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PHASE EQUILIBRIA IN THE Cu_2Se-$SnSe$-Sb_2Se_3 SYSTEM ALONG THE $SnSe$-Cu_3SbSe_3 SECTION

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Abstract. Phase equilibria in the Cu_2Se-$SnSe$-Sb_2Se_3 system were studied along the $SnSe$-Cu_3SbSe_3 section by means of differential-thermal and X-ray phase analysis and its phase diagram was constructed. It was found that the $SnSe$-Cu_3SbSe_3 section is stable below the solidus and is non-quasibinary thanks to the incongruent melting of the Cu_3SbSe_3 compound.

Keywords: Cu_2Se-$SnSe$-Sb_2Se_3 system, $SnSe$-Cu_3SbSe_3 section, phase diagram.

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1. INTRODUCTION

Ternary and complex copper chalcogenides have attracted much attention thanks to their outstanding photoelectric, thermoelectric, non-linear optic and etc. properties [1-3]. In particular, the Cu-Sb-Sn-X (X = S, Se) systems are of great interest for the development of new ecologically safe thermoelectric materials [4–6]. In recent years, these compounds are very interesting due to the possibility of increasing their thermoelectric gure of merit. One of the ways to increase the thermoelectric gure of merit of these materials is to obtain solid solutions based on them. For this purpose, it is expedient to study phase equilibria in the corresponding systems [7, 8].

Earlier we carried out a multitude of comprehensive studies [9–11] of phase equilibria and thermodynamic properties of complex systems based on copper chalcogenides.

The purpose of this work is to clarify the phase equilibria in the Cu_2Se-$SnSe$-Sb_2Se_3 quasiternary system along the $SnSe$-Cu_3SbSe_3 polythermal section.

Tin monoselenide SnSe melts congruently at 1134 K [12] and crystallizes in the orthorhombic system, space group *Pcmn*, with following lattice parameters: $a = 4.46$, $b = 4.19$, $c = 11.57$ Å; $Z = 4$ [13].

The Cu_3SbSe_3 compound melts incongruently at 808 K [2] and crystallizes in the orthorhombic system, space group *Pnma*, with $a = 7.9865(8)$, $b = 10.6138(9)$ and $c = 6.8372(7)$ Å; $Z = 4$ [14]. Recent studies have shown that this compound due to its environmentally-friendly constituent elements, ultralow thermal conductivity, and moderate thermopower, could be a potentially useful thermoelectric material [15–17], as well as the compound SnSe exhibit exceptionally good thermoelectric properties at high temperatures above ~800 K, including a very low thermal conductivity [18, 19].

2. EXPERIMENTAL

2.1. Materials and syntheses

The initial compounds SnSe and Cu_3SbSe_3 were synthesized by melting of elementary components of high purity (99.999 %) in vacuumed (~ 10^{-2} Pa) quartz ampoules. The synthesis was carried out at temperatures 50 °C higher than the melting points of the synthesized compounds. Further ampoule with tin selenide was slowly cooled to room temperature. The ampoule with Cu_3SbSe_3 according to the recommendations of [20] was rapidly cooled from the melt and then annealed at 600–673 K. Synthesized compounds SnSe and Cu_3SbSe_3 were identi ed by differential-thermal analysis (DTA) and powder X-ray diffraction (XRD) method.

A series of $SnSe$-Cu_3SbSe_3 alloys with compositions of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 95 mol % Cu_3SbSe_3 was prepared for the investigation. Alloys were prepared from pre-synthesized starting compounds by melting in a vacuum.

In order to achieve the equilibrium state in alloys, cast non-homogenized samples obtained by slow cooling of melts were ground into a powder, thoroughly mixed and pressed into tablets with a mass of 0.8–1g, and then annealed at 700 K for 500 hours.

2.2. Methods

Studies carried out by DTA and XRD methods.

The differential-thermal analysis was carried out in the temperature range from room temperature to 1400 K with a heating rate of 10 $K \cdot min^{-1}$ on a differential scanning calorimeter (NETZSCH 404 F1 Pegasus system). The measurement results were processed using the NETZSCH Proteus Software. The accuracy of the temperature measurement was within ±2 K.

X-ray phase analysis was carried out at room temperature on a Bruker D8 ADVANCE diffractometer with $CuK\alpha_1$ radiation. The X-ray images were indexed using Topas V3.0 software Bruker.

3. RESULTS AND DISCUSSION

The results of XRD of annealed alloys showed that they are two-phase mixtures of the starting compounds. This indicates the stability of this section below the solidus. For example, Fig. 1 shows X-ray image of the alloy with composition 40 mol % SnSe – 60 mol % Cu_3SbSe_3 and con rmed its biphasic composition. As can be seen, the XRD pattern of this alloy is entirely composed of diffraction peaks of the SnSe (circles) and Cu_3SbSe_3 (triangles).

