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PHASE RELATIONS IN THE AGI-AG$_7$GESE$_5$I-GESE$_2$ SYSTEM

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Phase equilibria in the AgI-Ag_7GeSe_5I-$GeSe_2$ system were studied by differential thermal and X-ray diffraction analysis. T-x phase diagrams of boundary systems, liquidus surface projection and a number of internal vertical sections of the T-x-y diagram were constructed. It was found that all three boundary systems are quasi-binary and form eutectic phase diagrams. The AgI-Ag_7GeSe_5I-$GeSe_2$ system is a quasi-ternary plane of the corresponding quaternary system and belongs to the type with invariant eutectic crystallizing at 525 ^{0}C. The liquidus surface projection consists of 3 regions corresponding to the primary crystallization of the α-phase based on Ag_7GeSe_5I, as well as high-temperature modifications of the AgI and $GeSe_2$ compounds. The liquidus surfaces of HT-$GeSe_2$ and the α-phase, which have a higher melting point, occupy very large areas, while the liquidus surface of the HT-AgI phase is located in a small region near the corresponding vertex of the concentration triangle.

Keywords: silver iodide, germanium diselenide, argyrodite, phase equilibria

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INTRODUCTION

Silver chalcogenides with p^2 - elements are valuable functional materials with interesting semiconductor, photoelectric, thermoelectric, etc. properties [1–4]. Among these materials, the argyrodite family compounds occupy a special place. Their physicochemical study began in the 60s of the last century. As is known, the argyrodite family includes compounds with the general formula $A^{m+}_{(12-n)/m}B^{n+}X^{2-}_6$. Here, A^{m+} is usually mono- (Cu^+, Ag^+, Li^+) or divalent (Zn^{2+}, Cd^{2+}, Hg^{2+}) cations, B^{n+} is Ga^{3+}, Si^{4+}, Ge^{4+}, Sn^{4+}, P^{5+}, As^5, cations, and X^{2-} is S^{2-}, Se^{2-}, Te^{2-} anions. These compounds are valuable environmentally safe functional materials that exhibit thermoelectric, photoelectric, and optical properties and have great potential for application in solar converters, as well as in various photovoltaic processes [5-12].

In addition to chalcogenide argyrodites, there are also argyrodites with multiple quaternary anion substitutions of the type $A^I_7B^{IV}X_5Y$ (Y=Cl, Br, I), in which one of the 6 chalcogen atoms in their formula is replaced by a halogen [5, 9]. Many of these compounds have high ionic conductivity and are promising for use as ion-selective electrodes, solid electrolytes, etc. [9, 13-19].

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One of the most effective ways to establish the physicochemical basis for obtaining new multicomponent phases is the study of phase equilibria in the relevant systems [9, 10, 20]. Recent studies have focused on phase equilibria in various systems significant for the exploration of new variable-composition phases within the argyrodite family of compounds [9, 10, 21-29].

The Ag_2Se-AgI-$GeSe_2$ solid-state plane of the Ag-Ge-Se-I four-component system is of interest in terms of the search for chalcogen→halogen-substituted phases based on argyrodite compounds. When planning experimental work to study this solid-state plane, it became clear that there is no information about it in the scientific literature.

Taking into account the above, we decided to study phase equilibria in the Ag_2Se-AgI-$GeSe_2$ system. The presented work presents the results of the study of this system in the AgI-Ag_7GeSe_5I-$GeSe_2$ solid-state plane.

The initial compounds of the system have been studied in detail. The AgI compound melts congruently at 558 °C and undergoes polymorphic transformation at 147 °C. The high-temperature modification (HT-AgI) crystallizes in a cubic structure (Sp.gr.*Im*3*m*, *a*=5.062 Å), while the low-temperature modification (RT-AgI) crystallizes in a hexagonal (Sp.gr. $P6_3mc$, *a*=4.99 Å, *c*=7.520 Å) structure [30, 31]. HT-AgI is a classic representative of cation-conducting (Ag^+) solid electrolytes. The electrical conductivity of this phase (~1 Om^{-1}cm^{-1}) was determined as early as 1914 by K. Tubandt and E. Lorenz [30]. Its anomalously high electrical conductivity is due to the properties of the crystal structure. There are 42 positions for Ag^+ ions in the elementary lattice, and 21 vacant positions fall on each silver cation in one elementary lattice. Silver ions can easily move from one of these positions to another, that is, they are delocalized. This leads to its high ionic conductivity [30-33].

