# Selective Chemical Vapor Transport as a Means of Varying the Composition of Nonstoichiometric Indium Sulfides

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Received March 1, 2007

Abstract—Investigation of halide vapor transport with the participation of indium and indium sulfides in a closed system indicates that applying a temperature gradient is insufficient for quantitative spontaneous indium transfer from the lower indium sulfides or for the transport of elemental indium. A major reason for this is that the vapor phase over indium and its lower sulfides is dominated by monohalides. Impossible under conventional experimental conditions, chemical vapor transport can be achieved by diluting indium with an inert substance, e.g., gold. Our results indicate that the vapor transport of indium is possible in systems of the form indium sulfide–indium chloride vapor–charge (Au–In) and that chloride vapor transport can be used to nondestructively control the composition of indium sulfides. The transport process is shown to be selective and reversible. Conditions are determined for nondestructive chemical transport control over the composition of indium sulfides.

DOI: 10.1134/S0020168507110039

#### **INTRODUCTION**

Selective chemical vapor transport (SCVT) is particularly attractive for finely tuning the composition (nonstoichiometry) of phases with a low vapor pressure [1, 2].

The basic principle of the method is that a selective transport reaction may proceed in the forward direction (extraction of a component from the material) or reverse direction (saturation of the material with the component being transported), depending on the process conditions. The process is run in a closed system (ampule) containing the sample and charge. The latter acts as a source or getter of the component to be transported (Fig. 1). The vapor phase in the ampule consists of several vapor species, which insure selective transport. According to earlier findings [1], the direction of selective vapor transport is only dependent on the sample temperature  $T_2$ , charge temperature  $T_1$ , and charge composition  $x_1$ . The sample and charge compositions stop varying when the system reaches a steady state, in which no mass transport occurs. The sample composition in the final state is determined by the same variables:  $T_2$ ,  $T_1$ , and  $x_1$ .

In this work, we focus on approaches for controlling the composition of solid phases in the In–S system using SCVT without recrystallization of the starting material.

## THEORETICAL ANALYSIS AND SELECTION OF COMPONENTS OF THE TRANSPORT SYSTEM

As pointed out earlier [3], indium chemical transport in the vapor transport system under consideration must be due to the selective reaction

$$2\mathrm{In''} + \mathrm{In}_{2}\mathrm{Hal}_{4}' = 4\mathrm{In}\mathrm{Hal'}, \tag{1}$$

$$K = \frac{p_{\rm InHal}^4}{p_{\rm In,Hal}},\tag{2}$$

where the primed and double-primed species are in the vapor phase and condensed phase, respectively  $(In_6S_7,$ 



**Fig. 1.** Schematic representation of the experimental geometry for varying the composition of low-volatility binary phases via SCVT: (1) two-zone furnace, (2) quartz ampule filled with transport agent vapor, (3) sample, (4) charge acting as a source or getter of the component being transported.

1090

1270 L 852 1070 78 751 752  $L_1 + L_2$ 68 638 In2.8S4 870 593  $T, \mathbf{K}$ 414 670 L + InS470 156 InS In<sub>2</sub>S<sub>3</sub> In + InS0 10 20 30 40 50 60 70 80 In mol % S

Fig. 2. *T*–*x* phase diagram of the In–S system [4].

 $In_{3-x}S_4$  is indium in the condensed phase, e.g., in an indium sulfide).

By analogy with previous studies of SCVT with the participation of gallium selenides [1, 2], we attempted to use metallic indium as a controlling charge, but we failed to control the sample composition in the system sample (In–S)–vapor (indium halides)–charge (In metal): independent of the process conditions, any of the known indium sulfides (InS,  $In_6S_7$ ,  $In_{3-x}S_4$ , and  $In_2S_3$  [4–7] (Fig. 2)<sup>1</sup>) converted to the most indium-rich phase, InS. Transport was impossible even in a simplified system, where the indium sulfide in the sample was replaced with pure indium.

The lack of transport can be interpreted as follows: According to Yasuo Kunia et al. [8–10], at temperatures above 400°C equilibrium (1) with the participation of pure liquid indium is shifted almost fully to the right  $(K \rightarrow \infty)$ . In<sub>2</sub>Hal<sub>4</sub>, which returns the halogen to the charge, is essentially missing in the vapor phase, and indium transport is impossible. Given the relation between K and the chemical potential of the indium present in the condensed phase in equilibrium with the vapor phase [11], the problem in hand can be formulated as the too high potential of indium  $(\mu_{1_{In}})$  in the metallic indium charge:

$$\mu_{1_{\text{in}}} = 1/2RT\ln K + F(T).$$
(3)

Here, F(T) is related to standard potentials and depends on temperature only.

Two approaches have been proposed to reduce the chemical potential  $\mu_{In}$ :<sup>2</sup>

to dilute the charge with an inert component R such that a homogeneous solution can be obtained over the entire concentration range of interest;

to bind the component to be transported (In) in a distinct chemical compound.

