Influence of the In-Ga substitution on the physical properties of layered $CuInP_2S_6$ crystals

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Introduction: Recently, all over the world, interest in two-dimensional materials has significantly increased, which is associated with the promising nature of their use in modern electronic products [1]. Of particular interest are 2D ferroelectrics, for example, $CuInP_2S_6$, on the basis of which diodes, transistors, memory cells, electronic equivalents of synapses, etc. have already been developed. The main advantage of this material is believed to be its ferroelectric properties in ultrathin layers at room temperature (up to 4 nm [2]), the orientation of spontaneous polarization perpendicular to the structural layers, the possibility of integration with modern 2D materials such as MoS_2 and graphene [3]. One of the drawbacks of the practical application of these crystals is the relatively low temperature of the phase transition to the paraelectric phase ~ 315K. Therefore, the search for an increase in the temperature of the $CuInP_2S_6$ phase transition is very actual. This problem can be solved, for example, by hydrostatic or uniaxial compression of these crystals [4] or by changing its chemical composition, for example, by enriching it with indium [5]. Our results indicate that the partial replacement of indium by gallium also leads to an increase in the phase transition temperature.

Experiment: For our research, we used solid solutions 80%$CuInP_2S_6$- 20%$CuGaP_2S_6$ grown at the Faculty of Chemistry of UzhNU. The chemical composition of the obtained crystals was confirmed by the extraction-photometric method [6] and by the EDAX. The resulting layered samples were 2×3, 3×3 mm^2 in size, 50-100 µm thick, light yellow in color, slightly lighter than pure $CuInP_2S_6$ crystals. To study the electrophysical properties, electrodes made of silver paste were applied to the opposite planes of the samples. The temperature dependence of the dielectric constant was measured at a frequency of 10 kHz, in the temperature range 80-400K. To assess the homogeneity of the crystals as well as the surface quality (which is very important in the case of 2D crystals), studies were carried out using a TESCAN MIRA 3 Scanning Electron Microscope, the results of which are presented in Figure 1. As we can see, the surface is rather heterogeneous, with inclusions of microcrystallites. Further studies are required to determine the homogeneity of the chemical composition of the samples, since the method used by us for determining the chemical composition is integral over the scanning beam diameter (within a few millimeters), microscopic inhomogeneities most likely remained unnoticed.

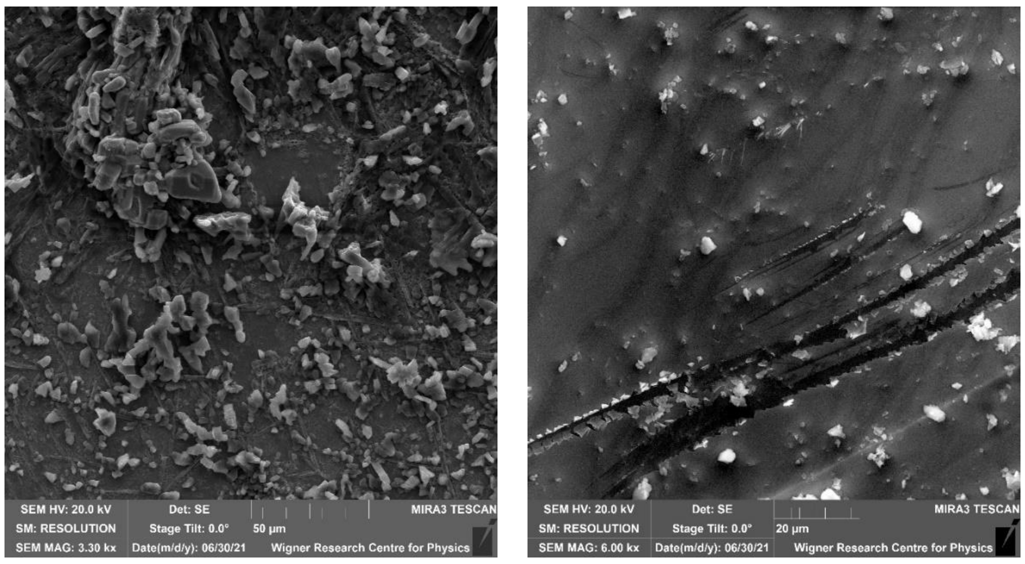

Figure 1. Images of the surface of 80%$CuInP_2S_6$- 20%$CuGaP_2S_6$ crystals obtained using a scanning electron microscope at a magnification of 3300 (a) and 6000 (b) in different parts of the sample

