Abstract

The paper presents the phase diagram of the Sn–As–Ge system. The diagram of polythermal Sn–GeAs section was constructed using the results of X-ray powder diffraction analysis and differential thermal analysis. We found that in a concentration interval with arsenic content of less than 50 mol%, four-phase peritectic equilibria $L + SnAs \leftrightarrow GeAs + Sn_4As_3$ (834 K) and $L + GeAs \leftrightarrow Ge + Sn_4As_3$ (821 K) are present. When the temperature is close to the melting point of pure tin, non-variant equilibrium with tin, germanium and $Sn_4As_3$ is implemented as well. The study of $Sn_0.39As_0.61–Ge_0.28As_0.72$, $SnAs–Ge_0.4As_0.6$ and $SnAs–GeAs_2$ sections and elaboration of the type of the $SnAs–GeAs$ phase diagram demonstrated that polythermal sections $SnAs–GeAs$ and $SnAs–GeAs_2$ can perform phase subsolidus demarcation of the phase diagram of the Sn–As–Ge system. There are also invariant peritectic equilibria $L + GeAs_2 \leftrightarrow GeAs + SnAs$ (840 K) and $L + As \leftrightarrow SnAs + GeAs_2$ (843 K) in the system.

Keywords: Phase diagram; germanium arsenide; tin arsenide; ternary system

1. Introduction

A large number of experimental and theoretical studies of the properties of graphene have provoked considerable scientific interest in layered structures, and compounds of the AIVB$V$ class in particular. AIVB$V$ compounds are of great practical value for two reasons: their anisotropic electrophysical characteristics resulting from low-symmetry structure; and their layered crystal structure which allows for the intercalation of ions and molecules into the interlayer space.$^{1-5}$ The presence of volatiles makes it rather difficult to synthesise such compounds, which is why attempts were made to obtain GeP samples in the presence of tin.$^5$ In that study, Sn-doped materials with peculiar semiconductor properties were obtained. However, the lack of information about the phase equilibria of AIV–B$V$–Sn ternary systems makes further research in this area rather problematic. Therefore, since the synthesis of multicomponent alloys is based on information about phase equilibria, the study of the phase diagram of the Sn–As–Ge system is of great importance.

This paper presents the results of an experimental study of Sn–GeAs, $Sn_{0.39}As_{0.61}–Ge_{0.28}As_{0.72}$, $SnAs–Ge_0.4As_0.6$, $SnAs–GeAs$ and $SnAs–GeAs_2$ polythermal sections, which was performed using differential thermal analysis and X-ray phase analysis methods. $T$–$x$ diagrams of the sections were constructed, and the nature of phase equilibria in the ternary Sn–As–Ge system was analysed.

2. Experimental

2.1. Materials and Synthesis

The number of ternary alloys with compositions corresponding to Sn–GeAs, $Sn_{0.39}As_{0.61}–Ge_{0.28}As_{0.72}$, $SnAs–Ge_0.4As_0.6$, $SnAs–GeAs$ and $SnAs–GeAs_2$ polythermal sections were prepared from the preliminary obtained binary compounds using high purity tin Sn–5N (99.999%), arsenic As–5N (99.9997%) and polycrystalline zone purified germanium Ge–5N–6N (99.9999%). Weighing was performed on an AR2140 balance with an accuracy of ± 0.001 g. The preparation of samples was carried out using the one-temperature method in thick-walled quartz ampoules vacuumised up to the residual pressure of 0.05 Pa. During the synthesis of the samples, the temperature was measured using a chromel–alumel thermocouple with a TK–
5.11 contact thermometer. The alloys were subjected to homogenizing annealing for 150 hours at 800–815 K.

2. 2. Research Methods

The study of the samples obtained was carried out on the differential thermal analysis (DTA) setup with a programmable heating of the furnace using OWEN TRM–151 and TRM–202 proportional-integral-differential controllers. The signal received from chromel-alumel thermocouples was digitized and processed by the MasterSCADA software package. In our experiments, the heating rate of DTA-setup was 5 K min–1.

Thermoanalytical studies were carried out using Stepanov’s quartz vessels. The experimental substance was ground and placed in the vessels so as to fill the maximum volume, after which the vessels were vacuumised up to the residual pressure of 0.05 Pa. Anhydrous analytically pure aluminium oxide was used as the reference substance. Chromel-alumel thermocouples, used as temperature sensors, were calibrated according to the phase transitions temperatures of pure metals, often used as standards. Furthermore, Sn, As and Ge were used. Their physical and chemical properties are similar to the properties of the objects we were studying. The precision of determining the temperature of phase transition by the DTA-setup was within the limit of ± 2 K.

