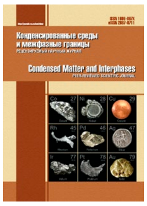

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Review

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Phases with layered (AB) and “defective” (A_2B_3) structures in A^{III}–B^{VI} systems. Part 2. Phase diagrams and approaches to some problems of reproducible synthesis in A^{III}– B^{VI} systems. Review

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Abstract

The paper analyzes phase diagrams of A^{III}–B^{VI} systems and phase equilibria involving crystalline compounds formed in these systems. The location of each solid binary phase mainly related to mono- and sesquisulfides families and selenides of aluminum, gallium, and indium on *T*-*x*-diagrams is discussed in detail. The homogeneity regions of these phases were also analyzed if the necessary data were available. For polymorphic (or close to them) transformations, the nature of the occurring structural transformations was described and the temperature stability of various modifications of similar composition was analyzed. Using examples of several systems, it was shown how, by changing the experimental conditions, it is possible to reproducibly obtain compounds with the required structure (even for different polytypes of structures with very similar structures of individual layers) and the required composition (including those within the regions of phase homogeneity). Various methods of reproducible inorganic synthesis were considered, taking into account the features of the phase diagram and phase equilibria. In conclusion, current and partially still unresolved issues concerning the characteristics of the $A_2^{III}B_3^{VI}$ and $A_1^{III}B_1^{VI}$ compounds were analyzed.

Keywords: Chalcogenides, *A*(III)*B*(VI), Stoichiometric vacancies, Phase diagrams, Phase equilibria

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1. Introduction

This series of review articles is devoted to the description of two large groups of inorganic substances with very unusual structures and properties: mono- and sesqui-chalcogenides of Al, Ga, and In compounds. The first part of the study considers the structural features of phases of[*] $A_1^{III}B_1^{VI}$ and $A_2^{III}B_3^{VI}$ families and the possible areas of practical use of these compounds based on structural features. This second part of the study aimed to summarize and reconcile the data on phase diagrams and equilibria in $A^{III}–B^{VI}$ systems. The main attention was paid to the relationship between a specific phase diagram and the conditions of formation of certain modifications of crystalline phases of the families of mono- and sesquisulfides and selenides of aluminum, gallium, and indium. In this part of the study we also considered the basics of new methods for precision variation of both the phase and non-stoichiometric composition of already synthesized crystalline chalcogenides. The search for such methods is due to the fact that traditional methods of regulating the composition of the solid phase through vapor (for example, during directional crystallization with controlled vapor pressure) are almost unsuitable for $A^{III}B^{VI}$ chalcogenides due to the very low values of saturated vapor pressures above condensed phases even under conditions of contact with melts (S - L - V equilibrium) [1]. Both the previous and the present (second) parts of the review are based on the analysis of both third-party literary data and the results of the studies of authors of this review and other VSU employees.

2. Al-S and Al-Se systems

2.1. The T-x-diagram and phase equilibria in the Al-S system

When mentioning the aluminum-sulfur system, any chemist will immediately recall the existence of only one compound, Al_2S_3, which is easily obtained by direct synthesis (for example, by igniting a mixture of powdered Al + S). Until recently, this aluminum sulfide was considered unpromising for high-tech materials science. Indeed, Al_2S_3 is easily destroyed in air and liquid water (the latter interaction is a well-known convenient method for obtaining gaseous hydrogen sulfide). Despite the above, the example of the Al – S system clearly demonstrates how the phase diagram can become the basis for the creation of a new and possibly very promising chemical technology even in the case when solid intermediate phases cannot be obtained at room temperature (as AlS), or they quickly degrade in the atmosphere (as Al_2S_3).

The detailed analysis clearly demonstrates that the Al – S system is not so simple. Thus, back in 1940, Murakami and Shibata [2] showed that, along with Al_2S_3, there is also ***mono***-aluminum sulfide AlS, which can only be obtained at temperatures around 1000 °C. However, the region of existence of AlS (~50 °C) can be easily “skipped”, since when the upper limit of existence is exceeded, aluminum monosulfide decomposes according to a peritectic reaction (see Fig. 1):

$$AlS = L_2 + \gamma\text{-}Al_2S_3. \quad (1)$$

As the temperature decreases, the AlS phase also decomposes. Moreover, it has not yet been possible to preserve aluminum monosulfide even with rapid quenching. The decomposition of AlS during cooling results in almost pure molten aluminum (L_1 liquid) and aluminum sesquisulfide [3]:

$$AlS = L_1 + \gamma\text{-}Al_2S_3. \quad (2)$$

The authors of later studies [4-8] conducted a number of experiments using thermal and X-ray diffraction analysis (XRD), as well as optical metallography. The results of these studies demonstrated that aluminum monosulfide AlS melts peritectically at ~1058 °C (reaction 1) and Al_2S_3 sesquisulfide melts congruent at ~ 1073 °C. The general appearance of the diagram is shown in Fig. 1, and the most important data on phase equilibria are summarized in Table 1.

Among the features of the presented diagram, in addition to the already mentioned AlS, observed on T-x-diagram in a narrow temperature

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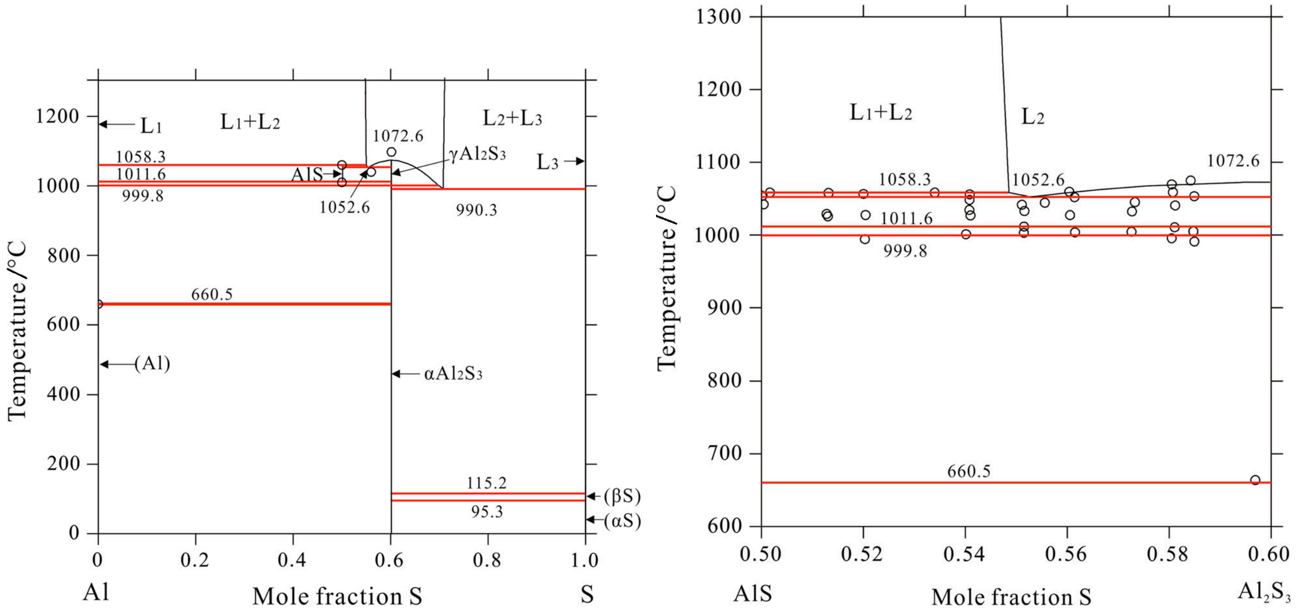
[*] Various $A^{III}B^{VI}$ modifications, related by solid-phase transformations, are often characterized by similar but different compositions (for example, $\gamma Ga_{2+\delta}S_3$ and $\alpha' Ga_2S_3$). This contradicts the classical definition of polymorphism, according to which different structures must have the same composition. Taking into account the proximity of structural $A_2^{III}B_3^{VI}$ motifs we discussed phases of the sesqui-chalcogenide families (Ga_2S_3, Ga_2Se_3 etc.), trying to avoid using the term “polymorphism”. We also discussed phases of the monochalcogenide families.



a b

Fig. 1. *T-x*-diagram for the Al – S system [3] (*a*) and an enlarged fragment of this diagram in the region for a sulfur content from 50 to 60 mol. % (*b*) [3] (*b*). The results of the CALPHAD calculation using the substitution solution model are given together with the experimental data

range, two modifications of Al_2S_3 should be noted (α and γ; the latter melts congruently), as well as three liquid phases separated by wide areas of stratification: L_1 - almost pure molten aluminum, L_3 – almost pure liquid sulfur and L_2 – a melt close in composition to the Al_2S_3. In addition, the authors of a new detailed analysis of the Al – S system [3] came to the conclusion that the upper limit of the existence of aluminum monosulfide is associated not with the peritectic (1), but with a very rare among phase equilibria synthetic transformation, in which a solid phase can be obtained by cooling two immiscible melts (shift to the right of equilibrium 3):

$$AlS = L_1 + L_2 \tag{3}$$

Structurally, AlS monosulfide has not yet been studied. The reason for this is the high aggressiveness of "low-valent" aluminum compounds in relation to almost any solid materials and the impossibility of hardening AlS without decomposition. Several polymorphic modifications have been identified for Al_2S_3, but, according to the data of [8] and [3], which have recently been confirmed by the results of experimental [9] and computational [10, 11] studies, only two modifications can be stable: the hexagonal form α-Al_2S_3 (SG $P6_1$, exists from room temperatures to ~1000 °C) and γ-Al_2S_3 phase with a trigonal structure of corundum (SG $R\bar{3}c$). The γ-phase exists at high temperatures: from ~1000 °C to the congruent melting point (~1070 °C). The α-modification, since it is the one that has a structure with stoichiometric vacancies, is of greatest interest. This structure is derived from the crystal lattice of "defective" wurtzite and was discussed in detail above in the analysis of "defective" gallium sesquisulfides of the α-Ga_2S_3 modification.

