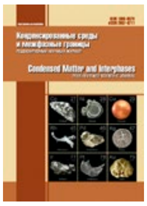
Condensed Matter and Interphases. 2024;26(4): 745–754



ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2024.26/12450

Phase subsolidus separation of the Ge–P–Sn ternary system

G. V. Semenova✉, T. P. Sushkova, A. N. Golentsova

Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

2D materials are becoming increasingly attractive for use in modern electronic devices due to new properties that can arise from reduced dimensionality and the quantum confinement of charge carriers. Many studies are aimed at the search for materials characterized by a layered structure, which allows obtaining chemically stable atomic layers without surface broken bonds. Binary compounds of elements of IV (Si, Ge, Sn) and V (P, As) groups form layered structures in which two-dimensional layers with covalent bonds are bound by weak van der Waals forces, and from this point of view they can be considered as being promising 2D materials. However, it should be noted, that obtaining crystals of compounds of this class is associated with significant difficulties due to the high vapor pressure of phosphorus. Attempts have been made to obtain the GeP samples from tin melt solutions, which can significantly soften the synthesis conditions. The study of phase equilibria and the construction of a phase diagram of the Ge–P–Sn ternary system would allow approaching the production of both bulk and two-dimensional samples of germanium phosphide, as well as determining the possibility of alloying them with tin.

In this study, based on the investigation of several alloys of the Ge–P–Sn ternary system using the X-ray phase analysis, it was established that the phase subsolidus separation of the state diagram is carried out by the Sn_4P_3–Ge, Sn_4P_3–GeP, Sn_3P_4–GeP and SnP_3–GeP sections. The composition of the alloys corresponded to the figurative points of the intersecting sections. A scheme of phase equilibria in the Ge–P–Sn system was proposed. This scheme assumes the existence of a nonvariant peritectic equilibrium L+Ge ↔ Sn_4P_3+GeP and eutectic processes L ↔ Ge+Sn+Sn_4P_3 and L ↔ Sn_4P_3+GeP+SnP_3.

The study of alloys using the differential thermal analysis method allowed determining the temperatures of these processes, equal to 795 K, 504 K, and 790 K, respectively. The *T-x* diagram of the Sn–GeP polythermal cross section, which experimentally confirms the proposed scheme, was constructed.

Keywords: Phase diagrams, Germanium phosphide, Tin phosphides, Ge–P–Sn system, Subsolidus phase separation

Acknowledgements: X-ray powder diffraction studies were performed using the equipment of the VSU Centre for Collective Use of Scientific Equipment.

For citation: Semenova G. V., Sushkova T. P., Golentsova A. N. Phase subsolidus separation of the Ge–P–Sn ternary system. *Condensed Matter and Interphases*. 2024;26(4): 745–754. https://doi.org/10.17308/kcmf.2024.26/12450

Для цитирования: Семенова Г. В., Сушкова Т. П., Голенцова А. Н. Фазовое субсолидусное разграничение системы Ge–P–Sn. *Конденсированные среды и межфазные границы*. 2024;26(4): 745–754. https://doi.org/10.17308/kcmf.2024.26/12450

✉ Galina V. Semenova, e-mail: semen157@chem.vsu.ru

1. Introduction

The $A^{IV}B^{V}$ compounds have been known for a long time and have been quite well studied [1, 2]. However, their wide application was extremely limited due to the complex conditions of their synthesis. Recently, interest in these compounds has significantly increased due to the possibility of obtaining 2D materials based on them. Along with research into graphene, black phosphorus, and arsenic subgroup elements [3–9], an active search for binary compounds that can be used as 2D materials is being carried out. $A^{IV}B^{V}$ compounds are characterized by a layered structure with unequal bonds, which allow to obtain these phases in the form of atomically thin layers [10–14]. GeP samples in the form of two-dimensional layers were obtained in [10], however, the harsh synthesis conditions significantly limit widespread use of this material, therefore attempts to obtain this phase from a melt solution in tin are being made. The authors [10] believed that the addition of a low-melting component such as tin, should soften the conditions for the production of germanium phosphide, lowering the synthesis temperature and the vapor pressure of phosphorus in the system. However, in addition to germanium phosphide, the presence of tin phosphide was detected in the samples. In order to predict the composition of the obtained samples, it is necessary to know the nature of the phase diagram of the ternary Ge-P-Sn system. The process, as well as the optimal conditions for obtaining materials with the required composition and the characteristics can be selected based on the nature of phase equilibria.

At the same time, information about the phase diagram in the literature is very limited. The following circumstances make the analysis of the Ge–P–Sn ternary system quite difficult. If the Ge–Sn binary system is characterized by a eutectic type of phase diagram [15], then in the other two Ge–P and Sn–P binary systems there are intermediate phases. The Ge–P system has been studied quite well; germanium monophosphide GeP is the only compound and melts by a peritectic reaction at a temperature of 998 K and a pressure of about 4.6 MPa [16]. The nature of the equilibria in the Sn–P binary system has not yet been definitively established, especially in the region of high phosphorus content. The system contains three intermediate phases with a similar rhombohedral structure and space group $R\bar{3}m$: Sn_4P_3, Sn_3P_4 and SnP_3 [17]. There is also information about the existence of high-pressure phases, in particular, SnP with tetragonal and cubic structures [18]. The existence of tin monophosphide at normal pressures was first reported in [19], and $P321$, $P\bar{3}m1$, $R\bar{3}m1$ were indicated as the possible space groups. On the other hand, in a metallographic study of the Sn–P system for an equimolar composition Vivian [20] demonstrated a eutectic mixture of Sn_4P_3 and Sn_3P_4. The author [21] thinks that the contradictory results may be related to the metastability of the SnP phase.