The $GeSe_2$ compound melts congruently at 742 °C. This compound also has a polymorphic transformation. The low-temperature (25-579°C) modification is rhombic (Sp.gr.*Pmnm*, *a*=6.950, *b*=12.220, *c*=23.040 Å z=24), while the high-temperature (579-742°C) modification crystallizes in the monoclinic syngony (Sp.gr. $P2_1/c$, *a*=7.030, *b*=16.840, *c*=11.820 Å, α = 90°74′, z = 16) [34, 35].

The compound Ag_7GeSe5_I melts congruently at 870 °C and crystallizes in a cubic structure (Sp.gr. $F\bar{4}3m$, a=10.72.2(7) Å [14], a=10.986 Å [36] or a=11.034 (5) Å [37], It is a characteristic superionic conductor [13].

EXPERIMENTAL

To study the nature of the physicochemical interaction in the AgI-Ag_7GeSe_5I-$GeSe_2$ system, initial binary compounds (20 grams each) were synthesized. The synthesis was carried out by co-melting mixtures of high-purity simple substances (Ag- rod, 99.997%, CAS 7440-22-4; Ge- ingot, 99.999%, CAS 7440-56-4; Se- granule, 99.999%, CAS 7782-49-2; I-powder, 99.999%, CAS 7553-56-2, AgI-powder) taken in stoichiometric proportions in quartz ampoules under vacuum conditions (10^{-2} Pa).

Since the saturated vapor pressures of iodine (T_b=184 °C) and selenium (T_b=685 °C [38]) at the melting temperatures of the compounds are high, the synthesis of all three compounds was carried out in a two-zone mode in an inclined furnace.

For the synthesis of AgI, Ag_7GeSe_5I, and $GeSe_2$ compounds, a quartz ampoule with a length of ~15 cm and an internal diameter of ~1.4-1.6 cm, previously cleaned with a chromium mixture, was used. Due to the volatility of elemental iodine, for the synthesis of the first two compounds, the required amount of silver was first weighed and placed in the ampoule, then iodine was added to the ampoule cooled in ice water, and was vacuumed and sealed.

During the synthesis of all three compounds, a part of the ampoule (~ 6 cm) remained outside the furnace. To control the vapor pressure of the volatile element and prevent the ampoule from exploding, the part of the ampoule remaining outside the furnace ("cold" zone) was cooled with water. The furnace was gradually heated to a temperature 30–500 °C higher than the melting point of the synthesized compound ("hot zone"). In the "cold" zone, the volatile component condensed and returned to the "hot" zone and entered the reaction. During the reaction, the amount of the volatile component gradually decreased and after a while, it was practically completely consumed. After that, the ampoule was completely inserted into the furnace, kept at 580 °C (AgI), 780 °C ($GeSe_2$), or 900 °C (Ag_7GeSe_5I) for 1 hour, and then slowly cooled.

The individuality of the synthesized samples was confirmed by DTA and XRD methods. Two thermal effects were detected in the DTA heating curves of AgI, $GeSe_2$ compounds: 147 °C and 558 °C (AgI), 579 and 742 °C ($GeSe_2$). Small peaks with lower temperatures (147 and 579 °C) correspond to the polymorphic transition temperatures of these compounds, and high-temperature endoeffects (558 and 742 °C) to their melting temperatures. Only one peak (870 ^{0}C) was detected on the DTA heating curve of the Ag_7GeSe_5I compound, corresponding to the melting temperature of this compound. These indicators are in full agreement with the literature data [30-37].