2.2. Physicochemical principles of using equilibria involving aluminum sulfides. Obtaining metallic aluminum using the carbosulfide method

Despite the apparent "academic nature" of the question of the existence of the AlS monosulfide on the phase diagram, which is formed only over a narrow temperature range and is not preserved upon hardening, the control of the processes of synthesis and decomposition of this substance seems very important for the development of a new scheme for the industrial production of metallic aluminum (see below). The search for new ways of obtaining metallic aluminum is connected with the fact that the traditional technology of smelting aluminum using electrolysis (the Hall-Héroult process) is accompanied by emissions of environmentally harmful carbon fluorides. These

Table 1. Three-phase equilibria of condensed phases in the Al – S system according to from a number of literary sources. In the columns “Compositions” the numerical values are given for the phases listed in accordance with the corresponding equations of phase reactions. All calculated (according to different models) data of the table refer to the work [3], the experimental values – to the sources [6–8]

Equation	Phase reaction type	*T*, °C	Compositions, mol. % S*			Source of information
$L_1 = Al_s + \alpha\text{-}Al_2S_3$	Eutectic (degenerate)	~ 660	–	0	60	Experiment, [6]
		660.5	0	0	60	Substitutional solution model (SSM)
		660.5	0	0	60	Associate model (AM)
$L_1 + L_2 = A1S$	Synthetic	1060.0	–	–51	50	Experiment, [6]
		1058.3	0	54.3	50	SSM
		1059.9	4.1	54.8	50	AM
$L_1 = AlS + \gamma\text{-}Al_2S_3$	Eutectic	1040.0	56.0	50.0	~ 59	Experiment, [6]
		1052.6	55.3	50.0	60	SSM
		1052.6	55.7	50.0	60	AM
$A1S = L_1 + \gamma\text{-}Al_2S_3$	Catatectic	1010.0	50.0	...	< 60	Experiment, [6]
		1011.6	50.0	0	60	SSM
		1011.5	50	2.6	60	AM
$L_2 = \gamma\text{-}A1_2S_3 + L_3$	Monotectic	973.0	–	...	...	Experiment, [7]
		990.3	70.7	60	100	SSM
		970.6	63.6	60	100	AM
$L_3 = \alpha\text{-}Al_2S_3 + \beta\text{-}S$	Eutectic (degenerate)	~ 115	~ 100	60	~ 100	Experiment, [8]
		115.2	100	60	100	SSM
		115.2	100	60	100	AM
$\beta\text{-}S = \alpha\text{-}Al_2S_3 + \alpha\text{-}S$	Eutectoid (degenerate)	~ 95.5	~ 100	60	~ 100	–
		95.3	100	60	100	SSM
		95.3	100	60	100	AM

fluorides (CF_4 with admixture of C_2F_6) are released as by-products at the sacrificial graphite anode, which is immersed in an $Al_2O_3 – Na_{3x}K_x[AlF_6]$ melt.

***Step* 1.** *Carbosulfidization of aluminum ore containing mostly* Al_2O_3 [12]

One of the most promising alternative methods of obtaining Al is based on the so-called carbosulfide method, which consists of the following three stages. The Loutfy method is based on the reaction of aluminum ore (Al_2O_3) with coal (graphite) and sulfur vapor at a temperature of 1027 – 1227 °C with the formation of an Al_2S_3 melt (4):

$$Al_2O_{3\,(s)} + 3C_{(s)} + 1.5S_{2\,(g)} = Al_2S_{3\,(l)} + 3CO_{\,(g)}. \quad (4)$$

A slightly different way of obtaining aluminum sesquisulfide was proposed by Sportel and Verstraten. According to this scheme $\gamma\text{-}Al_2O_3$ reacts with carbon disulfide vapors at a slightly lower temperature (⩾ 750 °C), but under pressure from 5 to 35 atm:

$$Al_2O_{3\,(g)} + 3CS_{2\,(g)} = Al_2S_{3\,(l)} + 3CO_{\,(g)} + 1.5S_{2\,(g)}. \quad (5)$$

Since CO and sulfur vapor react to form carbon monoxide sulfide, the latter equation is sometimes represented as:

$$Al_2O_{3\,(s)} + 3CS_{2\,(g)} = Al_2S_{3\,(l)} + 3COS_{\,(g)}. \quad (6)$$

The carbon disulfide used in this scheme can be obtained directly in the same reactor by reacting natural gas with sulfur vapor:

$$CH_{4\,(g)} + S_{2\,(g)} = CS_{2\,(g)} + 2H_{2\,(g)}. \quad (7)$$

***Step* 2.** *Incongruent sublimation of the* Al_2S_3 *melt*. The resulting melt is heated under reduced pressure to temperatures from ~1330 to ~1630 °C. This results in the removal of some of the sulfur from the melt and the composition of the liquid (L_2) shifts to a composition with a sulfur content of 53–54 mol. %:

$$Al_2S_{3\,(l)} \rightarrow L_{2\,(\sim AlS)} + S_{2\,(g)}. \quad (8)$$

Step 3. *Release of* Al *during the catathetic decay* of AlS. Decrease in melt temperature of L_2, obtained in the previous step, causes crystallization of the AlS phase (Fig. 1). Further cooling to $t < 1010$ °C causes a disproportionation of aluminum monosulfide according to reaction (2). As a result, along with solid Al_2S_3, almost pure liquid aluminum is formed. The molten metal flows into the bottom of the reactor and the aluminum sesquisulfide is redirected for reheating for the removal of the sulfur.

Recently, other applications of aluminum sesqui-chalcogenides have been discovered. In particular, α-Al_2S_3 was used in promising chemical power sources (CPS) [13, 14]. Al-S batteries operate at relatively low temperatures (~85 °C) due to the transfer of electrons from the anode (metallic Al or Al alloy) to the cathode – sulfur (S^0). Free sulfur is intercalated into graphite-like boron nitride (α-BN) or distributed in an array of carbon nanotubes. When the battery discharges, sulfur turns into microcrystalline α-Al_2S_3. During charging, Al^{3+} ions are removed from the sulfide, and sulfur is converted to its original oxidized state S^0. It should be emphasized that the possibility of fast charging of Al-S batteries is probably associated with the structural features of α-Al_2S_3, which contains *stoichiometric vacancies* V_{Al}, which facilitates the diffusion of Al^{3+} ions in the solid phase. For the transfer of Al^{3+} ions in a liquid electrolyte, an ionic liquid is used in which the cations are represented by nitrogen-organic ions (for example, the cation of 1-ethyl-3-methylimidazolium), and the anions are $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ ions. There are also reports on the high potential of such chemical power sources in which sulfur in the cathode material is partially or completely replaced by selenium [15], [16], and such CPS can be used even at room temperature.

2.3. The Al – Se system and aluminum selenide Al_2Se_3

In this part of the review, together with the Al – S system, we will also consider the corresponding selenium system. This is due to the fact that aluminum selenides have been less studied than sulfides, and the practical application of the only intermediate phase of this system, aluminum sesquiselenide (Al_2Se_3), is at the initial stage.

According to [3], a congruently melting narrowly homogeneous compound exists in this system at pressures close to atmospheric (Fig. 2), the monoclinic (Cc) structure of which is characterized by an ordered arrangement of vacancies and is considered in more detail in Chapter 2.1 (when considering the α'-Ga_2S_3 isostructural phase). At the same time, we note that the diagram presented in Fig. 2 is the result of calculations based on certain solution models and needs to be verified. The fact that this selenide was previously assigned the formula Al_3Se_4, may indicate a noticeable shift in the composition towards excess of aluminum relative to the ideal stoichiometry with a selenium content of 60 mol. % (compare with phase composition γ-$Ga_{2+\delta}S_3$ in the following described system).

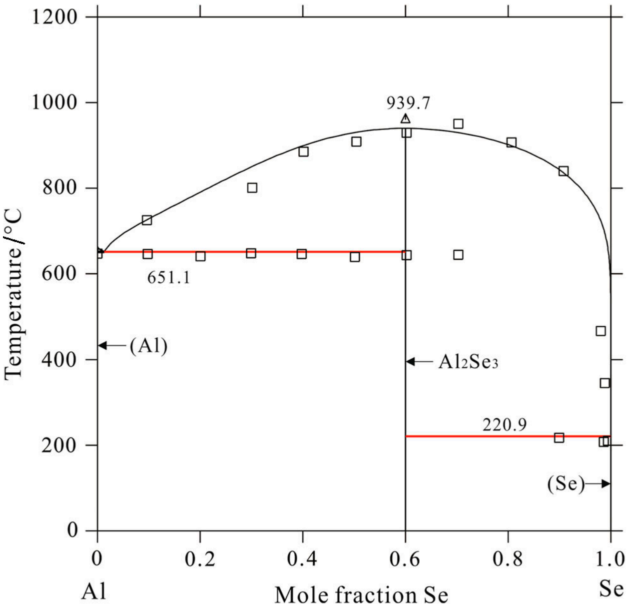


Fig. 2. *T*-*x*-diagram for the Al – Se system [3]. The results of the CALPHAD calculation using the substitution solution model are given together with the experimental data

3. The Ga – S system

When searching for ways of reproducibly synthesizing crystalline phases, especially in the case of the existence of many polymorphic modifications, it is highly desirable to find conditions under which these phases are stable relative to other compounds of this system*. In

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* Definitely, synthesis can be performed in a way that allows immediately obtaining a metastable or even unstable (under reaction conditions) compound. However this approach has the risk of non-reproducibility of the method.

other words, when choosing such a strategy, the resulting modification must be present in the equilibrium phase diagram of the given system. In this case it is possible to obtain this phase under conditions close to equilibrium and then harden it. In our opinion, unsuccessful and mutually exclusive descriptions of the paths of formation of certain volumetric structures are associated with contradictory data on phase equilibria and on the phase diagram. The Ga – S system is an example of the need for a detailed study of the *P-T-x-* (or at least, *T-x-*) diagram.

Until now, the fact that this system contains solid congruently melting phases with the GaS and Ga_2S_3 stoichiometries, and also the fact that the latest stoichiometry corresponds to several modifications with “defective” crystal lattices, based on sphalerite or wurtzite structural types have not caused controversy [17], [18]. In addition, there was no question that the saturated vapor over gallium sulfides was represented by Ga_2S and S molecules. In this case, GaS sublimates incongruently with the formation of almost only Ga_2S, and for Ga_2S_3 in the homogeneity region there are congruently evaporating compositions [19, 20]. It should be noted that other chalcogenides of aluminum, gallium, and indium behave similarly during sublimation [1, 21].

However, until now, it has not been clear what other phases can be realized in this system and what is the structure of the corresponding diagram. In particular, in the studies of famous authors [20] and [19] GaS and Ga_2S_3 sulfides were considered as *the only* crystalline intermediates in this system (Fig. 3). However, the study [22] provides a completely different pattern, where in addition to gallium mono- and sesquisulfide, subsulfide (Ga_2S), as well as Ga_4S_5, both with an incongruent melting type, were indicated. In relatively modern reference studies [23] and [24] the Ga – S system is also presented in accordance with [22] (Fig. 4). In addition, the existence of Ga_2S and Ga_4S_5 phases was confirmed in an independent study [25].

