Pressure behaviour of the birefringence in $Sn_2P_2(S_{1-x}Se_x)_6$ crystals in the vicinity of the Lipshitz point

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Abstract

The temperature dependences of the birefringence of $Sn_2P_2(S_{1-x}Se_x)_6$ ferroelectric crystals with x=0; 0.1 and 0.2 at high hydrostatic pressures (to 0.4 GPa) have been investigated. On the base of the analysis of the birefringence behaviour in the region of the phase transition the β critical exponent of the order parameter and the α thermal capacity have been determined. The pressure dependences for investigation of crystals in the vicinity of the Lifshitz point have been built.

Key words: birefringence, ferroelectrics, phase transitions, hydrostatic pressure

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Introduction

$Sn_2P_2(S_{1-x}Se_x)_6$ crystals are the proper ferroelectrics. In their p,T,x-diagram the line of policritical points – the Lifshitz points (LP) is realized [1]. At atmospheric pressure the $Sn_2P_2S_6$ crystals undergo the phase transition of the second type at T=336 K with the symmetry change $Pc \rightarrow P2_1/c$. The Lifshitz point is realized at p_{LP}=0.18 GPa and T_{LP}=295 K. The increase of the Se concentration leads to the shift of the LP towards the region of less pressure [1].

In the paper under consideration the results of the investigation of birefringence in the $Sn_2P_2(S_{1-x}Se_x)_6$ crystals (for x<0.3) along the p,T-diagram are given. As it is known, for the proper ferroelectrics the anomalous part of the birefringence is proportional to the square of spontaneous polarization $\Delta n \sim P_s^2 \sim \tau^{-2\beta}$ (where $\tau=(T-T_0)/T_0$ – reduced temperature), but the first derivative by temperature is proportional to the anomalous part of the specific heat $d\Delta n(T)/dT \sim C_p \sim \tau^{-\alpha}$. This gives the opportunity to determine the behaviour of the critical exponent by the experimental dependences $\Delta n(T)$ and to estimate the behaviour of the coefficients of the thermodynamic potential decomposition for these crystals in the vicinity of the Lifshitz point.

Experimental

In the given work the investigation of the temperature dependence of the $\Delta n(T)$ birefringence of the $Sn_2P_2(S_{1-x}Se_x)_6$ crystals with x=0, 0.1, 0.2 at different fixed values of hydrostatic pressure was carried out. Measuring of $\Delta n(T)$ was conducted by the Senarmont method on the wave length λ=0,6328 μm. In the experiment the change of rotation angle $\Delta\varphi$ of the analyzer was fixed. It was proportional to the change of Δn birefringence.

The $Sn_2P_2(S_{1-x}Se_x)_6$ monocrystals under investigation, obtained by the gas-transport reaction method, were made in the form of

plates (001) and (010) section with linear dimensions 1×3×3 mm^3. The sample was inside the three-window optic chamber, where pressure was made by means of the high pressure setting. Technical benzene of fine purification was used as the working liquid. The β value was determined by the inclination of $\Delta\varphi \sim f(\tau)$ dependences, built in the double logarithmic scale with correlation $\ln(\Delta\varphi) \sim 2\beta\ln(\tau)$.

Result and discussion

Anomalies are observed on the temperature dependences of $\Delta\varphi(T)$ for $Sn_2P_2(S_{1-x}Se_x)_6$ crystals in the temperature region T_0=336 K for x=0, T_0=316 K for x=0.1, T_0=298 K for x=0.2. These anomalies are connected with the presence of the ferroelectric phase transition of the second type in the given materials. The increase of the value of hydrostatic pressure leads to the shift of these anomalies towards the area of low temperatures with baric coefficients:
dT_0/dp= -220 K/GPa for x=0,
dT_0/dp= -224 K/GPa for x=0.1 and
dT_0/dp= -226 K/GPa for x=0.2, which are coordinated with the results of dielectric investigations. Fig.1 presents the dependences of the anomalous part of $\Delta\varphi$ on the temperature for $Sn_2P_2(S_{1-x}Se_x)_6$ crystals at different values of hydrostatic pressure. As it can be observed the increase of p leads to the decrease of the birefringence values in the ferroelectric phase and to more sudden alternation in the region of the phase transition.