X-ray phase analysis also confirmed the homogeneity of the synthesized samples. The powder diffractograms had diffraction patterns known from the literature for low-temperature modifications of both compounds. The crystal lattice parameters calculated on their basis coincide with those given in the literature [30-37].

By melting mixtures of the obtained initial compounds in various proportions in vacuumed quartz ampoules, the AgI-$GeSe_2$, 0,2Ag_7GeSe_5I-$GeSe_2$, and 0,2Ag_7GeSe_5I-AgI side systems, as well as alloys with 3 internal sections ([A] – $GeSe_2$, [B] – AgI and 0.2 Ag_7GeSe_5I- [C], [A], [B], [C] – compositions corresponding to a 1:1 molar ratio of the components on the sides of the concentration triangle) were prepared. To maximally approach the equilibrium state, the samples were gradually cooled to 450 °C and thermally treated at this temperature for 500 hours.

The studies were carried out in closed ampoules by DTA (NETZSCH 404 F1Pegasus system, heating rate 10 deg. / min, chromel-alumel thermocouples) and XRD (Bruker D8 ADVANCE diffractometer, $CuK_{\alpha1}$ radiation, 2θ = 5-75 °). The temperature was determined with an error of ±2°, and the crystal lattice parameters with an error of ±0.00001 Å.

RESULTS AND DISCUSSION

As a result of the combined analysis of the XRD and DTA results of the heat-treated samples, a full scheme of the phase equilibria in the AgI-Ag_7GeSe_5I-$GeSe_2$ system was obtained. Before the formula of the compound Ag_7GeSe_5I in the concentration triangle and the corresponding sections, the coefficient 0.2 is written so that the expression of the composition in this composition region is the same as in the concentration triangle Ag_2Se-AgI-$GeSe_2$.

Boundary quasi-binary systems

Powder diffractograms of annealed samples of boundary systems are given in Fig. 1.

As can be seen, the diffraction patterns of the intermediate alloys in all three systems consist of sets of diffraction reflections of the corresponding initial compounds. There are no new diffraction lines in the alloys, the reflection angles of the equilibrium phases are the same as the diffraction lines of the corresponding initial compounds. This indicates that all three boundary systems are stable in the subsolidus, i.e., they consist of 2-phase mixtures of the corresponding initial compounds, and there are no areas of homogeneity that can be felt based on these compounds.

Based on the DTA and XRD data, the phase diagrams of the AgI-$GeSe_2$, 0,2Ag_7GeSe_5I-$GeSe_2$, and 0,2Ag_7GeSe_5I-AgI were constructed.