The authors of this study previously [22] detected the SnP phase using X-ray phase analysis (XRD) and X-ray electron microscopy in alloys with equimolar composition, but after prolonged annealing the phase decomposed. A conclusion about the fairly high kinetic stability of SnP below 773 K was made, but the question of thermodynamic stability remained open. In [23], the phase composition of samples obtained for establishing equilibrium between tin and phosphorus at given values of temperature and phosphorus vapor pressure was determined. Moreover, the tin monophosphide phase was not recorded under any conditions, which may also indicate the metastability of this phase.

In [24,25], based on the study of samples of the Sn–P system using differential thermal analysis (DTA), X-ray phase analysis and local X-ray structural microanalysis, the existence of a eutectic equilibrium $L \leftrightarrow Sn_4P_3 + SnP_3$ at 824 K was established. The Sn_3P_4 intermediate phase was formed in the solid state according to the peritectoid scheme at a temperature of less than 673 K. The coordinates of the points of four-phase equilibrium were established by studying the temperature dependence of the saturated vapor pressure using the optical-tensimetric method: synthetic equilibrium ($Sn_4P_3 + V + L_1 + L_2$) was realized at 836 K and 0.6 atm; the eutectic equilibrium point ($L + V + Sn_4P_3 + SnP_3$) existed at 820 K and 2.8 atm. However, the SnP phase was not detected, which confirms the version about its metastability. Tin triphosphide, according to [20], decomposes into two liquids of different compositions, but the temperature of this synthetic equilibrium has not been established.

In [26], we studied the alloys of the Ge–Sn_4P_3 polythermal secttion of Ge–P–Sn ternary system using differential thermal and X-ray phase analysis methods. The samples were shown to be a heterogeneous mixture of two phases: germanium and tin phosphide with a Sn_4P_3 composition. Neither tin lines nor germanium phosphide reflexes were detected on X-ray diffraction patterns. Two endothermic effects, with the low-temperature effect occurring at the same temperature (800 K) were revealed on the thermograms of the samples. Thus, it was concluded that this section is partially quasi-binary (due to the synthetic transformation in the tin-phosphorus system, since the stratification of the liquid phase characteristic of a binary system can affect the nature of the liquidus surface of the ternary diagram in general, and, in particular, on the appearance of the considered section). However, in the study [26], when considering the division of the diagram into partial systems below the solidus, the appearance of the Sn_3P_4 by the peritectoid reaction was not taken into account, which requires additional experimental research.

The aim of this study was the identification of the nature of the phase subsolidus separation and the presentation of a possible scheme of phase equilibria in the Ge–P–Sn ternary system.

2. Experimental

The samples were obtained using a single-zone furnace SNOL 4/1100 ALSCO1220. The synthesis was carried out in quartz ampoules, which were pre-graphitized to prevent any possible interaction of the phosphorus with the walls of the ampoule. The OSCH-9-5 red phosphorus, OVCH-000 tin, and polycrystalline zone-purified germanium GOST 16154-80 were used to obtain the samples. The weighing was performed on AR2140 scales with an error of ± 1 10^{-3} g. The ampoules with the weighed portions of the starting substances were evacuated to a residual pressure of $5\cdot10^{-2}$ Pa and sealed.

The furnace heating mode was as follows: heating for 1 h to 693 K, then holding for two h at the specified temperature, and then heating for 7 h to 1233 K and holding for 1.5 h. The samples were then annealed for 150 h at a temperature below the expected solidus. The annealing temperature was selected based on the nature of equilibria in binary systems. For majority of the studied alloys it was 623 K.

The samples were studied using differential thermal analysis (DTA) in a programmable furnace heating system at a heating rate of 3.5 K/min, using calcined aluminum oxide as a standard. The samples and standards were kept in Stepanov quartz evacuated vessels. The signal from the chromel-alumel thermocouples was digitized and processed using the "MasterSCADA" computer program.

The X-ray diffraction was performed using an ARL X'TRA diffractometer with Bragg–Brentano Θ–Θ focusing geometry; the source of radiation was an X-ray tube with a copper anode: λ(Cu-Kα1) = 0.1541 nm; λ(Cu-Kα2) = 0.1544 nm; a step size of 0.04° and a counting time of 3 seconds. The diffraction patterns were interpreted using the ICDD PDF2 database.

3. Results and discussion

It should be noted that all binary compounds in the analyzed system do not melt congruently, as is assumed in the classical version of singular triangulation. Thus, germanium phosphide melts by a peritectic reaction [16], Sn_4P_3 and SnP_3 decompose into two liquids of different composition (synthetic equilibrium) [20], and Sn_3P_4 is formed in the solid state according to the peritectoid scheme [24, 25]. Therefore, only phase subsolidus separation is characteristic of the studied triple system [27].

Possible variants for separation in the Ge–P–Sn ternary system are shown in Fig. 1. The position of the secant cuts may vary, therefore experimental research is required for the determination of the correct separation pattern in the solid state.

To determine the subsolidus separation scheme of the phase diagram, alloys with compositions corresponding to the intersection points of the sections (Fig. 2) were prepared, and their phase analysis was carried out.

