Journal of Physics: Conference Series **121** (2008) 022015 doi:10.1088/1742-6596/121/2/022015

Optical and dielectric properties of $CuInP_2S_6$ layered crystals at high hydrostatic pressure

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Abstract. Effect of hydrostatic pressure on the birefringence and dielectric properties of $CuInP_2S_6$ crystals is studied. The pressure behaviour of the phase transition temperature confirms that the phase transition in these crystals belongs to the order/disorder type. An additional line of birefringence anomalies in the ferrielectric phase is revealed. Based on the studies of the optical and dielectric properties of $CuInP_2S_6$ crystals their (p,T) diagram was constructed.

1. Introduction

$CuInP_2S_6$ crystals belong to layered ferrielectrics, where ferrielectric polarization arises normally to the layers and results from anticollinear contributions due to copper ion ordering and indium ion displacement [1]. A first - order phase transition in these crystals at atmospheric pressure occurs at T=315 K. In the paraelectric phase the crystal structure belongs to monoclynic syngony: – C2/c , in the ferrielectric phase – Cc [1]. The spontaneous polarization value is P_s=2,55 μC/cm^2 [2]. Observation of a high-pressure induced first-order phase transition in $CuInP_2S_6$ crystals at p=4.0 GPa and room temperature from the monoclynic to a trigonal phase is reported, based on Raman scattering measurements [3].

Here we report on the studies of dielectric permeability and birefringence of $CuInP_2S_6$ crystals at hydrostatic pressure $p$atm<p<250 MPa in the temperature interval 77 K<T<400 K.

2. Experimental

$CuInP_2S_6$ crystals were grown by Bridgman technique. They were shaped in 0.2–2-mm thick plates, with silver paste or aquadag electrodes applied to the largest faces. Complex dielectric permeability was measured at the measuring field frequencies of 1 kHz and 1MHz.

Birefringence was studied by Senarmont technique at laser wavelength 0.63 μm. The light beam propagated along the normal to the layer. The measurements were performed in a three-window optical high-pressure chamber, benzene being used as a pressure medium.

3. Results and discussion

Figure 1,2 shows temperature dependences of $CuInP_2S_6$ dielectric permeability, obtained at measuring field frequencies of 1 kHz and 1 MHz. At atmospheric pressure the dielectric permeability maximum, corresponding to the phase transition temperature in the crystals under investigation, is achieved at the temperature T_c≈315 K. The increase of the dielectric permeability value at 1 kHz (curve 1 in Fig. 1) in the range T>330 K results from the ionic conductivity of Cu ions [1]. It should be noted that for the samples under study a temperature hystheresis of the phase transition is observed, ΔT ≈1.7 K. This value is essentially below that observed for the same crystals in [1] and coincides with the results of [4].

The performed studies of the dielectric properties of the $CuInP_2S_6$ crystals at atmospheric pressure have shown a considerable dependence of the dielectric permeability value on the sample thickness. This, in our opinion, can be responsible for a considerable data spread for the maximal dielectric permeability values (140<ε_{max}<900), obtained by different authors [1,4].

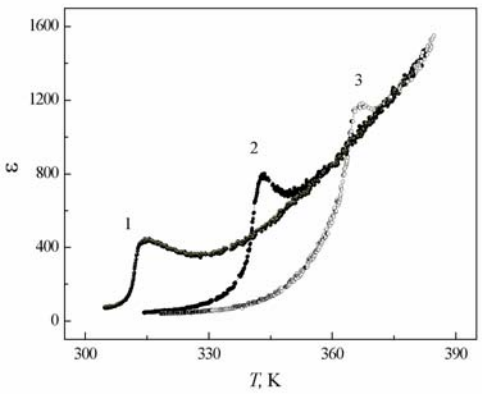

Figure 1. Temperature dependences of the dielectric permeability of $CuInP_2S_6$ crystals at the measuring field frequency 1 kHz at different values of hydrostatic pressure p: $p=p_{atm}$ (1), 128 MPa (2), 248 MPa (3).