### DILUTION OF THE COMPONENT TO BE TRANSPORTED (CONTINUOUS SERIES OF SOLUTIONS)

Consider the first approach. It is reasonable to expect that indium dilution will be accompanied by a decrease in activity and will reduce  $\mu_{1_{in}}$  according to the well-known relation

$$\mu_{1_{\text{In}}} = \mu_{1_{\text{In}}}^0 + RT \ln a_{\text{In}}, \tag{4}$$

where  $\mu_{1_{In}}$  is the chemical potential of the indium in the charge, and  $\mu_{1_{In}}^{0}$  is the chemical potential of pure metallic indium.

According to Eq. (4), the decrease in activity will cause a reduction in K and, hence, a rise in the content of  $In_2Hal_4$ , necessary for indium chemical transport.

Transport selectivity imposes the following requirements on the diluent R:

(1) It must have a negligible vapor pressure.

(2) It must be nonreactive with the transport agent.

(3) The forming solution should not exhibit large positive deviations from ideality.

As the diluent, we used gold, which meets all of the requirements above [3]. The Au–In system contains several low-melting-point intermetallic phases (Fig. 3) [12]. The use of melts appears more attractive compared to intermetallic-based solid solutions from the viewpoint of the rate of indium exchange in the bulk of the charge.

As the transport agent, we used chlorine (in the form of InCl), first, because indium chlorides have higher vapor pressures than do bromides and iodides [3] and, second, because, by analogy with halides of some elements (Ga, Ge, Si, and others), we assumed that the

<sup>&</sup>lt;sup>1</sup> Various designations have been proposed in the literature for phases close in composition to  $In_2S_3$ . The  $In_{3-x}S_4$  phase is often designated  $\beta$ -In<sub>2</sub>S<sub>3</sub> [3], whereas in [4, 5]  $\beta$ -In<sub>2</sub>S<sub>3</sub> is used to denote the low-temperature phase with a sulfur content close to 60 mol %.

<sup>&</sup>lt;sup>2</sup> The problem might possibly be resolved by using another transport agent. We, however, failed to find substances that would selectively and reversibly react with crystalline indium sulfides without dissolving in them.



**Fig. 3.** *T*–*x* phase diagram of the In–Au system [12].

oxidized form of indium halides  $(In_2Hal_4)$  would be more stable in the chlorine compound.

To verify and refine these considerations in experiment, the problem of controlling the composition of indium sulfides via SCVT using a gold-diluted indium charge was divided into the following steps:

1. First, the feasibility of the chloride transport of indium was assessed using a simplified, sulfur-free system: sample (In metal)–vapor (indium chlorides)– charge (Au metal).

2. We examined the possible relationships between the compositions of the In–S sample and indium–diluent (R) charge (during the process and in the final state, in equilibrium with respect to indium).

3. Next, we experimentally determined the interrelated changes in the compositions of the sample and charge in the closed isothermal system sample (In–S)– vapor (indium chlorides)–charge (In–Au melt) and compared them with the prediction results (particular attention was paid to the correspondence between the sample and charge compositions in equilibrium with respect to In).

4. Finally, we examined the possibility of reversible changes in the sample and charge compositions upon variations in their temperatures in the above system.

Selective chemical transport of indium in the system sample (In metal)-vapor (indium chlorides)charge (Au metal). In the context of the first problem, we examined chloride transport of indium in a simplified, sulfur-free system. To reduce the chemical potential of indium in the charge, we used an indium-free substance, pure gold ( $\mu_{1_{In}} \longrightarrow -\infty$ ), as the charge and metallic indium as the sample. Indium transport, i.e., mass transfer between the sample and the charge, was examined using static gravimetry, a method used earlier in studies of similar systems [1, 3].

In our preparations, about 1 g of metallic indium (In-00) was placed at one end of an ampule, and a plate of refined gold (~0.1 g) was placed at the other end. The ampule also contained indium monochloride in an open capillary. InCl was synthesized by melting a weighed portion of AgCl and an excess of indium metal [3]. The amount of InCl was chosen so as to ensure an unsaturated vapor pressure  $p_{\text{InCl}} = 2.5 \times 10^4$  Pa.

Indium transport and dissolution in gold were easily observable: the Au plate fully melted at a temperature well below the melting point of gold, and the In–Au melt changed in color from yellowish to silvery white. According to the rate data (Fig. 4), indium was transported most rapidly in the initial stages of the process, when the indium activity in the charge was lowest. As the gold was diluted with indium, the indium concentration and activity in the melt increased; at 55 mol % In, the transport almost ceased. The rate data (0.1 mol % accuracy in the compositions of In–Au alloys) were checked by an independent technique: after the experiment, the In–Al alloy was weighed. The compositions evaluated by the two methods coincided to within 1 mol %.

Experiments under nonisothermal conditions showed that temperature variations did not reverse the



**Fig. 4.** (a) Amount of indium transferred to the gold getter and (b) getter composition as functions of time; sample and getter temperatures, 823 and 773 K, respectively;  $C_{\text{InCl}} = 7 \text{ mol/m}^3$ .

direction of mass transport, which implies that, in the system under consideration, the gold and the forming In–Au solution act solely as an indium getter, rather than as a donor. This seems to be due to the large difference in chemical potential,  $\mu_{2_{In}} - \mu_{1_{In}}$ , especially in the case of Au-rich In–Au solutions. Thus, our results demonstrate that indium dilution with an inert (in the vapor phase) substance ensures indium vapor transport in at least one direction.