However, in our latest detailed studies [26-31] we obtained a *T-x-* diagram of the Ga-S system (Fig. 5), significantly different from either of the two images shown above. Moreover, the diagram in Fig. 5 turned out to be close to the images published in little-known French-language studies [18, 32]. It should be emphasized that the ideas about the system and equilibria corresponding to Fig. 5 were obtained using various methods that confirm each other: X-ray diffraction analysis (XRD, HTXRD – up to 600 °C), *in situ* X-ray analysis using synchrotron X-ray radiation for high-temperature (up to ~

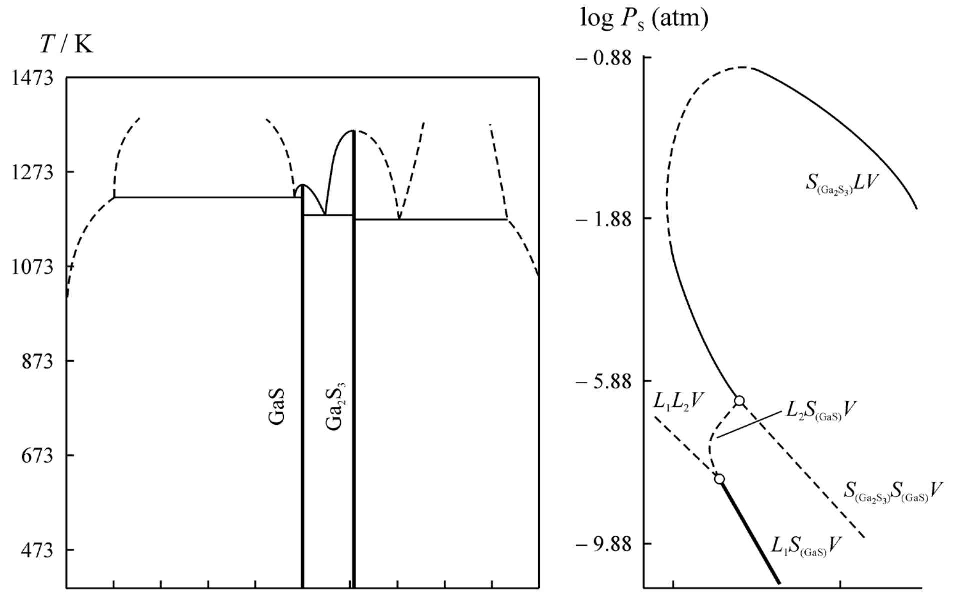

Fig. 3. *T-x* diagram for the Ga-S system according to the data of [19, 20]

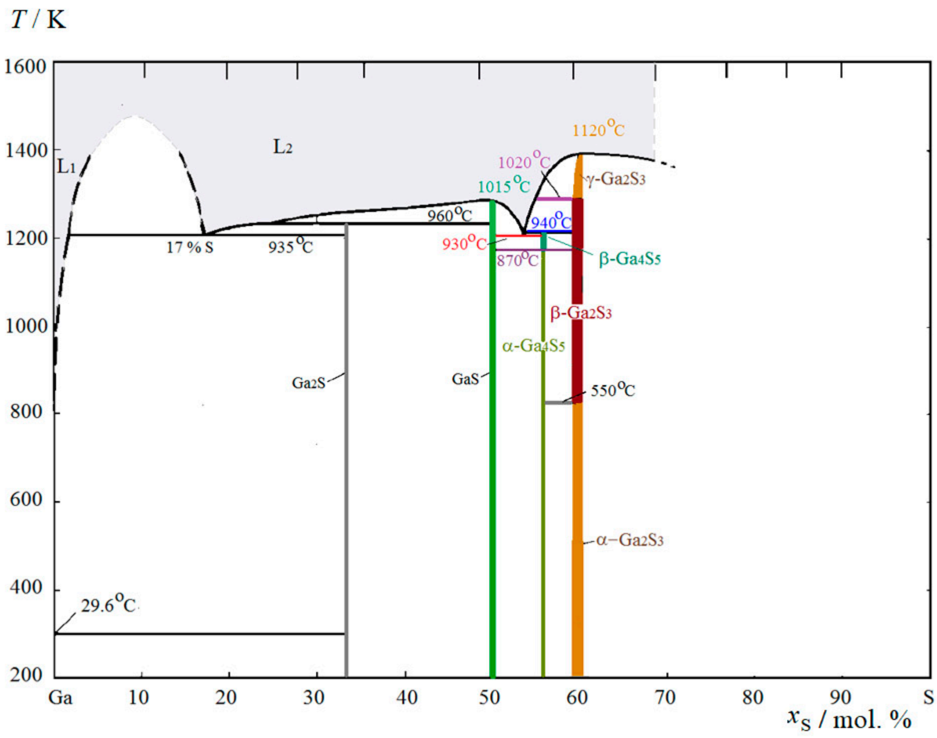

Fig. 4. *T-x* диаграмма системы Ga-S по данным [22]

1030 °C) studies of phase equilibria, differential thermal analysis (DTA) together with a new static method of thermal analysis [33], and methods of transmission electron microscopy (HRTEM, SAED). This diagram and the phases present in it are analyzed in detail in a recently published article [31]. We will not discuss this study in detail, just list the main features of the Ga – S system.

1. The existence of a Ga_2S solid phase was not confirmed experimentally. Moreover, there are no structural data on this substance in the literature. Most probably, the false ideas about solid gallium subsulfide arose from an analysis of the gross composition of the product of resublimation of gallium monosulfide from the hot zone to the cold zone. Indeed, the sublimation of GaS occurs incongruently with the predominant formation of Ga_2S vapor. However, upon condensation, the subsulfide vapors disproportionate, yielding a sample of Ga + GaS heterogeneous powder.

2. For the Ga_4S_5 phase found in [22], most likely, an error in the determination of the composition was made. Probably, in this study the authors obtained one of the phases of the Ga_2S family, namely, γ-$Ga_{2+\delta}S_3$ with a sulfur content of about 59.3 mol. %.

3. If gallium monosulfide is a practically completely stoichiometric compound, for gallium sesquisulfide there is a whole family of phases with “defective” structures of sphalerite or wurtzite. In this case, the phase with the highest ordering of stoichiometric vacancies during genesis from the wurtzite α′- Ga_2S_3 structure is, according to the ideas [18], the only phase that is stable at room temperature. Moreover, like GaS, it is narrowly homogeneous and almost completely stoichiometric. Other phases of this family can be stable (relative to other phases) only at high temperatures. In this case, it is mostly shifted towards gallium relative to the ideal composition – up to 0.7 mol. % – “defective-sphalerite” modification γ-$Ga_{2+\delta}S_3$, which is realized on the phase diagram in a narrow temperature region of about 900 °C. Higher temperature forms – α- and β-Ga_2S_3 are grouped closer to the composition of 60 mol. % S. All of them can be isolated individually and stored at room temperature after annealing under equilibrium conditions, followed by quenching.

4. Obtaining one or another modification of the Ga_2Se_3 family, probably, is very dependent on the presence of even small concentrations of impurities, as evidenced by the following facts.

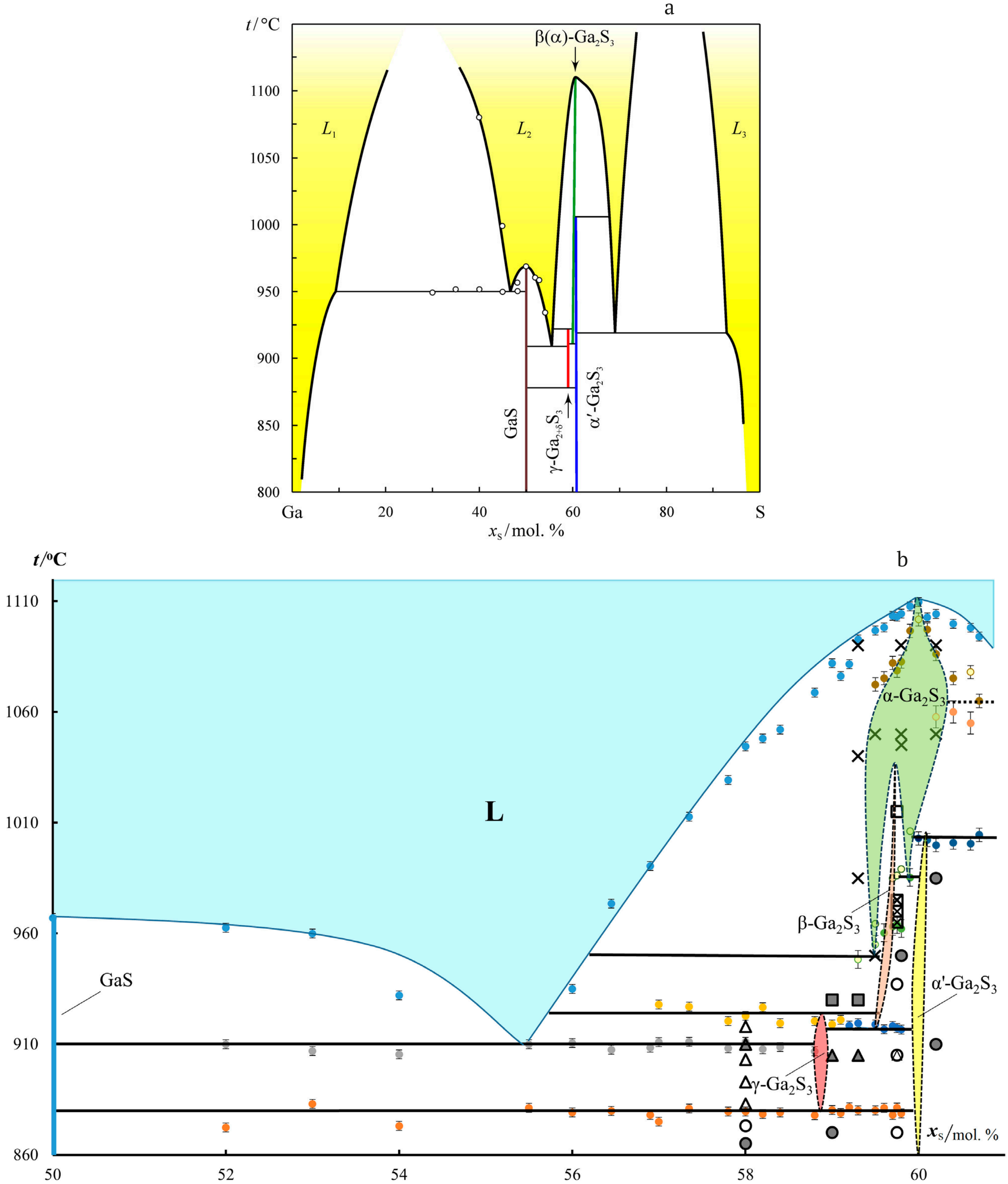

Fig. 5. New data on the *T-x* diagram of Ga – S: general view [29] (*a*) and a detailed fragment in which 4 “defective” modifications of the Ga_2S_3 family are realized [31] (*b*)

a). In particular, we observed stabilization of the cubic γ-$Ga_{2+\delta}S_3$ phase when introducing already 0.5 mol. % iron [34]. Hexagonal modifications, α- and β-Ga_2S_3, are stabilized by the addition of manganese [35]. These modifications were observed at temperatures much lower than those allowed for this system by the phase diagram of the Ga – S system, even taking into account a small possible supercooling.

b). The authors of [36] reported the isolation of a cubic form during crystallization from potassium iodide or lead chloride melts [36]. Moreover, in the latest study, the order of releasing of equilibrium phases of the Ga_2S_3 family at different temperatures turned out to be completely different than it follows from *T-x*-diagrams of the Ga – S system (compare Fig. 5 and Fig. 6).

c). A cubic γ-phase was also released during the crystallization of glasses of the Ga-Ge-S system (the Ga_2S_3 – GeS_2 section) at 750 °C. It should be noted that for pure gallium sesquisulfide the γ-$Ga_{2+\delta}S_3$ phase becomes metastable at temperatures below 878 °C and quickly turns into α'-Ga_2S_3 at t < 840 °C (with slow cooling or annealing) [37].

d). In the production of gallium sesquisulfide by the oxidation of molten gallium triiodide with elemental sulfur at 500 °C the γ-$Ga_{2+\delta}S_3$ cubic high-temperature modification was also released; with a slight increase in temperature (up to 650 °C) another phase with a hexagonal structure was released ($P6_1$) [38]. It should be noted that for *pure* gallium sesquisulfide both modifications should at the specified temperatures unambiguously transform into monoclinic α'-Ga_2S_3*.

