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PREPARATION OF THE SULFIDES OF P-ELEMENTS OF GROUPS III–IV OF THE PERIODIC TABLE VIA THEIR VOLATILE IODIDES♣

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Thermodynamic analysis of «p-element iodide – sulfur» systems for the elements of groups III–IV of the Periodic Table in the temperature range of 300–500°C was carried out by the method of equilibrium constants. The sulfides of aluminum(III), gallium(III), indium(III), germanium(IV) were prepared by interaction of their volatile iodides with sulfur in an evacuated two-section quartz glass reactor at the temperature of 350–400°C. The yield of sulfides was 95, 93, 68 and 72%, respectively. The content of iodine in the prepared sulfides was at the level of 1.8–4.2 at. %.

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1. Introduction

The sulfides of p-elements of groups III–IV of the Periodic Table are promising materials for infra-red optics and semiconductor engineering. They are individual semiconductors entering into the composition of complex sulfides and chalcogenide glasses. The traditional method of preparation of these compounds consists in joint melting of simple substances in evacuated quartz glass ampoules at 800–1200°C for several dozens of hours [1]. It complicates the selection of structural materials and contributes to the contamination of sulfides with impurities entering from the walls of quartz reactor which degrades their target properties.

With the aim of decreasing the temperature and duration of synthesis it is proposed to use oxides or hydroxides and hydrogen sulfide instead of simple substances of p-elements as the source of sulfur [2]. Another approach is the reaction between hydrogen sulfide and organic compound of p-element in liquid alkanes [3]. The drawbacks of these methods consist in the presence of noticeable amounts of unreacted oxide and organic impurities in the prepared sulfide, low efficiency and the use of toxic hydrogen sulfide.

The goal of this work was to investigate the interaction of volatile and low-melting iodides with sulfur and the subsequent preparation of the sulfides of aluminum, gallium, indium and germanium. The expected merits of this method are in the considerable decrease in temperature and duration of synthesis, the possibility to load the components into the reactor by vacuum evaporation, absence of toxic reagents and products of synthesis.

2. Experimental

To estimate the possibility of preparing the sulfides of p-elements by the interaction of their iodides with sulfur, the «p-element iodide – sulfur» systems were subjected to

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thermodynamic analysis by the method of equilibrium constants. The proposed thermodynamic model is based on the following reaction

$$eMeI_x(cr) + y/8S_8(g) \leftrightarrows Me_eS_y(cr) + xe/2I_2(g), \quad (1)$$

$$n/8S_8(g) \leftrightarrows S_n(g), \quad (2–7)$$

where Me is Al, Ga, In, Si, Ge, Sn; n = 2–7. It was assumed that the investigated systems comprised three phases: the melt of «p-element iodide–sulfur–iodine», the vapor phase, the crystal phase represented by the corresponding sulfide. It was also assumed that the melt of «p-element iodide–sulfur–iodine» is the ideal solution; the vapor phase complies with the equations of the state of the ideal gases mixture; the vapor pressure of the sulfide is negligible as compared with the total pressure in the system; dissociation of molecular iodine does not take place. The equilibrium constants of the reactions (1)–(7) were calculated using the data on the thermodynamic properties of individual substances [4, 5]. The system of mathematical equations describing this thermodynamic model is considered in detail in [6]. The result of the calculation was the determination of the content of the components in all assumed phases.

The possibilities of the proposed method were experimentally tested. Aluminum(III) iodide, gallium(III) iodide, indium(III) iodide and germanium(IV) iodide were synthesized from simple substances. The prepared iodides interacted with sulfur in the two-section evacuated quartz glass reactor (Fig.1). Programmable thermoregulators Thermolux-010, equipped with chromel-alumel thermocouples, were used to control the temperature of the processes. The lower section was heated up to 350–400°C which led to intensive emission of iodine vapors. Their condensation in the upper section precluded explosion. The temperature gradient throughout the reactor height provided the selective removal of iodine from the melt and the shift of reaction equilibrium (1) to the formation of the p-element sulfide. The duration of synthesis was 2 hours. After the synthesis the prepared substances were annealed in the lower section at 500°C for one hour with the purpose of providing a more complete removal of the iodine.

