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Formation pattern and growing of $CuInP_2S_6$ 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_2S_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 $CuInP_2S_6$ tetrary compounds. $CuInP_2S_6$ compound is generated of sintectic reaction at T=1088±5 K. $CuInP_2S_6$ compound is crystallized in the C2/c space group with unit cell parameters: a = 6,096; b = 10,564; c = 13,623 Å and β = 107,101°. The technological requirements of single crystals of $CuInP_2S_6$ tetrary compound are developed by the chemical transport reaction method and the directed crystallization of fusion.

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

Поторий М. В., Приц И. П., Мотря С. Ф., Милян П. М, Микайло О. А. Характер образования, выращивание монокристаллов $CuInP_2S_6$. Методами дифференциального термического и рентгеновского фазового анализов исследован характер физико-химического взаимодействия в системе $CuInS_2$ – “P_2S_4”. Построена Т-х диаграмма состояния указанной системы. Установлено, что изученный разрез является частично квазибинарным. Система характеризуется образованием тетрарного соединения $CuInP_2S_6$. Соединение $CuInP_2S_6$ образуется по синтектической реакции при Т = 1088±5 К. $CuInP_2S_6$ кристаллизуется в моноклинной сингонии, пространственная группа *C2/c* с параметрами элементарной ячейки а = 6,096; b = 10,564; c = 13,623 Å; β = 107,101°. Разработаны технологические условия получения монокристаллов тетрарного соединения $CuInP_2S_6$ методами химических транспортных реакций и направленной кристаллизацией расплава.

Ключевые слова: фазовая диаграмма, тетрарное соединение, монокристаллы.

Поторій М. В., Пріц І. П., Мотря С. Ф., Милян П. М., Микайло О. А. Характер утворення, вирощування монокристалів $CuInP_2S_6$. Методами диференціального термічного та рентгенівського фазового аналізів досліджено характер фізико-хімічної взаємодії в системі $CuInS_2$ – “P_2S_4”. Побудовано Т-х діаграму стану вказаної системи. Встановлено, що вивчений розріз є частково квазібінарним. Система характеризується утворенням тетрарної сполуки $CuInP_2S_6$. Сполука $CuInP_2S_6$ утворюється по синтектичній реакції при Т = 1088±5 К. $CuInP_2S_6$ кристалізується в моноклінній сингонії, просторова група С2/с з параметрами елементарної комірки а = 6,096; b = 10,564; c = 13,623 Å; β = 107,101°.

Розроблено технологічні умови одержання монокристалів тетрарної сполуки $CuInP_2S_6$ методами хімічних транспортних реакцій та направленої кристалізації розплаву.

Ключові слова: фазова діаграма, тетрарна сполука, монокристали.

Statement of scientific problem and its importance. $CuInP_2S_6$ compound is the isoelectronic analogues of the known $Sn_2P_2S_6$ ferroelectric. $CuInP_2S_6$ 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 $CuInP_2S_6$ a ferroelectric phase transition at T_c = 315 K [1]. Information about the crystal

structure and the synthesis and of $CuInP_2S_6$ crystals as yellow thin films by the chemical transport reactions method was given by authors [2].

It was described in [3] that the phase transition temperature for $CuInP_2S_6$ crystals depends on the obtaining conditions. The presence of Cu_2S excess in the initial mixture for crystals results to the temperature drop of the phase transition, and In_2S_3 surplus - to its increase as compared to crystals, got from the stoichiometric composition mixture.

All that facts indicates actuality of phase diagrams investigations of the systems in which $CuInP_2S_6$ compound appear. Information about is absent in literature.

Preparation of the basic material and study the results of research. The main aim of this research was studying of physico-chemical interaction in $CuInS_2$ – "P_2S_4" system, then the construction of proper phase diagrams and development on the basis of derived results the technological requirements for single crystals growing of $CuInP_2S_6$ tetrary compound.

For the choice of the quasibinary cross-section, on which $CuInP_2S_6$ compound appear, the experimental triangulation of Cu_2S – In_2S_3 – "P_2S_4" quasiternary system was made (fig.1).