Compounds from the gallium sesquisulfide family should be very promising for materials science (luminescent properties [39], [40], nonlinear optics [40], etc.). However, the incomplete reproducibility of the isolation of each individual modification significantly limits their use. We hope that a refined phase diagram of the Ga–S system, as well as detailed studies of the ternary diagrams Ga–S–X (X is an impurity), especially taking into account the extremely high sensitivity of the stability of various modifications to very small concentrations of impurities will contribute to the solution of the question of the use of phases of the Ga_2S_3 family in modern materials science.

4. The Ga – Se system

Currently, the Ga–Se system appears to be the poorest among A^{III} – B^{VI} based on the number of intermediate solid phases [3, 21]. The *T-x*-diagram of the discussed system contains two polymorphic modifications of layered gallium monoselenide [40] and two modifications of gallium sesquiselenide [41], [42] (Fig. 7).

“Defective” compounds of the Ga_2Se_3 family are represented by a high-temperature β-Ga_2Se_3 modification with a sphalerite structure (with disordered vacancies) and a low-temperature

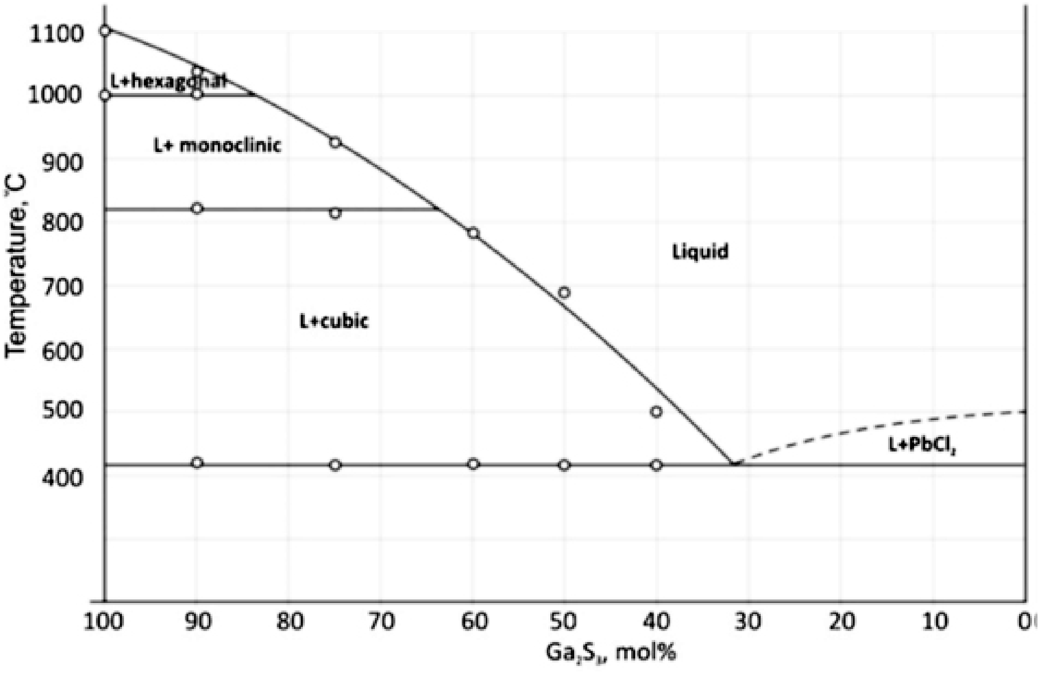

Fig. 6. *T-x* diagram for the Ga_2S_3 – $PbCl_2$ according to the data of [36]

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* The authors [38] for the hexagonal modification with SG $P6_1$ used the name β-Ga_2S_3. In the majority of literary sources and in our studies this phase appears as α-Ga_2S_3, and the designation β-Ga_2S_3 was assigned to the wurtzite-like “defective” form with SG $P6_3mc$.

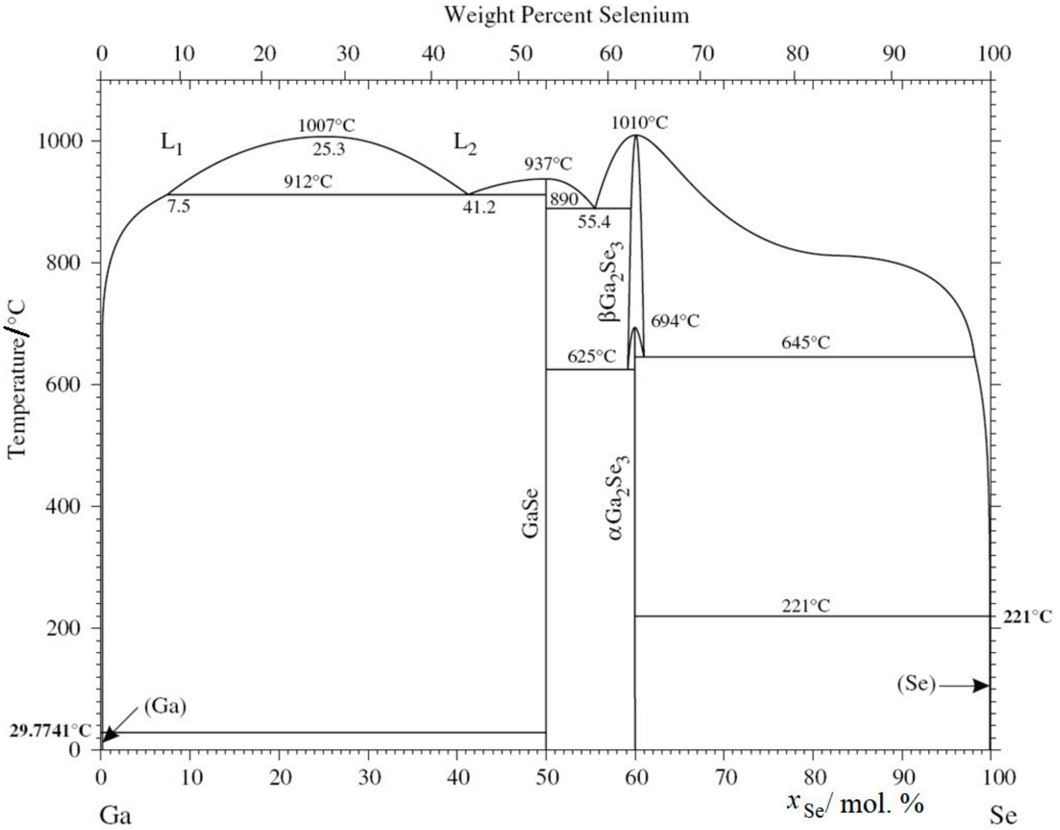

Fig. 7. *T-x* diagram for the Ga-Se system according to the data of [41, 42]

monoclinic α-Ga_2Se_3 form, which is isostructural to α'-Ga_2S_3 (with ordered vacancies) [41, 42]. At the same time, it should be noted that in our preliminary studies we have not yet been able to confirm the equilibrium existence of high-temperature α-phases, despite a fairly detailed study. In the latter, in addition to DTA, *in situ* X-ray powder analysis with X-ray synchrotron radiation was used. This allowed the Ga–Se system sample to be annealed under specific high-temperature conditions for several hours to establish equilibrium.

4.1. Regulation of the GaSe polytypic structure and composition by the SSCTR method

In our study, we were able to reproducibly obtain individual polytypes of layered gallium monoselenide [43–45]. For this purpose, a non-isothermal version of phase composition control (both phase and within the homogeneity region) was used using the method of selective chemical transport reactions (SSCTR).

The essence of the SSCTR is the introduction or removal of one of the components of the solid phase (in our case, Ga) during a selective gas transport reaction. In an experiment on regulating the phase composition using the SSCTR method, the initial sample is placed at one end of the ampoule, and the batch, which is the source of the transported component, is placed at the other end. Also, a certain amount of transport agent is introduced into the ampoule, which, under experimental conditions, produces unsaturated vapor. Then, after removing the air, the sealed ampoule is placed in an oven in a way that the higher temperature (T_2) corresponds to the sample, and the lower temperature (T_1) corresponds to the batch. In the system, selective transfer of only one component between the batch and the sample occurs. It should be emphasized that this transfer gradually ceases as the controlled sample reaches a certain phase composition (i.e. a certain structure) and a certain non-stoichiometry (i.e. a specific composition within the homogeneity region). As a result, a steady state without mass transfer is realized in the system, in which the sample can exist for an indefinite period of time at the fixed temperatures of the hot and cold zones (T_2, T_1) [46].

In our studies [43], [46], to regulate the composition and structure of gallium selenides, pure gallium was used as a batch and gallium triiodide was used as a transport agent. The chemistry of selective transfer was reduced to a reversible reaction (9):

$$2Ga^{\text{in the composition of Ga selenides}} + GaI_3^{\text{vapor}} \rightleftarrows 3GaI^{\text{vapor}}. \quad (9)$$

It should be noted that at temperatures up to ~ 900 °C gallium selenides have only small values of saturated vapor (Ga_2Se, Se_2 pressure does not exceed several mm Hg [1, 21]). This fact, as well as the absence of stable forms of binary and ternary selenium iodides in the pair, lead to the fact that the role of selenium or its compounds in mass transfer is minimal. The latter allows the selective nature of iodide chemical mass transfer of gallium selenides.

