*Dielectric properties of $Cu_6P(S_{0,1}Se_{0,9})_5I$ superionic crystals under high hydrostatic pressures

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Abstract

The influence of temperature on dielectric properties of $Cu_6P(S_{0,1}Se_{0,9})_5I$ superionic crystals at high hydrostatic pressures in the region of the phase transition (PT) has been investigated. The temperatures of superionic and ferroelastic PT and baric coefficients of their shift have been determined. The character of PT has been established.

Key words: superionic crystals, phase transitions, hydrostatic pressure

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Superionic crystals of Cu_6PS_5I are compounds of argyrodites type with mixed ion-electronic conductivity [1]. In the given crystals the two phase transitions (PT) take place: a low-temperature superionic PT at a temperature T_s and a high-temperature ferroelectric PT at a temperature T_c [2]. The given transitions arc accompanied by a space symmetry change from monoclinic *m* to cubic $F\bar{4}3m$ [1]. Based on optical investigations the superionic PT was observed in $Cu_6P(S_{0,1}Se_{0,9})_5I$ crystals in the region of temperatures T_s~213–230 K, the information about ferroelectric PT is absent [3] The pressure effect on physical properties has useful information about the disorder mechanism in $Cu_6P(S_{0,1}Se_{0,9})_5I$ superionic crystals. That is why we have investigated the influence of temperature (80-400 K) and hydrostatic pressure (to 500 MPa) on dielectric properties of $Cu_6P(S_{0,1}Se_{0,9})_5I$ crystals, dielectric permeability ε, the dielectric loss tangent $tan(\sigma)$ and specific conductance σ.

$Cu_6P(S_{0,1}Se_{0,9})_5I$ single crystals were grown by the method of chemical transport reactions. For dielectric measurements the crystals were oriented along crystallographic direction *[100]* and were of 0,5x2x3 mm^3 dimensions. The measurement *of* $\varepsilon(T)$, $tan\delta(T)$ and $\sigma(T)$ was performed with the help of *E7-12* bridge at a frequency of ν=1*MHz* in the dynamic mode. Temperature was changed with the speed of 0,3K/*mm.* A silver paste was used for providing electric contacts.

In figure 1 temperature dependencies of ε, $tan(\delta)$, σ in heating and cooling modes at hydrostatic compression are given. The anomaly in the form of maximum for $tan\,\delta(T)$ (at $p=p_{atm}$), which occurs at the temperature $T_s^c = 220$ K and a sharp increase in $\varepsilon(T)$ and $tan\,\delta(T)$ are assigned to the superionic PT. The given PT is accompanied by the temperature hysteresis ΔT=5 *K,* that gives a reason to classify it as the first-order phase transition. Within the temperature range of *250-350 K* additional peculiarities of the studied parameters are observed which are surely assigned to

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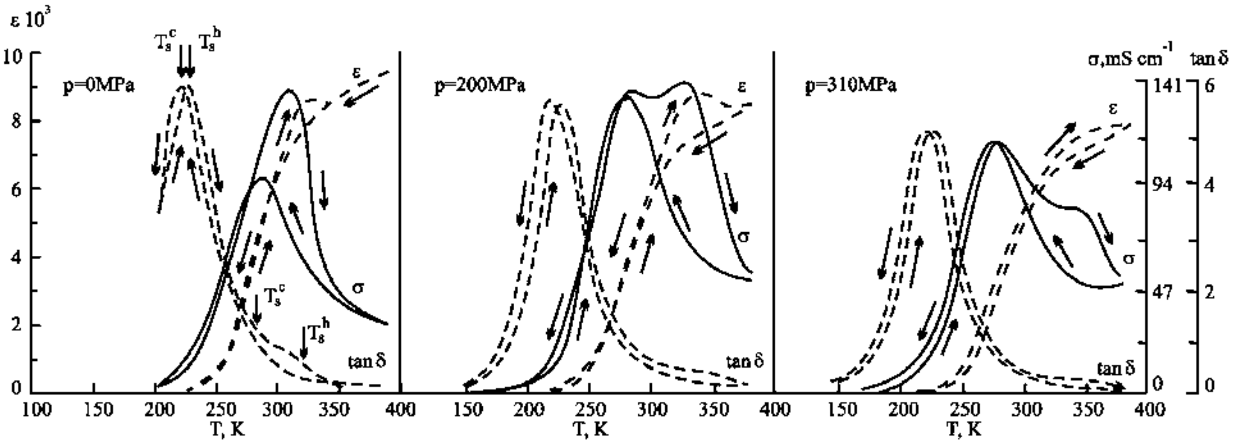