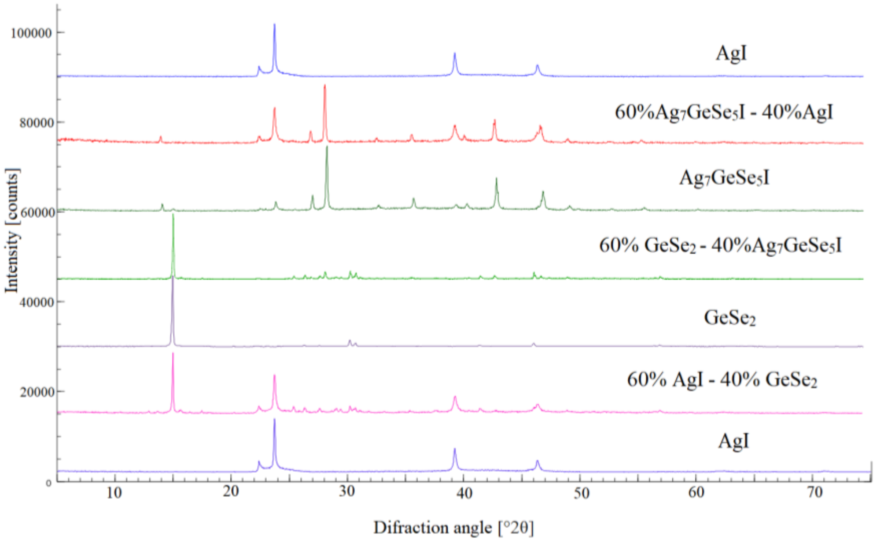

Figure 1. Powder diffractograms of samples of boundary systems

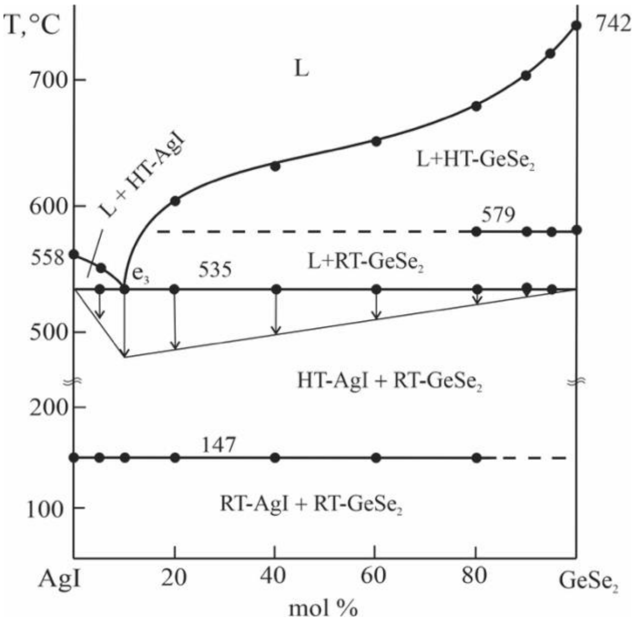

Figure 2. Phase diagram of the AgI-GeSe$_2$ system

As can be seen from Fig.2, the *AgI-GeSe$_2$* system is quasi-binary and has a eutectic-type phase diagram. The eutectic has a 10 mol % GeSe$_2$ content and crystallizes at 535 °C.

In the 0,2Ag$_7$GeSe$_5$I-AgI system, the eutectic crystallizes at the composition of 92 mol% AgI and 545 °C (Fig.3). At the eutectic temperature, there is a solid solution area of 7-8 mol % based on Ag$_7$GeSe$_5$I. The polymorphic transformation temperature of the AgI compound in the system is constant and has the same value as that of pure AgI. This indirectly indicates that the solubility in AgI is very small.

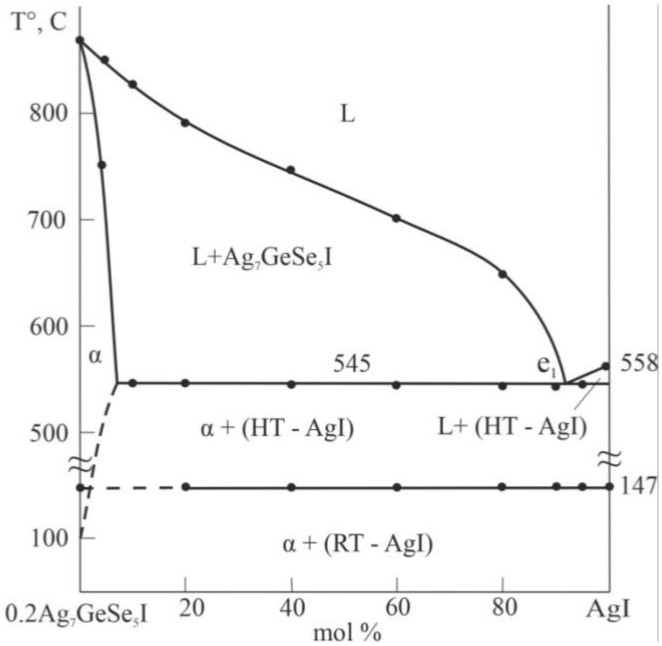

Figure 3. Phase diagram of the 0,2Ag_7GeSe_5I-AgI system

0.2Ag_7GeSe_5I-$GeSe_2$ system (Fig.4). In this system, the eutectic has coordinates 40 mol % $GeSe_2$ and 542 °C. The fact that the polymorphic transformation temperature of the $GeSe_2$ compound remains constant indicates that its solubility is very low.

