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SOLUBILITY OF GERMANIUM DISELENIDE IN THE Cu_3AsSe_4

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Differential thermal analysis and powder X-ray diffraction methods were used for phase equilibria studying in the Cu_3AsSe_4 - GeSe_2 system. It was established that wide (up to 30 mol.%) solid solutions based on Cu_3AsSe_4 are formed. GeSe_2 -rich alloys consist of various heterogeneous mixtures, including phases outside the T-x plane of this section.

Keywords: copper-based chalcogenides, copper-arsenic selenide, solid solutions, phase equilibria.

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Introduction

Ternary and complex copper chalcogenides attract attention as promising functional materials due to their photoelectric, thermoelectric, nonlinear optical, and other properties [1–3]. In particular, copper-based chalcogenides with arsenic subgroup elements are synthetic analogs of multiple copper minerals, such as tetraedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), famatinite (Cu_3SbS_4), enargite (Cu_3AsS_4), etc., are promising thermoelectric (TE) materials due to their excellent transport properties and relatively low thermal conductivity [4–10]. These phases are one of the most studied in recent years' compounds, since their good thermoelectric performance, as well as widespread inexpensive and non-toxic constituents. However, the thermoelectric figure of merit of such phases is too low to use in practice due to the low concentration of charge carriers and, as a consequence, poor electrical conductivity. Substitution doping and obtaining non-stoichiometric phases is the best and proven strategy for changing the electronic structure and TE performance of a material [11]. For this purpose, it is necessary to investigate phase equilibria in the corresponding systems [12, 15]. In a number of works [16, 17], complex systems based on copper chalcogenides were studied and new nonstoichiometric phases were discovered in them.

In this work, the Cu_3AsSe_4 - GeSe_2 section of the Cu-Ge-As-Se system was investigated to search and study solid solutions with As→Ge substitution. Similar studies were carried out in Cu_3SbX_4 - GeX_2 (X – S, Se) systems [18, 19], and a region of solubility based on Cu_3SbX_4

up to 15 mol% was found in both systems.

Here, some physico-chemical properties of the starting compounds Cu_3AsSe_4 and GeSe_2 . Cu_3AsSe_4 melts congruently at 773 K and has a polymorphic transition at 715 K [20]. The high-temperature modification crystallizes in the cubic system, while the low-temperature modification crystallizes in a tetragonal structure (Sp. gr. *I42m*) with lattice parameters: $a = b = 5.53$ Å; $c = 11.83$ Å; $\alpha = \beta = \gamma = 90$ [21].

Germanium diselenide melts on distectic reaction at 1015 K [22]. 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; $\beta = 90.65(5)^\circ$ [23].

Experimental part

The initial Cu_3AsSe_4 and GeSe_2 compounds were preliminarily synthesized for the experiments from 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%). Synthesis was performed by fusion of simple substances in stoichiometric ratios in evacuated to $\sim 10^{-2}$ 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.

All synthesized compounds were control-

led 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.

About fifteen $\text{Cu}_3\text{AsSe}_4\text{--GeSe}_2$ alloys were prepared by alloying the initial compounds under vacuum conditions. Further, cast alloys obtained by rapid cooling of melts were annealed at 650 K within 700 hours in order to achieve a state as close as possible to equilibrium.

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

was within $\pm 2^\circ$.

PXRD was carried out at room temperature on a D8 ADVANCE diffractometer (Bruker) with $\text{CuK}\alpha_1$ radiation. The X-ray patterns were indexed using the Topas V3.0 Software Bruker.

Results and discussion

XRD analysis of the annealed $\text{Cu}_3\text{AsSe}_4\text{--GeSe}_2$ alloys showed that samples containing no more than 30 mol.% GeSe_2 are single-phase. Their PXRD patterns have diffraction peaks identical for the pure Cu_3AsSe_4 compound with a slight shift to the big angles (i.e. right) (Figure 1).