2. Possible relationships between the compositions of the In–S sample and indium–diluent (R) charge. Consider mass transport conditions in a closed isothermal vapor transport system of the form sample (In–S)–vapor (indium chlorides)–charge (In–R). Note that, in this system, the transport agent has no effect on the final state (equilibrium with respect to indium) of the sample and charge, which is defined by the wellknown equality

$$\mu_{1_{In}} = \mu_{2_{In}}, \tag{5}$$

where subscripts 1 and 2 refer to the charge and sample, respectively.

Indeed, if indium sulfide samples had a significant indium vapor pressure  $(p_{\text{In}}, p_{\text{In}})$ , Eq. (5) might be fulfilled through physical transport of indium, that is, with no transport agent. Our purpose is to predict how the final sample composition (equilibrium In content) then varies at a fixed temperature. Let us plot the sample composition against the charge composition. It follows from Eqs. (4) and (5) that to each equilibrium (with respect to In) charge composition corresponds a particular sample composition, i.e., an indium sulfide of certain stoichiometry and structure. Let us follow the variation in the indium content of the sample as the charge is diluted with R (Fig. 5a). Assume that selective indium transport is conducted at a fixed temperature, e.g., at 600°C, where the In-S system contains five phases:  $L_{In}$  (indium-based melt), InS, In<sub>6</sub>S<sub>7</sub>, In<sub>3-d</sub>S<sub>4</sub>, and  $L_{\rm S}$  (sulfur-based melt) (Fig. 5b).

In the initial stages of the process, a gradual variation in charge composition will be accompanied by a gradual variation in the composition of the  $L_{In}$  solution (Fig. 5a, segment *AB*), and, at a higher diluent (R) content, the equilibrium (with respect to indium) sample will contain more sulfur (nontransportable component). At a certain charge composition, the equilibrium chemical potential of indium in the sample will reach the value characteristic of the phase boundary of  $L_{In}$ . The same potential of indium and, hence, the same charge composition will correspond to the In-rich phase boundary of the neighboring phase, InS (Fig. 5a, point *C*). Moreover, this charge composition will correspond to a heterogeneous mixture of these phases, independent of their contents (Fig. 5a, vertical segment *BC*).

Further raising the diluent concentration in the charge will gradually increase the content of the nonvolatile component (S) within the homogeneity range of the InS phase (Fig. 5a, segment CD). At the sulfurrich phase boundary of indium monosulfide, the same charge composition will correspond to the compositions of two coexisting phases: InS and In<sub>6</sub>S<sub>7</sub>. In this manner, we obtain the broken line A-J in Fig. 5a. Thus, to nonstoichiometric compositions of each phase corresponds a certain composition range of the In-R solution. The use of such a solution as a charge must enable the preparation of each intermediate phase (any sulfide) with controlled stoichiometry, while maintaining the selectivity of the process. The only obstacle to implementing this approach is that it is desirable to use the maximum possible amount of the charge. Otherwise, both the sample and charge compositions will vary markedly during the evolution of the system. This may reduce the accuracy in predicting the final sample composition.

The above considerations must apply to both physical and selective chemical transport of indium. The only role of the transport agent is to drastically accelerate indium transfer between the sample and charge. This statement, however, only applies to isothermal SCVT systems.



**Fig. 5.** (a) Diagram illustrating the predicted relationship between the compositions of In–S samples and In–R charges (isothermal section at  $T \approx 870$  K; R is a diluent forming a continuous series of solutions with In). (b) Partial *T*–*x* phase diagram of the In–S system; the homogeneity ranges of the phases are represented only schematically.

3. Isothermal mass transport in the system sample (In-S)-vapor (indium chlorides)-charge (In-Au melt) and sample and charge compositions at equilibrium (with respect to In). In all our experiments, samples ( $\sim 0.1$  to  $\sim 1$  g) consisted of a particular In–S phase. To raise the reaction rate, the samples were ground to a particle size no greater than 1 mm. The charges used were weighed portions (~0.2 to 0.5 g) of In–Au alloys containing 0 to 80 mol % Au. The process was run in quartz ampules at temperatures from 550 to 650°C and a chlorine content corresponding to  $p_{\text{InCl}} =$  $10^4$  Pa. After annealing for a certain time, the ampules were quenched. To this end, cold water was poured onto them so that the indium chlorides condensed in the central part of the ampule and did not contaminate the sample or charge, which were located at the ends of the ampule. Next, the substances were withdrawn from the ampule and weighed on a VLM-2000 analytical balance to determine the weight change. This procedure allowed us to evaluate the compositional changes caused by indium transport. After the measurements, the experiment was continued and the above procedure was repeated. The compositions of the heat-treated materials were correlated with x-ray diffraction and, occasionally, static gravimetry data.

After 200 h of annealing, the sample and charge weights stopped varying, suggesting that an equilibrium (with respect to In) state had been reached. According to x-ray microanalysis and roentgenoluminescence data for the condensed phases, the charge contained no sulfur, and the sample contained no gold.

These results confirm that the transport process is selective.

