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Dielectric properties of $CuInP_2S_6$ crystals under high pressure

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Dielectric properties of $CuInP_2S_6$ layered crystals in the range of ferrielectric phase transition are studied under hydrostatic pressure. The pressure dependence of the phase transition temperature testifies to the phase transition being of the order/disorder type. The (p,T) phase diagram of $CuInP_2S_6$ crystals has been constructed.

Key words: *phase transitions, ferrielectrics, pressure, dielectric properties*

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1. Introduction

Monoclinic $CuInP_2S_6$ crystals undergo a phase transition from paraelectric (C2/c) to ferrielectric (Cc) phase. The studies of ferrielectric phase transition in the layered $CuInP_2S_6$ crystals at atmospheric pressure have shown [1,2] that polarization in these crystals arises at the first-order phase transition, normally to the layers, and results from anticollinear contributions due to copper ion ordering and indium ion displacement. The sponatneous polarization value is $P_s = 2.5\ \mu\mathrm{C}\cdot\mathrm{cm}^{-2}$.

While physical properties at high hydrostatic pressures of “3–D” $Sn_2P_2S_6$-type crystals have been well investigated earlier [3,4] the studies of “2–D” (layered) hypothiodiphosphates under high pressure are at the initial stage. The only paper devoted to this problem reported on a pressure-induced first-order phase transition from the monoclinic to the trigonal phase observed in $CuInP_2S_6$ crystals at $p = 4.0$ GPa at room temperature from Raman measurements [5].

The present paper is devoted to the study of the hydrostatic pressure effect ($p_{\mathrm{atm}} < p <$ 0.4 GPa) on the dielectric properties of $CuInP_2S_6$ crystals and to the determination of their (p,T) phase diagram.

2. Experimental

The crystals were grown using the Bridgman techniques. The samples were the plates 0.2 to 1.6 mm thick with the silver paste or aquadag electrodes applied to their surfaces. The complex dielectric permeability was measured in the temperature range from 77 to 450 K with temperature variation rate of 1 K/min, using an AC bridge at frequencies of 1 kHz and 1 MHz.

3. Results and discussion

Figure 1 presents temperature dependences of dielectric permeability of $CuInP_2S_6$ crystals obtained at the measuring field frequencies of 1 kHz and 1 MHz. At atmospheric pressure the maximum of dielectric permeability, corresponding to the phase transition temperature in the crystals under investigation is observed at the temperature $T_{\mathrm{c}} \approx 315$ K. The increase of dielectric permeability at 1 kHz (curve 1 in figure 1) in the temperature range above 330 K is due to ionic conductivity of Cu atoms [1]. It should be noted that for the investigated samples, a temperature hystheresis $\Delta T \approx 1.7$ K of the phase transition is observed. This value is much lower than those observed for $\mathrm{CuInP_2S_6}$ crystals in [1] and is in good agreement with the results of [2].

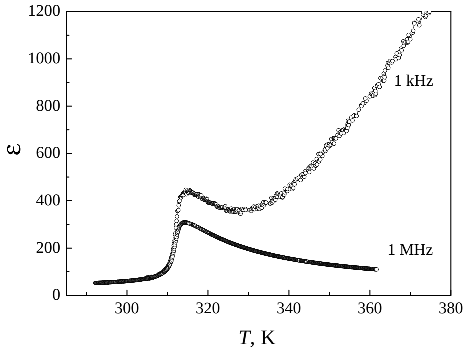

Figure 1. Temperature dependences of $\mathrm{CuInP_2S_6}$ crystals dielectric permeability in the heating mode at the measuring field frequencies of 1 kHz (1) and 1 MHz (2).

The studies of dielectric properties of $\mathrm{CuInP_2S_6}$ crystals at atmospheric pressure have shown a considerable dependence of the dielectric permeability on the sample thickness. In our opinion, it can be responsible for the difference in the dielectric permeability maximum values ($140 < \varepsilon_{\max} < 900$) obtained by different authors [1,2].