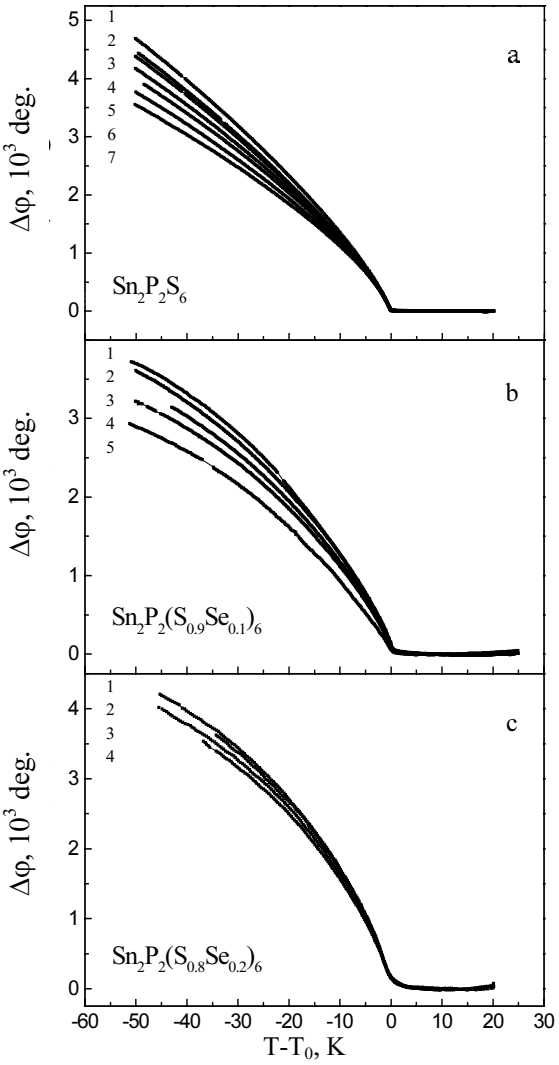

Fig.1. Temperature dependences of the anomalous part of rotation angle of $Sn_2P_2(S_{1-x}Se_x)_6$ crystals at different values of hydrostatic pressure, bar: a) 1–0; 2–170; 3–510; 4–700; 5–1020; 6–1290; 7–1640. b) 1–100; 2–135; 3–405; 4–740; 5–1120. c) 1–30; 2–65; 3–195; 4–300.

By means of the dependences of $\Delta\varphi(T)$ and $d\Delta\varphi/dT$ for $Sn_2P_2(S_{1-x}Se_x)_6$ crystals the values of the critical exponent for the α the thermal capacity and for the β order parameter were defined. In the ferroelectric phase of $Sn_2P_2(S_{1-x}Se_x)_6$ the anomalous part of birefringence satisfies the correlation of $d\Delta\varphi/dT \sim \tau^{-\alpha}$ with the critical exponent $\alpha \approx 0.5$. Taking into account the contribution of static defects, in the paraelectric phase the anomalous part of birefringence can be represented as: $d\Delta\varphi/dT \sim A\tau^{-0.5}+B\tau^{-1.5}$. Here coefficient A determines the contribution of fluctuations, coefficient B determines the contribution of defects [2]. On the change of the chemical composition in $Sn_2P_2(S_{1-x}Se_x)_6$ crystals from the value x=0 to x=0.2 (Fig.2) the increase of the contribution of defects into critical anomaly from B/A=10^{-3} to 10^{-2} is observed. The increase of the protraction on the dependences of $d\Delta\varphi/dT$ in paraelectric phase testifies to that fact. Analogus behaviour of A and B coefficient relation for these solid solutions was observed also in [3]. The increase of hydrostatic pressure

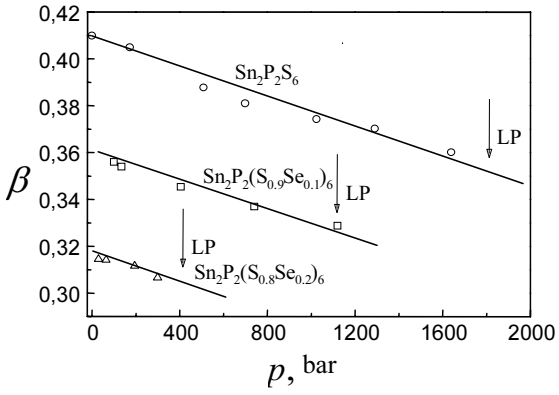

Fig.2. The pressure dependences of the β critical exponent of order parameter of $Sn_2P_2(S_{1-x}Se_x)_6$ crystals.