The $Ge_{0.30}P_{0.30}Sn_{0.40}$ (No. 1) sample corresponds to the intersection of Sn_4P_3–Ge and Sn–GeP sections. As shown in [26], it is a heterophase mixture of germanium and tin phosphide Sn_4P_3, which confirms the conclusions presented earlier. The Sn_4P_3–Ge section separates the secondary Sn_4P_3–Ge–Sn system, in which L↔Sn_4P_3+Ge+Sn

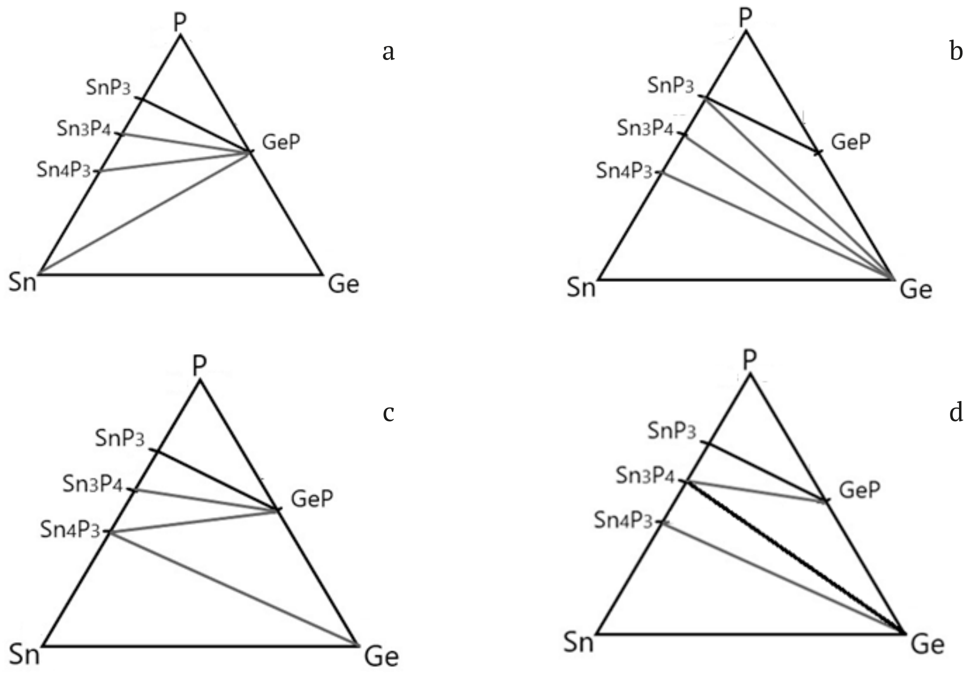


Fig. 1. Possible separation schemes in the Ge–P–Sn ternary system

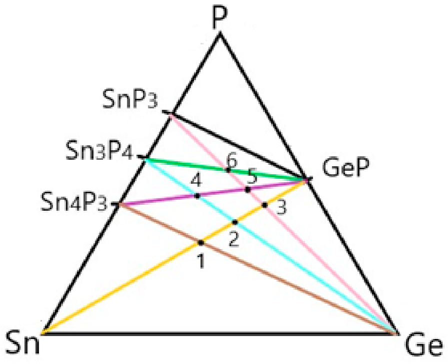


Fig. 2. Alloy compositions corresponding to the intersection of sections in the Ge–P–Sn system

equilibrium will be realized. This suggests that the diagram partitioning presented in Fig. 1a is incorrect. This conclusion was also confirmed by the results of X-ray phase analysis of $Ge_{0.36}Sn_{0.28}P_{0.36}$ (No. 2) and $Ge_{0.41}Sn_{0.15}P_{0.44}$ (No. 3) alloys, the diffraction patterns of which are shown in Fig. 3a, b. The alloys did not contain a tin-based phase, and the samples were a mixture of three phases: germanium, germanium phosphide, and Sn_4P_3. Since the figurative points of these alloys are the intersection points of the Sn_3P_4–Ge and SnP_3–Ge sections with the Sn–GeP section, it can be concluded that the indicated cuts will not be secant cuts as the presence of neither Sn_3P_4 nor SnP_3 were recorded in the samples.

From this point of view, out of the variants of the diagram division presented in Fig. 1, the correct variant is 1c. In this case, the compositions of the $Ge_{0.36}Sn_{0.28}P_{0.36}$ (No. 2) and $Ge_{0.41}Sn_{0.15}P_{0.44}$ (No. 3) samples belong to the triangle formed by the figurative points of the germanium, germanium phosphide and Sn_4P_3 phases, which also indicates that the Sn_4P_3–Ge and Sn_4P_3–GeP sections are secant sections below the solidus.

If the division of the state diagram of the considered system is performed by the Sn_4P_3–GeP section, then for $Ge_{0.17}Sn_{0.35}P_{0.48}$ (No. 4) and $Ge_{0.35}Sn_{0.16}P_{0.49}$ (No. 5) alloys we should observe the coexistence of two phases, germanium phosphide and Sn_4P_3. This is demonstrated by the diffraction pattern of the $Ge_{0.17}Sn_{0.35}P_{0.48}$ (No. 4) sample, shown in Fig. 3c. The diffraction pattern of the $Ge_{0.29}Sn_{0.18}P_{0.53}$ (No. 6) alloy, the figurative point of which represents the intersection of two sections: SnP_3–Ge and Sn_3P_4–GeP is shown in Fig. 3d. In the sample, GeP and Sn_3P_4 are the main phases.

Summarizing all the results obtained by the X-ray phase analysis, we can propose a scheme of phase subsolidus separation in the Ge–P–Sn system, performed by Sn_4P_3–Ge, Sn_4P_3–GeP, Sn_3P_4–GeP, and SnP_3–GeP sections.