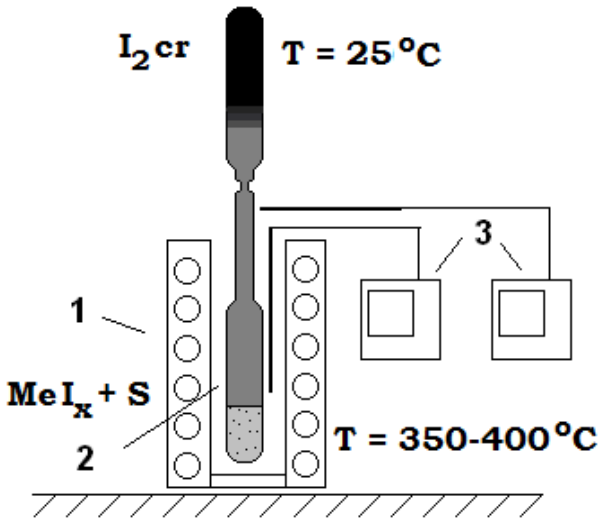

Fig. 1. Scheme of set-up for synthesis of sulfides.
1 – furnace; 2 – reactor; 3 – programmable temperature regulators.

Elemental composition of the prepared powders was determined by the method of the X-ray micro-analysis using the scanning electron microscope SEM-515 (Philips) equipped with the energy-dispersive analyzer EDAX-9900 (EDAX). The phase composition was determined by the method of X-ray phase analysis using the diffractometer XRD-6000 Shimadzu (CuKα-radiation).

3. Results and discussion

Fig. 2 presents the results of the solution to the system of the equations of the thermodynamic model in the form of the temperature dependence of the yield of p-element sulfide according to the reaction (1) in the temperature range of 300°C–500°C. The yield was calculated

as the ratio of the amount of sulfide substance in the equilibrium state with respect to the initial amount of iodide, taking into account the stoichiometric reaction coefficients. It follows from these results that the yield of aluminum(III) sulfide, gallium(III) sulfide and silicon(IV) sulfide in the investigated temperature range is close to 100%. The conversion degree of germanium(IV) iodide increases from 6 to 26%, of indium(III) iodide from 2 to 6%. The yield of tin(IV) sulfide at 500°C does not exceed 1%. The observed regularities are explained by the decrease in the thermodynamic stability of the sulfides in passing from aluminum to indium and from silicon to tin. The thermodynamic stability of iodides in the group changes in a non-monotonic way. Standard Gibbs energies during the formation of gaseous iodides at 298K in Al – Ga – In and Si – Ge – Sn series are -302.7, -200.7, -224.2 kJ/mol and -237.1, -192.6, -260.7 kJ/mol, respectively. The minimum thermodynamic stability of the iodides of gallium and germanium can be due to the fact that they are the first representatives of post-transition elements in their groups and their 18-electron shell provides an increased polarizing effect on the atoms of iodine with the destabilization of the molecule of iodide. Increase in size of the central atom, while passing from gallium to indium and from germanium to tin, decreases its polarizing ability which leads to the increase in iodide stability. Despite the greater thermodynamic stability of the iodides of the third group as compared with the forth group they more easily transform into corresponding sulfides due to the high stability of the latter. To increase the conversion degree of iodides during the synthesis of sulfides the process must be carried out in a two-section reactor. The condensation of iodine vapors in the upper "cold" section leads to its gradual removal from the melt which assists the shift of reaction equilibrium (1) to the formation of the corresponding sulfide.

