UDC 544.344.015.3: 546.56/57'23

PHASE EQUILIBRIA ALONG THE Cu_2GeSe_3 – Ag_2GeSe_3 ISOPLETH SECTION OF THE Cu_2Se – Ag_2Se – GeSe_2 SYSTEM**V.A.Abbasova**

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Received 03.04.2019

DTA and XRD methods were used to study phase equilibria along the Cu_2GeSe_3 – Ag_2GeSe_3 isopleth section of the Cu_2Se – Ag_2Se – GeSe_2 system and its phase diagram was constructed. It was established that this section is non-quasibinary. In the composition range 0–55 mol% Cu_2GeSe_3 , solid solutions on the basis of high-temperature modification of Ag_8GeSe_6 primarily crystallize from the melt, and in the range 55–100 mol% Cu_2GeSe_3 solid solutions based on Cu_2GeSe_3 . Based on Cu_2GeSe_3 , solid substitution solutions were identified, the length of which at 900 K is 20 mol%, and at room temperature – 10 mol%.

Keywords: copper-germanium selenides, silver-germanium selenides, phase diagram, solid solutions.

<https://doi.org/10.32737/0005-2531-2019-3-52-56>

Introduction

Complex chalcogenides of copper and silver with elements of the germanium subgroup received a lot of attention over the years due to many phases based on them exhibit excellent properties that make them a good candidate for fabrication of novel high-performance functional materials [1–3]. In particular, $\text{A}_2\text{B}^{\text{IV}}\text{X}_3$ and $\text{A}_8\text{B}^{\text{IV}}\text{X}_6$ (A – Cu, Ag; B^{IV} – Ge, Sn; X – S, Se, Te) compounds and alloys based on them are possess thermoelectric, photoelectric, optical, and other properties [4–12].

In order to develop novel preparative methods and growth of single crystals of this kind of complex materials and in particular, to examine the formation of new intermediate phases it is necessary to investigate phase relationships and to plot phase diagrams of the respective systems [13–16].

This paper presents the results of a study of phase equilibria along a section Cu_2GeSe_3 – Ag_2GeSe_3 of a quasiternary system Cu_2Se – Ag_2Se – GeSe_2 . Earlier, a number of works presented phase diagrams of some similar systems in which continuous (Cu_2GeS_3 – Cu_2GeSe_3 [17, 18]) or wide (Cu_2SnS_3 – Cu_2SnSe_3 [19]), Cu_2GeS_3 – Ag_2GeS_3 [20]) areas of substitutional solid solutions were revealed.

Cu_2GeSe_3 compound melts at 1038 K [2] and crystallizes in a monoclinic structure: *Sp.Gr. Cm*, $a = 0.6772$, $b = 0.3956$, $c = 0.3958$ nm; $\beta =$

125.83° [21]. In the literature, until recently, there was conflicting information about the existence of the Ag_2GeSe_3 compound [2, 22]. A recently published work [23] proved the absence of this compound. It was shown that the alloy of composition " Ag_2GeSe_3 " is the Ag_2Se + GeSe_2 two-phase mixture.

Experimental part

For the investigations, Cu_2GeSe_3 , Ag_2Se and GeSe_2 were synthesized by the direct fusing of the high purity grade (not less than 99.999%) constituent elements in sealed (10^{-3} Pa) silica ampoules. The synthesis of the first two compounds was performed in the inclined two-zone furnace because of high vapor pressure of elemental selenium at high temperature. The "hot" zone of the furnace was 30–50 K higher than the melting point of the corresponding synthesized compound, whereas the temperature of the "cold" zone was about 900 K (lower than the boiling point of selenium [24]).

The alloys of the investigated system were prepared by melting the stoichiometric quantities of the pre-synthesized compounds in sealed silica ampoules under vacuum. All alloys were heated up to 1050 K and held at this temperature for about 3–4 h and were then annealed at 800 K for about 500 h. Finally, alloys slowly cooled down to room temperature.

DTA and XRD techniques were employed

to check the purity of the synthesized starting compounds and analyze the samples. Differential thermal analysis of the equilibrated alloys was carried out using a NETZSCH 404 F1 Pegasus system. The measurement was performed between room temperature and 1100 K with a heating and cooling rate of 10 K min^{-1} . Temperatures of thermal effects were taken mainly from the heating curves. XRD analysis was done with the Bruker D8 ADVANCE diffractometer ($\text{CuK}\alpha_1$ -radiation).

DTA and XRD data confirmed that the pre-synthesized compounds were phase-pure. Powder XRD data for synthesized compounds were found to be very close to data of Reference [2, 21].

Results and discussion

Based on powder X-ray diffraction patterns of the homogenized samples, it was shown that the solubility of Cu_2GeSe_3 at room temperature about 10 mol% (γ -phase). A sample has a diffraction pattern identical to Cu_2GeSe_3 (Figure 1). Solutions containing 30–80 mol% Cu_2GeSe_3 were three-phase, while 0–20 mol% Cu_2GeSe_3 were two-phase. Here β - GeSe_2 , δ are solid solutions based on high-temperature cubic modification of Ag_8GeSe_6 . Figure 2 presents the X-ray powder diffraction patterns of Ag_8GeSe_6 , GeSe_2 compounds and an alloy of this system