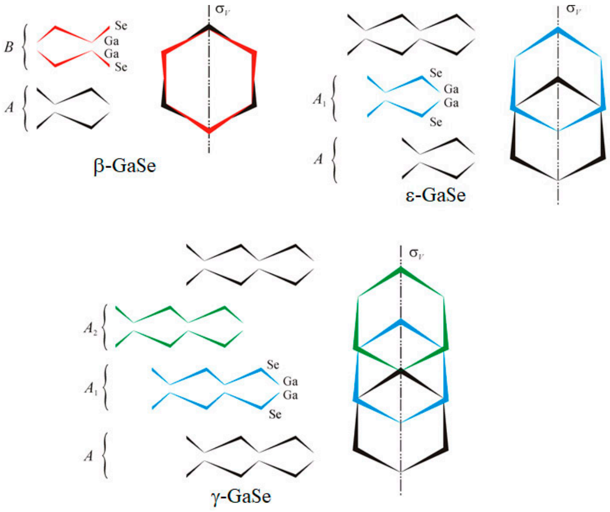

Fig. 8. Structures of some polytypes of GaSe (according to [44])

The results of the study showed that γ-modification of GaSe (alternating packets of the ...ABCABC...type, Fig. 8) exists on the phase diagram only with an excess of selenium and only at high temperatures close to the melting point. The ε-GaSe polytype (alternating packets of the ...ABAB-...type, Fig. 8) always turns out to be stable relative to other phases at low temperatures (up to ~700 °C), as well as at temperatures up to melting in the case of high gallium content within the homogeneity region [43, 44]. On the *T*-*x*-diagram these polytypes according to our research data are shown in Fig. 9.

Thus, it is possible to solve a rather complex problem of reproducible obtaining of a certain polytype. The deformation nature of the

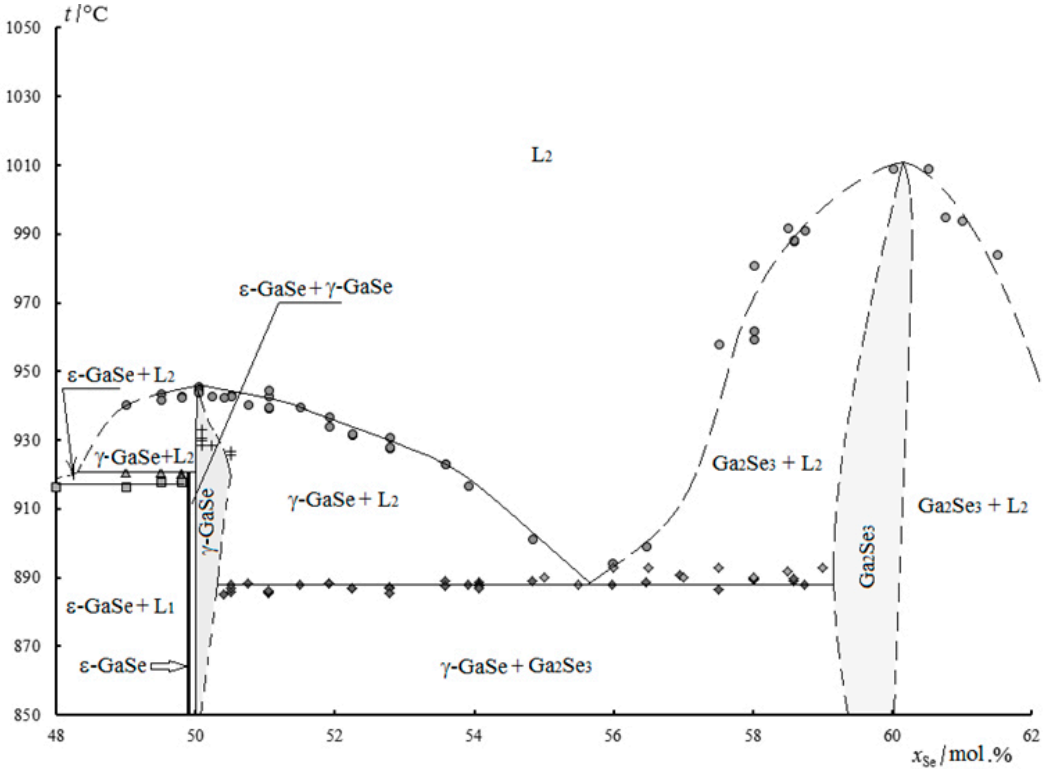

Fig. 9. High-temperature region of *T*-*x*-diagram for the Ga – Se system according to [45]

transformation of one polytype into another allows in this case to preserve single crystals of substances without their destruction. It also should be noticed that in [43], [44] the possibility of regulating not only the polytypic structure, but also the composition within the homogeneity regions of these phases is shown.

5. The In – S system

When moving to indium chalcogenides, a much greater variety of intermediate phases is observed. This is usually associated with the greater tendency of indium to form compounds with a larger proportion of the ionic component of the chemical bond (especially compared to gallium) with a variety of charge states (In^{+1}, In^{+3}, to a lesser extent In^{+2}). Thus, on the In – S phase diagram ([47–49], Fig. 10) there are InS phases (two modifications: the low-temperature form InS, which transforms via a distectoid path into the high-temperature form), In_6S_7, $In_{3\text{-}x}S_4$ (according to a number of sources, it is also α-In_2S_3), as well as polymorphic modifications of indium sesquisulfide: low-temperature β-In_2S_3 and high temperature γ-In_2S_3. The high temperature InS form, as well as n_6S_7 and $In_{3x}S_4$ melt incongruently. The γ-In_2S_3 is the most resistant to high temperatures and melts congruently at 1097 °C [49] (1090 °C according to [50]).

Taking into account the relatively low values of partial pressures over indium sulfides, their incongruent sublimation and the difficult kinetics of establishing equilibria between condensed phases and their own vapor, it is difficult to use classical tensimetric research methods for the In–S system, as well as classical methods for regulating the composition of these sulfides through the vapor phase. For this reason, the auxiliary component (AC) method seems to be promising both for a detailed analysis of the considered system and for tasks on the synthesis of indium sulfides.

The In–S system was studied by the AC method, primarily using hydrogen with the aid of a spectrophotometric technique [47], [48], [51]. The studied equilibrium in this case can be written as (10):

$$S^{\text{in the composition of In sulfides}} + H_2^{\text{gas}} \rightleftarrows H_2S^{\text{vapor}}. \qquad (10)$$

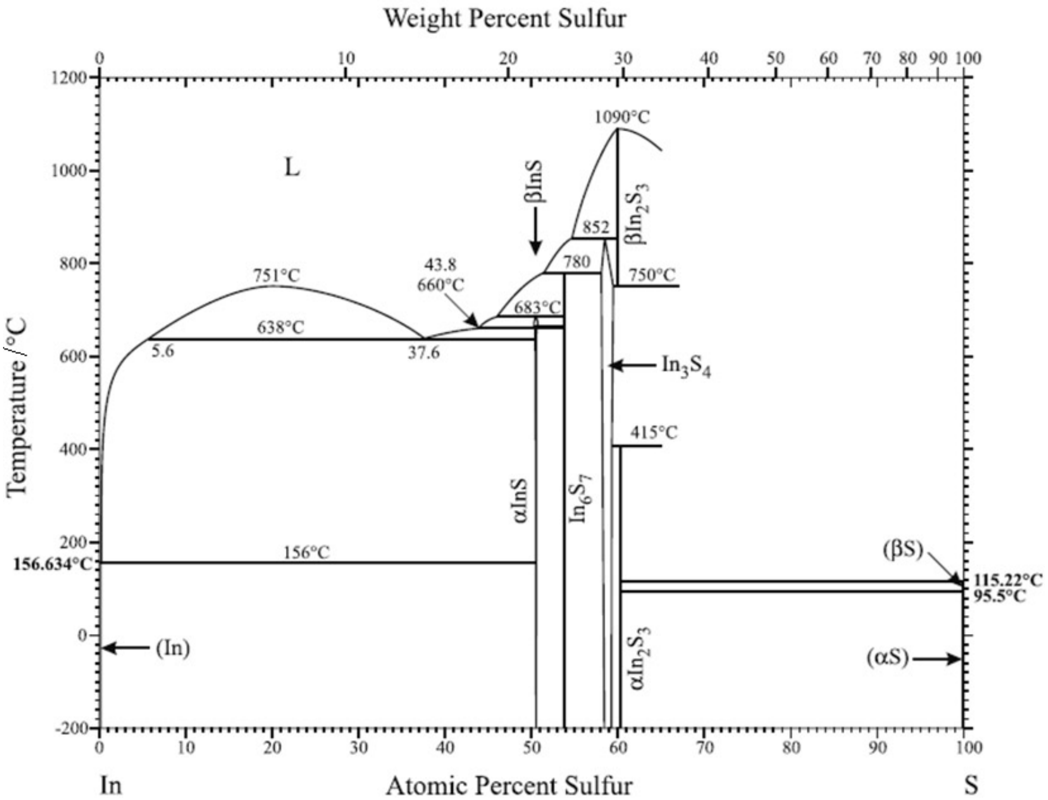

Fig. 10. *T-x* diagram for the In – S [50] system, based on the data of [49]

To achieve equilibrium, the studied sample of the In – S system was kept in contact with hydrogen at a temperature of 400 to 725 °C. After such annealing for many hours, the reactor with the substances (a sealed quartz cuvette) was quenched and the absorption spectrum in the region of hydrogen sulfide absorption was studied ().

In addition to the previously established set of intermediate phases of the In – S system (InS, In_6S_7, $In_{3-x}S_4$, In_2S_3 modifications) it was established that the $In_{3-x}S_4$[*] phase has a wide homogeneity range: from ~ 58.0 to 59.8 mol. % S. In this case, the behavior of the concentration dependences of the chemical potential of sulfur[**] in this area of homogeneity turned out to be very unusual. These dependences consisted of alternating almost horizontal and inclined sections, which, according to the authors [51], may indicate a tendency of this cubic phase to disintegrate into separate independent modifications with similar but different compositions.

The auxiliary component method was also used to solve problems related to the synthesis of substances with a given composition, both phase and within homogeneity regions. In these experiments, the goal was to specifically vary the composition of pre-synthesized indium sulfides, both fine-crystalline films and bulk samples [52-54]. For this purpose, chlorine in the form of indium chlorides was used as an auxiliary component (also known as a transport agent). In this case, transfer via a reversible reaction (11) was used, similar to (9):

$$2\mathrm{In}^{\text{in the composition of In sulfides}} + \mathrm{InCl}_3^{\text{vapor}} \rightleftarrows 3\mathrm{InCl}^{\text{vapor}}. \quad (11)$$

In this case, the sulfur atoms chemically bound in indium sulfide practically do not pass into vapor, which allows us to discuss the selectivity (11). However, the use of metallic indium as a control charge in such experiments turned out to be impossible because indium produces much more stable In^{+1} halides compared to similar gallium compounds. As a result, equilibrium (11) turns out to be extremely shifted to the right in the equilibria of the $InCl_3$ vapor with $In_{met.}$ To circumvent this difficulty, we used the dilution of indium in the batch with a chemically inert diluent. This allowed to reduce the activity of indium towards higher halides. Indeed, when using In–Au melt solutions, it was possible to change the direction of indium mass transfer between the sample and the batch and reproducibly obtain a sulfide of the required composition and structure depending on the gold content in the batch [44, 53]. In [54] the possibility of regulating the composition of indium sulfides using a batch of heterogeneous mixtures of indium sulfides (for example, In_6S_7 $In_{3-x}S_4$) instead of expensive gold was demonstrated.