Alloys of the Ge–P–Sn system were also studied using differential thermal analysis. Since the samples belong to different polythermal sections,

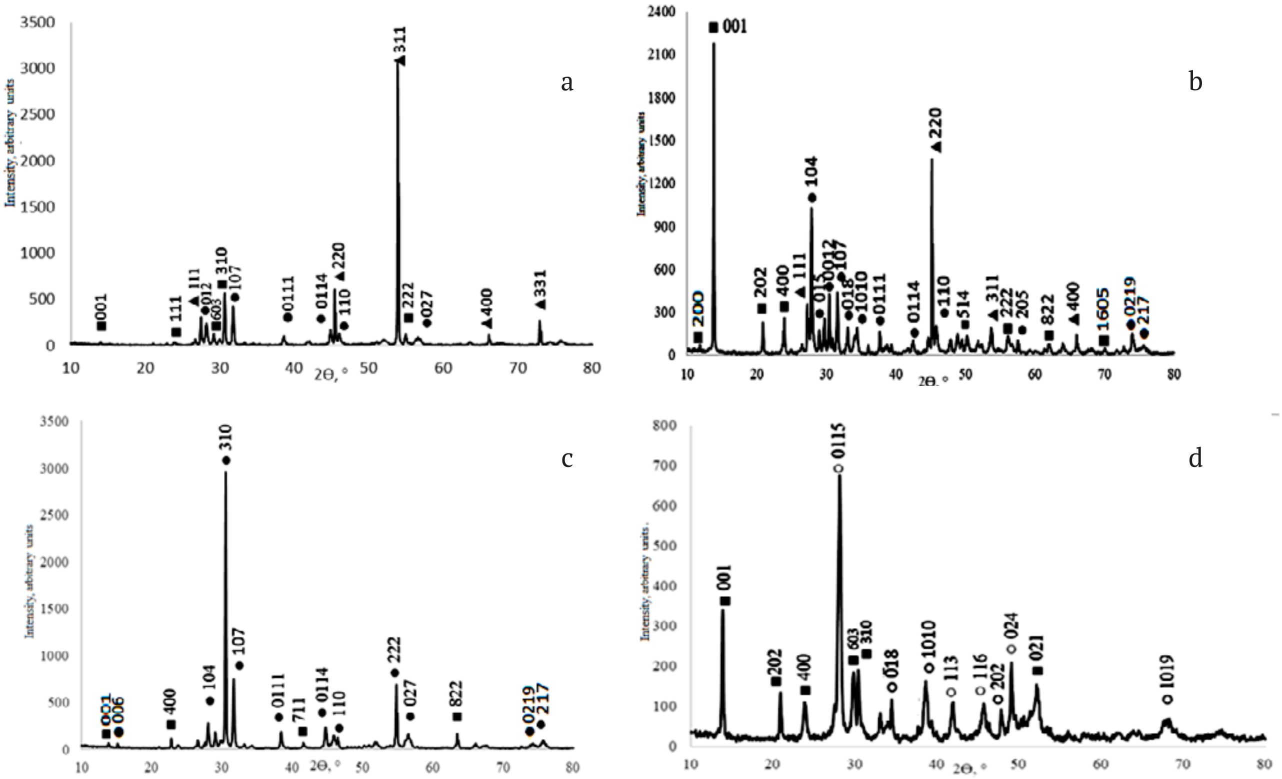


Fig. 3. Diffraction patterns of samples of the Ge–P–Sn system: a – $Ge_{0.36}P_{0.36}Sn_{0.28}$; b – $Ge_{0.41}P_{0.44}Sn_{0.15}$; V - $Ge_{0.17}P_{0.48}Sn_{0.35}$; g – $Ge_{0.29}P_{0.53}Sn_{0.18}$. ▲ – Ge; ● – Sn_4P_3; ■ – GeP; ○ – Sn_3P_4

information can only be obtained by comparing the lowest temperature effects on the heating curves. Such effects correspond to invariant equilibria involving a melt and three crystalline phases. At the same time, even lower temperature transformations in the solid state are possible (with the participation of Sn_3P_4), but they are usually rarely recorded by the DTA method. The temperatures of the onset of the first effects for the studied alloys are shown in Table, and thermograms of $Ge_{0.41}Sn_{0.15}P_{0.44}$ (No. 3) and $Ge_{0.29}Sn_{0.18}P_{0.53}$ (No. 6) samples are shown as the example in Fig. 4.

Alloys of the compositions $Ge_{0.36}Sn_{0.28}P_{0.36}$ (No. 2) and $Ge_{0.41}Sn_{0.15}P_{0.44}$ (No. 3) are characterized by the same temperature of the onset of the first effect (795±1 K). Because their figurative points belong to the Ge–GeP–Sn_4P_3 triangle, it can be stated that at this temperature a four-phase invariant process is carried out in the system with the participation of the melt and these three solid phases. Germanium phosphide is formed according to the peritectic scheme, then in the ternary system the L + Ge ↔ GeP monovariant process should occur, and the four-phase transformation should also be peritectic. Accordingly, the following diagram of phase equilibria in the germanium – phosphorus – tin system can be proposed (Fig. 5).

The pU_1 line corresponds to the L + Ge ↔ GeP monovariant process and along the e_6U_1 curve the L ↔ Ge + Sn_4P_3 process takes place, which is also monovariant. At the U_1 point, a four-phase L + Ge ↔ GeP + Sn_4P_3 transformation takes place.