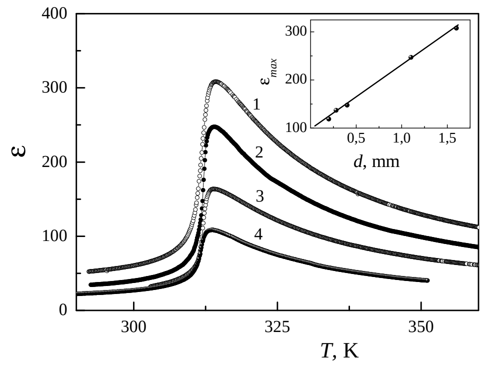

Figure 2. Temperature dependences of $\mathrm{CuInP_2S_6}$ crystal dielectric permeability at different values of the crystal thickness D: 0.2 mm (1); 0.4 mm (2); 1.1 mm (3); 1.3 mm (4) at the measuring field frequency of 1 MHz. The insert shows the dependence of the dielectric permeability maximum value on the crystal thickness.

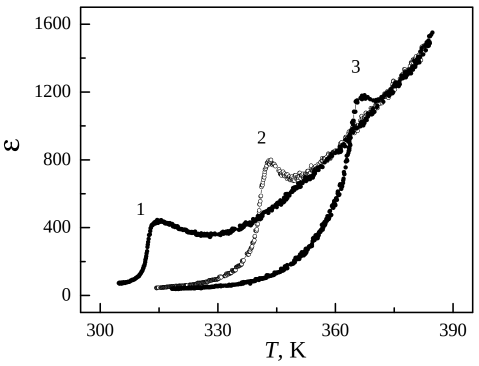

Figure 3. Temperature dependences of $\mathrm{CuInP_2S_6}$ crystal dielectric permeability at the measuring field frequency of 1 kHz at atmospheric pressure (1) and at hydrostatic pressure values of 128 MPa (2) and 248 MPa (3).

Temperature dependences of dielectric permeability of $\mathrm{CuInP_2S_6}$ crystals ware measured for the samples of the same cross-section ($S \approx 12$ mm^2) but of different thickness. As seen in figure 2, the dielectric properties essentially depend on the crystal thickness in the whole temperature range under study. The coefficient of the dielectric permeability maximum value variation with thickness is $\partial\varepsilon_{\max}/\partial D = 220$ mm^{-1}. A similar dependence of dielectric permeability on the sample thickness in the phase transition vicinity was observed earlier for a number of ferroelectrics: TGS [6],

Pb_5GeO_{11} [7], $Sn_2P_2S_6$ [8]. In particular, in $Sn_2P_2S_6$ crystals it is related to the existence of subsurface layers with small ε due to the presence of near-electrode spatial charges. Besides, in $CuInP_2S_6$ crystals we have revealed the increase of the dielectric loss angle tangent in both phases with the decrease of the crystal sample thickness as well as the increase of the Curie-Weiss constant C_W from $2 \cdot 10^3$ K to $7.5 \cdot 10^3$ K at the sample thickness increase from 0.2 to 1.6 mm. Evidently, the dependence of dielectric properties on thickness in layered $CuInP_2S_6$ crystals is much more complicated than in $Sn_2P_2S_6$ and is determined by more factors, e.g. the defects in the interlayer spaces.

The results quoted below were obtained for the 1.6-mm thick $CuInP_2S_6$ crystal. Figure 3 shows the temperature dependences of $CuInP_2S_6$ crystal dielectric permeability obtained at the measuring field frequency $f = 1$ kHz. With the increase of the hydrostatic pressure the curves shift towards higher temperatures. As seen from figure 3, the pressure increase has practically no effect on the character of the temperature dependence of ionic conductivity in the paraelectric phase. The pressure increase is accompanied by the increase of the step at the phase transition. This is due to the absence of ionic conductivity contribution to the dielectric permeability. According to our calculations, in the pressure range of $p \geqslant 400$ MPa, the anomaly of the dielectric permeability will be completely masked by copper ion conductivity.