Figure 6 illustrates the variations in the sample and charge compositions and presents the final (equilibrium) compositions. The plot in Fig. 6 is analogous to the composition relationship diagram in Fig. 5.<sup>3</sup> The compositions may refer to the materials in the initial, intermediate, and final (equilibrium with respect to In) states of the vapor transport system. This allows one to follow compositional changes and to correlate the final compositions of the condensed phases in the system.

The data in Fig. 6 were obtained at 650°C. The arrows indicate the variations in the sample and charge compositions during the evolution of the system to the equilibrium (with respect to In) state. These data lead us to the following conclusions:

1. The transport direction at  $T_2 = T_1$  is governed by the initial sample and charge compositions. At high diluent (gold) contents, indium is transported to the charge, and the indium content of the sample decreases. At lower gold contents of the charge, indium is transported to the sample and dissolves in it.

<sup>&</sup>lt;sup>3</sup> Clearly, the equilibrium (with respect to In) state of the isothermal vapor transport system under consideration is also determined by the temperature and, to a far lesser extent, by the pressure. The diagram in question must then be represented in four dimensions (sample composition-charge composition-temperature-pressure). Thus, the two-dimensional diagrams below are isobaric-isothermal sections of the composition relationship diagrams.



**Fig. 6.** Diagram illustrating the relationship between the compositions of In–S samples and In–Au charges, as inferred from the gravimetric data for the system sample (indium sulfides)–vapor (indium chlorides)–charge (In–Au melt); (1, 3, 4) evaluated from the weight change of the charge (In–Au alloy), (2) evaluated from the weight change of the In–S sample. The arrows indicate the evolution of the sample and charge compositions from the initial to final (200 h of annealing) state. The heavy segments represent the sample and charge compositions in the equilibrium (with respect to In) state of the system at  $650^{\circ}$ C.

2. Further evidence that the vapor transport system under consideration can reach the equilibrium (with respect to In) state is provided by the fact that a given composition can be obtained at higher and lower diluent contents, corresponding to the opposite transport directions (different directions of the arrows in Fig. 6).

3. The final sample composition can be obtained using different initial states (see the points near 57 mol % S and 55 mol % Au). Since the charge is homogeneous, the evolution trajectory depends not only on the initial compositions but also on the initial amounts of the sample and charge.

4. The sample and charge compositions are interrelated: increasing the diluent content of the charge reduces the indium content of the sample. Each point corresponding to a final, equilibrium state must be only determined by the temperature (at slight variations in total pressure) and is independent of the other factors (the nature of the transport agent, the amount of solids, etc.).

5. As would be expected, the composition ranges in which the sample is heterogeneous (two-phase) are represented by vertical segments, which reflect the relationship between the equilibrium (with respect to In) sample and charge compositions. On the other hand, the monotonic segments of the final state indicate that the sulfide sample consists of a single phase with a considerable homogeneity range.

In addition, the data in Fig. 6 lead us to some conclusions about the homogeneity ranges of the intermediate phases in the In–S system. In particular, it seems likely that the homogeneity range of the  $In_{3-\delta}S_4$  phase is several percent in width and extends from ~58.3 to 60.3 mol % S at 650°C, that is, it includes the stoichiometric composition  $In_2S_3$ . The inflection in the composition relationship line in the  $In_{3-\delta}S_4$  phase region provides indirect evidence that different point defects dominate in different composition regions of this phase.

The results of similar experiments performed at other temperatures (700 and 750°C) indicate that moderate changes in temperature (on the order of 100°C) have little effect on the relationship between the sample and charge compositions.

In addition, it was important to ascertain whether the indium transport between the sample and charge was indeed due to an increase in the  $In_2Cl_4$  (oxidized form) concentration in the vapor phase. We assumed that, at lower chemical potentials of indium in the condensed phases (sample and charge) at partial equilibrium, the equilibrium vapor phase was richer in  $In_2Cl_4$  compared to InCl. In addition, we expected that quenching had an insignificant effect on the relative amounts of these vapor species, which, therefore, can be assessed by analyzing the condensed phases.

Qualitative information can be gained from the color of the condensed phases. It is well known that, with increasing Cl content, solid In-Cl phases change from colorless  $(In_2Cl_4 \text{ and } InCl_3)$  to yellow-orange (InCl) [13, p. 56]. The observed color changes in the condensed chlorides were consistent with the above assumptions. The highest indium content (maximum  $\mu_{In}$ ) of the equilibrium charge (>55 mol % In) and sample (InS phase) corresponds to a bright orange color of the condensed phases. When such condensed phases are in equilibrium with indium chloride vapors, the fraction of molecules with the lowest chlorine content (InCl) must be the highest. With decreasing indium concentration in the sample, the color of the condensed chlorides became less intense. For example, a pale orange color corresponded to the In-S sample with a final sulfur content of 58.5 mol %, and a pale yellow color corresponded to sulfur contents above 59 mol %. Thus, our results demonstrate that a reduction in the indium content of the sample and charge is accompanied by an increase in the In<sub>2</sub>Cl<sub>4</sub> (oxidized form) concentration in the vapor phase.