X-ray powder diffraction (XRD) analysis of alloy samples of the sections Sn–GeAs, SnAs–Ge0.0As0.6, SnAs–GeAs were performed using a powder diffractometer AR-LX'TRA with the following characteristics: CuKα-radiation, exposure step 0.06⁰, exposure time 3.0 seconds. The samples of the sections Sn0.39As0.61–Ge0.28As0.72 и SnAs–GeAs were performed using a powder diffractometer DRON 4–07 (CoKα-radiation, exposure step 0.1⁰, exposure time 3.0 seconds). The intermediate phases in the Ge–Sn–As system have the following crystal structure: SnAs – Cubic, space group Fm3m; Sn4As3 – Rhombohedral, space group R3m; GeAs – Tetragonal, space group 14mm; GeAs2 – Orthorhombic, space group Pbam. The recorded X-ray powder diffraction patterns were interpreted using the Powder Diffraction File cards of International Centre for Diffraction Data (ICDD PDF-2 2007).

3. Results and Discussion

In our previous experimental study of polythermal sections Sn4As3–GeAs and SnAs–GeAs3 it was showed that a peritectic equilibrium L + SnAs ↔ Sn4As3 + GeAs was achieved in the Ge–As–Sn system at the temperature of 834 K. This conclusion we confirmed by the study of the alloys of the polythermal cross section of Ge–SnAs,8 this corresponds to the four-phase process L + GeAs ↔ Ge + Sn4As3. The second effect at 939 K was noted for the samples in the range of 82-94 mol.% GeAs compositions. The high-temperature effect corresponding to the liquidus on the heating curves was not very distinct, but was well reproduced on the cooling curves. For samples with a monoarsenide germanium content of less than 60 mol.%, the effect at 821 K was absent, for all the alloys analysis showed that when the content of germanium arsenide is more than 60 mol. % three endothermic effects were fixed, and the low-temperature effect was observed at the same temperature of 821 K. According to our data obtained from the study of the polythermal cross section of Ge–SnAs,8 this corresponds to the four-phase process L + GeAs ↔ Ge + Sn4As3. The second effect at 939 K was noted for the samples in the range of 82-94 mol.% GeAs compositions. The high-temperature effect corresponding to the liquidus on the heating curves was not very distinct, but was well reproduced on the cooling curves. For samples with a monoarsenide germanium content of less than 60 mol.%, the effect at 821 K was absent, for all the alloys

Figure 1. XRD patterns of the alloys of the polythermal section Sn–GeAs: a – 0.33; b – 0.82 mol. f. GeAs. The symbols denote: • – Sn4As3; □ – Ge; ■ – Sn; ● – GeAs.

In this paper, the alloys belonging to the Sn–GeAs section were studied. An X-ray diffraction analysis showed that for all the samples in the solid state, the presence of three phases is detected: irrespective of the composition, the lines of germanium and tin arsenide Sn4As3 are fixed. Depending on the third phase contained in the alloys, the samples can be divided into two groups. When the content of germanium arsenide is up to 60 mol.%, the alloys are a heterophase mixture of tin and germanium, as well as Sn4As3 (e.g., the X-ray diffraction pattern in Fig. 1a). For the alloys with germanium arsenide content of 67-94 mol.%, there are no reflexes characteristic of tin; on the contrary, lines indicating the presence of germanium monoarsenide in the solid phase appear, and the intensity of these lines increases with the enrichment of the alloys with this component (Fig. 1b).

The investigation of the alloys by differential thermal
of a given concentration interval, an endothermic effect is realized at 505 K.

Fig. 2 shows phase equilibria in the Sn–As–Ge system within the concentration interval of less than 50 mol.% As. This allows for correct interpretation of the experimental results of studying the T-x diagram of the Sn–GeAs system.

The presence of a horizontal section on the T-x cut chart (the first effect on heating curves) corresponds to an invariant four-phase equilibrium in the ternary system. According to an X-ray diffraction analysis in the composition range of less than 60 mol.% GeAs, there are three solid phases: tin, germanium and Sn₄As₃. Thus, we can assume the existence of a four-phase equilibrium \( L \leftrightarrow \text{Sn₄As₃} + \text{Ge} + \text{Sn} \) in the system, which is realized at a temperature of 505 K. Tin is absent in the region of compositions rich in GeAs, but three solid phases are still recorded: Ge, Sn₄As₃ and GeAs.