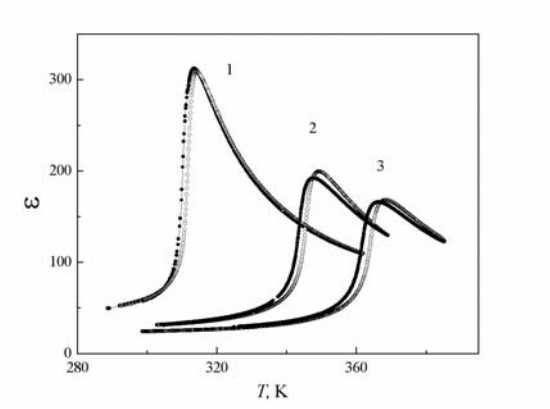

Figure 2. Temperature dependences of the dielectric permeability (open circles – heating, dark circles – cooling) at the measuring field frequency 1 MHz for $CuInP_2S_6$ crystals at different values of hydrostatic pressure p: $p=p_{atm}$ (1), 152 MPa (2), 249 MPa (3).

Temperature dependences of the dielectric permeability of $CuInP_2S_6$ crystals at the measuring field frequency f=1 kHz are shown in Fig. 1. With the hydrostatic pressure increase the curves shift towards higher temperatures. As seen from Fig. 1, the pressure increase practically does not affect the character of the ionic conductivity in the paraelectric phase. The pressure increase is accompanied with the increase of the step of ε at the phase transition. This results from the lack of contribution of ionic conductivity into the dielectric permeability in the ferrielectric phase. According to our calculations, in the pressure range near p=400 MPa the anomaly of the dielectric permeability will be completely masked by Cu ion conductivity.

The results of hydrostatic pressure effect on the temperature dependences of the dielectric permeability for $CuInP_2S_6$ crystals, obtained at the measuring field frequency f=1 MHz, are presented in Fig. 2.

The shift of the ε anomalies is accompanied by a decrease of its maximal values at the constant temperature hystheresis of the phase transition, what is the evidence for the character of the phase transition remaining unchanged. The Curie-Weiss constant value which in the paraelectric phase at atmospheric pressure is $C_W=7.5\cdot10^3$ K, decreases with pressure. The coefficient $\frac{dC_W}{dp}=-2.8\text{K/MPa}$. The phase transition is accompanied by a maximum of the tanδ value, coinciding with the temperature of the dielectric permeability maximum. The increase of loss in the high-temperature range is due to the ionic conductivity of the Cu atoms.

Temperature dependences of the $CuInP_2S_6$ crystal birefringence at different values of hydrostatic pressure are shown in Figs. 3 and 4. The pressure increase results in a slight change of the birefringence in the high-temperature range and to its essential increase in the ferrielectric phase. At the temperature dependences of the anomalous part of the birefringence a step and a temperature hystheresis of ~2K are observed, what is the evidence for the phase transition in this material being of the first order. For proper ferroelectrics the anomalous part of birefringence is known to be proportional to the squared spontaneous polarization P_s^2: $\Delta n=M P_s^2$.

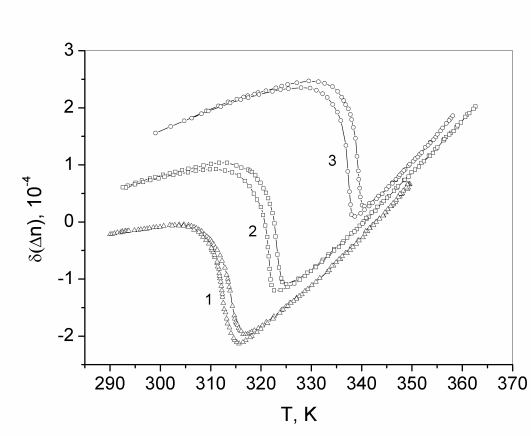

Figure 3. Temperature dependences of birefringence of $CuInP_2S_6$ crystals at different values of hydrostatic pressure p: $p=p_{atm}$ (1), 40 MPa (2), 120 MPa (3).

