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PHASE EQUILIBRIA ALONG THE Cu_3SbSe_4-$GeSe_2$ SECTION OF THE Cu-Ge-Sb-Se SYSTEM

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Abstract. Phase equilibria in the Cu_3SbSe_4-$GeSe_2$ system were studied by differential thermal analysis and powder X-ray diffraction method (PXRD). It was found that in the system the Cu_3SbSe_4 based solid solutions with Sb→Ge substitution (α-phase) are formed. The extent of solid solutions is up to 15 mol.%. In the $GeSe_2$-rich region phase equilibria are complex. The phase compositions of the alloys in the entire range of compositions of the investigated section were determined by the PXRD method: α+Cu_2GeSe_3+Sb_2Se_3+Se (15-58 mol.% $GeSe_2$); Cu_2GeSe_3+Sb_2Se_3+Se (60 mol.% $GeSe_2$); Cu_2GeSe_3+Sb_2Se_3+$GeSe_2$+Se (more than 60 mol% $GeSe_2$).

Keywords: *copper-based chalcogenides, Cu_3SbSe_4-$GeSe_2$ system, copper-antimony selenide, solid solutions, phase equilibria.*

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1. Introduction

Ternary and complex copper chalcogenides attract attention as promising functional materials due to their photoelectric, thermoelectric, nonlinear optical, and other properties (Ahluwalia, 2016; Babanly *et al.*, 1993). In particular, copper-based chalcogenides p-type semiconductors, such as $CuInTe_2$, $Cu_2ZnSnSe_4$, $Cu_2CdSnSe_4$, Cu_3SbX_4 (X = Se, S) and etc., are promising thermoelectric (TE) materials due to their excellent transport properties and relatively low thermal conductivity (Dou *et al.*, 2020; Deng *et al.*, 2020; Luo *et al.*, 2015; Kosuga *et al.*, 2014; Liu *et al.*, 2016; Fan *et al.*, 2011, 2012; Liu *et al.*, 2012; Irfan *et al.*, 2018). Among these phases, Cu_3SbSe_4 is one of the most studied compounds, since it has a large effective mass of carriers (i.e., high electrical conductivity), a small band gap, as well as widespread inexpensive and non-toxic constituents (Shyam Prasad & Rao, 2019; Xie *et al.*, 2018; Liu *et al.*, 2017; Chen *et al.*, 2016). Cu_3SbSe_4 has a famatinite crystal structure, which can be described as a three-dimensional Cu-Se framework of distorted [$CuSe_4$] tetrahedra with a one-dimensional array of inserted [$SbSe_4$] tetrahedra. This configuration results in two copper positions with different Cu-Se bond lengths. This structure provides adequate electron transfer properties and inefficient phonon propagation (Garsia *et al.*, 2018), which is an excellent property for TE applications. However, the thermoelectric figure of merit of Cu_3SbSe_4 is too low ($ZT\approx0.3$ at 570 K (Li *et al.*, 2015)) to use it in practice due to the low concentration of charge carriers and, as a consequence, poor electrical conductivity. Substitution doping is the best and proven strategy for changing the electronic structure and TE performanceof a material (Zeier *et al.*, 2016). The optimized

concentration of carriers in Cu_3SbSe_4 in order to increase its ZT can be achieved by doping the Sb or Se site with some potential dopants. Recent studies have shown that the replacement of Sb, which is in the 5^+ state, with elements with low valence, such as with IIIA (M = Al, Ga, In, Tl) and IVA (M = Si, Ge, Sn, Pb) elements significantly increases the concentration of hole carriers and, as a consequence, the electrical conductivity (Do & Mahanti, 2015; Zhao *et al.,* 2017; Zhang *et al.,* 2016; Ghanwat *et al.,* 2016; Chang *et al.,* 2017; Li *et al.,* 2013). Therefore, it would be advisable to study the formation of substitutional solid solutions based on this compound in various systems containing the above dopant elements. For this reason, it is necessary to investigate phase equilibria in the corresponding systems (Babanly *et al.,* 2017, 2019; Imamaliyeva *et al.,* 2019, 2020).

Earlier, in a number of works (Alverdiyev *et al.,* 2017; Mashadiyeva *et al.,* 2017a, 2017b, 2020; Ismailova *et al.,* 2019), we carried out similar studies of complex systems based on copper and silver chalcogenides, in which new nonstoichiometric phases were discovered and their primary crystallization regions were determined.

The *aim* of this work was to search and study solid solutions based on the Cu_3SbSe_4 compound with Sb→Ge substitution along the Cu_3SbSe_4-$GeSe_2$ section of the Cu-Ge-Sb-Se system.