The triangle formed by the figurative points of tin, germanium and tin phosphide Sn_4P_3, also has a four-phase transformation point (E_1), at a temperature probably very close to the melting point of tin:

Table. Temperatures of the onset of the first effect for alloys of the Ge–P–Sn system

	Alloy composition	*T*, K		Alloy composition	*T*, K
№ 1	$Ge_{0.30}P_{0.30}Sn_{0.40}$	800 ± 1	№ 4	$Ge_{0.17}P_{0.48}Sn_{0.35}$	794 ± 1
№ 2	$Ge_{0.36}P_{0.36}Sn_{0.28}$	795 ± 1	№ 5	$Ge_{0.35}P_{0.49}S_{n0.1}6$	795 ± 1
№ 3	$Ge_{0.41}P_{0.44}Sn_{0.15}$	796 ± 1	№ 6	$Ge_{0.29}P_{0.53}Sn_{0.18}$	789 ± 1

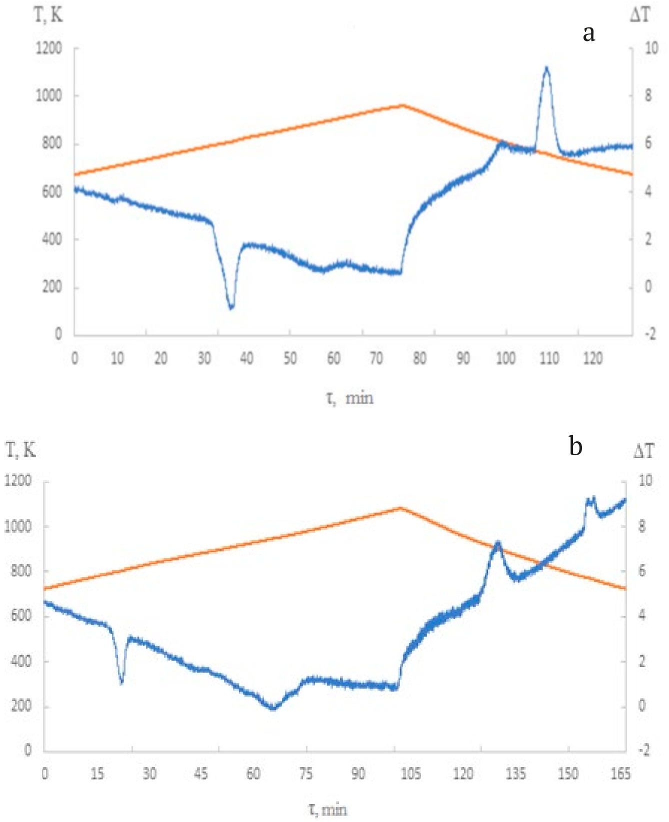


Fig. 4. Thermograms of alloys of the Ge–P–Sn system: a – $Ge_{0.41}P_{0.44}Sn_{0.15;}$ b – $Ge_{0.29}P_{0.53}Sn_{0.18}$

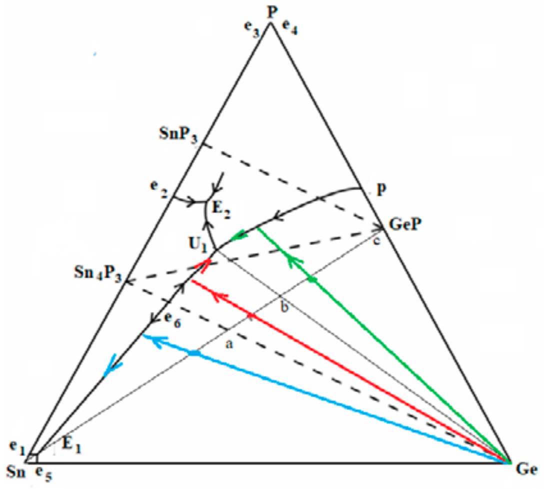


Fig. 5. Scheme of phase equilibria in the Ge–P–Sn system and crystallization processes of the alloy of the Sn–GeP cross section

e_1E_1	L ↔ Sn + Sn_4P_3
e_5E_1	L ↔ Sn + Ge
e_6E_1	L ↔ Ge + Sn_4P_3
E_1	L ↔ Ge +Sn + Sn_4P_3

It should be noted that the phase diagram of the Sn_4P_3–Ge section constructed in [21] based on differential thermal analysis data is a eutectic type diagram with coordinates of the eutectic point e_6 800 K, 15 mol. % Ge. Thus, in e_6 point, the L ↔ Ge + Sn_4P_3 process is non-variant, carried out at constant temperature and composition of the melt.

Since the thermogram of the $Ge_{0.29}Sn_{0.18}P_{0.53}$ (No. 6) sample, shown in Fig. 5c, demonstrates a lower temperature than the other alloys, it can be assumed that the crystallization of this alloy ends at the point of four-phase equilibrium, located inside the triangle formed by the figurative points of the solid phases: Sn_4P_3, SnP_3, and GeP. Accordingly, the following processes occur:

U_1E_2	L ↔ Sn_4P_3 + GeP
e_2E_2	L ↔ SnP_3 + Sn_4P_3
E_2	L ↔ Sn_4P_3 + SnP_3 +GeP

The processes occurring in areas with high phosphorus content and characterized by high saturated vapor pressure require additional research. Nevertheless, based on the data presented in this study, it can be concluded that in the Ge–P–Sn ternary system, the invariant peritectic equilibrium L + Ge ↔ Sn_4P_3 + GeP and the eutectic process L ↔ Sn_4P_3 + GeP + SnP_3 are realized.

This diagram does not contradict the *T-x* diagram of the Sn–GeP polythermal section (Fig. 6), constructed in this work. The investigation of this section was interesting from a practical point of view to explain the possibility of using tin as a solvent, which was proposed by the authors [10].

