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Influence of hydrostatic pressure on the dielectric properties of $CuInP_2S_6$ and $CuInP_2Se_6$ layered crystals

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Abstract. The studies of dielectric permeability of $CuInP_2S_6$ and $CuInP_2Se_6$ crystals at hydrostatic pressure $p_{atm}<p<600$ MPa in the temperature range 77 K<T<400 K are reported. The sign of the pressure-related shift of ferrielectric phase transition temperature is shown to be opposite in $CuInP_2S_6$ and $CuInP_2Se_6$ crystals what is the evidence for the difference in the phase transition mechanisms in these materials.

1. Introduction

$CuInP_2S_6$ and $CuInP_2Se_6$ crystals belong to layered ferrielectrics [1,2]. Ferrielectric polarization in these crystals arises normally to the layers and results from anticollinear contributions due to copper ion ordering and indium ion displacement.

A first-order order-disorder type phase transition at atmospheric pressure in $CuInP_2S_6$ crystal occurs at T=315 K. In the paraelectric phase the crystal structure belongs to monoclynic syngony (*C2/c*), in the ferrielectric phase – Cc [1]. In the paraelectric phase the crystal structure of $CuInP_2Se_6$ belongs to - *P-31c* syngony, in the ferrielectric phase – to *P31c* [3]. According to the data of [4], for $CuInP_2Se_6$ crystals both second-order and first-order phase transitions are observed at T_i=248.5 K and T_c=235.5 K, respectively. The phase transitions in $CuInP_2Se_6$ crystal are also of the order-disorder type. The authors of [4] consider the intermediate phase to be an incommensurate one. The longitudinal ultrasound velocity studies revealed anomalies for two phase transitions at the temperatures 228 K and 236 K [5]. The effect of hydrostatic pressure on the phase transitions in $CuInP_2Se_6$ crystals has not been studied yet.

Here we report on the studies of dielectric permeability of $CuInP_2S_6$ and $CuInP_2Se_6$ crystals at hydrostatic pressure $p_{atm}<p<600$ MPa in the temperature range 77 K<T<400 K.

2. Experimental

0.2- to 2-mm thick Bridgman-grown $CuInP_2S_6$ crystals and 0.05- to 0.2-mm thick $CuInP_2Se_6$ crystals, grown by vapour transport were studied. Complex dielectric permeability was measured at the measuring field frequencies 1 kHz and 1MHz in a high hydrostatic pressure chamber. Silver paste was used for contacts. Benzene was used as a pressure medium.

3. Results and discussion

Temperature dependences of dielectric permeability ε of $CuInP_2S_6$ crystals, obtained at the measuring field frequencies 1 kHz are shown in Figures 1.

At atmospheric pressure the maximum of the dielectric permeability, corresponding to the phase transition temperature in the crystals under investigation, is achieved at the temperature T_c≈315 K. In the paraelectric phase at T>330 K at the frequency f=1 kHz an increase of the dielectric permeability value is observed what is evidently due to the ionic conductivity of Cu atoms [2]. Note that for the crystals under study a temperature hystheresis of the phase transition is observed:

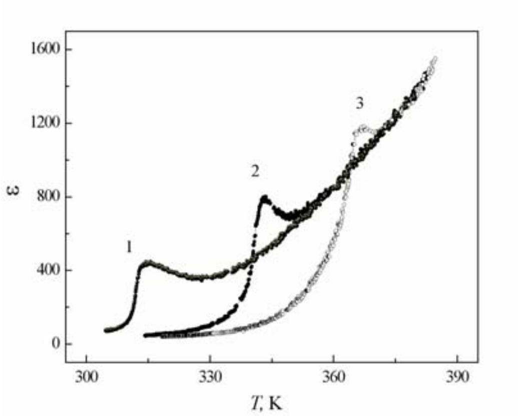

Figure 1. Temperature dependences of the dielectric permeability of $CuInP_2S_6$ crystals at the measuring field frequency 1 kHz at different values of hydrostatic pressure p: $p=p_{atm}$ (1), 128 MPa (2), 248 MPa (3).