The starting compounds of the studied Cu_3SbSe_4-$GeSe_2$ section have been studied in detail. Cu_3SbSe_4 melts congruently at 755 K and crystallizes in a tetragonal structure (Sp. gr. I*4*2m) with lattice parameters: a = b = 5.6609 (8) Å; c = 11.280 (5)Å (Pfitzner, 1994).

Germanium diselenide melts with an open maximum at 1015 K (Massalski, 1990). $GeSe_2$ crystallizes in a monoclinic structure (space group P21/c) with lattice parameters: a = 7.016(5) Å; b = 16.796(8) Å; c = 11.831(5) Å; β = 90.65(5)° (Abrikosov *et al.,* 1969).

2. Experimental part

For the experiments, the initial compounds Cu_3SbSe_4 and $GeSe_2$ were synthesized by fusion of simple substances in stoichiometric ratios in evacuated to ~10^{-2} Pa and sealed quartz ampoules at temperatures 50° higher than the melting temperatures of the synthesized compounds. The ampoules with the obtained melts were kept at these temperatures for 3-4 hours and then cooled in the switched off furnace to room temperature. We used simple substances from the company EVOCHEM ADVANCED MATERIALS GMBH (Germany) of high purity: copper in granules (Cu-00029; 99.9999%), antimony in granules (Sb-00002; 99.999%), Germanium pieces (Ge-00003; 99.9999%), selenium granules (Se-00002; 99.999%).

The individuality of all synthesized compounds was monitored by differential thermal analysis (DTA) and PXRD methods. The obtained values of the melting temperatures and the crystal lattices parameters for all synthesized compounds within the error limit (±3 K and ±0.0003 Å) were close to the above literature data.

To carry out experiments by alloying the initial compounds under vacuum conditions, about 20 alloys were prepared along the Cu_3SbSe_4-$GeSe_2$ section. According to DTA data for cast non-homogenized alloys, it was shown that their crystallization from melts is completed at temperatures not lower than 680 K. Taking this into account, to achieve a state as close as possible to equilibrium, cast alloys obtained by rapid cooling of melts were annealed at 650 K within 700 hours.

The prepared samples of the studied system were investigated by DTA and PXRD methods. DTA was performed on a 404 F1 PEGASUS SYSTEM differential scanning calorimeter (NETZSCH). The heating rate was 10 $K \cdot min^{-1}$. The DTA measurement results were processed using the NETZSCH Proteus Software. The temperature measurement accuracy was within ±2°.

PXRD was carried out at room temperature on a BRUKER D8 ADVANCE diffractometer with $CuK_{\alpha 1}$ radiation. The X-ray patterns were indexed using the Topas V3.0 Software Bruker.

3. Results and discussion

XRD analysis of the annealed samples showed that Cu_3SbSe_4-$GeSe_2$ alloys containing no more than 15 mol.% $GeSe_2$ are single-phase and have diffraction peaks identical to those for the pure Cu_3SbSe_4 compound with a slight shift to the right (Fig. 1).