Reversible changes in the composition of phases during nonisothermal SCVT in the system sample (In-S)-vapor (indium chlorides)-charge (In-Au melt). One would expect that, in a nonisothermal  $In_mS_n$ -vapor (In-Cl)- $In_{1-x}Au_x$  system, the chemical transport direction can be reversed by adjusting the chemical potential of indium in the sample or charge via temperature variations. As shown earlier [1, 2], the direction of mass transport under nonisothermal conditions depends not only on the charge composition but also on the sample and charge temperatures ( $T_2$  and  $T_1$ , respectively). (It is convenient to use the difference  $\Delta T = T_2 - T_1$  instead of  $T_2$  or  $T_1$ : at constant  $T_2$  or  $T_1$ , increasing  $\Delta T$  reduces the concentration of the component being transported [1, 2]. The reversibility of nonisothermal indium transport was examined using static gravimetry.

First, a ground In–S alloy containing 48.0 mol % S was used as the sample. The alloy consisted of In and InS, as determined by x-ray diffraction. As the charge, we used a weighed amount of pure gold. The sample temperature was 823 K, and the charge temperature was 783 K ( $\Delta T = 40$  K). Curves *I* in Figs. 7a–7c show the time dependences of the sample weight, sample composition, and charge composition. It follows from these data that indium extraction from the sample ceases at 50 mol % S (InS). The corresponding charge composition in this steady state is 55 mol % Au. It seems likely that the chemical potential of indium in this melt is too high for further indium extraction via InS conversion to In<sub>6</sub>S<sub>7</sub>.





**Fig. 7.** (a) Amount of indium transferred, (b) sample composition, and (c) charge composition as functions of time for nonisothermal vapor transport at a sample temperature of 823 K: (*I*) In + InS sample ( $\Delta T = 40$  K), (*2*) further indium transport owing to InS conversion to In<sub>6</sub>S<sub>7</sub> ( $\Delta T = 55$  K), (*3*) insignificant transport ( $\Delta T = -110$  K), (*4*) reverse indium transport ( $\Delta T = -240$  K). The error of determination is represented by the size of the data points.

At the same time, InS conversion to  $In_6S_7$  proved possible when the charge temperature was reduced by 15 K ( $T_2 = 823$  K,  $T_1 = 768$  K,  $\Delta T = 55$  K). As a result, we observed further indium transport from the sample to the charge, which ceased when the charge composi-

1000

tion was 49.6 mol % Au (Fig. 7, curves 2). The final sample composition was 50.5 mol % S, which corresponds to a mixture of InS and  $In_6S_7$ . As the indium content of the sample decreased, that of the charge increased, which probably prevented full conversion of InS to  $In_6S_7$ .

To reverse the direction of indium transport, we increased  $T_1$  (compared to the previous experiment), without changing the temperature  $T_2$  of the InS + In<sub>6</sub>S<sub>7</sub> sample. After a relatively small increase in  $T_2$ , the rate of indium transport was rather slow (Fig. 7, curves 3;  $T_2 = 823$  K,  $T_1 = 933$  K,  $\Delta T = -110$  K). At the same time, after the charge temperature  $T_1$  was raised to 1063 K (Fig. 7, curves 4;  $\Delta T = -240$  K), the rate of indium transport to the In–S sample was initially relatively fast. Under those conditions, mass transport ceased when a steady state with 49.9 mol % S (which corresponds to InS within the present experimental accuracy) was reached.

Therefore, our results demonstrate that the direction of mass transport in the system under consideration depends on the thermal conditions of the process.

Thus, the charge dilution approach offers the following advantages:

1. Varying the concentration component of the chemical potential, one can control the equilibrium state of the system, which offers the possibility of using those phase compositions of the sample and transport agent which are commonly believed to be unsuitable for reversible mass transport.

2. The proposed approach notably extends the capabilities of isothermal selective transport. It was pointed out earlier [2] that, if the charge belongs to the same binary system as the sample, a single-zone process allows one to reproducibly obtain only samples with compositions at the limits of the homogeneity range. In the approach in question, control over the activity of the component being transported allows one to obtain compositions with the desired nonstoichiometry.

3. To control the sample composition in the course of isothermal selective chemical transport, it is necessary to scan the composition relationship diagram of the system. Such diagrams are similar to classical phase diagrams in that they represent phase assemblages under equilibrium conditions.

4. In nonisothermal SCVT, a variety of sample compositions can be obtained by varying only three parameters: the sample and charge temperatures and charge composition.

## A WAY OF BINDING THE ACTIVE COMPONENT OF THE CHARGE IN DISTINCT CHEMICAL COMPOUNDS: EXPERIMENTAL AND RESULTS

**Theoretical analysis.** Consider the latter of the above approaches to reducing the chemical potential of the component being transported in the charge. The

basic principle of this approach is to bind this component in distinct chemical compounds with significant, but limited homogeneity ranges. Component Q, which forms a number of compounds (AQ,  $A_2Q_3$ , and others) with the component to be transported (A), must meet almost the same requirements as the diluent R in the approach involving the formation of a continuous series of solutions:

It must have a negligible vapor pressure.

It must be nonreactive with the transport agent.