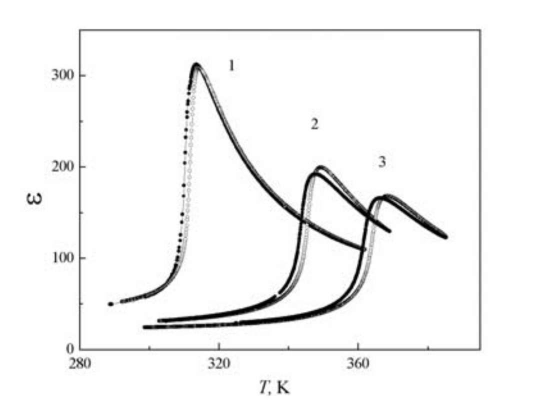

Figure 2. Temperature dependences of the dielectric permeability (open circles – heating, dark circles – cooling) at the measuring field frequency 1 MHz for $CuInP_2S_6$ crystals at different values of hydrostatic pressure p: $p=p_{atm}$ (1), 152 MPa (2), 249 MPa (3).

$\Delta T \approx 1.7$ K. This value is essentially below the one reported for these crystals in [2]; meanwhile, it coincides with the results of [6]. The pressure increase practically does not affect the character of the temperature dependence of the dielectric permeability due to the ionic conductivity in the paraelectric phase. In the ferrielectric phase there is no contribution to the dielectric permeability due to the ionic conductivity. The pressure increase is accompanied by the increase of the ε step value at the phase transition. As one can estimate, in the pressure range p>400 MPa the dielectric permeability maximum will be totally masked by Cu ion conductivity.

Figure 2 shows the results on the influence of the hydrostatic pressure on the temperature dependences of the dielectric permeability of $CuInP_2S_6$ crystals, obtained at the measuring field frequency f=1 MHz. The shift of the ε anomalies is accompanied by the decrease of the maximal values at the constant value of the phase transition temperature hystheresis what is the evidence for the phase transition character remaining unchanged. The Curiee-Weiss constant value which in the paraelectric phase equals $C_W=7.5\cdot10^3$ K, decreases with pressure. The coefficient value $\frac{dC_W}{dp} = -2.8$ K/MPa. The phase transition is accompanied by the maximum of the tanδ value, coinciding with the temperature of the maximum of dielectric permeability.

In the pressure range under investigation, the increase of p results in a linear increase of the ferrielectric phase transition temperature at a rate dT_c/dp = 210 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 this type of phase transitions .

The results of the studies of high hydrostatic pressure effect on the dielectric permeability of $CuInP_2Se_6$ are shown in Figure 3. In $CuInP_2Se_6$ crystals the hydrostatic pressure increase leads to a shift of anomalies of the dielectric permeability ε, dielectric loss angle tangent tanδ towards lower temperatures, what is not typical for order/disorder type phase transitions. At amospheric pressure in $CuInP_2Se_6$ crystals two phase transitions are observed at T_c=224.5 K and T_i=332 K what is in better agreement with the data of [5] than with [4]. The temperatures of both phase transitions decrease with pressure, a slight increase of the maximum of the dielectric permeability ε being observed. The temperature hystheresis value $\Delta T_c \approx 2$ K (at $p = p_{atm}$) remains practically unchanged with pressure.

Within the temperature range 145 K < T < T_i a considerable hystheresis of the dielectric permeability in the intermediate and the ferrielectric phases is observed.

Based on the dielectric studies of $CuInP_2S_6$ and $CuInP_2Se_6$ crystals, their (*p,T*) phase diagram was built (Figures 4 and 5). As seen from Figure 5, the (*p,T*) phase diagram of $CuInP_2Se_6$ crystals is nonlinear. In the range of the lower pressures the pressure-related shift of the phase transition temperature dT_i/dp = –11 K/GPa, and at p>150 MPa dT_i/dp = –42 K/GPa. The shift of the anomaly, responsible for the second phase transition, is dT_c/dp = –46 K/GPa what is the evidence for the broadening of the intermediate phase under hydrostatic pressure. A similar pressure-related broadening of the intermediate incommensurate phase was observed in $Sn_2P_2S_6$-type crystals [7].