For alloys with a tin content of more than 40 mol. % , lines of germanium, tin, and tin phosphide of the Sn_4P_3 composition were recorded on the diffraction patterns. The X-ray diffraction data for the $Ge_{0.20}P_{0.20}Sn_{0.60}$ sample are shown as an example in Fig. 7a. In the thermograms of samples in this concentration range, the first endothermic effect is realized at a temperature close to the melt point of tin (Fig. 8a). This confirms the presence of a four-phase equilibrium L ↔ Ge + Sn + Sn_4P_3 (E_1 point), and since double eutectics in binary systems are degenerate, then the E_1 point of the triple eutectic also exists in the region of very high tin concentrations.

With a lower tin content in alloys, GeP lines appeared in alloys along with Ge and Sn_4P_3 reflexes, which can be seen in the spectrum

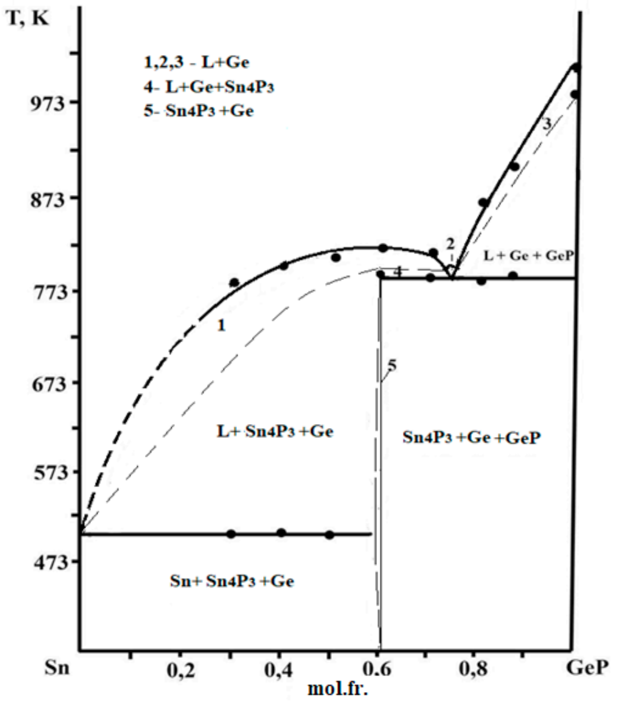


Fig. 6. The *T-x* diagram of the Sn–GeP polythermal cross section

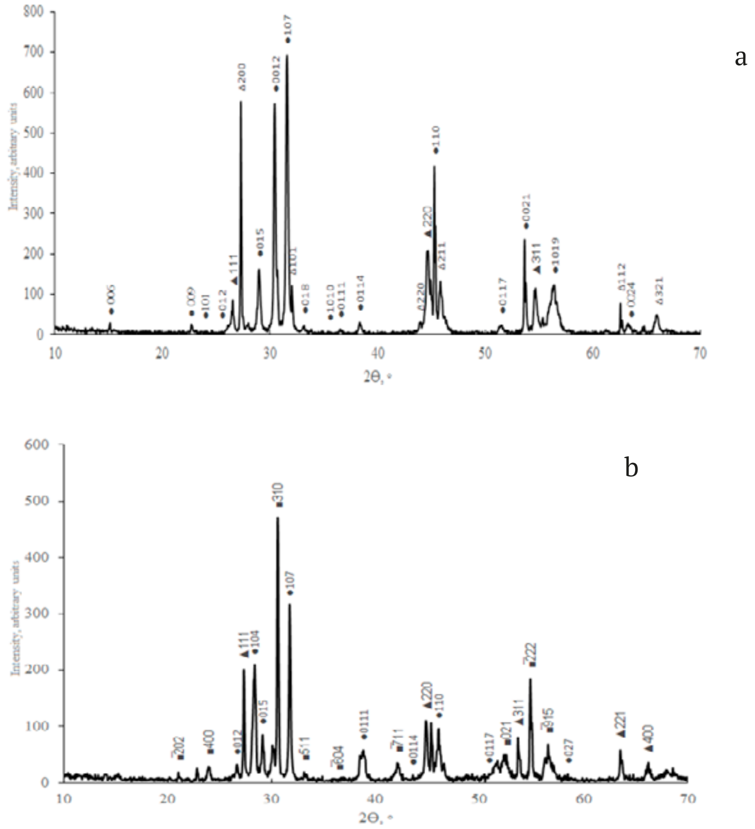


Fig. 7. Diffraction patterns of samples of the Sn–GeP polythermal cross section: a –$Ge_{0.2}P_{0.2}Sn_{0.6}$; b –$Ge_{0.35}P_{0.35}Sn_{0.3}$. ▲ – Ge; ● – Sn_4P_3; ■ – GeP; Δ – Sn

