Formation pattern and growing of CuInP$_2$S$_6$ single crystals

The work was performed at the Department of Inorganic Chemistry and Institute for Physics and Chemistry of Solid State, Uzhgorod National University

The nature of physico-chemical interaction in CuInS$_2$ – “P$_2$S$_4$” system by the methods of differential thermal and X-ray phase analysis was investigated. The T-x phase diagram for this system was plotted. It is established that the studied cross-section is partially quasibinary. The system is characterized by formation of CuInP$_x$S$_{6-x}$ tetra compounds. CuInP$_2$S$_6$ compound is generated of sintectic reaction at $T=1088\pm 5$ K. CuInP$_2$S$_6$ compound is crystallized in the C2/c space group with unit cell parameters: $a = 6,096$; $b = 10,564$; $c = 13,623$ Å and $\beta = 107,10^{\circ}$. The technological requirements of single crystals of CuInP$_2$S$_6$ tetra compound are developed by the chemical transport reaction method and the directed crystallization of fusion.

Key words: phase diagram, tetra compound, single crystals.

Statement of scientific problem and its importance. CuInP$_2$S$_6$ compound is the isoelectronic analogues of the known Sn$_2$P$_2$S$_6$ ferroelectric. CuInP$_2$S$_6$ can be examined as phase was obtained by the substitution of 2Sn$^{2+}$ on (Cu$^+$ + In$^{3+}$). The heightened interest to the study of these compounds is explained the existence in CuInP$_2$S$_6$ a ferroelectric phase transition at $T_c = 315$ K [1]. Information about the crystal

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The quasibinary CuInS₂ – “P₂S₄” cross-sections of Cu₃S – In₂S₃ – “P₂S₄” triple system were chosen for the study of formation character of CuInP₂S₆ compound.

The synthesis of alloys of the investigational system was carried out by one temperature method from CuInS₂ ternary compound with addition of the expected amounts of phosphorus, sulphur in the vacuumed quartz ampoules. The choice of CuInS₂ ternary compound as an initial components is explained by the reason that the elementary initial components application during the alloys synthesis leads to the situation when the compound of In₄(P₂S₆)₃ appears in the first place, as more thermodynamics steady. Their interaction with a metallic copper with formation of CuInP₂S₆ tetry compound is labored.

With the purpose of complete interaction providing of initial components and in order to avoid the partial sublimation of reaction products, top of ampoules supported at the temperature on 50−60 K higher in comparison with bottom during the synthesis.

A maximal temperature of alloys heating with participation of sulphur was 1000 K. The alloys were maintained during three weeks at these temperatures.

The synthesized samples were investigated by the methods of differential thermal and X-ray phase analysis and also the measuring of individual compounds density.

On results of the differential thermal analysis the phase diagram of CuInS₂ – “P₂S₄” system is built (fig. 2).
It is obvious (Fig. 2), that CuInP$_2$S$_6$ compound appears due to a synthetic reaction from two liquids L$_1$ and L$_2$ at the temperature 1088 ± 5 K. The eutectic between CuInS$_2$ and CuInP$_2$S$_6$ compounds conforms the composition of 75 mol. % CuInS$_2$ and melts at the temperature 1088 ± 5 K.

It was performed from the calculation of CuInP$_2$S$_6$ diffraction patterns that this phase is crystallized in C2/c space group of monoclinic system and Z = 2 with cell parameters: a = 6.956; b = 10.564; c = 13.623 Å; γ = 107.101º.

The specific density of CuInP$_2$S$_6$, certained by the hydrostatic weighing method in toluene, was 3.425·10$^3$ kg/m$^3$.

The single-crystals of both compounds could be obtain by the method of chemical transport reactions, we have used before, and the directional crystallization of fusion one.

Both compounds possess, in all likelihood, the considerable homogeneity regions on the different directions in Cu$_2$S – In$_2$S$_3$ – “P$_2$S$_4$” quasiternary system, that in turn should affect on the values of phase transitions temperatures, and also on the peak forms of dielectric conductivity for crystals with deviations from stoichiometry.

In present work the CuInP$_2$S$_6$ single-crystals growth by the methods of chemical transport reactions (CTR) and the directional crystallization of fusion from the charge mixture of stochiometric composition was performed. The single-crystals growth process of these compounds has carried out by the CTR method in quartz ampoules by 20–24 mm diameter and 140–160 mm long. Iodine (V-4) with 4–6 mg/cm$^3$ concentration of ampoule free volume, and also CuI were used as transport substances.