The enthalpy of formation of the compounds must be significant:  $\Delta_f H(T) \ll 0$ .

Consider the system sample (A-Q)-vapor-charge (A-Q) under isothermal conditions. Assume that there is a vapor-phase indium exchange between the sample  $(A_xB_y)$  and a phase  $(A_wQ_z)$  of the charge.

Assume that, at temperature  $T_i$ , the A–Q system contains the phases  $\alpha$  (A-based phase),  $\beta$  (intermediate compound), and  $\gamma$  (Q-based phase) (Fig. 8c). At this temperature, the A–B system also contains three condensed phases:  $\alpha'$  (A-based solution),  $\beta'$ , and  $\gamma'$ (B-based solution) (Fig. 8b).

Let us examine how the content of component A in the sample varies with increasing content of component Q in the charge (Fig. 8a). Like in the case of charge dilution, we expect that, at a low content of component Q in the charge, the equilibrium (with respect to component A) phases are  $\alpha$  (charge) and  $\alpha'$  (sample); the dependence for partial equilibrium must be continuous and monotonic (Fig. 8a, segments  $DE_1$ ,  $DE_2$ ). At a higher content of the binding component Q in the charge, the equilibrium sample must contain more component B (nontransportable).

As the content of component Q in the charge increases, two situations are possible.

1. The mutual chemical affinity of the interacting components (Q and A) in the  $\alpha$  phase of the charge is high, and increasing the concentration of the binding component Q sharply reduces the chemical potential  $\mu_A$ in the charge. Even at a relatively low concentration of component Q in the charge (which also corresponds to the  $\alpha$  phase), the chemical potential  $\mu_A$  in the sample will then take the value corresponding to the phase boundary of the  $\alpha'$  phase (Fig. 8a, point  $E_1$ ). The neighboring phase,  $\beta'$ , will have the same value of the chemical potential. Thus, the composition relationship line will have a vertical segment,  $E_1F_1$ , representing the selective equilibrium between the homogeneous charge of particular composition and a mixture of arbitrary amounts of the  $\alpha'$  and  $\beta'$  phases. Further increasing the content of component Q in the  $\alpha$  phase will change the composition of the  $\beta'$  phase within its homogeneity range (segment  $F_1G_1$ ).

2. A different situation occurs when the mutual chemical affinity of the interacting components Q and A in the  $\alpha$  phase of the charge is low throughout the homogeneity range of this phase. Even significant com-



**Fig. 8.** Possible types of diagrams illustrating the relationship between the compositions of A–B samples and A–Q charges, where Q is an inert binder forming distinct condensed phases ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) with component A: (a) isothermal section of the composition relationship diagram, (b, c) partial *T*–*x* phase diagrams of the A–B and A–Q systems, respectively.

positional changes then have little effect on  $\mu_A$  in the charge. As a result, the corresponding change in the sample composition will also be relatively small, and the  $\alpha$  phase in the charge will reach its phase boundary before the  $\alpha'$  phase in the sample (Fig. 8a, point  $E_2$ ). In this instance, to the same composition of the  $\alpha'$  solution corresponds the boundary of the  $\beta$  phase in the charge, which is adjacent to the  $\alpha$  phase. Thus, a horizontal segment,  $E_2F_2$ , appears in the composition relationship diagram.

As the concentration of the binding component Q in the  $\beta$  phase of the charge increases further, two scenarios are again possible.

(1) The  $\mu_A$  in the charge is also a weak function of concentration. Even "traversing" the entire homogeneity range of the  $\beta$  phase is then incapable of reducing the chemical potential of component A to an extent sufficient for reaching, in equilibrium with the sample, another phase, poorer in component A ( $\beta$ ). As a result, we obtain the curved segment  $F_2G_2$  and then the horizontal segment  $G_2H_2$  in the composition relationship line (Fig. 8a).

(2) If the chemical potential of indium in the homogeneity range of the  $\beta$  phase is a strong function of the concentration of component Q, increasing the concentration of this component may bring the sample composition to the  $\alpha'-\beta'$  phase boundary (Fig. 8a, vertical segment  $G_3H_3$ ) and then change the composition of the  $\beta'$  phase within its homogeneity range (curved segment  $H_3I_3$ ).

It is, therefore, reasonable to assume that, if a combination of distinct phases is used as the charge, the composition relationship line may consist of three types of segments:

curved segments, corresponding to gradual variations across the homogeneity ranges of phases close in the chemical potential of the component being transported;

vertical segments (homogeneous, single-phase charge and two-phase sample);

horizontal segments (two-phase charge and sample composition within the homogeneity range).

It is easily seen that the last situation is best suited for accurate control of the sample composition within the homogeneity range of a given phase in the sample.

Selection of the transport agent and charge material. In the proposed approach for controlling the composition of indium sulfides, hydrogen is used as the

transport agent, which makes it possible to introduce sulfur into sulfides or to extract it. Hydrogen has many advantages over other transport agents, the most important of which are the insignificant solubility of hydrogen in most semiconductors (including all of the indium sulfides) and the high selectivity of the reactions involved.