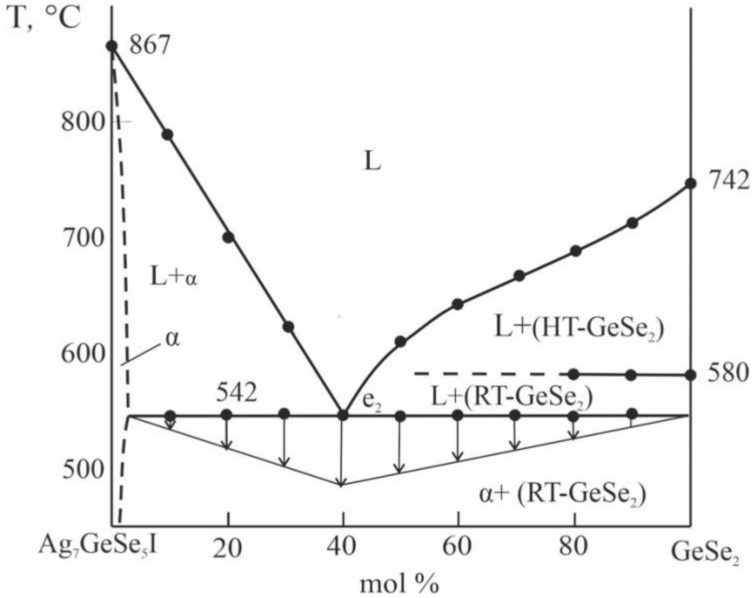

Figure 4. Phase diagram of the 0,2Ag7GeSe5I-GeSe2 system

Liquidus surface of the AgI-Ag7GeSe5I-GeSe2 system

The fact that all three sides of the 0,2Ag_7GeSe_5I- AgI- $GeSe_2$ concentration triangle are quasi-binary allows it to be characterized as an independent subsystem of the Ag_2Se-AgI-$GeSe_2$ quasi-ternary system.

Based on the DTA results, a projection of liquidus surface projection of the 0,2Ag_7GeSe_5I- AgI- $GeSe_2$ system was constructed (Fig. 5). As can be seen, the system belongs to the eutectic type. The liquidus consists of 3 areas corresponding to the initial crystallization of the α-phase based on Ag_7GeSe_5I, as well as high-temperature modifications of the AgI and $GeSe_2$ compounds. While the liquidus surfaces of the HT-

$GeSe_2$ and α-phases, which have a higher melting temperature, occupy very large areas, the liquidus surface of the HT-AgI phase is located in a small area near the corresponding vertex of the composition triangle. Liquidus surfaces are bounded by eutectic curves reflecting the following

L↔α+(HT-AgI) (e_1E curve; 545-525 °C) (1)

L↔α+(HT-$GeSe_2$) (e_2E curve; 542-525 °C) (2)

L↔(HT-AgI)+(HT-$GeSe_2$) (e_3E curve; 535-525 °C) (3)

monovariant equilibria.

Crystallization ends at 525 °C via a nonvariant process

L↔α+(RT-$GeSe_2$)+(HT-AgI) (4)

The composition of the crystallizing liquid (E) according to this scheme is approximately 75 mol% AgI and 10 mol% $GeSe_2$.

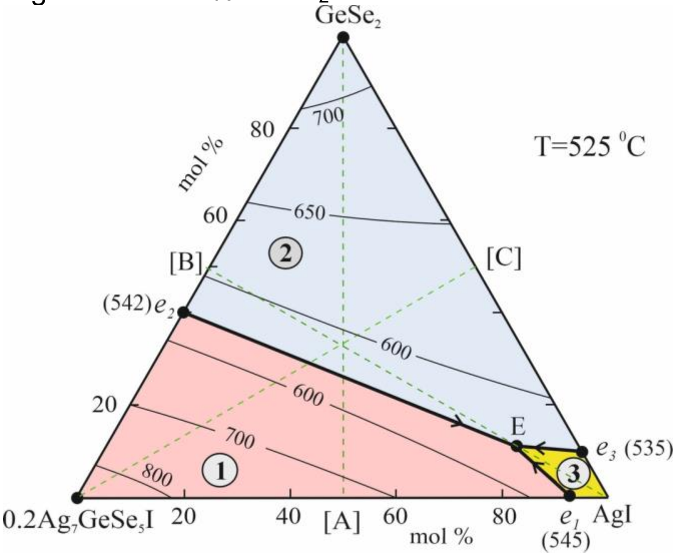

Figure 5. The liquidus surface projection of the $0,2Ag_7GeSe_5I$- AgI- $GeSe_2$ system