6. The In – Se system

According to our latest studies [30, 55] and data of other authors [56, 57], the *T-x* diagram of the In – Se system is distinguished by a huge variety of phases even in comparison with the In – S system. Solid selenides are realized in a small concentration range (40–60 mol. % S) and demonstrate pronounced polymorphism (Fig. 11). These are In_4Se_3 selenides (however, there is no similar sulfide, or gallium chalcogenides with such a stoichiometry), InSe (a layered structure similar to ε-GaSe), In_6S_7 and In_2Se_3 (several modifications). In our latest studies, which were carried out using a new spectrophotometric technique with an auxiliary component ([58-60]), the following was discovered [30], [56].

1. It was shown that high temperature (650–890 °C) modification of δ-In_2Se_3, is wurtzite-like (SG $P6_3mc$; may contain stoichiometric vacancies), while in the literature it is classified as SG $P\bar{3}m1$.

2. Near the composition corresponding to the stoichiometry of In_6Se_7, there are two phases with similar but different structures and compositions. When this was revealed, alloys of the In – Se system with a selenium content of 54.0 and 57.5 mol. % Se were studied using X-ray phase analysis. Before the study, the alloys were homogenized in repeated long-term annealing

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[*] The indium mono- and sesquisulfides differ from the structures of other $A^{III}B^{VI}$ mono- and sesquichalcogenide compounds (except γ-In_2S_3). In particular, the $In_{3-x}S_4$ phase (often not quite correctly called β-In_2S_3) has the structure of a “defective” inverted spinel (see Part 1 of this review).

[**] More precisely, we are discussing the value (let’s denote it $\ln(K_P^{\#})$, see [51]), which at a constant temperature T is linearly related to chemical potential μ_S in the solid phase [51]: $\ln(K_P^{\#}) = \frac{\mu_S}{RT} + Y$, where Y is a constant value (at T = const).

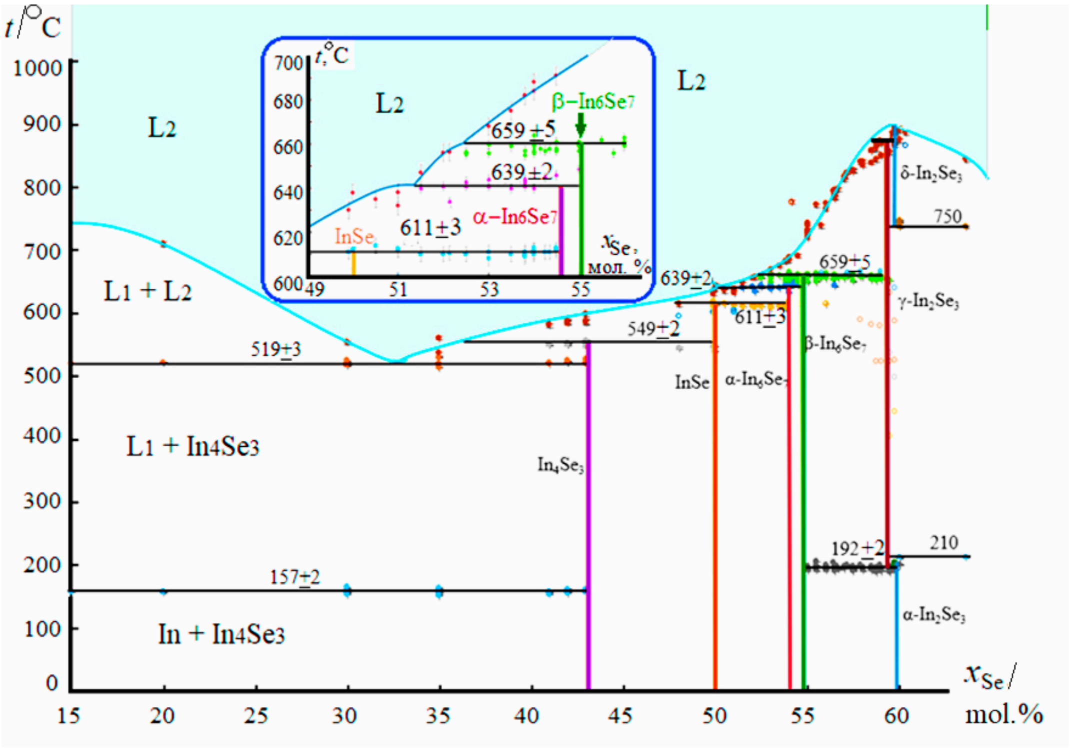

Fig. 11. *T*-*x*-diagram of the In – Se system in the composition range of 15.0 – 63.4 mol. % Se Se [30]

procedures (500 °C, 72 h) and grinding the powder (2 cycles in total). It was found that the first sample was represented by a monoclinic (SG $P2_1$) structure, and the second turned out to be a mixture of two phases and contained α-3R-In_2Se_3 as an impurity. The main phase of the sample with an increased selenium content (57.5 mol. %) compared to the stoichiometry of In_6Se_7 was identified as monoclinic and resembled the In_6Se_7 structure described above. However, it was well described by *another* space group ($P2_1/m$) and, therefore, was a *separate* phase. Both structures ($P2_1$ And $P2_1/m$) are mentioned in scientific papers, however, for the description of the In_6Se_7 structure [61-64] the second SG is used more often [61]. It is assumed that the crystal lattice of the compound with SG $P2_1/m$ corresponds to the phase with the stoichiometry In_9Se_{11} described in a number of studies [62, 63], but still not structurally characterized. The composition of this phase, which we designate as β-In_6Se_7 [30], was close to 55.0 mol. % Se. The composition of the modification with SG $P2_1$ is richer in indium (we denote it as β-In_6Se_7 [30]) better corresponds to the stoichiometry of In_6Se_7 (~54 mol. %Se).

3. In our study of this diagram, we did not find any structures that could correspond to the stoichiometries of In_5Se_7 and In_3Se_4. Phases with such compositions have not been confirmed either by X-ray powder diffraction studies or by thermographic or tensiometric experiments.

Thus, the main compounds of indium and selenium are In_4Se_3(P_{nnm}), InSe ($P6_3/mmc$), In_6Se_7 (two similar modifications, but differing in composition: $P2_1$ And $P2_1/m$) and In_2Se_3 (represented by at least three modifications, 3R-α-In_2Se_3, γ-In_2Se_3, as well as δ-In_2Se_3). Most of these phases decompose upon heating by peritectic reactions (except for congruently melting δ-In_2Se_3). Over the course of thermal analysis (DTA, chemiluminescence analysis [33]), we obtained the following quantitative data on the temperature stability of condensed phases of the In – Se system and equilibria involving these phases (Table 2).

Out of the issues that are not yet completely clear, we note that this system requires additional studies of samples with compositions close to 60 mol. % selenium content. In these studies, it is still necessary to determine in more detail the positions of the modifications of the In_2Se_3 family on the corresponding phase diagram. Today, only the exact position of the low-temperature 3R-α-In_2Se_3phase does not raise questions.

Table 2. Observed effects and phase equilibria in the In – Se system

No	Number of exp. points	Temperature at which the effect was observed, *t*, °C	The compound or range of compounds for which the effect was observed x_{Se}, mol. %	Corresponding phase equilibrium effect
1	9	156.5±2	30.0–43.01	In_4Se_3 + In ⇔ L, eutectic
2	9	519±2	30.0–43.01	L_1 + In_4Se_3 ⇔ L_2, monotectic
3	7	549±3.7	41.0–49.9	In_4Se_3 ⇔ InSe + L, peritectic
4	25	611±3.3	49.9–55.0(54.5)	InSe ⇔ α-In_6Se_7 + L, peritectic
5	15	639±2.0	51.5–55.0	α-In_6Se_7 ⇔ β-In_6Se_7+L, peritectic
6	30	659±4.5	53.5–59.5	β-In_6Se_7 ⇔ γ-In_2Se_3+L, peritectic
8	18	191±2.0	55.0–60.0	β-In_6Se_7 + α-In_2Se_3 ⇔ γ-In_2Se_3, eutectoid
9	2	890±5.0	60.0	σ-In_2Se_3 ⇔ L, congr. melting
10	52	от ~520 до ~891	15.0–63.35	S ⇔ L (liquidus)
11	3	211±2.0	60.0–63.5	α-In_2Se_3 ⇔ γ-In_2Se_{3+} L, peritectic

7. Conclusions

In conclusion of our review, we will summarize the most important results of the study. First of all, let's analyze, *what do we know* about A^{III}–B^{VI} systems, as well as phases of families $A_1^{III}B_1^{VI}$ and $A_2^{III}B_3^{VI}$, to which this study is mainly devoted.

1. In all the discussed systems, non-molecular crystalline compounds with $A_1^{III}B_1^{VI}$ and $A_2^{III}B_3^{VI}$ stoichiometries are realized. A partial exception is aluminum monoselenide, but, as we already noted, this compound is also realized in the form of films.

2. $A_1^{III}B_1^{VI}$ **mono**chalcogenides form typical layered structures that have significant similarities with graphite (analogues of graphene, nanotubes and other nanoformations, intercalation reactions, including those during which there is partial damage to the structure of the intercalated crystal itself). Among the monosulfides and monoselenides of indium and gallium, the only partial exception is indium monosulfide, in which, despite the four-layer structure, the bonds between the individual layers can no longer be exclusively classified as van der Waals.

3. **Sesqui-chalcogenides** of aluminum, gallium and indium provide families of "defective" semiconductors, in which crystalline compounds with ordered and disordered stoichiometric vacancies based on wurtzite and sphalerite structures, containing stoichiometric vacancies as structural units, are realized. A partial exception is the In–S system: of the three modifications, close in stoichiometry to indium sesquisulfide, only the highest-temperature one can be classified as a "diamond-like defective" structure based on sphalerite or wurtzite. The other two forms, despite the fact that they also contain stoichiometric vacancies, are derivatives of defective spinel.

4. All intermediate solid compounds in A^{III} – B^{VI} systems are characterized by kinetic difficulties and "sticking" in metastable states. This is especially important when working with thermal analysis methods. In particular, in DTA experiments we observed the effect of "switching"

from one type of phase diagram to another when the heating rate threshold was exceeded by more than 13 K/min [49]. Sufficiently reproducible and clearly interpretable results appear only at the lowest heating rates (0.5–2 K/min). The static method of thermal analysis was developed for the elimination of this problem [33]. In addition, in order to circumvent the difficulties with kinetic difficulties, the auxiliary component method can be recommended [54], which can be used both in solving research problems and for the synthesis of substances with precisely specified compositions [46].