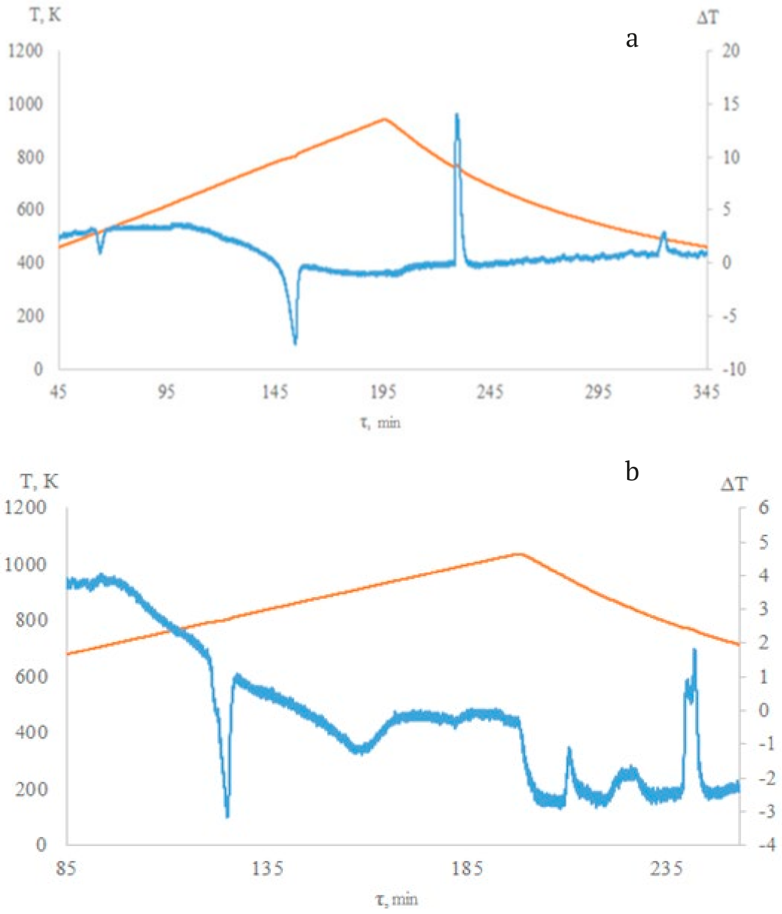


Fig. 8. Thermograms of alloys of the Ge–P–Sn system: a –$Ge_{0.20}P_{0.20}Sn_{0.60;}$ b –$Ge_{0.35}P_{0.35}Sn_{0.30}$

shown in Fig. 7b. The alloy, corresponding to the intersection of the studied section with the Sn_4P_3–Ge section, was a two-phase mixture of germanium and tin phosphide, which confirms the partially quasi-binary nature of the Sn_4P_3–Ge section. A study of alloys with a tin content of less than 40 mol. % by differential thermal analysis showed that the lowest endothermic effect in temperature was recorded at a temperature of 795 K. When cooling samples whose composition lies in the ab range, after the primary precipitation of germanium L ↔ Ge, the melting point falls on the curve of the monovariant equilibrium e6U1. For alloys with even lower tin content (*bc* segment) after the primary crystallization follows the L + Ge ↔ GeP secondary process (the pU_1 monovariant equilibrium line). However, after, in any case, for all alloys a four-phase process L + Ge ↔ GeP + Sn_4P_3, occurred, which corresponded to a temperature of 795 K. This is demonstrated by the thermogram of the $Ge_{0.35}P_{0.35}Sn_{0.30}$ alloy shown in Fig. 8b.

4. Conclusions

Based on the study of a number of alloys of the Ge–P–Sn ternary system using the X-ray phase analysis method, it was established that the phase subsolidus separation of the state diagram is performed by the Sn_4P_3–Ge, Sn_4P_3–GeP, Sn_3P_4–GeP and SnP_3–GeP sections. Taking into account the type of phase diagrams of binary systems and the established phase partition of the state diagram of a ternary system, a scheme of phase equilibria in the Ge–P–Sn system was proposed, which assumes the existence of a nonvariant peritectic equilibrium L + Ge ↔ Sn_4P_3 + GeP and the eutectic processes L ↔ Ge + Sn + Sn_4P_3 and L ↔ Sn_4P_3 + GeP + SnP_3. The study of alloys using the DTA method allowed determining the temperatures of these processes, equal to 795 K, 504 K, and 790 K, respectively. The *T*-x diagram of the Sn–GeP polythermal cross section, experimentally confirming the proposed scheme, was constructed.

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. Goncharov E. G. *Semiconductor phosphides and arsenides of silicon and germanium**. Voronezh: VSU Publ.; 1989. 208 p. (In Russ.)

2. Semenova G. V., Goncharov E. G. *Solid solutions with the participation of elements of the fifth group**. Moscow: MFTI Publ.; 2000. 160 p. (In Russ.). Available at: https://www.elibrary.ru/item.asp?id=25882424

3. Khan K., Tareen A. K., Khan Q. U., Iqbal M., Zhang H. and Guo Z. Novel synthesis, properties and applications of emerging group VA two-dimensional monoelemental materials (2D-Xenes). *Materials Chemistry Frontiers*. 2021;5: 6333-6391. https://doi.org/10.1039/D1QM00629K

4. Yu X., Liang W., Xing Ch., ... Zhang H. Emerging 2D pnictogens for catalytic applications: status and challenges. *Journal of Materials Chemistry A*. 2020;8: 12887–12927. https://doi.org/10.1039/D0TA04068A

5. Tao W., Kong N., Ji X., ... Kim J. S. Emerging two-dimensional monoelemental materials (Xenes) for biomedical applications. *Chemical Society Reviews*. 2019;48: 2891-2912. https://doi.org/10.1039/C8CS00823J

6. Carrasco J. A., Congost-Escoin P., Assebban M., Abellán G. Antimonene: a tuneable post-graphene material for advanced applications in optoelectronics, catalysis, energy and biomedicine. *Chemical Society Reviews*. 2023;52: 1288–1330. https://doi.org/10.1039/D2CS00570K

7. Pang J., Bachmatiuk A., Yin Y., ... Rümmeli M. H. Applications of phosphorene and black phosphorus in energy conversion and storage devices. *Advanced Energy Materials*. 2018;8(8): 1702093. https://doi.org/10.1002/aenm.201702093

8. Niu T. New properties with old materials: layered black phosphorous. *Nano Today*. 2017;12: 7–9. https://doi.org/10.1016/j.nantod.2016.08.013