Polythermal sections of the phase diagram

To demonstrate the processes of crystallization from the melt, some polythermal sections of the volume phase diagram are constructed: [A] – $GeSe_2$, [B] – AgI, and 0.2 Ag_7GeSe_5I – [C]. Here [A], [B], and [C] – are the compositions corresponding to the 1:1 molar ratio of the components on the sides of the concentration triangle.

[A]–$GeSe_2$ section (Fig.6a). This section passes through the initial crystallization areas of the Ag_7GeSe_5I and HT-$GeSe_2$ phases (RT-$GeSe_2$ in a very small composition interval). The intersection point of the liquidus curve (~25 mol % $GeSe_2$) (2) corresponds to the monovariant eutectic equilibrium. This process occurs in all samples with a content of >10 mol % $GeSe_2$. In the concentration range of 0–10 mol% $GeSe_2$, after the initial crystallization of the α-phase, a monovariant equilibrium (1) is observed. In all alloys, crystallization ends at 525 °C according to the nonvariant eutectic reaction (4). The horizontal lines at temperatures of 580 and 147 °C reflect polymorphic transformations of the $GeSe_2$ and AgI compounds.

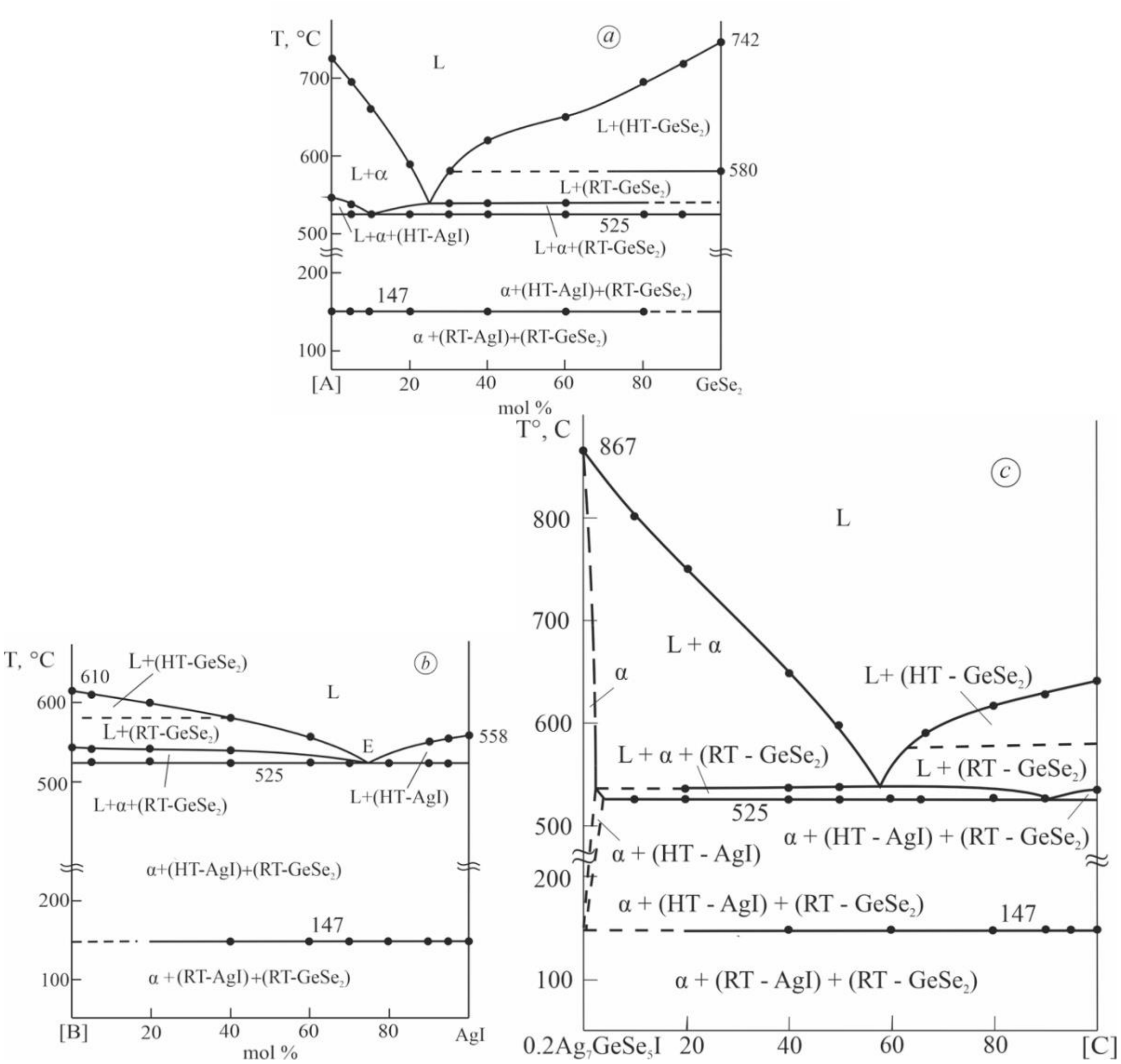

Figure 6. Some polythermal sections of the phase diagram of the Ag_2Se-AgI-$GeSe_2$ system

[B]–AgI cross section (Fig. 6b). Comparison of this cross section with the liquidus surface projection (Fig. 3) shows that it passes through the liquidus surfaces of $GeSe_2$ and AgI compounds and the triple eutectic point (E). Although thermal effects corresponding to the polymorphic transformation of the $GeSe_2$ compound are not detected in the DTA curves (this may be due to their very small intensity), this transformation is marked by broken lines at 780 °C in Fig. 4b.