The alloys the compositions of which correspond to the concentration region \( ab \) (Fig. 2) of the polythermal section lie in the region of primary crystallization of the germanium monoarsenide \( L \leftrightarrow \text{GeAs} \). Secondary crystallization is connected with the three-phase equilibrium line \( e₁E₁ \), along which the process \( L \leftrightarrow \text{GeAs} + \text{Ge} \) is carried out. The crystallization ends at \( U₁ \) point: \( L + \text{GeAs} \leftrightarrow \text{Ge} + \text{Sn₄As₃} \). The segment \( cd \) intersects the field of primary crystallization of germanium. After the primary crystallization, the figurative point of the liquid falls on the curve \( U₁E₁ \). The process ends with eutectic crystallization at the point \( E₁ \) (the temperature of this four-phase transformation noted by the DTA method is 505 K). The sequence of processes will be as follows: \( L \leftrightarrow \text{Ge} \); \( L \leftrightarrow \text{Ge} + \text{Sn₄As₃} \); \( L \leftrightarrow \text{Ge} + \text{Sn₄As₃} + \text{Sn} \). The segment \( cd \) also crosses the field of primary crystallization of tin. However, taking into account the degenerate nature of the eutectic processes \( e₁E₁ \) and \( e₂E₁ \), it should be assumed that the four-phase and preceding three-phase processes will occur in a narrow concentration interval (\( E₁ \) is degenerated) and it is not possible to investigate them. The presented reasoning makes it possible to interpret the data of differential thermal analysis and construct the T-x diagram of the polythermal section of Sn–GeAs (Fig. 3).

While studying the SnAs–GeAs polythermal section it was suggested that this section is quasibinary and can be presented as a eutectic phase diagram with coordinates of the eutectic point 840 K and 20 mol% GeAs. The results of the experimental study of the polythermal section SnAs–Ge₃₀₄₄As₆₀₆ allowed us to elaborate the T-x diagram of SnAs–GeAs. The polythermal section SnAs–Ge₃₀₄₄As₆₀₆ starts from the figurative point of tin monoarsenide and from the double eutectic point (GeAs₂+GeAs) in the

![Figure 2](image-url)

**Figure 2.** Crystallization processes of the alloys of the polythermal section Sn–GeAs.

![Figure 3](image-url)

**Figure 3.** T-x diagram of the polythermal section Sn–GeAs.

![Figure 4](image-url)

**Figure 4.** XRD patterns of the alloys of the polythermal section SnAs–Ge₃₀₄₄As₆₀₆: a – 0.15; b – 0.75 mol.f. SnAs. The symbols denote: ● – SnAs; ■ – GeAs₂; ▲ – GeAs.
Ge–As system. The alloys of the polythermal section SnAs–Ge0.4As0.6 are the mixtures of GeAs, GeAs2, and SnAs. XRD patterns of some of the alloys are given as an example in Fig. 4 a, b.

The results of the differential thermal analysis showed that the first endothermic effect for all the samples of the SnAs–Ge0.4As0.6 section was observed at the temperature of 840 K. In Fig. 5 as an example, thermograms of alloys of two sections are presented: SnAs–GeAs and SnAs–Ge0.4As0.6. For the alloys of the section SnAs–GeAs (Fig. 5a), two endothermic effects are observed, and for the cut SnAs–Ge0.4As0.6, there are three effects, which can be clearly seen on the cooling curves. The beginning of the first endothermic effect is the same for both samples - 840 K. For greater clarity, on Fig. 6 the thermograms in the coordinates ΔT-T are compared.

If there is an eutectic equilibrium with three solid phases SnAs + GeAs + GeAs2, a lower temperature corresponding to the melting of the triple eutectic should be expected. The results obtained can be explained, if we assume that the ternary Sn–As–Ge system includes a peritectic four-phase equilibrium L + GeAs2 ↔ GeAs + SnAs. Taking this into account, a T-x diagram of the polythermal section SnAs–Ge0.4As0.6 was constructed, and the form of the polythermal section SnAs–GeAs was specified (Fig. 7 a, b).