9. Goswami A., Gawande M. B. Phosphorene: current status, challenges and opportunities. *Frontiers of Chemical Science and Engineering*. 2019;13(2): 296–309. https://doi.org/10.1007/s11705-018-1783-y

10. Lee K., Synnestvedt S., Bellard M., Kovnir K. GeP and $(Ge_{1-x}Sn_x)(P_{1-y}Ge_y)$ (x~0.12, y~0.05): synthesis, structure, and properties of two-dimensional layered tetrel phosphides. *Journal of Solid State Chemistry*. 2015;224: 62–70. https://doi.org/10.1016/j.jssc.2014.04.021

11. Barreteau C., Michon B., Besnard C., Giannini E. High-pressure melt growth and transport properties of SiP, SiAs, GeP, and GeAs 2D layered semiconductors. *Journal of Crystal Growth*. 2016;443(1): 75–80. https://doi.org/10.1016/j.jcrysgro.2016.03.019

12. Cheng A-Q., He Z., Zhao J., Zeng H., Chen R-Sh. Monolayered silicon and germanium monopnictide semiconductors: excellent stability, high absorbance, and strain engineering of electronic properties. *ACS Applied Materials & Interfaces*. 2018;10(6): 5133–5139. https://doi.org/10.1021/acsami.7b17560

13. Zhou L., Guo Y., Zhao J. GeAs and SiAs monolayers: novel 2D semiconductors with suitable band structures. *Physica E: Low-dimensional Systems and Nanostructures*. 2018;95: 149–153. https://doi.org/10.1016/j.physe.2017.08.016

14. Ramzan M. S., Bacic V., Jing Y., Kuc A. Electronic properties of a new family of layered materials from groups 14 and 15: first-principles simulations. *The Journal of Physical Chemistry C*. 2019;123(41): 25470–25476. https://doi.org/10.1021/acs.jpcc.9b07068

15. Olesinski R. W., Abbaschian G. J. The Ge–Sn (Germanium–Tin) system. *Bulletin of Alloy Phase Diagrams*. 1984;5(3): 265–271. https://doi.org/10.1007/bf02868550

16. Ugai Ya. A., Sokolov L. I., Goncharov E. G., Pshestanchik V. R. *P-T-x* diagram of the state of the Ge-P system and the thermodynamics of the interaction of the components. *Russian Journal of Inorganic Chemistry*. 1978;23(7): 1907–1911. (In Russ.). Available at: https://www.elibrary.ru/item.asp?id=29096578

17. Olofsson O. X-ray investigation of the tin-phosphorus system. *Acta Chemica Scandinavica*. 1970;24: 1153 -1162. https://doi.org/10.3891/acta.chem.scand.24-1153

18. Donohue P. C. The synthesis, structure and superconducting properties of new high-pressure forms of tin phosphide. *Inorganic Chemistry*. 1970;9(2): 335–348. https://doi.org/10.1021/ic50084a032

19. Katz G., Kohn Y. A., Broder Y. D. Crystallographic data for tin monophosphide. *Acta Crystallographica*. 1957;9: 607–609. https://doi.org/10.1107/s0365110x57002170

20. Vivian A. C. The tin-arsenic system. *Journal of the Institute of Metals*. 1920;23: 325–336.

21. Gullman J. The crystal structure of SnP. *Journal of Solid State Chemistry*. 1990;87: 202–207. https://doi.org/10.1016/0022-4596(90)90083-a

22. Sushkova T. P., Kononova E. U., Savinova Y. A., Dorokhina E. S., Semenova G. V. Intermediate phases in Sn-P system. *Condensed Matter and Interphases*. 2014;16(2): 210–214. Available at: https://www.elibrary.ru/item.asp?edn=sitfep

23. Ritcher A. Pressure dependence of the tin-phosphorus phase diagram. *Monatshefte für Chemie – Chemical Monthly*. 2012;143(12): 1593–1602. https://doi.org/10.1007/s00706-012-0861-y

24. Proskurina E. Yu., Semenova G. V., Zavrazhnov A. Yu., Kosyakov A. V. *P-T-x* diagram of Sn - P system. *Condensed Matter and Interphases*. 2015;17(4): 498–509. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.asp?id=25946590

25. Zavrazhnov A. Yu., Semenova G. V., Proskurina E. Yu., Sushkova T. P. Phase diagram of the Sn - P system. *Journal of Thermal Analysis and Calorimetry*. 2018;134(1): 475–481. https://doi.org/10.1007/s10973-018-7123-0

26. Semenova G. V., Leont'eva T. A., Sushkova T. P. Analysis of phase equilibria in the Ge–P–Sn ternary system. *Condensed Matter and Interphases*. 2019;21(2): 249–261. (In Russ., abstract in Eng.). https://doi.org/10.17308/kcmf.2019.21/763

27. Khaldoyanidi K. A. *Phase diagrams of heterogeneous systems with transformations*[*]. F. A. Kuznetsov (ed.). Novosibirsk: INKh RAN Publ.; 2004. 382 c. (In Russ.)

Information about the authors

Galina V. Semenova, Dr. Sci. (Chem.), Full Professor, Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0003-3877-985X

semen157@chem.vsu.ru

Tatiana P. Sushkova, Cand. Sci. (Chem.), Associate Professor, Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0003-1969-7082

sushtp@yandex.ru

Angelina N. Golentsova, Engineer of 1 category, Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0009-0002-0824-8062

An.golentsovaa@mail.ru

Received 11.07.2024; approved after reviewing 03.09.2024; accepted for publication 16.09.2024; published online 25.12.2024.

Translated by Valentina Mittova