At temperatures above 300°C, free hydrogen readily reacts with any solid sulfides according to the following, well known reaction, reversible to a significant degree:

$$H'_2 + S'' = H_2 S'.$$
 (6)

(Here, like in the above schemes, the primed and double-primed species are in the vapor phase and condensed phase (combined sulfur), respectively.) In the case of indium sulfides, the selectivity of reaction (6) is due to the fact that there are no stable indium hydrides or sulfohydrides.

Recall that experiments on controlling the composition of indium sulfides were to be conducted in a closed isothermal system (ampule). The sample and charge were placed at the opposite ends of the ampule. The charge (sulfur source or getter) must consist of a substance which also reacts with hydrogen according to scheme (6) under the experimental conditions of interest.

The question that now arises is how the charge composition must be selected in order to vary the sample composition in the desired direction. Selective transport in an isothermal system is governed by the relationship between the chemical potentials of the component being transported (sulfur) in the sample and charge. The chemical potential of sulfur, in turn, determines the vapor pressure of this element  $(p_{S_2})$ :

$$\mu_{s}(\text{solid}) = \mu_{s_{2}}(\text{vapor});$$
  

$$\mu_{s_{2}}(\text{vapor}) = \mu_{s_{2}}^{0}(p) + RT \ln p_{s_{2}}$$
(7)  
(at  $x_{s}(\text{solid}) = \text{const}).$ 

The charge can then be selected according to the equilibrium sulfur vapor pressure over it, even if this vapor pressure is extremely low. Namely, if the  $p_{S_2}$  over the charge is higher than that over the sample, vapor transport will be toward the sample, which will become richer in sulfur. Otherwise, the charge will act as a sulfur getter, and the sample will lose sulfur. The final state (equilibrium with respect to sulfur) will be reached when the sulfur vapor pressure over the sample will be equal to that over the charge as a result of compositional changes. In the above reasoning, only one assumption was made, that changes in the total pressure in the system upon the formation of an atmosphere containing the transport agent (H<sub>2</sub> + H<sub>2</sub>S) have little or no effect on the chemical potential of sulfur.

The sulfur vapor pressure is well known for many low-volatility sulfides, which facilitates the selection of the charge material. An additional requirement for the charge material is fully incongruent vaporization: only sulfur molecules must vaporize.

The phases of the Cu–S system meet all of these requirements.

In the temperature range 430–708 K, the Cu–S system contains three phases:

The "high-temperature" phase  $Cu_2S$  (chalcosine), which decomposes peritectoidally at 708 K to form anilite and copper;

anilite, a phase with a broad homogeneity range, from  $Cu_{1.96}S$  to  $Cu_{1.75}S$ , which melts congruently at 1378 K;

covellite, CuS, which decomposes peritectically at 780 K to form liquid sulfur and anilite.

Earlier data [14, 15] and our mass spectrometry results for the In–S system can be used to compare the partial sulfur vapor pressures over In–S and Cu–S phases at different temperatures (table).

The data in the table lead us to a number of assumptions.

Under conditions that insure a constant sulfur vapor pressure over the charge (a large amount of the substance or the use of a mixture of two neighboring phases), an In–S sample, independent of its initial composition,

must convert to  $In_2S_3$  if the charge consists of CuS, CuS + Cu<sub>1.75</sub>S, or Cu<sub>1.75</sub>S (clearly, the composition of  $In_2S_3$  will vary within its homogeneity range, depending on the nature of the charge);

must convert to  $In_6S_7$  if the charge consists of  $Cu_2S$  and Cu.

Controlling the composition of indium sulfides using hydrogen and a Cu–S charge. Hydride vapor transport of sulfur was conducted as follows: First, a quartz ampule and containers for sample and charge powders were prepared. To this end, a bulbous joint with a neck was made at one end of a cylindrical quartz tube ~3 cm in diameter, and then containers with the powdered sample and charge (1-2 g) were inserted into the ampule. Next, a second neck with a bulbous joint was made, and the ampule was ready to fill with hydrogen. The distance between the containers was about 1 cm, the ampule length was approximately 12 cm, and the ampule volume was about 75 ml.

The ampule was then filled with dry hydrogen prepared by the aluminate process (aqueous KOH + Al). The amounts of the reagents were chosen so as to pass 30 l of hydrogen (~400 ampule volumes) through the system. After filling the ampule with hydrogen, the joints were sealed off, and the ampule was placed in the isothermal zone of a horizontal cylindrical furnace.

The samples consisted of an In–S alloy containing 56 mol % sulfur. According to our phase-diagram and