5. Phase equilibria in $A^{III}–B^{VI}$ systems, especially with the participation of “defective” phases of families are very sensitive even to small concentrations of impurities. Doping with even small concentrations of impurities can fundamentally change the pattern of phase equilibria and the appearance of phase diagrams of systems, which can no longer be considered binary, but must be considered as multi- (at least three-) component.

Let us now turn to the problems that remain open to the discussed systems and phases of $A_1^{III}B_1^{VI}$ ***and*** $A_2^{III}B_3^{VI}$ ***families.***

1. Now, the relationship between different defects in phases can be considered as an open problem. In particular, *a priori* it is assumed that in the γ-$Ga_{2+\delta}S_3$ cubic modification a noticeable phase deviation from ideal stoichiometry (59.3 instead of 60.0 mol. % S) occurs due to the “healing” of part of the stoichiometric vacancies by gallium atoms. However, this assumption has not yet been verified by anyone.

2. Another issue is related to finding a more adequate definition of what stoichiometric vacancies are. The point is that in some cases of ordering (for example, for α′-Ga_2S_3), it is no longer possible to discuss such vacancies, since a new type of crystal lattice is formed, in which the stoichiometry corresponds to a new structural type. At the same time, many properties (the possibility of creating interlayers during epitaxy, high diffusion coefficients, preserved radiation resistance, etc.) indicate the presence of such vacancies as independent structural units in crystal lattices.

3. For the monochalcogenides there is still no understanding of when, under what conditions and by what reagents intercalation interactions can be carried out, and when such reactions are impossible. This also includes the question of which areas are affected by intercalation if it occurs and which areas are not affected (and for what reason). There is currently no understanding of the question of how intercalation can be carried out, achieving equilibrium in a way, that this equilibrium can be controlled by changing the concentration of the guest substance in the layered crystal and its ordered or disordered arrangement in the van der Waals gaps.

These questions await answers in future studies.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Piacente V., Bardi G., Di Paolo V., Ferro D. The vapour pressure over Ga_2S_2 and Ga_2Se_2. *The Journal of Chemical Thermodynamics*. 1976;8(4): 391–401. https://doi.org/10.1016/0021-9614(76)90080-x

2. Murakami T., Shibata N. The action of sulfur against metals at high temperatures. 3-rd report. The action of sulfur against aluminum alloys. *Nippon Kinzoku Gakk*. 1940;4: 221–228. https://doi.org/10.2320/jinstmet1937.4.8_221

3. Shi C., Yang B., Hu B., Du Y., Yao S. Thermodynamic description of the Al–X (X = S, Se, Te) systems. *Journal of Phase Equilibria and Diffusion*. 2019;40: 392–402. https://doi.org/10.1007/s11669-019-00733-z

4. Kohlmeyer E. J., Retzlaff H. W. Aluminum sulfide, silicon sulfide and the Al – Si – S system. *Zeitschrift für anorganische Chemie*. 1950;261: 248–260. https://doi.org/10.1002/zaac.19502610314

5. Forland T., Gomez J., Ratkje S. K., Ostvold T. Measurements of phase equilibria in the aluminum-aluminum sulfide system. *Acta Chemica Scandinavica*. 1974;28a(2): 226–228. https://doi.org/10.3891/acta.chem.scand.28a-0226

6. Sharma R. C., Chang Y. A., The Al – S (aluminum-sulfur) system. *Journal of Phase Equilibria*. 1987;8(2): 128–131. https://doi.org/10.1007/BF02873197

7. Flahaut J. A variety of aluminum sulfide stable at high temperature. *Comp. Rend*. 1951;232: 2100–2102.

8. Flahaut. J. Contribution a l’e´tude du sulfure d’aluminium. *Annales de Chimie*. 1952;12: 632–696.

9. Huda N., Rhamdhani M. A., Brooks G. A., Monaghan B. J., Prentice L. Aluminium production route through carbosulfidation of alumina utilizing H_2S. In: *Light*

Metals. B. A. Sadler (ed.). 2013: 1299–1304. https://doi.org/10.1007/978-3-319-65136-1_219

10. Ramadhan M. R., Khansa S. A., Zulindra Q., Handayania D. P., Wardania N. A., Astuti F. Electronic structure calculation of α-Al_2X_3 system (X = O, S) based on r++scan functional. *East European Journal of Physics*. 2023;4: 210–215. https://doi.org/10.26565/2312-4334-2023-4-26

11. Shimomura Y., Ohno S., Hayashi K., Akamatsu H. Quadruple-well ferroelectricity and moderate switching barrier in defective wurtzite α-Al_2S_3: a first-principles study. *arXiv: Condensed Matter – Materials Science*. 2024;2406.04084: 1-35. https://doi.org/10.48550/arXiv.2406.04084

12. Rhamdhani M. A., Huda N., Khaliq A., … Prentice L. Novel multi-stage aluminium production: part 1 – thermodynamic assessment of car-bosulphidation of Al_2O_3/bauxite using H_2S and sodiothermic reduction of Al_2S_3. *Mineral Processing and Extractive Metallurgy*. 2017;127: 1–12. https://doi.org/10.1080/03719553.2017.1293352

13. Klimpel M., Kovalenko M. V., Kravchyk K. V. Advances and challenges of aluminum–sulfur batteries. *Communications Chemistry*. 2022;77(5): 1–12. https://doi.org/10.1038/s42004-022-00693-5

14. Meng J., Hong X., Xiao Z. Rapid-charging aluminium-sulfur batteries operated at 85 °C with a quaternary molten salt electrolyte. *Nature Communications*. 2024;15(596): 1–10. https://doi.org/10.1038/s41467-024-44691-8

15. Gordon L. W., Jay R., Jadhav A. L., Bhalekar S. S., Messinger R. J. Elucidating consequences of selenium crystallinity on its electrochemical reduction in aluminum–selenium batteries. *ACS Materials Letters*. 2024;6(7): 2577–2581. https://doi.org/10.1021/acsmaterialslett.4c00531

16. Wu S. C., Ai Y., Chen Y.-Z. High-performance rechargeable aluminum–selenium battery with a new deep eutectic solvent electrolyte: thiourea – $AlCl_3$. *ACS Materials Letters*. 2020;12: 27064–27073. https://doi.org/10.1021/acsmaterialslett.4c00531

17. Hahn H., Klingler W. Über die Kristallstrukturen von Ga_2S_3, Ga_2Se_3 und Ga_2Te_3. *Zeitschrift für anorganische Chemie*. 1949;259(1-4): 110–119. https://doi.org/10.1002/zaac.19492590111

18. Pardo M. P., Tomas A., Guittard M. Polymorphisme de Ga_2S_3 et diagramme de phase Ga-S. *Materials Research Bulletin*. 1987;22: 1677–1684. https://doi.org/10.1016/0025-5408(87)90011-0

19. Greenberg J. *Thermodynamic basis of crystal growth: P-T-X phase equilibrium and nonstoichiometry*. Springer-Vcrlag Berlin Heidelberg, Berlin; 2002. 247 p. https://doi.org/10.1007/978-3-662-04876-4

20. Zlomanov V. P., Novoselova A. V. *P-T-x-state diagrams of metal-chalcogen systems**. V. B. Lazarev (ed.). Moscow: Nauka Publ.; 1987. 187 p. (In Russ.). Available at: https://f.eruditor.link/file/1843241/

21. Ider M., Pankajavalli R., Zhuang W., Shen J. Y., Anderson T. J. Thermochemistry of the Ga-Se system. *ECS Journal of Solid State Science and Technology*. 2015;4(5): Q51–Q60. https://doi.org/10.1149/2.0011507jss

22. Rustamov P. G., Mardakhaev B. I., Safarov M. G. Study of the phase diagram of the gallium-sulphur system. *Izvestiya Akademii Nauk SSSR Neorganicheskie Materialy*. 1967;3(3): 479–484. (In Russ.)

23. Massalski T. *Binary alloy phase diagrams. Materials Information Soc*. 2-nd Ed., Volume. 2. Materials Park, Ohio; 1990. 1269 p.

24. Predel B., Ed.: O. Madelung. Ga-S (Gallium-Sulfur) System. In: *Phase equilibria, crystallographic and thermodynamic data of binary alloys*. Berlin: Springer; 1996;2(1-2): 2. https://doi.org/10.1007/10501684_1396

25. Spandau H., Klanberg F. Thermische Untersuchungen an Sulfiden. II. Das thermische Verhalten der Sulfide des Galliums. *Zeitschrift für anorganische und allgemeine Chemie*. 1958;295(5-6): 300–308. https://doi.org/10.1002/zaac.19582950504

26. Berezin S. S., Zavrazhnov A. Y., Naumov A. V., Nekrylov I. N., Brezhnev N. Y. The phase diagram of the Ga–S system in the concentration range from 48.0 to 60.7 mol % S. *Condensed Matter and Interphases*. 2017;19(3): 321–335. (In Russ., abstract in Eng.). https://doi.org/10.17308/kcmf.2017.19/208

27. Zavrazhnov A., Berezin S., Kosykov A., Naumov A., Berezina M., Brezhnev N. The phase diagram of the Ga–S system in the concentration range of 48.0–60.7 mol % S. *Journal of Thermal Analysis and Calorimetry*. 2018;134: 483–492. https://doi.org/10.1007/s10973-018-7124-z

28. Volkov V. V., Sidey V. I., Naumov A. V., Nekrylov I. N., Brezhnev N. Y., Malygina E. N., Zavrazhnov A. Y. The cubic high-temperture modification of gallium sulphide (xs = 59 mol %) and the *T*, *x*-diagram of the Ga – S system. *Condensed Matter and Interphases*. 2019;21(1): 37–50. (In Russ., abstract in Eng.). https://doi.org/10.17308/kcmf.2019.21/715

29. Volkov V. V., Sidey V. I., Naumov A. V., … Zavrazhnov A. Yu. Structural identification and stabilization of the new high-temperature phases in A(III) – B(VI) systems (A = Ga, In, B = S, Se). Part 1: high-temperature phases in the Ga – S system. *Journal of Alloys and Compounds*. 2022;899: 163264. https://doi.org/10.1016/j.jallcom.2021.163264

30. Brezhnev N. Yu. *Ga-S and In-Se systems: crystal structure of intermediate phases and T-x-diagrams**. Cand. chem. sci. diss. Voronezh; 2023. 28 p. (In Russ.). Available at: https://rusneb.ru/catalog/000199_000009_012131968/