After the initial crystallization of the HT-$GeSe_2$ and RT-$GeSe_2$ phases from the melt, monovariant eutectic crystallization (2) occurs. This leads to the formation of a three-phase region L+α+(RT-$GeSe_2$) on the T–x diagram. A sample with a 75 mol % $GeSe_2$ content has a eutectic composition (E) and crystallizes invariantly at 525 °C. In samples richer in AgI, the (HT-AgI) and then the ternary eutectic crystallizes first.

0.2 Ag_7GeSe_5I – [C] section (Fig. 6c). In this section, from left to right, the α-phase and 2 modifications of the $GeSe_2$ compound crystallize. At the intersection of the liquidus curves, monovariant crystallization of the α+(RT-$GeSe_2$) eutectic mixture occurs. This process occurs in all samples with a content of >10 mol% 0.2 Ag_7GeSe_5I. In the 0–10 mol% 0.2 Ag_7GeSe_5I content interval, after the initial crystallization of (RT-$GeSe_2$), co-crystallization of the (HT-AgI)+(RT-$GeSe_2$) eutectic mixture takes place. As in other sections, crystallization is completed by the monovariant eutectic process (4), and at 147°C, the (HT-AgI) → (RT-AgI) polymorph transition occurs in this mixture.

CONCLUSION

Thus, in this work, phase relationships in the quasi-ternary AgI-Ag_7GeSe_5I-$GeSe_2$ system were studied using physicochemical analysis methods. Phase diagrams of the side systems, projections of the liquidus surface, and a number of the cross sections of the volume diagram were constructed. It was shown that all three side systems are eutectic type quasi-binary systems. In the studied system, the ternary eutectic point crystallizes at 525°C.

The obtained experimental data can be used to select alloy compositions that are of interest as potential environmentally friendly thermoelectric materials with anomalously low thermal conductivity and mixed ionic-electronic conductors.

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