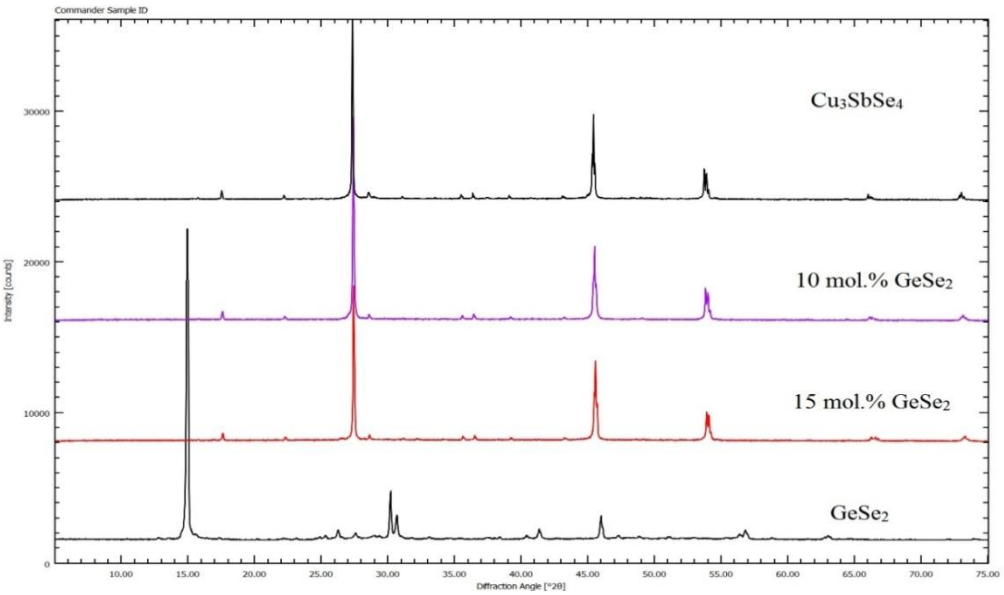

Figure 1. PXRD patterns for the Cu_3SbSe_4-$GeSe_2$alloys

This indicates the formation of up to 15 mol% solid solution based on the Cu_3SbSe_4 compound. The following lattice parameters were calculated by indexing these powder diffraction patterns:

Cu_3SbSe_4 a=5.6531 Å; c=11.2606 Å;
$(Cu_3SbSe_4)_{0.1}(GeSe_2)_{0.9}$ a=5.6409 Å; c=11.243 Å;
$(Cu_3SbSe_4)_{0.15}(GeSe_2)_{0.85}$ a=5.6351 Å; c=11.2307 Å;

The formation of solid solutions in the Cu_3SbSe_4-$GeSe_2$ system was also confirmed by the DTA results (Fig. 2). However, we found that the Cu_3SbSe_4-$GeSe_2$ system is generally non-quasi-binary and is characterized by a complex interaction. The DTA data for alloys with a high $GeSe_2$ content could not be interpreted. Therefore, Fig. 2 shows a fragment of the phase diagram of the Cu_3SbSe_4-$GeSe_2$ system.

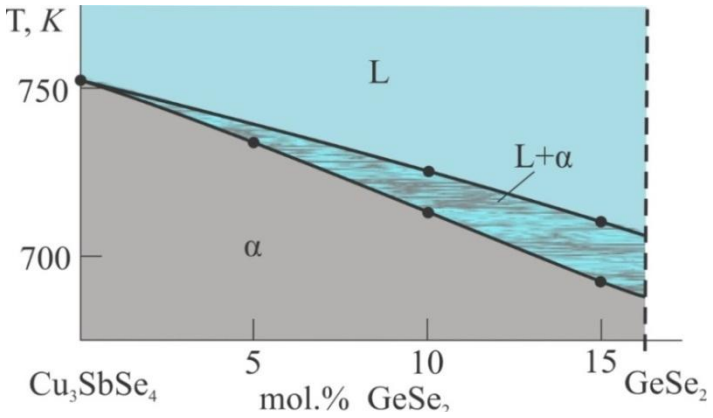

Figure 2. A fragment of the phase diagram of the Cu_3SbSe_4-$GeSe_2$ system

We determined the phase compositions of the alloys in the entire range of compositions of the investigated section by means of PXRD method. It was found that in the 15-58 mol% $GeSe_2$ compositions range alloys consist of a 4-phase mixture α+Cu_2GeSe_3+Sb_2Se_3+Se. The alloy with a composition of 60 mol% $GeSe_2$ is 3-phase: Cu_2GeSe_3+Sb_2Se_3+Se. Alloys containing more than 60 mol% $GeSe_2$ consist of a 4-phase mixture Cu_2GeSe_3+Sb_2Se_3+$GeSe_2$+Se. For example, Fig. 3 shows a powder X-ray diffraction pattern of an alloy containing 80 mol% $GeSe_2$ with an indication of the phase composition.