This indicates the formation of up to 30 mol% solid solution based on the Cu_3AsSe_4 compound. The following lattice parameters were calculated by indexing these powder diffraction patterns:

Cu_3AsSe_4	$a=5.5427 \text{ Å}$;	$c=11.8411 \text{ Å}$;
$(\text{Cu}_3\text{AsSe}_4)_{0.1}(\text{GeSe}_2)_{0.9}$	$a=5.6389 \text{ Å}$;	$c=11.8382 \text{ Å}$;
$(\text{Cu}_3\text{AsSe}_4)_{0.15}(\text{GeSe}_2)_{0.85}$	$a=5.6305 \text{ Å}$;	$c=11.8309 \text{ Å}$;
$(\text{Cu}_3\text{AsSe}_4)_{0.20}(\text{GeSe}_2)_{0.80}$	$a=5.6235 \text{ Å}$;	$c=11.8245 \text{ Å}$;
$(\text{Cu}_3\text{AsSe}_4)_{0.30}(\text{GeSe}_2)_{0.70}$	$a=5.6158 \text{ Å}$;	$c=11.8129 \text{ Å}$;

Fig. 1. PXRD patterns for the $\text{Cu}_3\text{AsSe}_4\text{--GeSe}_2$ alloys.

The formation of solid solutions in the Cu_3AsSe_4 – GeSe_2 system was also confirmed by the DTA results (Figure 2). However, we found that the Cu_3AsSe_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, Figure 2 shows a fragment of the phase diagram of the Cu_3AsSe_4 – GeSe_2 system.

Fig. 2. A fragment of the phase diagram for the Cu_3AsSe_4 – GeSe_2 system.

The nature of phase equilibria in a similar system Cu_3SbSe_4 – GeSe_2 was studied in more detail in [18]. It has been shown that the Cu_3SbSe_4 – GeSe_2 section is located in 4-phase regions $\text{Cu}_3\text{SbSe}_4 + \text{Cu}_2\text{GeSe}_3 + \text{Sb}_2\text{Se}_3 + \text{Se}$ and $\text{Cu}_2\text{GeSe}_3 + \text{Sb}_2\text{Se}_3 + \text{GeSe}_2 + \text{Se}$ 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 . Our preliminary data suggest that the nature of phase equilibria in the Cu_3AsSe_4 – GeSe_2 system is qualitatively similar to the indicated system.

Conclusion

An experimental study of phase equilibria in the Cu_3AsSe_4 – GeSe_2 system has been carried out by means of DTA and PXRD methods. The solubility based on Cu_3AsSe_4 reaches up to 30 mol% GeSe_2 . Phase equilibria in the GeSe_2 -rich area are complex and alloys consisting of various heterogeneous mixtures, including phases outside the T-x plane of this section. The obtained solid solutions are interesting as potential environmentally friendly functional materials.

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GERMANIUM DİSELENİDİN Cu_3AsSe_4 BİRLƏŞMƏSİNDƏ HƏLL OLMASI

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Differensial termiki analiz və toz rentgenoqrafiyası üsulları ilə Cu_3AsSe_4 – GeSe_2 sistemində faza tarazlıqları öyrənilmişdir. Müəyyən edilmişdir ki, sistemdə Cu_3AsSe_4 birləşməsi əsasında geniş (30 mol%-ə qədər) bərk məhlul sahəsi mövcuddur. GeSe_2 ilə daha zəngin xətlələr müxtəlif fazaların, o cümlədən tərkibcə bu kəsin T–x müstəvisində olmayan fazaların heterogen qarışıqlarından ibarətdir.

Açar sözlər: mis əsasında xalkogenidlər, mis-arsen selenidləri, bərk məhlullar, faza tarazlıqları.

РАСТВОРИМОСТЬ ДИСЕЛЕНИДА ГЕРМАНИЯ В Cu_3AsSe_4

З.Т. Гасанова

Методами дифференциального термического анализа и порошковой рентгенографии изучены фазовые равновесия в системе Cu_3AsSe_4 – GeSe_2 . Установлено, что в системе образуются широкая (до 30 мол.%) область твердых растворов на основе Cu_3AsSe_4 . Сплавы с большим содержанием GeSe_2 состоят из различных гетерогенных смесей, включая фазы вне Т–х плоскости этого сечения.

Ключевые слова: халькогениды на основе меди, селениды меди-мышьяка, твердые растворы, фазовые равновесия.