t, °C	$p(\mathbf{S}_2)$ , Pa					
	InS–In <sub>6</sub> S <sub>7</sub> –V	$In_6S_7 - In_3S_4 - V$	$In_2S_3(60\%)-V$	CuS–Cu <sub>1.75</sub> S–V	$Cu_{1.75}S-Cu_2S-V$	Cu <sub>2</sub> S–Cu–V
360	$9 \times 10^{-26}$	$9 \times 10^{-16}$	$1 \times 10^{-11}$	16	$2 \times 10^{-5}$	$8 \times 10^{-15}$
380	$5 \times 10^{-24}$	$1 \times 10^{-14}$	$7 \times 10^{-11}$	40	$8 \times 10^{-5}$	$4 \times 10^{-14}$
400	$2 \times 10^{-22}$	$9 \times 10^{-14}$	$4 \times 10^{-10}$	96	$2 \times 10^{-4}$	$2 \times 10^{-13}$
420	$1 \times 10^{-20}$	$7 \times 10^{-13}$	$2 \times 10^{-9}$	218	$8 \times 10^{-4}$	$8 \times 10^{-13}$
440	$3 \times 10^{-19}$	$5 \times 10^{-12}$	$9 \times 10^{-9}$	471	$2 \times 10^{03}$	$3 \times 10^{-12}$
460	$1 \times 10^{-17}$	$3 \times 10^{-11}$	$4 \times 10^{-8}$	978	$6 \times 10^{-3}$	$1 \times 10^{-11}$
480	$2 \times 10^{-16}$	$2 \times 10^{-10}$	$1 \times 10^{-7}$	1953	$2 \times 10^{-2}$	$3 \times 10^{-11}$

S<sub>2</sub> vapor pressures over phases in the Cu-S and In-S systems

x-ray diffraction data, the alloy consisted of roughly equal amounts of two phases,  $In_6S_7$  and  $In_3S_4$ . The charge consisted of a Cu–S alloy: Cu<sub>2</sub>S, Cu<sub>1.76</sub>S, or CuS. Accordingly, three series of experiments were planned, with each type of charge.

Experiments were conducted in steps, for 50, 100, and 200 h at 410°C. The temperature was chosen so as, on the one hand, to achieve favorable kinetics of selective transport and, on the other, to maintain a sufficient phase diversity in the Cu–S system. In particular, under

our experimental conditions, the composition  $Cu_2S$  corresponded to a mixture of chalcosine and a small amount of copper ( $Cu_{2-x}S + Cu$ ),  $Cu_{1.76}S$  corresponded to anilite with a stoichiometry close to its sulfur-rich phase boundary, and CuS corresponded to covellite (sulfur removal during vapor transport might lead to the formation of a mixture with anilite,  $Cu_{1.76}S + CuS$ ). The vapor pressure in the system was evaluated from the ideal gas law, for room temperature and atmospheric pressure in the initial state and for a constant number of



**Fig. 9.** Diagram illustrating the relationship between the compositions of In–S samples and Cu–S charges, as inferred from experimental data for the system sample (In–S)–vapor ( $H_2 + H_2S$ )–charge (Cu–S) (isobaric–isothermal section); the dashed line represents the sample and charge compositions in the equilibrium (with respect to S) state at 680 K.

moles of vapor species in reaction (6) ( $\sim 0.25$  MPa at  $410^{\circ}$ C).

After each experiment, the ampule was broken, and the containers were weighed (VLM-200 balance,  $5 \times 10^{-5}$  g accuracy). The weighing results were compared with those obtained before annealing to assess the annealing-induced weight and composition changes. After weighing, the containers were again placed in an ampule, and the hydrogen annealing cycle was repeated. The results are presented in Fig. 9.

In combination with x-ray diffraction data, these results lead us to the following conclusions:

1. Long-term (above 100 h) annealing transfers the system into a state which seems to be close to partial equilibrium (compositional changes decrease with increasing annealing time and become insignificant after 200 h of annealing).

2. The mass transport direction depends on the nature of the charge. In particular, the use of the CuS and Cu<sub>1.76</sub>S alloys causes the indium sulfide sample to transform into In<sub>2</sub>S<sub>3</sub> of variable stoichiometry: after annealing with the CuS alloy, the In<sub>2</sub>S<sub>3</sub> sample contains more sulfur (61.0 mol % S) than it does after annealing with the Cu<sub>1.76</sub>S alloy (60.1 mol % S in In<sub>2</sub>S<sub>3</sub>). Note that in each of those experiments, the sample changed color to bright red, characteristic of  $\beta$ -In<sub>2</sub>S<sub>3</sub>.

3. In the presence of a charge with an initial sulfur content of 30 mol % (a mixture of Cu and Cu<sub>2</sub>S), sulfur is transported toward the charge, but the compositional changes are not very large: the selective transport, most likely, ceases as the copper-based phase in the charge disappears, and the composition of anilite varies within its homogeneity range. (In<sub>3</sub>S<sub>4</sub> + In<sub>6</sub>S<sub>7</sub> mixtures can then be used as charges for controlling the composition of the Cu<sub>2-x</sub>S phase.)

The high selectivity of SCVT in this implementation was confirmed by roentgenoluminescence measurements (VRA-30 spectrometer): in the annealing products, the indium sulfides contained no copper, and the Cu–S alloys contained no indium.

The above results lead us to the following conclusion: for nondestructive control over the composition of solids via SCVT in the case of binding the component being transported in distinct condensed compounds, the most promising approach is to fix particular nonstoichiometric compositions. This can be achieved by selecting two-phase mixtures such that the appropriate chemical potential of the sample is equal to that of the charge. For example, near 400°C a mixture of  $Cu_{1.76-\delta}S$  and CuS can be used to enrich the  $\beta$ -In<sub>2</sub>S<sub>3</sub> phase with sulfur (to ~61 mol % S).

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