

ANALYSIS OF CONDITIONS OF CuInS_2 OBTAINING FROM THE $\text{CuCl-In}_2\text{S}_3\text{-H}_2\text{O}$ SYSTEM

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The presented work is devoted to conditions of CuInS_2 obtaining solar energy material, from $\text{CuCl-In}_2\text{S}_3\text{-H}_2\text{O}$ system. The material composition was subjected to chemical analysis. X-ray powder analyses showed that the compounds were single phase with tetragonal structure.

Several members of the I-III-VI family of semiconductors have recently received considerable interest because of their potential application in solar cells. These compounds crystallize in the chalcopyrite structure and are direct bandgap semiconductors. Of these many ternary compounds, CuInS_2 is particularly well suited for solar cell application due to its bandgap of 1.55 eV, which is close to the ideal value for optimum solar energy conversion via the photovoltaic effect [1]. A calculation by Meese et al. [2] concludes that solar energy efficiencies between 27 and 32% are theoretically achievable in CuInS_2 p-n homojunction. Thin film CuInS_2 solar cells with an efficiency of 3.6% were reported in 1977 [3]. Kazmersky L.L. et al. have reported an efficiency of 3.55% for CdS/CuInS_2 heterojunctions [4].

Stoichiometric mixtures of constituent elements (Cu, In and S) were sealed in evacuated 10^{-6} torr quartz ampoules and prereacted in the furnace as follows. The furnace temperature was raised to 600°C , held for several hours to prevent an explosion [6-8], then raised to 1175°C and held for 2 days for the purpose of complementing their uniformity. Various slow cooling rates were employed to obtain large homogenous single crystals.

It is known that the obtaining of semiconductor materials by simple technology and the least expenses is one of the urgent problems of solid-state electronics. Development of very simple and cheap method of obtaining of compound CuInS_2 instead of a method of synthesis which requires a lot of time and energy and is frequently accompanied by explosion of an ampoule can be considered as an important step in the direction of the solution of this problem.

Taking into account that In_2S_3 is used at obtaining CuInS_2 from the water environment and in this process InCl_3 is also obtained, we considered

expedient to investigate the influence pH on them. The solution of NH_4OH with 5% is gradually added to the solution of InCl_3 with $\text{pH}=2$. It is established that $\text{In}(\text{OH})_3$ is formed at $\text{pH}=3.5$. The received deposit is not dissolved at raising pH even up to 11. 30-40 ml of distilled water is added to the definite amount of In_2S_3 and its change is registered depending on pH (by ammonia). It is established that any change do not occur up to $\text{pH}=11$, i. e. In_2S_3 is not dissolved in the excess NH_4OH . In_2S_3 gradually decays at small values pH beginning from 0.5. So In_2S_3 is steady in the strong acid (with HCl) environment.

Taking into consideration the complexity of synthesis CuInS_2 the purpose of the presented work is working out a simple method of obtaining of this compound. The basic essence of this method is that the exchange reaction is occurred by exerting influence on In_2S_3 with ammonia complex of CuCl in the water environment and as a result CuInS_2 is obtained.

At addition of ammonia solution of CuCl on freshly prepared In_2S_3 the brightly yellow colour turns into the brown one beginning from the first drop. With increase in amount of the deposition agent the suspension In_2S_3 will be turned into crystalline deposit and the bright blue colour of the excess CuCl appears on the solution. The deposit is filtered, is reached up to the constant mass at 105°C and weighed. As it is visible from the table 1 the practical output CuInS_2 is higher than the theoretical one.

Table 1. The unity of turning In_2S_3 to CuInS_2 .

Taken $\text{In}_2\text{S}_3, \text{g}$	Obtained CuInS_2, g	
	practically	calculated
0.3251	0.4439	0.3628
-----	0.4400	-----
-----	0.4462	-----
-----	0.4320	-----

To obtain the full deposit the amount CuCl should be taken more than the preliminary calculated one. But as CuCl is used as an ammonia complex in water it cannot give the deposit. copper (I) hydroxide. It is supposed that at high values of pH InCl_3 allocated from the reaction is hydrolyzed and mix up with CuInS_2 , so high results are obtained.

To specify this assumption the experiments have been carried out in the wide (1-9) interval of pH. At addition of plenty of solution CuCl onto In_2S_3 pH of the environment achieves up to 10. In

all experiments the value of pH achieves up to 10. Then the 10% hydrochloric acid is used for an establishment of the fixed value of pH. After the filtration the obtained deposits are weighed.

As it is visible from the table 2 the deposits obtained up to pH=4 practically coincide with the theoretical calculations. The great values at pH>4 are explained with the hydrolysis InCl_3 allocated from the reaction.

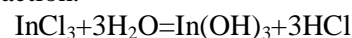


Table 2. The influence of pH on the full deposition of CuInS_2

№	Taken In_2S_3 ,g	pH of the environment	Obtained CuInS_2	
			practically	calculated
1	0,4620	1	0,5142	0.5156
2	-----	2	-----	0.5142
3	-----	3	-----	0.5122
4	-----	3.5	-----	0.5120
5	-----	4	-----	0.6210
6	-----	5	-----	0.6312
7	-----	6	-----	0.6340
8	-----	8	-----	0.6282
9	-----	10	-----	0.6260

The influence of temperature on deposition CuInS_2 from the solution is investigated. The experiments have been carried out at the temperatures 20°C , 50°C and 90°C . It is established that the temperature factor does not influence on the results.

The material composition is determined using the following techniques. The dry deposit in amount of 0,5321g decays by the nitric acid diluted in the ratio 1:1. Then the rest of nitric acid is evaporated up to a wet condition of products of

decay. As a result by means of being oxidized the copper (I) ions turn into the copper (II) ions, the sulphide ions turn into the sulphate ions. The solution is evaporated up to a wet condition.