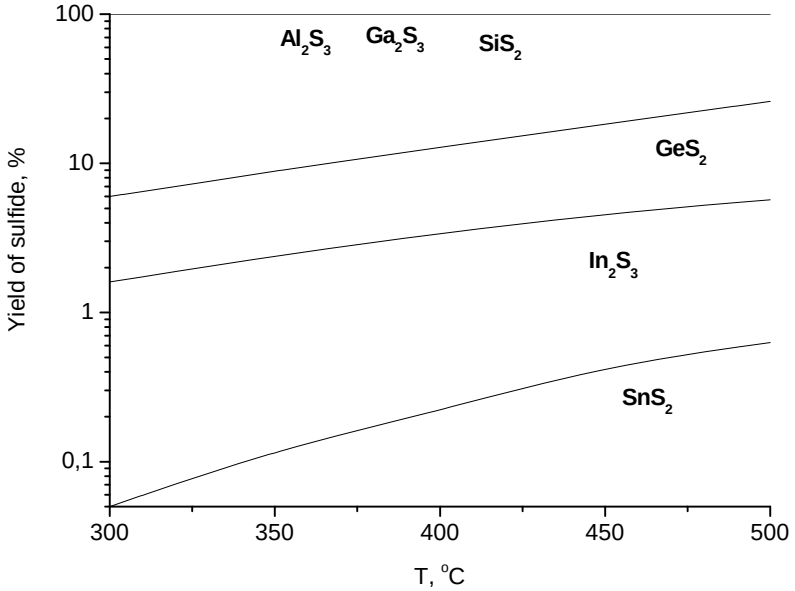

Fig. 2. Thermodynamically specified yield of sulfide depending upon temperature.

The compositions of the prepared sulfides of aluminum, gallium and germanium are given in Table 2. The samples for the analysis were in the form of tablets compressed from ground powder. The ratio in the content of sulfur to the p-element in the prepared powders is the same as in the corresponding sulfide within the error of measurement which is equal to 15%. Despite annealing the sulfides at 500°C for 1 hour the content of iodine in them is at the level of 1.8–4.2 at. %. Perhaps, the difficulty in the removal of iodine is due to the fact that it does not appear in the form of free molecules of I_2, but is chemically connected with the atoms entering the sulfide composition. This assumption is proved by the values of bond energies Me – I which greatly exceed the dissociation energy of molecular iodine [7]. The composition of the prepared aluminum sulfide was not determined due to its intensive hydrolysis in air.

Table 1. Composition of prepared sulfides.

	Sulfide composition, at. %				Yield, %
	E	S	I	S/E	
Al	–	–	–	–	95
Ga	39.4	58.8	1.8	1.49	93
In	38.9	57.3	3.8	1.47	68
Ge	31.7	64.1	4.2	2.02	72

Fig. 2 gives the X-ray patterns of the prepared powders of sulfides. All the samples are polycrystalline and characterized by phase homogeneity. The synthesized gallium(III), indium(III), aluminum(III) and germanium(IV) sulfides have a cubic (PDF No. 43-0916), tetragonal (PDF No. 73-1366), hexagonal (PDF No. 81-1811) and orthorhombic (PDF No. 75-1978) elementary cell, respectively [8]. The substantial degree of amorphism in the sample of the aluminum sulfide is, probably, due to its hydrolysis in air during the preparation and measurements of the sample.

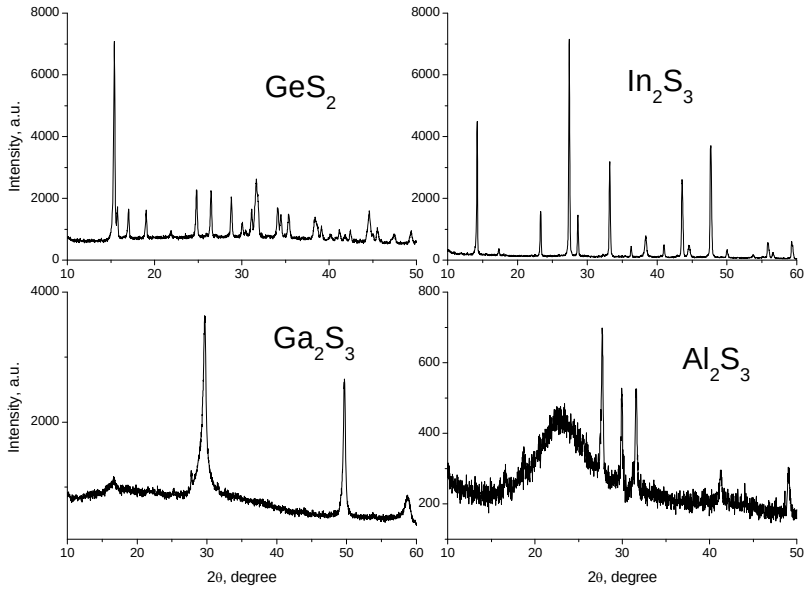

Fig. 3. X-ray patterns of the prepared sulfide powders.