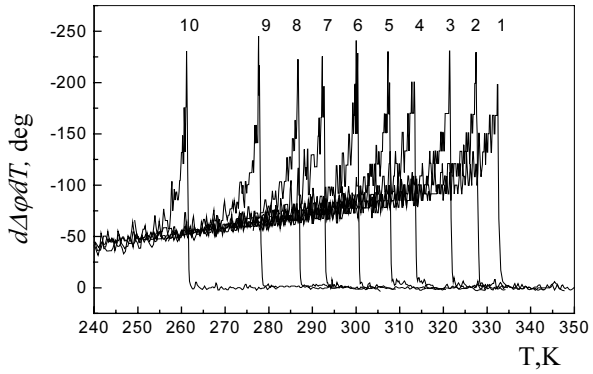

Fig.3. The temperature dependences of the derivative from the anomalous component of birefringence $d\Delta\varphi/dT$ for $Sn_2P_2S_6$ crystals at different p, bar: 1–0; 2–170; 3–510; 4–700; 5–1020;6–1290; 7–1640: 8–2300; 9–2590; 10–3500.

essentially did not change the B/A proportion for the given crystals.

Fig. 2 gives the pressure dependencies of the β critical exponent of the order parameter for $Sn_2P_2(S_{1-x}Se_x)_6$ crystals. It is evident, that at the atmospheric pressure, the increase of the Se content decreases the β value from 0.41 for x=0 to 0.3 for x=0.2.

It can be explained by approaching the Lifshitz point on the concentration x,T-diagram $(x_{LP}=0.28)$, that it well agrees with the results of work [2]. The pressure increase leads to the linear decrease of β from the values β_{atm}=0.41 at p=p_{atm} to β_{LP}=0.35 for $Sn_2P_2S_6$ and from β_{atm}=0.36 to β_{LP}=0.33 for $Sn_2P_2(S_{0.9}Se_{0.1})_6$ and from β_{atm}=0.32 to β_{LP}=0.3 for $Sn_2P_2(S_{0.8}Se_{0.2})_6$. Thus, on the line of polycritical points at the p,T,x-diagram of $Sn_2P_2(S_{1-x}Se_x)_6$ crystals the critical index of the order parameter decreases and gets the value from β_{LP}=0.35 for $Sn_2P_2S_6$ to β_{LP}=0.3 for $Sn_2P_2(S_{0.8}Se_{0.2})_6$ and is close to the theoretically expected value β=1/3, which is received for the LP on the approaching the medium field [3-5].

It is known, that the derivation by the temperature of the anomalous part of birefringence is proportional to the anomalous part of $d\Delta\varphi/dT \sim C_p$ thermal capacity.

Hence by means of transformation of temperature dependencies of the $d\Delta\varphi/dT$ (Fig.3) value it is possible to estimate the pressure behaviour of B and C coefficients of the thermodynamic potential density

$$F=F_o+AP_s^2+BP_s^4+CP_s^6+$$

$$\delta(dP_s/dz)^2+g(d^2P_s/dz^2)^2+\dots\ .$$

For the $Sn_2P_2S_6$ crystal such an estimation displays that the increase of the hydrostatic pressure on approaching the polycritical point leads to the increase of the B and C values. It testifies to the fact that a polycritical point at the p,T-diagram of $Sn_2P_2S_6$ crystals is realized at the positive values β and this point is the Lifshitz point. The hydrostatic pressure causes the removal from the possible tricritical LP.

References

1. Slivka A.G., Gerzanich E.I., Guranich P.P. et.al. Ferroelectrics, **103** (1990) 71.
2. Isaverdiyev A.A., Lebedyev N.I., Levanyuk A.P. et.al., Fiz. Tverd. Tela, **31** (1989) 272 (in Russian).
3. Vysochanskii Yu.M., Mytrovcij V.V., Grabar A.A. et.al., Ferroelectrics, **237** (2000) 193.
4. Folk R., Moser G., Phys. Rev. B, **47** (1993) 1392.
5. Nasser I., Abdel-Hady A., Folk R., Phys. Rev. B, **56** (1997) 154.