The wet deposit is dissolved in the distilled water. Cu^{++} ions are determined by the known method, the ions of sulphate are determined by BaCl_2 and the indium (III) ions are determined by the trilon B. The results of the chemical analysis are presented in the table 3.

Table 3. Chemical analysis of CuInS_2

Taken	Determined, g					
	copper		indium		sulphur	
	practic.	theor.	practic.	theor.	practic.	theor.
0.5321g, deposit	0.1388	0.1393	0.2532	0.2520	0.1386	0.1409

The note: The data indicated in the table are the average values of the four parallel carried experiments.

By the performed calculations on the results of the analyses it is proved that the obtained compound is CuInS_2 .

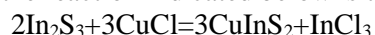
The amount of the indium in the solution is determined. The ammonia complex CuCl is added to the In_2S_3 of 0,6214 g until the light blue colour appears on the surface of the solution. Then pH of the environment is reduced up to pH=3 by the 10% nitric acid.

After the filtration and washing the deposit the filtrate is determined.
by the distilled water the amount of the indium in

Table 4. The determination of the amount of the indium entering the solution

Taken In_2S_3 ,g	Obtained CuInS_2 ,g		the amount of the indium entering the solution
	practically	calculated	
0.6214	0.6920	0.6934	0.1553
-----	0.6876	-----	0.1532
-----	0.6900	-----	0.1525
-----	0.6911	-----	0.1535

From the table it is possible to conclude that after the reaction the amount of the indium entering the solution is 1/4 part of the total taken indium. The rest 3/4 parts are contained in CuInS_2 . It proves once again that the reaction indicated below is true:



From the diffractogramm of the obtained compound it is established that these samples belong to the tetragonal structure. The position and the intensity of the observable five sharp maxima allow to conclude that this compound is CuInS_2 .

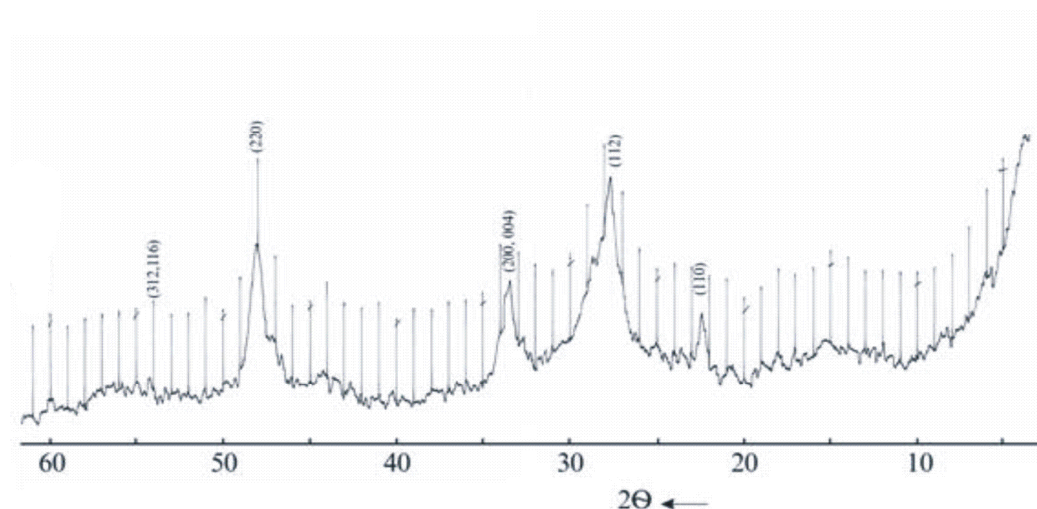


Fig. X-ray diffraction pattern of a CuInS_2 powder obtained from the $\text{CuCl-In}_2\text{S}_3\text{-H}_2\text{O}$ system.

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CuCl-In₂S₃-H₂O SİSTEMİNDƏN CuInS₂-nin ALINMA ŞƏRAİTİNİN TƏDQIQI***B.Z.Rzayev, M.H.Hüseynəliyev, A.B.Rzayeva***

CuCl-In₂S₃-H₂O sistemindən günəş enerji materialı olan CuInS₂ birləşməsinin alınmasının yeni üsulu işlənilib hazırlanmışdır. Müəyyən edilmişdir ki, otaq temperaturunda pH=2-4 qiymətlərində In₂S₃-ün 3/4 hissəsi CuInS₂ birləşməsinin alınmasında iştirak edir, 1/4 hissəsi isə duz formasında məhlulə keçir. Çöküntünün elementlərə görə analizi onun CuInS₂ formuluna uyğun gəldiyini təsdiq etmişdir. Alınan birləşmənin rentgen analizi onun tetragonal strukturda kristallaşdığını göstərmişdir.

ИССЛЕДОВАНИЕ УСЛОВИЙ ПОЛУЧЕНИЯ CuInS₂ ИЗ СИСТЕМЫ CuCl-In₂S₃-H₂O***Б.З. Рзаев, М.Г. Гусейналиев, А.Б. Рзаева***

Разработан новый способ получения CuInS₂ из системы CuCl-In₂S₃-H₂O. Установлено, что при комнатной температуре при pH=2-4 3/4 часть In₂S₃ участвует при образовании CuInS₂, 1/4 часть в форме соответствующих солей переходит в раствор. Анализ элементарного состава осадка подтвердил формулу, соответствующей CuInS₂. Рентгенографический анализ полученного соединения показал, что оно кристаллизуется в тетрагональной структуре.