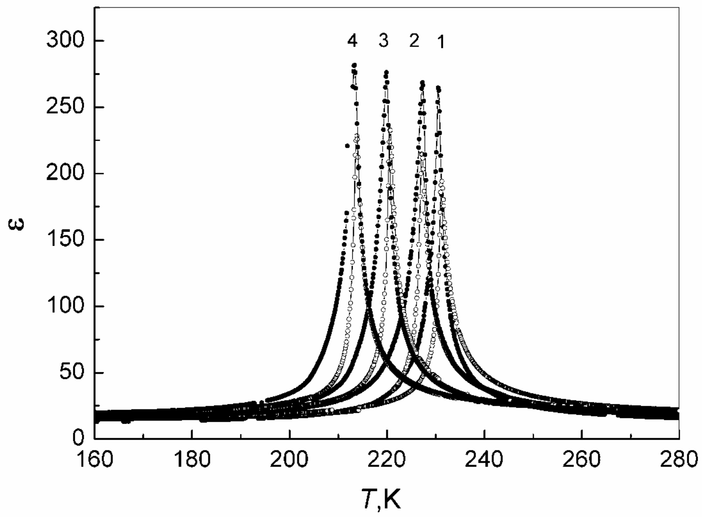

Figure 3. Temperature dependences of $CuInP_2S_6$ crystal dielectric permeability (heating – open symbols, cooling – dark symbols) at the measuring field frequency 1 MHz at atmospheric pressure (1) and at hydrostatic pressure values of 190 MPa (2), 370 and 540 MPa (4)

The results of structural analysis have shown that in $CuInP_2Se_6$ crystals copper and indium ion displacements in the low-temperature phase are considerably smaller than in their sulphide analog compound. Substitution of S by Se (with bigger ion radius) results in the decrease of the potential relief for copper ions in $CuInP_2Se_6$ with respect to $CuInP_2S_6$. Evidently, for this reason the main role at the phase transition is played by indium displacements, not by copper ion ordering. The opposite signs of the pressure-related shifts of the ferrielectric phase transitions in the selenide and the sulphide crystals indicates the difference in the mechanism of the phase transformations in these materials.

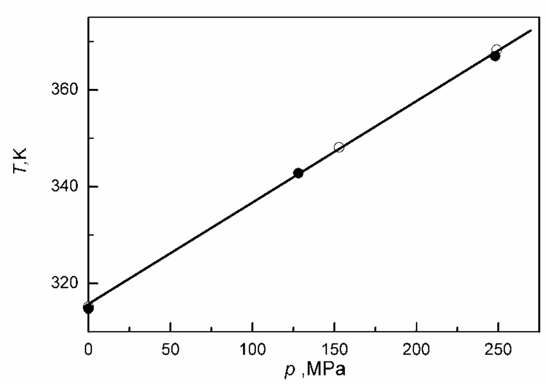

Figure 4. (*p, T*) phase diagram of $CuInP_2S_6$ crystals (dark symbols – dielectric data at the frequency *f*=1 kHz (circles) , open circles – dielectric data at the frequency *f*=1 MHz).pressure p: $p=p_{atm}$ (1), 40 MPa (2), 120 MPa (3).

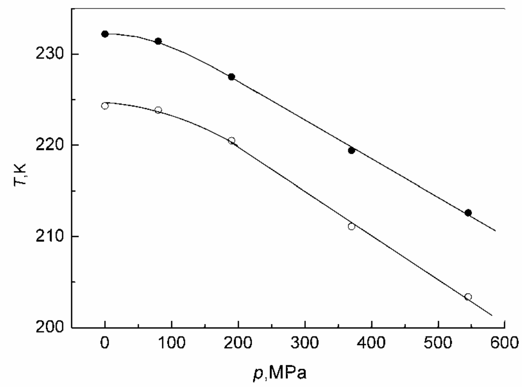

Figure 5 (*p, T*) phase diagram of $CuInP_2Se_6$ crystals (open circles – T_c; dark circles – T_i).

4. Conclusions

Dielectric properties of $CuInP_2S_6$ and $CuInP_2Se_6$ crystals at high hydrostatic pressures are studied. It has been found that the opposite signs of the pressure-related shifts of the ferrielectric phase transitions in the selenide and the sulphide crystals indicate the difference in the mechanism of the phase transformations in these materials. The (*p, T*) phase diagram of $CuInP_2S_6$ and $CuInP_2Se_6$ crystals is built.

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