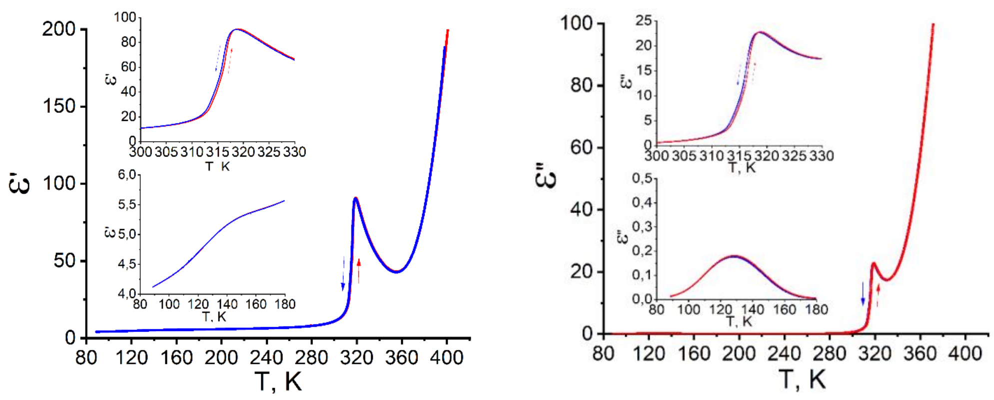

Figure 2. Temperature dependency of real and imaginary parts of complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\cdot\varepsilon''$ of 80%$CuInP_2S_6$- 20%$CuGaP_2S_6$ solid solution

Results and discussion: As can be seen in Figure 2, the phase transition temperature for this composition is 318K, which is 3 degrees higher than that of a pure crystal $CuInP_2S_6$. The anomaly in the temperature dependence of the dielectric constant caused by the phase transition is not blurred, and the maximum value of ε' and ε" at the phase transition practically coincides with that for pure crystals, which indicates the absence of degradation of the electrophysical parameters of solid solutions 80%$CuInP_2S_6$- 20%$CuGaP_2S_6$ with the replacement of indium by the gallium. We can also note a decrease in the temperature hysteresis of the dielectric constant to 0.1K (which is clearly visible on the inserts of fig. 2), in contrast to a pure crystal, where this phenomenon has an amplitude of 1-2K at a temperature change rate of 0.1 K/min in both cases.

At temperatures below 200K (more precisely, at 120-140K at 10 kHz), a "step" is observed on the temperature dependence of the real part of the dielectric constant, and a maximum on the temperature dependence of the imaginary part of the dielectric constant. Moreover, frequency dispersion of the dielectric permittivity can be observed at low frequencies for 80%$CuInP_2S_6$- 20%$CuGaP_2S_6$ as well as in pure $CuInP_2S_6$. As shown in [5], such dielectric dispersion is typical for dipolar glasses. However, this conclusion requires clarification, since a similar behavior at low temperatures is observed both in other ferroelectrics of the $Me_2P_2S_6$ family, for example, $Sn_2P_2S_6$, and in crystals that are not ferroelectrics, for example, $CuFeP_2S_6$.

Conclusions: From our data, we can conclude that partial replacement of indium with gallium makes it possible to raise the phase transition temperature of crystals; however, to clarify the maximum value of this phenomenon, additional studies are required using a wider set of X%$CuInP_2S_6$- Y%$CuGaP_2S_6$ solid solutions with different gallium concentrations.

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