with a composition of 10 mol% Cu_2GeSe_3 . As can be seen, the diffraction pattern of this alloy consists of a set of reflection lines of Ag_8GeSe_6 and GeSe_2 compounds. Figure 3 shows the T – x diagram of the Cu_2GeSe_3 –“ Ag_2GeSe_3 ” section. As can be seen, this section is non-quasibinary. Liquidus consists of two curves. From left to right, they correspond to the primary crystallization of γ –(~55–100 mol% Cu_2GeSe_3) and δ -phases. Since the region of homogeneity of the γ -phase is located in the plane of the section, the tie-lines in the two-phase region $L+\gamma$ are practically in the plane of the section. The region of homogeneity of the γ -phase is maximum at 900 K and about 20 mol%. Below liquidus, crystallization takes place according to monovariant eutectic reactions: $L \leftrightarrow \gamma + \delta$ (30–80 mol% Cu_2GeSe_3) and $L \leftrightarrow \beta + \delta$ (0–30 mol% Cu_2GeSe_3). In the region of 0–25 mol% Cu_2GeSe_3 , crystallization is completed by the second scheme and a two-phase field $\beta + \delta$ is formed. Near room temperature, the δ phase decomposes according to the monovariant scheme $\delta \rightarrow \delta_2$, resulting in the formation of $\beta + \delta + \delta_2$ three-phase and $\beta + \delta_2$ two-phase areas (δ_2 -solid solutions on the basis of low-temperature modification of Ag_8GeSe_6). The heating thermogram of a sample with a composition of 10 mol% Cu_2GeSe_3 (Figure 4a) clearly displays these processes.

Fig. 1. XRD patterns of the 90 mol% Cu_2GeSe_3 and pure Cu_2GeSe_3 .

Fig. 2. XRD patterns of the 10 mol% Cu_2GeSe_3 , Ag_8GeSe_6 and GeSe_2 .

Fig. 3. Polythermal section Cu_2GeSe_3 – Ag_2GeSe_3 of the phase diagram of the Cu_2Se – Ag_2Se – GeSe_2 .

Fig. 4. Heating thermograms of samples of the Cu_2GeSe_3 – Ag_2GeSe_3 polythermal section: *a* – 10 mol% Cu_2GeSe_3 , *b* – 70 mol% Cu_2GeSe_3 .

In the region of 25–85 mol% Cu_2GeSe_3 crystallization is completed by the formation of a triple eutectic E at 820 K (mixture $\beta+\gamma+\delta$). From the heating thermogram of the sample of 70 mol% Cu_2GeSe_3 (Figura 4, *b*), it is seen that upon heating at 820 K initially invariant melting

occurs (eutectic E), then 2 polythermal endo-effects in the temperature range of 820–915 K and 915–970 K take place. These effects reflect the monovariant eutectic process $L \leftrightarrow \gamma+\delta$ and the dissolution of the remaining γ -phase crystals in the melt, respectively.

Conclusion

The T – x diagram of the Cu_2GeSe_3 –“ Ag_2GeSe_3 ” isopleth section of the Cu_2Se – Ag_2Se – GeSe_2 quasi-ternary system is constructed. Solid solutions based on Cu_2GeSe_3 are found in the system, the length of which at 900 K is 20 mol%, and at room temperature – 10 mol%. The obtained phases of variable composition are of interest as potential thermoelectric materials.

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Cu₂Se–Ag₂Se–GeSe₂ SİSTEMİNİN Cu₂GeSe₃–Ag₂GeSe₃ POLİTERMİK KƏSİYİ ÜZRƏ FAZA TARAZLIQLARI

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DTA və RFA üsulları ilə Cu₂Se–Ag₂Se–GeSe₂ sisteminin Cu₂GeSe₃–Ag₂GeSe₃ politermik kəsiyi üzrə faza tarazlıqları öyrənilmiş, faza diagramı qurulmuşdur. Müəyyən edilmişdir ki, bu kəsik qeyri-kvazibinardır, 0–55 mol% Cu₂GeSe₃ tərkib intervalında ərintidən ilkin olaraq Ag₈GeSe₆ birləşməsinin yüksək temperaturu modifikasiyası əsasında bərk məhlullar, 55–100 mol% Cu₂GeSe₃ intervalında isə – Cu₂GeSe₃ əsasında bərk məhlullar kristallaşır. Sistemdə Cu₂GeSe₃ əsasında bərk məhlul sahəsi 900 K-də 20 mol%, otaq temperaturunda isə 10 mol% təşkil edir.

Açar sözlər: mis-germanium selenidləri, gümüş-germanium selenidləri, faza diagramı, bərk məhlullar.

ФАЗОВЫЕ РАВНОВЕСИЯ ПО ПОЛИТЕРМИЧЕСКОМУ РАЗРЕЗУ Cu₂GeSe₃–Ag₂GeSe₃ СИСТЕМЫ Cu₂Se–Ag₂Se–GeSe₂

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Методами ДТА и РФА изучены фазовые равновесия по политермическому разрезу Cu₂GeSe₃–Ag₂GeSe₃ системы Cu₂Se–Ag₂Se–GeSe₂ и построена ее фазовая диаграмма. Показано, что разрез – неквазибинарный, в области составов 0–55 мол.% Cu₂GeSe₃ из расплава первично кристаллизуются твердые растворы на основе высокотемпературной модификации соединения Ag₈GeSe₆, а в области 55–100 мол.% Cu₂GeSe₃ – твердые растворы на основе Cu₂GeSe₃. При 900 К области гомогенности твердых растворов Cu₂GeSe₃ составляют 20 мол.%, а при комнатной температуре – 10 мол%.

Ключевые слова: селениды меди-германия, селениды серебра-германия, фазовая диаграмма, твердые растворы.