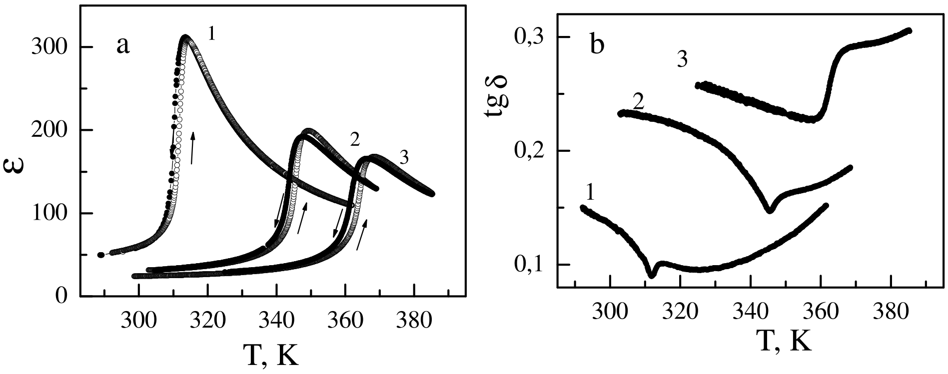

Figure 4. Temperature dependences of $CuInP_2S_6$ crystal dielectric permeability (a) (heating – open symbols, cooling – dark symbols) and dielectric loss angle tangent (b) at the measuring field frequency 1 MHz at atmospheric pressure (1) and at hydrostatic pressure values of 152 MPa (2) and 249 MPa (3).

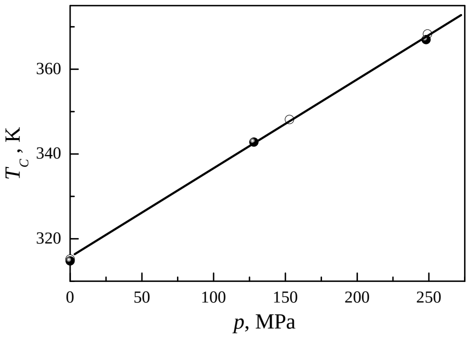

Figure 5. (p, T) phase diagram of $CuInP_2S_6$ crystals (open circles – $f = 1$ kHz; dark circles – $f = 1$ MHz).

Figure 4 illustrates the results of the hydrostatic pressure effect on the temperature dependences of $CuInP_2S_6$ crystal dielectric permeability and dielectric loss angle tangent obtained at the measuring field frequency $f = 1$ MHz. The shift of anomalies is accompanied by the decrease of its maximum values at the constant value of the phase transition thermal hystheresis. This is the evidence for the phase transition character remaining the same. The Curie-Weiss constant which is equal to $7.5 \cdot 10^3$ K at the atmospheric pressure in paraelectric phase, decreases with pressure. The pressure coefficient $\partial C_\mathrm{W}/\partial p = -2.8$ K/MPa. The phase transition also corresponds to the maximum of the tgδ value (figure 4b). The temperature of tgδ maximum exactly coincides with the dielectric permeability maximum temperature. The loss increase in the high-temperature range is determined by copper ion conductivity. The pressure increase causes a considerable increase of dielectric loss in both phases as well as changes the temperature behaviour at the phase transition.

Figure 5 shows the corresponding (p, T) diagram built based on the studies of temperature and pressure dependences of $\mathrm{CuInP_2S_6}$ crystal dielectric properties. In the pressure interval under study the increase of p causes a linear increase of the phase transition temperature with a coefficient of $\partial T_\mathrm{c}/\partial p = 210$ K/GPa. This coefficient is positive which is typical of the order/disorder phase transitions and its value is high enough in comparison with other materials possessing this type of phase transitions [9].

4. Conclusions

Dielectric properties of $\mathrm{CuInP_2S_6}$ crystals at high hydrostatic pressures are studied. The pressure behaviour of Curie-Weiss constant, dielectric permeability maximum and phase transition temperature are studied. The dependence of dielectric parameters on the sample size is revealed. The pressure behaviour of the phase transition temperature confirms the phase transition in these crystals to be of the order/disorder type. The (p, T) phase diagram of $\mathrm{CuInP_2S_6}$ crystals has been constructed.

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Діелектричні властивості кристалів $\mathrm{CuInP_2S_6}$ при високих тисках

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Досліджено діелектричні властивості шаруватих кристалів $\mathrm{CuInP_2S_6}$ в області сегнетоелектричного фазового переходу при високих тисках. Барична поведінка температури фазового переходу свідчить про те, що цей фазовий перехід відноситься до типу лад-безлад. Побудовано фазову (p, T) діаграму кристалів $\mathrm{CuInP_2S_6}$.

Ключові слова: *фазові переходи, сегнетоелектрики, тиск, діелектричні властивості*

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