![Figure 5](image)

Figure 5. Thermograms for (SnAs)0.4(GeAs)0.6 (a) and (SnAs)0.15(Ge0.4As0.6)0.85 (b) alloys

![Figure 6](image)

Figure 6. The DTA results in ΔT – T coordinates for (SnAs)0.4(GeAs)0.6 (a) and (SnAs)0.15(Ge0.4As0.6)0.85 (b) alloys

![Figure 7](image)

Figure 7. T-x diagrams of polythermal sections SnAs–Ge0.4As0.6 (a) and SnAs–GeAs (b).
In order to establish the nature of phase equilibria in the Sn–As–Ge system within the concentration interval of more than 50 mol% of arsenic, an experimental study of the polythermal sections Sn$_{0.39}$As$_{0.61}$–Ge$_{0.28}$As$_{0.72}$ and SnAs–GeAs$_2$ was carried out. The X-ray diffraction analysis of the alloys belonging to the polythermal section SnAs–GeAs$_2$ allowed us to detect a heterophasic mixture of two phases – tin monoarsenide and germanium diarsenide (Fig. 8 a, b).

Using differential thermal analysis allowed us to detect the endothermic effect in the samples of all concentration range at the same temperature of 843 K. The polythermal section Sn$_{0.39}$As$_{0.61}$–Ge$_{0.28}$As$_{0.72}$ goes through the

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**Figure 8.** XRD patterns of the alloys of the polythermal section SnAs–GeAs$_2$: a – 0.25; b – 0.85 mol.f. GeAs$_2$. The symbols denote: ● – SnAs; □ – GeAs$_2$.

**Figure 9.** XRD patterns of the alloys of the polythermal section Sn$_{0.39}$As$_{0.61}$–Ge$_{0.28}$As$_{0.72}$: a – 0.10; b – 0.90 mol.f. Ge$_{0.28}$As$_{0.72}$. The symbols denote: ● – SnAs; □ – GeAs$_2$; △ – As.
double eutectic point (GeAs₂ + As) in the binary system Ge–As and through the eutectic point (SnAs + As) in the Sn–As system. The alloys whose compositions belong to the polythermal section Sn₀.３₉As₀.₆₁–Ge₀.₂₈As₀.₇₂ represent a heterophase mixture of arsenic, germanium diarsenide and tin monoarsenide (Fig. 9 a, b).

Phase diagram of the Sn₀.３₉As₀.₆₁–Ge₀.₂₈As₀.₇₂ section is shown in Fig. 10a. Differential thermal analysis demonstrated that in all the samples the first endothermic effect was observed at the same temperature of 843 K (Fig. 11, 12). Implementation of the same temperature at the section SnAs–GeAs₂ (Fig. 10b) allows us to conclude that there exists a peritectic invariant equilibrium L + As ↔ SnAs + GeAs₂.

Thus, there are four equilibria of peritectic character in the ternary system of Sn–As–Ge:
1. L + As ↔ SnAs + GeAs₂
2. L + GeAs₂ ↔ GeAs + SnAs
3. L + SnAs ↔ Sn₄As₃ + GeAs
4. L + GeAs ↔ Ge + Sn₄As₃

Given that the eutectic points on the tin side are degenerate in the Ge–Sn and Sn–As systems, we can expect that the coordinate of the four-phase equilibrium point E₁ will be implemented in the tin-rich area of the alloys. Eutectic crystallization of three solid phases L ↔ Ge + Sn + Sn₄As₃ takes place at the E₁ point (Fig. 13).

The analysis of the nature of phase equilibria in the ternary Sn–As–Ge system, as well as the experimental study of polythermal sections Sn–GeAs, Sn₄As₃–GeAs, Sn₀.₃₉As₀.₆₁–Ge₀.₂₈As₀.₇₂, SnAs–Ge₀.₄As₀.₆, SnAs–GeAs and SnAs–GeAs₂ using the methods of differential thermal and X-ray diffraction analysis, allowed us to construct a T-x-y diagram of the Sn–As–Ge system (Fig. 13).

It seemed impractical to use a 3D chart, whereas Sheila's scheme turned out to be quite informative and, most importantly, convenient for the analysis of the phase states and the processes of melting and crystallization, as well as for calculations and cross-sections building (Fig. 14).

The main objective was to reduce the three-dimensional diagram of the triple system to a one-dimensional scheme, which would give a clear idea of the phase equilibria in the system. We performed this reduction by taking into account nonvariant and monovariant transformations only, leaving out the concentration of phases and using only the temperature axis. The scheme shown in Fig. 14 illustrates phase equilibria and successive (with decreasing temperature) crystallization processes in the ternary Sn–As–Ge system.