31. Brezhnev N. Y., Dorokhin M. V., Zavrazhnov A. Y., Kolyshkin N. A., Nekrylov I. N., Trushin V. N. High-temperature gallium sesquisulfides and a fragment of the *T-x* diagram of the Ga – S system with these phases. *Condensed Matter and Interphases*. 2024;26(2): 225–237. https://doi.org/10.17308/kcmf.2024.26/11936

32. Pardo M., Guittard M., Chilouet A., Tomas A. Diagramme de phases gallium-soufre et études structurales des phases solides. *Journal of Solid State Chemistry*. 1993;102: 423–433. https://doi.org/10.1006/jssc.1993.1054

33. Berezin S. S., Berezina M. V., Zavrazhnov A. Yu., Kosyakov A. V., Sergeeva A. V., Sidei V. I. Phase transformations of indium mono- and sesquisulfides studied by a novel static thermal analysis technique. *Inorganic Materials*. 2013;49(6): 555–563. https://doi.org/10.1134/s0020168513060010

34. Zavrazhnov A. Yu., Nekrylov N. I., Berezina S. S., Zhuravlev I. A. Phases of the gallium sesquisulfide family stabilised by iron and manganese impurities. In: *Thermodynamics and Materials Science: Proc. XV Symposium with International Participation, 3–7 July 2023*. Novosibirsk: Nikolaev Institute of Inorganic Chemistry of the Siberian

Branch of the Russian Academy of Sciences; 2023. p. 35. https://doi.org/10.26902/THERM_2023_015

35. Zavrazhnov A. Yu., Nekrylov I. N., Berezin S. S., Brezhnev, N. Y. Zavaluev V. Y., Kosyakov A .V. Phase diagrams for the Ga – S and Mn – Ga – S systems. *XXIV International Conference on Chemical Thermodynamics in Russia (RCCT-2024), July 1-5, Ivanovo*. Ivanovo State University of Chemistry and Technology: 2024: 125. ISBN 978-5-6051371-2-2. Available at: https://rcct.isc-ras.ru/sites/default/files/collectionabstracts/56/rcct-2024.pdf

36. Kokh K. A., Huang Z. M., Huang J. G., Gao Y. Q., ... Andreev Yu. M. Study of Ga_2S_3 crystals grown from melt and $PbCl_2$ flux. *Materials Research Bulletin*. 2016;84: 462–467. https://doi.org/10.1016/j.materresbull.2016.08.046

37. Tyurina E. A., Velmuzhov A. P. Sukhanov M. V., ... Shiryaev V. S. Phase formation during crystallization of melts and glasses of the $Ga_xGe_{40-x}S_{60}$ system. *Journal of Non-Crystalline Solids*. 2023;622: 122686. https://doi.org/10.1016/j.jnoncrysol.2023.122686

38. Vel’muzhov A. P., Sukhanov M. V., Potapov A. M., Suchkov A. I., Churbanov M. F. Preparation of extrapure Ga2S3 by reacting GaI3 with sulfur. *Inorganic Materials*. 2014;50(7): 656–660. https://doi.org/10.1134/s0020168514070152

39. Lee J., Won Y. H., Kim H. N. Photoluminescence of Ga_2S_3 and Ga_2S_3:Mn single crystals. *Solid State Communications*. 1996;97(12): 1101–1104. https://doi.org/10.1016/0038-1098(95)00728-8

40. Kokh K., Lapin I. N., Svetlichnyi V., Galiyeva P., Bakhadur A., Andreev Y. Synthesis and bridgman growth of Ga_2S_3 crystals. *Key Engineering Materials*. 2016;683: 71–76. https://doi.org/10.4028/www.scientific.net/KEM.683.71

41. Kosyakov A. V., Nekrylov I. N., Brezhnev N. Y., Malygina E. N., Zavrazhnov A. Y. The *T-x* diagram of the Ga – Se system in the composition range from 48.0 to 61.5 mol % Se according to thermal analysis data. *Condensed Matter and Interphases*. 2019;21(4): 519–527. https://doi.org/10.17308/kcmf.2019.21/2363

42. Okamoto H. Ga-Se (Gallium-Selenium). *Journal of Phase Equilibria and Diffusion*. 2009;30: 659. https://doi.org/10.1007/s11669-009-9601-3

43. Zavrazhnov A. Yu., Naumov A. V., Kosyakov A. V., Ryazhskikh M. V. Ancillary component method: using in the research and synthesis of pure inorganic compounds. *Materials Science and Engineering B*. 2011:1(12): 906–912.

44. Zavrazhnov A.Yu., Naumov A. V., Pervov V. S., Riazhskikh M. V. Chemical vapor transport for the control of composition of low-volatile solids: II. The composition control of indium sulfides: Technique of the charge dilution *Thermochimica Acta*. 2012;532: 96–102. https://doi.org/10.1016/j.tca.2010.10.004

45. Zavrazhnov A. Yu., Naumov A. V., Turchen D. N., Zartsyn I. D., Zlomanov V. P. Chemical transport for controlling the composition of condensed bodies II. Control of the composition of gallium monoselenide within the homogeneity region and diagnostics of GaSe nonstoichiometry. *Condensed Matter and Interphases*. 2004;6 (4): 322–335. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.asp?id=29833369

46. Zavrazhnov A. Yu., Zartsyn I. D., Naumov A. V., Zlomanov V. P., Davydov A. V. Composition control of low-volatility solids through chemical vapor transport reactions. I. Theory of selective chemical vapor transport. *Journal of Phase Equilibria and Diffusion*. 2007;28: 510–516. https://doi.org/10.1007/s11669-007-9200-0

47. Kosyakov A.V., Zavrazhnov A. Y., Naumov A. V. Refinement of the In-S phase diagram using spectrophotometric characterization of equilibria between hydrogen and indium sulfides. *Inorganic Materials*. 2010;46(4): 398-401. 343–345. https://doi.org/10.1134/s0020168510040035

48. Kosyakov A. V., Zavrazhnov A. Yu., Naumov A. V., Sergeeva A. S. Specification of the phase diagram of system In - S according to spectrophotometric researches ofbalance between sulfides of indium and hydrogen. *Proceedings of the Voronezh State University. Series: Chemistry. Biology. Pharmacy*. 2009;2: 28–39. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.as-p?id=12992199

49. Zavrazhnov A. Yu., Naumov A. V., Anorov P. V., Goncharov E. G., Sidey V. I., Pervov V. S. *T*-x phase diagram of the In-S system. *Inorganic Materials*. 2006;42(12): 1294–1298. https://doi.org/10.1134/s0020168506120028

50. Okamoto H. In-S (Indium-Sulfur). *Journal of Phase Equilibria and Diffusion*. 2012;34(2): 149–150. https://doi.org/10.1007/s11669-012-0152-7

51. Zavrazhnov A., Kosyakov A., Naumov A., Sergeeva A., Riazhskikh M., Berezin S. Study of the In–S phase diagram using spectrophotometric characterization of equilibria between hydrogen and indium sulfides. *Thermochimica Acta*. 2013;566: 169–174. https://doi.org/10.1016/j.tca.2013.05.031

52. Naumov A. V., Sergeeva A. V., Semenov V. N. Oriented $In_{3-x}S_4$ films on the (100) surface of Si, GaAs, and InP single crystals. *Inorganic Materials*. 2017;53(6): 560–567. https://doi.org/10.1134/S0020168517060127

53. Zavrazhnov A. Yu., Naumov A. V., Sergeeva A. V., Sidey V. I. Selective chemical vapor transport as a means of varying the composition of nonstoichiometric indium sulfides. *Inorganic Materials*. 2007;43(11): 1167–1178. https://doi.org/10.1134/s0020168507110039

54. Zavrazhnov A., Naumov A., Kosyakov A., Riazhskikh M. Ancillary component method: using in the research and synthesis of pure inorganic compounds. *Materials Science and Engineering B*. 2011;1: 906–912. Available at: https://www.researchgate.net/publication/247931076_Ancillary_Component_Method_Using_in_the_Research_and_Synthesis_of_Pure_Inorganic_Compounds

55. Brezhnev N. Yu., Zavrazhnov A. Yu., Naumov A. V., Kosyakov A. V., Zavalyuev V. Yu. Refinement of the T-x diagram of the state of the In-Se system, as well as the structure of intermediate phases of this system. In: *Thermodynamics and Materials Science: Proc. XV Symposium with International Participation, 3–7 July 2023*. Novosibirsk: Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences; 2023. p. 74. https://doi.org/10.26902/THERM_2023_054

56. Okamoto H. In-Se (Indium-Selenium). *Journal of Phase Equilibria and Diffusion*. 2004;25: 201. https://doi.org/10.1007/s11669-004-0031-y

57. Liu L., Dong J., Huang J, ... Liu Z. Atomically resolving polymorphs and crystal structures of In_2Se_3. *Chemistry of Materials*. 2019;31: 10143–10149 https://doi.org/10.1021/acs.chemmater.9b03499

58. Zavrazhnov A. Yu., Kosyakov A. V., Sergeeva A. V., Berezina S. S., Chernenko K. K. High-temperature in situ vapor spectrophotometry as a static variant of the tensimetric method equilibria in the Ga – I system. *Condensed Matter and Interphases*. 2015;17(4): 417–436. Available at: https://journals.vsu.ru/kcmf/article/view/87

59. Zavrazhnov A. Y., Naumov A. V., Malygina E. N., Kosyakov A. V. Indium monochloride vapor pressure: the vapor-gauge and spectrophotometric experimaental data. *Condensed Matter and Interphases*. 2019;21(1): 60–71. https://doi.org/10.17308/kcmf.2019.21/717

60. Brezhnev N. Y., Kosyakov A. V., Steich A. V., Zavrazhnov A. Y. High-temperature spectrophotometry of indium chloride vapours as a method of study of the In – Se system. *Condensed Matter and Interphases*. 2021;23(4): 482–495. https://doi.org/10.17308/kcmf.2021.23/3667

61. Walther R., Deiseroth J. Redetermination of the crystal structure of hexaindium heptaselenide, In_6Se_7. *Zeitschrift für Kristallographie – Crystalline Materials*. 1995;210: 359–365. https://doi.org/10.1524/zkri.1995.210.5.359

62. Gödecke T., Haalboom T., Sommer F. Stable and metastable phase equilibria of the In-Se system. *Journal of Phase Equilibria*. 1998;19(6): 572–576. https://doi.org/10.1007/BF02701021

63. Vassilev G. P. Infrared spectroscopy and X-ray diffraction data of In–Se compounds. *Int. International Journal of Materials Research.* 2007;98(1): 60–63 https://doi.org/10.3139/146.101428

64. Peng Y.-H., Muhimmah L. C., Ho C.-H. Phosphorus-doped multilayer In_6Se_7: the study of structural, electrical, and optical properties for junction device. *JACS Au*. 2023;4(1): 58–71. https://doi.org/10.1021/jacsau.3c00653

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