The crystal growth process was performed in a few stages. In the first stage of this process, the cleaning of crystallization zone of growing ampoule from charge tailings and gas phase by the way of reverse gradient formation during 24 hours (the temperature of crystallization zone − 970 K, charge zone − 670 K) was made.

In the second stage, the generation process of the limited amount of crystallization centers by the way of optimum supersaturation formations in ampoules was carried out.

The temperature changing in the zones of evaporation and crystallization, the temperature gradients, length and diameter of growing ampoules, concentration and type of carrier, conception mechanism and the duration of growing processes could be allow to create the conditions which provided the selective origin of active centers on the ampoule walls in the crystallization zone.

In all cases, the transport is directed from hotter to colder zone, which specifies on the endothermic character of gas-transport reactions. The mechanism of these reactions behavior is has not studied in details.
The scheme of chemical transport reactions at single-crystals growing of CuInP$_2$S$_6$ compound it is possible to present by the equation: $2\text{CuInP}_2\text{S}_6 \leftrightarrow 2\text{CuI} + 2\text{P}_2\text{S}_5 + \text{S}_2$.

The final stage of the growth process of CuInP$_2$S$_6$ single-crystals consists of the gas phase strippant from the crystallization zone. This process was carried out by the way of the gradual lowering temperatures of “hot” zone at 20 K/h speed to 400 K with further control at this temperature during 12 hours.

The subsequent cooling was performed in the mode of the turned off oven. In the Table 1 the growing conditions of CuInP$_2$S$_6$ single-crystals compound by the CTR method are presented.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transport agent; mg/cm$^3$</th>
<th>Temperature</th>
<th>$\Delta T$, K</th>
<th>$\tau$, h</th>
<th>Transport substance, %</th>
<th>Dimensions, mm</th>
<th>Color and Habitus of crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInP$_2$S$_6$</td>
<td>$\text{I}_2$;$\text{CuI}$; 4−6</td>
<td>900</td>
<td>870</td>
<td>30</td>
<td>350</td>
<td>10x8x0,1</td>
<td>Thin plates of yellow-lemon colors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>910</td>
<td>860</td>
<td>50</td>
<td>300</td>
<td>6x6x0,1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>940</td>
<td>920</td>
<td>20</td>
<td>400</td>
<td>5x5x0,1</td>
<td></td>
</tr>
</tbody>
</table>

The growth of CuInP$_2$S$_6$ crystals of enough largeness by the directed crystallization of fusion method presents the considerable interest. The principle possibility of these single-crystals growth by this method follows from the investigated phase diagram for CuInS$_2$ – “P$_2$S$_4$” systems were done in present work.

The growth process by the directed crystallization of fusion (Bridgman technique) was performed from the stoichiometrical compositions charge of CuInP$_2$S$_6$ compound in cone-shaped quartz ampoules.

The length of ampoule “spout” was ~18−20 mm, and a diameter − 3−4 mm with the aim for forming of the nucleus of single-crystal. This process has done in preliminary calibrated two-region ovens and the zone temperatures were regulated by REEF-101 devices.

The perform of initial polycrystalline charge was 15−20 g. The ampoule was soldered to quartz rod and set on the center of two-region oven. The ampoule “spout” was placed at the level of crystallization zone. The initial charge in ampoules heated to the temperature on 50 K higher than the proper temperature of compound formation.

Farther the ampoule with the charge was put into the crystallization zone through the special mechanism and in cone-shaped part carried out the origin of single-crystal fuse which after exposed to the recrystallization annealing during 2−3 days. Then, the mechanism of growth container moving switched on and began the growth process of CuInP$_2$S$_6$ single-crystals. The optimum conditions of CuInP$_2$S$_6$ single-crystals growing by the directional crystallization of fusion method are given in table 2.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature of fusion zone, K</th>
<th>Temperature of annealing zone, K</th>
<th>$\Delta T$ of growth zone, K/mm</th>
<th>Growth rate, mm/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInP$_2$S$_6$</td>
<td>1100</td>
<td>870</td>
<td>3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Consequently, the monolithic “boules” of CuInP$_2$S$_6$ crystals by 14 mm diameter and long 20−25 mm long with well developed cleavage are obtained. General view of samles, obtained from CuInP$_2$S$_6$ single-crystals is presented on Fig. 3.
**Fig. 3.** Samples, obtained from CuInP$_2$S$_6$ single-crystals (Bridgman technique)

**Literature**


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