4. Conclusions

The polythermal sections of the phase diagram of the Sn–As–Ge ternary system were studied by differential thermal and X-ray analysis methods, which made it possible to represent the nature of phase equilibrium L + GeAs ↔ Ge + Sn₄As₃ (T = 821 K) in the system established ear-
Figure 13. Sn–As–Ge phase diagram.

Figure 14. Flow diagram of the Sn–As–Ge system.
lier during the study of the Ge–SnAs and Sn₄As₃–GeAs sections. It is also shown that, at a temperature close to the melting point of tin, an invariant equilibrium is realized involving a melt and three solid phases: tin, germanium monoarsenide and Sn₄As₃. This fact is not surprising, since in the binary systems Ge–Sn and Sn–As the eutectic points are degenerate. Investigation of alloys in the concentration region with an arsenic content of more than 50 mol. % allowed to establish the presence of two more invariant processes. For samples whose compositions correspond to the concentration triangle formed by the figurative points GeAs, GeAs₂ and SnAs, the temperature of the first endoeffect equal to 840 K was recorded by differential thermal analysis. This value coincides with the temperature of the first effect for alloys of the GeAs–SnAs cross section. This can be explained by the existence at a given temperature of the peritectic invariant equilibrium L + GeAs₂ ↔ GeAs + SnAs, since the triple eutectic with these phases should have a lower temperature than for the GeAs–SnAs section. Investigation of the SnAs–GeAs₂ cross section and comparison of the results obtained with DTA data for samples with a high arsenic content made it possible to conclude that the equilibrium L + As ↔ SnAs + GeAs₂ takes place at 843 K. Thus, in the Sn–As–Ge ternary system there are five invariant equilibria, which are presented in the paper as a flow diagram.

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6. References

1. C. Barreteau, B. Michon, C. Besnard, E. Giannini, J. Cryst. Growth. 2016, 443, 75–80. DOI:10.1016/j.jcrysgro.2016.03.019
2. F. Shojaei, HS Kang, J. Phys. Chem. C. 2016, 120, 23842–23850. DOI:10.1021/acs.jpcc.6b07903
3. K. Lee, S. Kamali, T. Ericsson, M. Bellard, K. Kovnir, Chem. Mater. 2016, 28(8), 2776–2785. DOI:10.1021/acs.chemmater.6b00567
4. M. Khatun, A. Mar, Z. Naturforsch. 2016, 71(5), 375–380. DOI:10.1515/znb-2015-0203
5. K. Lee, S. Synnestvedt, M. Bellard, K. Kovnir, J. Solid State Chem. 2015, 224, 62-70. DOI:10.1016/j.jssc.2014.04.021
6. G. Klancnik, J. Medved, A. Nagode, G. Novak, D. Stein et Petrovic, J. Therm. Anal. Calorim. 2014, 116, 295–302. DOI:10.1007/s10973-013-3536-y
7. E. Kononova, S. Sinyova, G. Semenova, T. Sushkova, J. Therm. Anal. Calorim. 2014, 117(3), 1171–1177. DOI:10.1007/s10973-014-3883-3
8. G. V. Semenova, E. Yu. Kononova, T.P. Sushkova, Russian J. Inorg. Chem. 2014, 59(12), 1517–1521. DOI:10.1134/S0036023614120225

Povzetek

V prispevku predstavljamo fazni diagram sistema Sn–As–Ge. Diagram v sistemu Sn–GeAs smo izdelali z uporabo rezultatov rentgenske praskovne difrakcijske analize in diferencialne termične analize. Ugotovili smo, da so v koncentracijskem intervalu z vsebnostjo arzena manj kot 50 mol% prisotne štiri fazne v peritektičnem ravnotežju L + SnAs ↔ GeAs + Sn₄As₃ (834 K) in L + GeAs ↔ Ge + Sn₄As₃ (821 K). Ko je temperatura blizu tališča čistega kositra, pride do invariantnega ravnotežja s kositrom, germanijem in Sn₄As₃. Podrobneje smo raziskali tudi sekcije Sn₀.₃⁹As₀.₆₁–Ge₀.₂₈As₀.₇₂, Sn₄As₃–GeAs₂ in Sn₄As₃–GeAs₂ in preučevali fazna diagrama SnAs–GeAs in SnAs–GeAs₂ v sistemu Sn–As–Ge. V sistemu smo tudi opazili invariantna peritektična ravnotežja L + GeAs₂ ↔ GeAs + SnAs (840 K) in L + As ↔ SnAs + GeAs₂ (843 K).