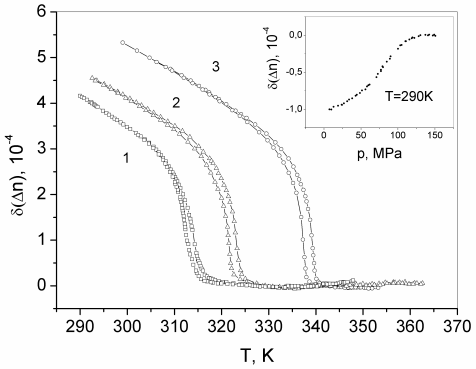

Figure 4. Temperature dependences of the anomalous part of the $CuInP_2S_6$ crystal birefringence at different values of hydrostatic pressure p: $p=p_{atm}$ (1), 40 MPa (2), 120 MPa (3). The insert shows the pressure dependence of the anomalous part of the $CuInP_2S_6$ crystal birefringence at constant temperature T=290 K.

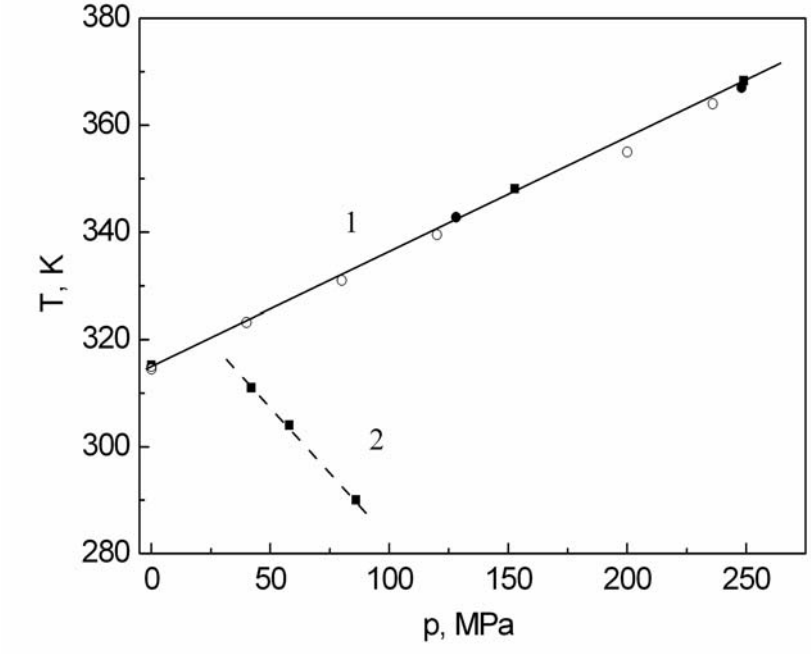

Figure 5. (p,T) phase diagram for $CuInP_2S_6$ crystals: *1* is the ferrielectric phase transition line, open circles being the birefringence data, dark symbols – dielectric data at the frequency f=1 kHz (circles) and f=1 MHz (squares), *2* is the line of birefringence anomalies in the ferrielectric phase.

Taking the spontaneous polarization value at normal conditions for $CuInP_2S_6$ crystals as P_s=2.55 μC/cm^2, one can estimate the proportionality coefficient M=0.587 m^4/C^2. In the range of the ferrielectric phase the studies of isothermal dependences of birefringence have revealed an additional anomaly in the form of a smeared jump (See the inset to Fig. 4). The position of this anomaly in the (p,T) space is extrapolated to the temperatures T≈335 K at atmospheric pressure. In this temperature range the authors of [1,2] observed the anomalies of the lattice parameters.

Based on the studies of the temperature and pressure dependences of the dielectric properties and birefringence of $CuInP_2S_6$ crystals, their (p,T) phase diagram was built, shown in Fig. 5. In the pressure range under investigation the increase of p results in a linear increase of the ferroelectric phase transition temperature at a rate $\frac{dT_c}{dp} = 210\text{K/GPa}$. This coefficient value is positive what is typical for order/disorder phase transitions and is high enough in comparison with other materials with such phase transition type [5]. Additional studies are required to elucidate the nature of the observed birefringence anomalies in the ferroelectric phase at high pressures.

4. Conclusions

Dielectric properties and birefringence of $CuInP_2S_6$ crystals at high hydrostatic pressures are studied. The pressure behaviour of the phase transition temperature confirms that the phase transition in these crystals belongs to the order/disorder type. An additional line of birefringence anomalies in the ferrielectric phase is revealed. The (p,T) phase diagram of $CuInP_2S_6$ crystals is built.

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