Hydrothermal synthesis of copper thioarsenites

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Recently, the interest in the production of metal chalcogenides by hydrothermal method with the use of thio- and selenoamides has increased. This method is widely used for the deposition of thin layers of metal chalcogenides and solid solutions based on them. It provides great opportunities for the synthesis of new compounds. Electrophysical properties of thin layers obtained by this method differ from the properties of thin layers obtained by other methods [1]. When the solution of metal thiocarbamide has the pH > 7, the reaction proceeds between Me^{+n} and S^{-2} ions. During the hydrolysis of thiocarbamide in alkaline solution, metal thiocarbamide complexes are formed primarily and then their decomposition occurs at the end. It has been defined that during the decomposition of copper(II) thiocarbamide complexes the reduction of copper occurs. Therefore, we used thiocarbamide as a sulfonating agent to synthesize copper(I) thioarsenites.

The solutions of 0.05 M $CuCl_2$, $NaAsO_2$ and $CS(NH_2)_2$ were used to synthesize copper(I) thioarsenites ($Cu_6As_4S_9$, Cu_3AsS_3 and $CuAsS_2$). The solutions at pH 7÷8 were mixed and placed in a teflon-made autoclave (100 ml) in accordance with the stoichiometric composition of the compounds. The samples were heated in microwave oven at 443 K for 48 hours. Obtained sediments were thermally processed at vacuumed quartz bulbs (~10^{-2} Pa) for 8 hours at 673 K after filtration.

The individuality of the obtained copper(I) thioarsenites has been confirmed by X-ray powder diffraction (2D PHASER "Bruker", CuK_α, 2θ, 20–80 deg.) and DTA (pyrometer HTP-70, device Thermoscan-2) methods. According to DTA results, Cu_3AsS_3 and $CuAsS_2$ compounds are melting congruently at 938 K and 898 Krespectively,but $Cu_6As_4S_9$ is melting incongruently at 762 K.

Micromorphology of the obtained compounds was studied by HITACHI TM3000 brand microscope (Figure).

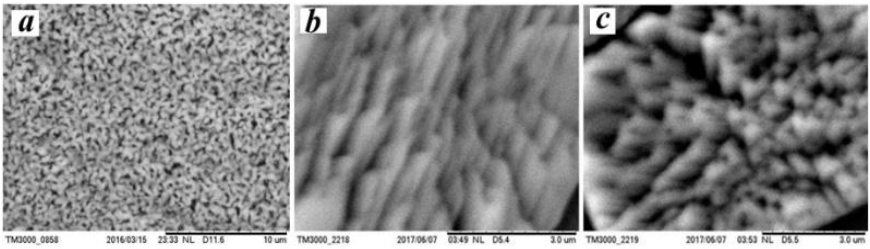

Fig. SEM photos of thermally processed $CuAsS_2$ (*a*), Cu_3AsS_3 (*b*) and $Cu_6As_4S_9$ (*c*) compounds at 673 K

The necessary requirements for thioarsenites synthesis were revealed and conditions of sulfide co-precipitation were determined. The most important were the determined pH, concentration of salts, thiocarbamides and ligands, as well as the degree of transformation of the initial salts into thiosalt, physical and chemical properties and solubility sum. The sulfonating of both metals depends on the amount of thiocarbamide in the reaction mixture. The following equation was used to calculate the equilibrium conditions in a system consisting of copper and arsenic:

$$\Delta p\alpha = \Delta pHH - pC_b - \Delta p\frac{\delta}{1-\delta},$$

where $\Delta p\alpha$ – the concentration difference of Me^{Z+} ions which does not form a complex; ΔpHH – solubility outcome difference of metal sulphides; pC_b – difference in the initial concentrations of metals; $\Delta p\frac{\delta}{1-\delta}$ – difference of metal salts to sulfide conversion rates.

It has been determined that such compounds as $Cu_{20}As_{13}S_{31}$ and $Cu_4As_2S_5$ were also obtained in aqueous solution, depending on the initial salts concentration. The $Cu_4As_2S_5$ compound decayed at 869 K and formed an alloy consisting of $Cu_{12+x}As_{4+y}S_{13}$ (here $0 \le x \le 1.72$; $0 \le y \le 0.08$). An elemental analysis of the obtained sediments was made (Launch Trion XL dilution refrigerator – OXFORD device) to estimate the precise stoichiometric composition of $Cu_6As_4S_9$,Cu_3AsS_3 and $CuAsS_2$ compounds. Mass and atomic ratios of copper, arsenic and sulfur in the compounds obtained were determined (Table).

Results of the elemental analysis of compounds

Compounds	The amount of elements, %					
	Cu		As		S	
	weight	at.	weight	at.	weight	at.
$Cu_6As_4S_9$	39.50	31.57	30.86	21.05	29.64	47.38
Cu_3AsS_3	52.89	42.85	20.66	14.28	26.45	42.87
$CuAsS_2$	31.51	24.98	36.93	24.97	31.56	50.09

According to the results presented in the table, the stoichiometric structure of the obtained sediments corresponds to $Cu_6As_4S_9$,Cu_3AsS_3 and $CuAsS_2$ compounds.

References

1. V. S. Zakhvalinsky, Thi Thao Pham, Thi Tham Khong [et al.]. Modern Science-Intensive Technologies (2013)6 : 58.