Fig.1. Temperature dependences *ε, tg δ* and *σ* of crystals $Cu_6P(S_{0,1}Se_{0,9})_5I$ at hydrostatic squeezing.

ferroelastic PT, that is observed in $Cu_6PS_5I(Br)$ crystals. It should mentioned noticeable difference in the temperature dependencies of $\varepsilon(T)$, $\tan\delta(T)$ and $\sigma(T)$ in the given region at warming and cooling. Specifically, in warming mode at $T_c^h = 325$ K there is a maximum on $\sigma(T)$ and on $\tan\sigma(T)$ an inflection is easily seen, at cooling the anomalies of $\delta(T)$ and $\tan\delta(T)$ don't appear. The appearance of temperature hysteresis of the indicated dependencies allows us to conclude that this PT is the first-order PT in contrast to $Cu_6PS_5I(Br)$ crystals.

The increase of hydrostatic pressure weakly influences the behaviour of $\varepsilon(T)$, $\tan\delta(T)$ and $\sigma(T)$ in a low-temperature region in the vicinity of PT at T_s. However, the increase in pressure causes a considerable transformation of the studied properties in a high-temperature region in the vicinity of ferroelastic PT. The changes in the conductivity σ behavior at warming is especially well expressed in particular increasing of pressure results in splitting the maximum into the two parts. It is interesting to note that the form of anomalies is almost not changed. The given results (see fig. 1) confirm the fact, that a high-temperature PT is the first-order PT. Also a strong temperature hysteresis occurs here. Since at warming of PT at T_c is shifted from superionic PT, the anomalies of $\varepsilon(T)$, $\tan\delta(T)$ and $\sigma(T)$ have a very distinct character. At cooling due to closeness of PT at T_s they are not well expressed. The increase in pressure causes the shift of ferroelastic PT into the region of high temperatures. The anomalies of $\varepsilon(T)$, $\tan\delta(T)$ and $\sigma(T)$ become more distinct in cooling mode.

Baric dependencies of $T_c^h(p)$ and $T_c^c(p)$ are shown in fig. 2. Under the action of hydrostatic pressure the anomalies $\varepsilon(T)$ and $\tan\delta(T)$ at ferroelastic PT are not distinct and are shifted the region of higher temperature with baric coefficient dT_c^h/dp=0,097 K/MPa. The similar behavior of $\varepsilon(T)$, $\tan\delta(T)$ and $\sigma(T)$ is observed in other crystals of the family of solid solutions $Cu_6P(S_{1-x}Se_x)_5I$ at $x \geq 80$.

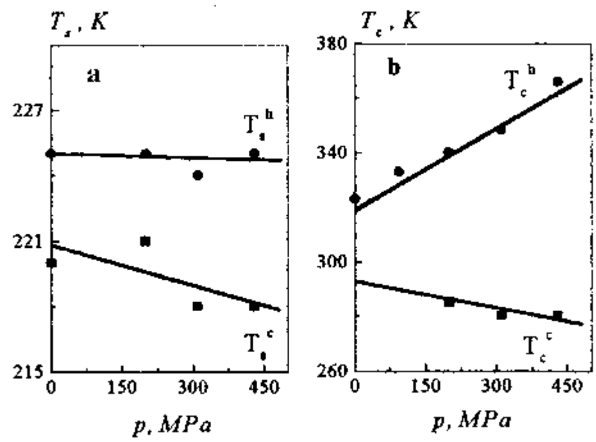

Fig.2. The phase p,T – diagrams of $Cu_6P(S_{0,1}Se_{0,9})_5I$ crystals: a-superionic PT, b – ferroelastic PT

Hence, studies of the influence of temperature and pressure on dielectric properties of $Cu_6P(S_{0,1}Se_{0,9})_5I$ crystals are performed here confirm the existence of the two first-order PT in these crystals. A low-temperature PT at T_s is assigned to the transition into superionic state, and a high-temperature one at T_c may be classified as ferroelastic.

Using the results of investigations the phase *p, T* - diagram of these crystals is suggested.

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