The yield of the prepared sulfides was determined by the mass of the annealed powder, taking into account the content of iodine (Table 1). It follows from the given results that the values of the theoretically calculated and experimentally obtained yield of the aluminum(III) sulfide and the gallium(III) sulfide are in good agreement. It is connected with the high reactivity of the iodides of these elements with respect to sulfur and the absence of thermostable sulfide-iodides whose formation complicates the preparation of sulfides. The lower values of the experimental results are, probably, connected with the partial evaporation of the sulfides formed during annealing due to transport reactions with iodine:

$$Al_2S_3 + 3I_2 \leftrightarrows 2AlI_3 + 3S;\ \ Ga_2S_3 + 3I_2 \leftrightarrows 2GaI_3 + 3S.$$

It is also proved by the presence of a certain amount of the sulfide in the upper section of the reactor which was not taken into account in the calculation of the yield due to the uncertainty in composition.

The experimentally determined values for the yield of the indium(III) sulfide and the germanium(IV) sulfide greatly exceed the thermodynamically specified conversion degree of iodides. It is connected with the fact that the synthesis in the two-section reactor makes it possible to greatly shift the equilibrium of reactions (1) to the formation of the sulfide. However, the

obtained values are lower than for the sulfides of aluminum and gallium. It is due to the fact that indium and germanium form sufficiently stable sulfide-iodides by reactions:

$$InI_3 + S \leftrightarrows InSI + I_2,$$
$$GeI_4 + S \leftrightarrows GeSI_2 + I_2,$$
$$2GeI_4 + 3S \leftrightarrows Ge_2S_3I_2 + 3I_2.$$

With the temperature gradient in the reactor the formed sulfide-iodides are partially decomposed:

$$3InSI \leftrightarrows In_2S_3 + InI_3,$$
$$2GeSI_2 \leftrightarrows GeS_2 + GeI_4,$$
$$2Ge_2S_3I_2 \leftrightarrows 3GeS_2 + GeI_4.$$

The evolved iodide condenses in the upper section of reactor together with the iodine which complicates its further interaction with sulfur. The assumed mechanism is experimentally proved by the presence of noticeable amounts of the iodides of germanium and indium in the collector for the iodine and by the formation of the orange-red crystals of InSI in the process of synthesis as well as of the vitreous sulfide-iodides of germanium decomposed during heating.

The sulfide-iodides and the products of their thermal decomposition are, probably, the main form of the iodine presence in the prepared sulfides after annealing. The concentration of iodine correlates with the stability of sulfide-iodides described in literature [2, 9–11]: the least content of iodine is observed in the gallium sulfide and the highest content is observed in the germanium sulfide. To provide a more complete removal of iodine it is necessary to anneal powders at higher temperatures.

It follows from the theoretical and experimental results obtained in the presented work that the formation of the sulfides of aluminum(III), gallium(III) and silicon(IV) from their volatile iodides attains its high yield at 350°C in 1.5–2 hours. The thermodynamically specified low yield of the sulfides of indium(III) and germanium(IV) can be increased up to 68–72% by synthesis in the reactor with two temperature areas. The formation of relatively stable sulfide-iodides is the main factor complicating the attainment of a higher yield of these sulfides. Synthesis under conditions providing thermal decomposition of sulfide-iodides will increase the yield of the sulfides of indium and germanium.

4. Conclusions

Thermodynamic analysis of «p-element iodide – sulfur» systems was carried out for the elements of groups III–IV of the Periodical Table in the temperature range of 300–500°C. The thermodynamically specified yield of the sulfides of aluminum(III), gallium(III) and silicon(IV) is close to 100%. The yield of the sulfides of indium(III), germanium(IV) and tin(IV) at 500°C was 6, 26 and <1%, respectively.

The possibility in principal to prepare refractory sulfides of p-elements of groups III–IV of the Periodical Table is demonstrated by the interaction of their iodides with sulfur at 350–400°C. Polycrystalline powders of the sulfides of aluminum(III), gallium(III), indium(III) and germanium(IV) with the yield of 95, 93, 68 and 72%, respectively, have been prepared. The high yield is provided by shifting the equilibriums to the formation of sulfides due to removal of iodine from the reaction area. After annealing at 500°C for one hour the residual content of iodine in the prepared sulfides was 1.8–4.2 at. %.

The proposed method is promising for the preparation of the sulfides of p-elements with high degree of purity by decreasing the temperature and the duration of synthesis as well as by the use of volatile iodides.

Acknowledgment

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