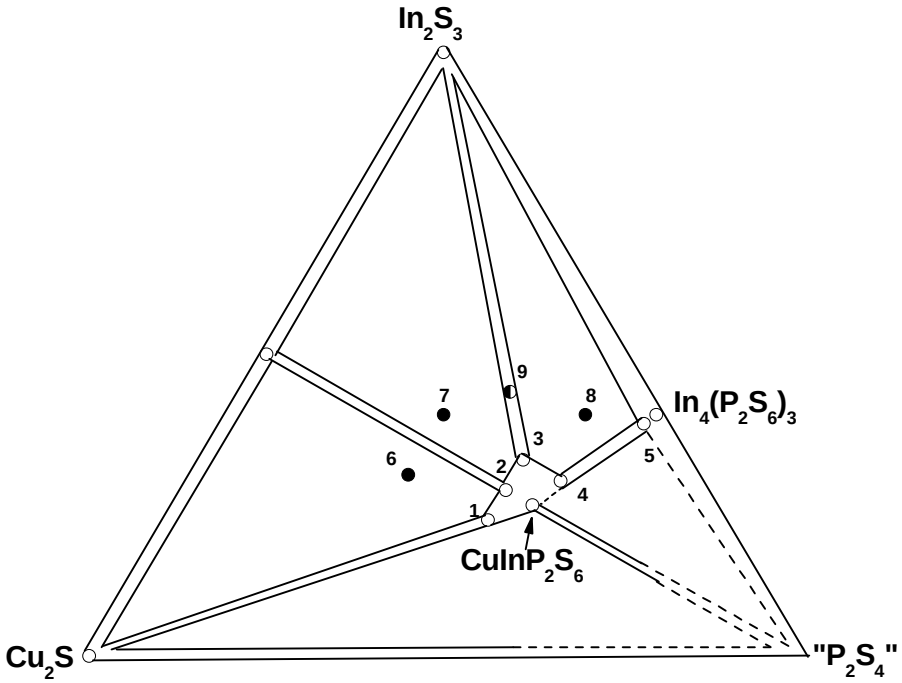

Fig. 1 *Phase equilibria in the Cu_2S – In_2S_3 – "P_2S_4" triple system*

The quasibinary $CuInS_2$ – "P_2S_4"cross-sections of Cu_2S – In_2S_3 – "P_2S_4" triple system were chosen for the study of formation character of $CuInP_2S_6$ compound.

The synthesis of alloys of the investigational system was carried out by one temperature method from $CuInS_2$ ternary compound with addition of the expected amounts of phosphorus, sulphur in the vacuumed quartz ampoules. The choice of $CuInS_2$ 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 $In_4(P_2S_6)_3$ appears in the first place, as more thermodynamics steady. Their interaction with a metallic copper with formation of $CuInP_2S_6$ tetrary 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 $CuInS_2$ – "P_2S_4" system is built (fig. 2).

