ, δ and g are the expansions coefficients which are generally pressure-dependent. The value $\alpha_0 = 1/\varepsilon_0 C_w$ value, where C_w - Curie-Weiss constant.

For second-order PT, that is the PT at p_0 and p_i, by the $\Delta\chi_V$ compressibility jump and the known of α_0, $\mathrm{d}T_0/\mathrm{d}p$ and $\mathrm{d}T_i/\mathrm{d}p$ and by using a common relation

$$\Delta\chi_V = \frac{\alpha_0}{2\beta}\left(\frac{\mathrm{d}T_{0(i)}}{\mathrm{d}p}\right)^2 \tag{2}$$

one may define the β coefficient in the thermodynamic potential expansion (1). In figure 4 the pressure dependencies of $\Delta\chi_V$, α_0, β values along the p,T-diagram are shown. At the pressure $p_{\mathrm{L}} = 180$ MPa corresponding to the Lifshitz point in the p,T-diagram an anomalous character of all three indicated values occurs. Thus, in the point of line splitting for continuous phase transitions $T_0(p)$ at $p = p_{\mathrm{L}} = 180$ MPa the α_0 value is the maximum value. The $\beta > 0$ coefficient undergoes a jump equal to $\Delta \approx 2.2 \cdot 10^8 Jm^5/Cl^4$. According to [8], under the given pressure the δ coefficient tends to 0, and the values of γ and g in the expansion (1) are practically not pressure-dependent ($\gamma \approx 3.5 \cdot 10^{10} Jm^9/Cl^6$, $g = 2.2 \cdot 10^{-27} Jm^5/Cl^2$).

The experimental behaviour of α_0 [9] testifies to the enhancement of ferroactive normal mode unharmonicity with approaching the Lifshitz point. The Δ jump in the change of β in this point confirms the results of theoretical investigations [10]. Thus, considering (1), and taking into account its elastic part and an additional higher-order term in the form of $(\frac{\lambda}{2})\eta^2\eta'^2$ it has been shown that between homogeneous and inhomogeneous deformations the "gap" Δ is formed, conditioned by long-range elastic forces.

So, the dilatometric investigations of the PT in $Sn_2P_2S_6$ crystal carried out at high pressures enabled us to define the change of the coefficients in the expansion of the thermodynamic potential and critical compressibility index in the vicinity of the Lifshitz point along the PT-diagram.

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Фазові переходи в сегнетоелектриках $Sn_2P_2S_6$ при високих тисках

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Проведені дилатометричні дослідження фазових переходів в сегнетоелектриках $Sn_2P_2S_6$ в умовах високих гідростатичних тисків. Встановлені баричні залежності коефіцієнтів розкладу термодинамічного потенціалу в ряд за степенями параметра порядку в околі точки Ліфшиця.

Ключові слова: *тиск, сегнетоелектрики, стисливість*

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