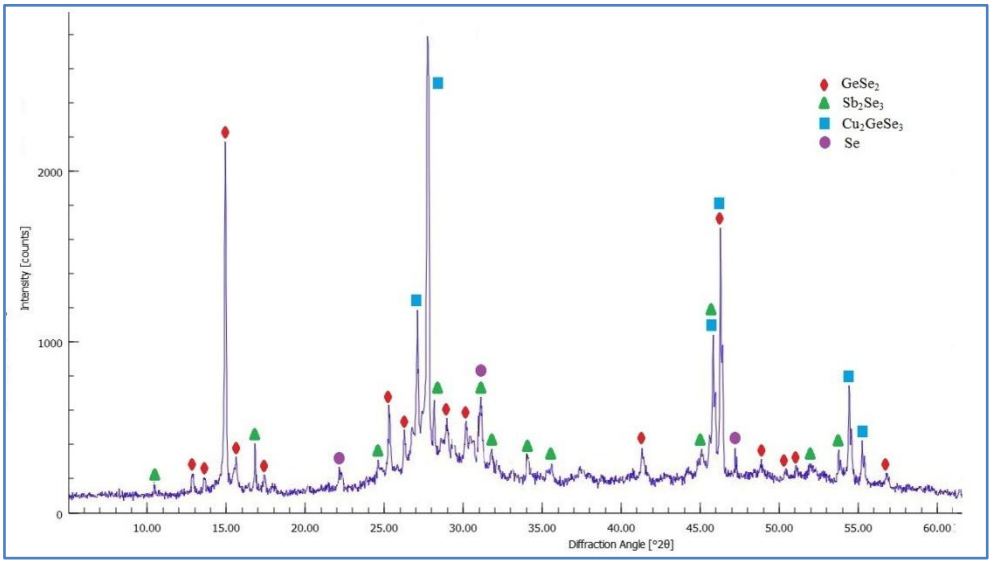

Figure 3. Powder diffraction pattern of the Cu_3SbSe_4-$GeSe_2$ alloy with a content of 80 mol% $GeSe_2$

Based on the data obtained, it can be concluded that the Cu_3SbSe_4-$GeSe_2$ section is located in 4-phase regionsCu_3SbSe_4+Cu_2GeSe_3+Sb_2Se_3+Se (area 1 in Fig. 4) and Cu_2GeSe_3+Sb_2Se_3+$GeSe_2$+Se (area 2 in Fig. 4) of the concentration tetrahedron Cu_2Se-$GeSe_2$-Sb_2Se_3-Se. These areas are delimited by a stable concentration triangle Cu_2GeSe_3-Sb_2Se_3-Se. The composition of the alloy located on the plane of this triangle corresponds to 60 mol% $GeSe_2$ (point A in Fig. 4).

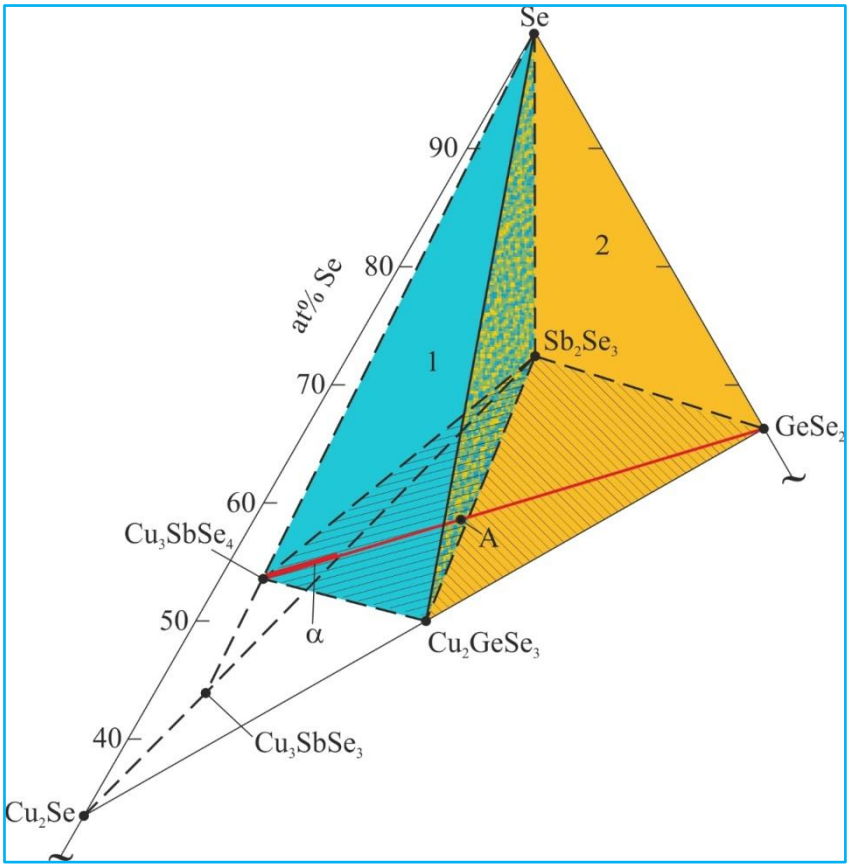

Figure 4. Concentration tetrahedron Cu_2Se-$GeSe_2$-Sb_2Se_3-Se

4. Conclusion

The character of phase equilibria in the Cu_3SbSe_4-$GeSe_2$ system has been established by DTA and PXRD methods. The formation in the system up to 15 mol% of solid solutions based on Cu_3SbSe_4 is shown. Phase equilibria in the $GeSe_2$-rich area are complex and alloys consist of various heterogeneous mixtures. The obtained solid solutions are interesting as potential environmentally friendly functional materials.

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