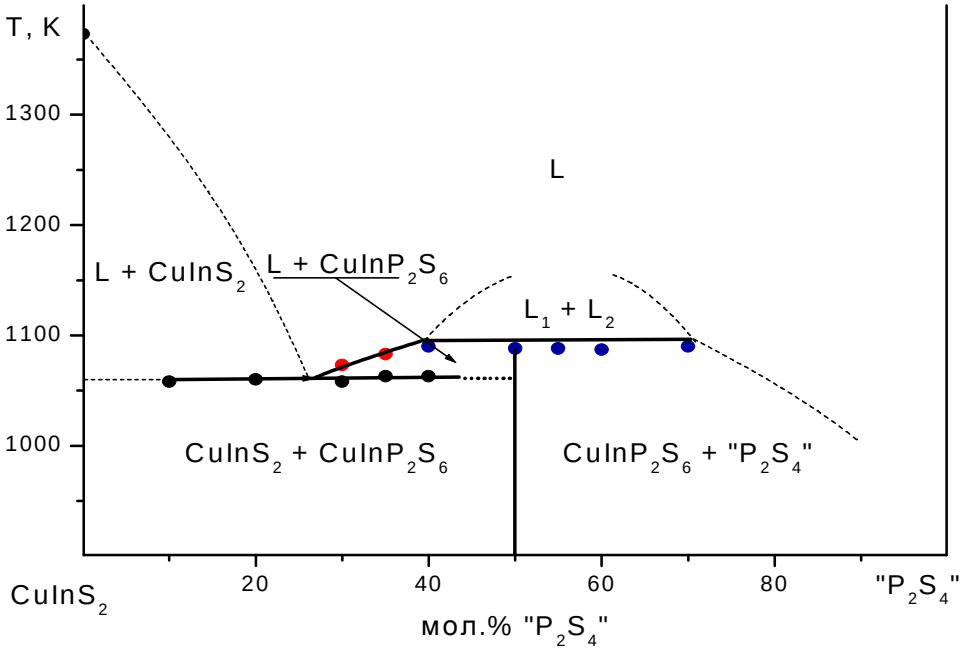

Fig. 2. *Diagram of the system $CuInS_2$ – "P_2S_4"*

It is obvious (Fig. 2), that $CuInP_2S_6$ compound appears due to a synthectic reaction from two liquids L_1 and L_2 at the temperature 1088 ± 5 K. The eutectic between $CuInS_2$ and $CuInP_2S_6$ compounds conforms the composition of 75 mol. % $CuInS_2$ and melts at the temperature 1088 ± 5 K.

It was performed from the calculation of $CuInP_2S_6$ 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 = 107,101°.

The specific density of $CuInP_2S_6$, certained by the hydrostatic weighing method in toluene, was $3{,}425 \cdot 10^3$ 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_2S – In_2S_3 – "P_2S_4" quasiternany 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 $CuInP_2S_6$ 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

yet. The scheme of chemical transport reactions at single-crystals growing of $CuInP_2S_6$ compound it is possible to present by the equation: $2CuInP_2S_6 \leftrightarrow 2CuI + 2P_2S_5 + S_2$.

The final stage of the growth process of $CuInP_2S_6$ 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 $CuInP_2S_6$ single-crystals compound by the CTR method are presented.

Table 1

The growing conditions of $CuInP_2S_6$ single-crystals by the CTR method

Formula of compound	Transport agent; мg/cm^3	Temperature		D T, K	t, h	Transport substance, %	Dimen-sions, mm	Color and Habitus of crystalls
		Evaporation zone	Crystallization zone					
$CuInP_2S_6$	I_2;CuI; 4–6	900	870	30	350	80	10x8x0,1	Thin plates of yellow-lemon colors
		910	860	50	300	95	6x6x0,1	
		940	920	20	400	70	5x5x0,1	

The growth of $CuInP_2S_6$ 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_2S_4" systems were done in present work.

The growth process by the directed crystallization of fusion (Bridgman teqnique) was performed from the stoichiometrical compositions charge of $CuInP_2S_6$ 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 $CuInP_2S_6$ single-crystals. The optimum conditions of $CuInP_2S_6$ single-crystals growing by the directional crystallization of fusion method are given in table 2.

Table 2

The optimum conditions of $CuInP_2S_6$ single-crystals growing by the directional crystallization of fusion method

Compound	Temperature of fusion zone, K	Temperature of annealing zone, K	DT of growth zone, K/mm	Growth rate, mm/day
$CuInP_2S_6$	1100	870	3	2,5

Consequently, the monolithic "boules" of $CuInP_2S_6$ crystals by 14 mm diameter and long 20−25 mm long with well developed cleavage are obtained. General view of samles, obtained from $CuInP_2S_6$ single-crystals is presented on Fig. 3.

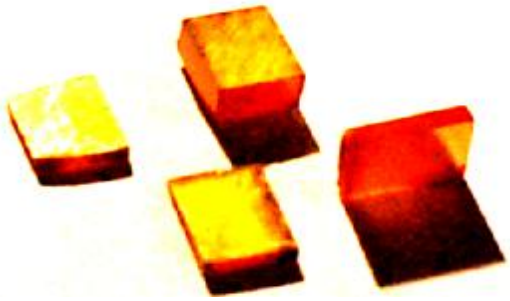

Fig. 3. *Samles, obtained from $CuInP_2S_6$ single-crystals (Bridgman teqnique)*

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