Based on the DTA data (Table), a phase diagram of the SnSe-Cu_3SbSe_3 section was plotted (Fig. 2). As can be seen, this section is a quasistable cross-section of the Cu_2Se-SnSe-Sb_2Se_3 system but is nonquasibinary due to the incongruent melting of the Cu_3SbSe_3 compound. Solubility on the basis of SnSe (β-phase) with an extension of ~3 mol % is observed. Liquidus of the SnSe-Cu_3SbSe_3 system consists of two branches, which characterize primary crystallization of the β-phase and solid solutions based on a high-temperature modi cation of Cu_2Se compound (α-phase) formed along the Cu_2Se-Sb_2Se_3 section [2]. Below the liquidus in the 0–30 mol % SnSe composition range, thermal effects related to the monovariant peritectic reaction $L+\alpha \leftrightarrow Cu_3SbSe_3$ are observed. During this reaction, a three-phase region $L+\alpha+Cu_3SbSe_3$ is formed. In the 30-95 mol % SnSe composition range the joint crystallization of the α- and β-phases takes place. The horizontal at 725 K corresponds to an invariant transition reaction $L+\alpha \leftrightarrow Cu_3SbSe_3+\beta$. Crystallization is completed by the formation of a two-phase mixture $Cu_3SbSe_3+\beta$.

Table. Results of DTA for SnSe-Cu_3SbSe_3 alloys

Composition, mol % Cu_3SbSe_3	Thermal effects, K
0 (SnSe)	1153
5	1105
10	725;1040
20	725; 950
30	725; 750; 880
40	725; 755; 835
50	725; 770; 800
60	725; 770
70	725; 810
80	725; 755; 850
90	725; 780; 890
95	725; 800; 920
100 (Cu_3SbSe_3)	808; 940

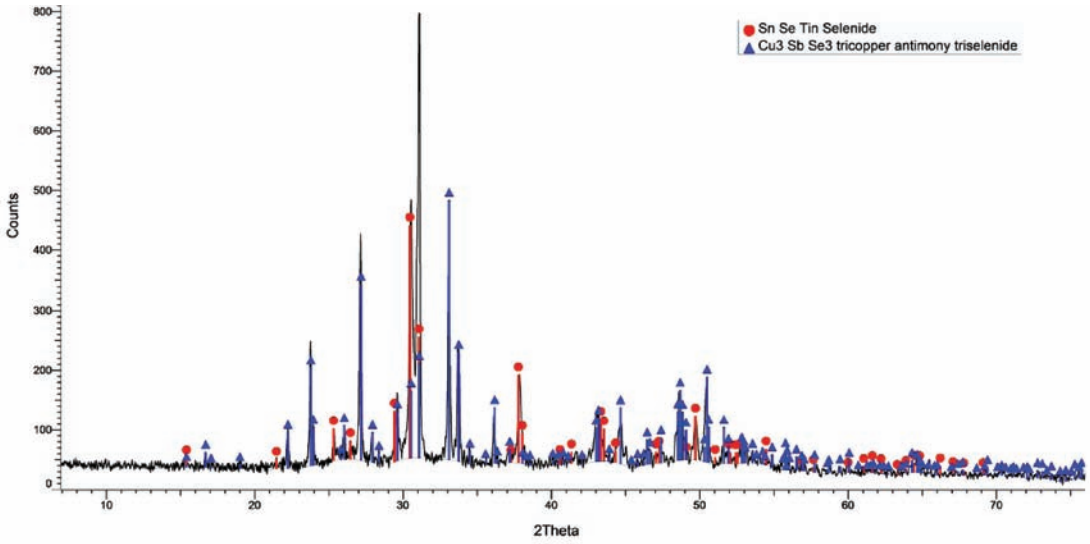

Fig. 1. Powder XRD pattern for the alloy 40 mol% SnSe-60 mol% Cu_3SbSe_3

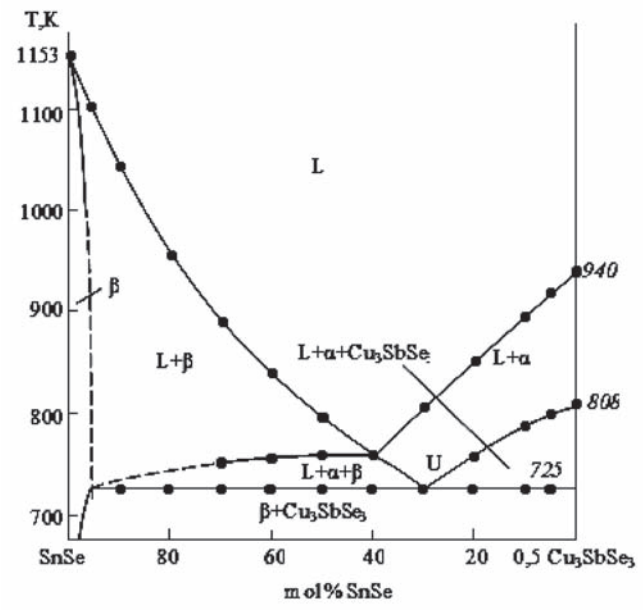

Fig. 2. Phase diagram of the SnSe-Cu_3SbSe_3 section

4. CONCLUSION

The SnSe-Cu_3SbSe_3 section is studied by means of the DTA and XRD methods and its phase diagram is constructed. It was established that the SnSe-Cu_3SbSe_3 is a nonquasibinary and stable below the solidus cross-section of the phase diagram of the Cu_2Se-SnSe-Sb_2Se_3 system.

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ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ Cu_2Se-SnSe-Sb_2Se_3 ПО РАЗРЕЗУ SnSe-Cu_3SbSe_3

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Аннотация. В работе приведены результаты исследования фазовых равновесий в квазитройной системе Cu_2Se-SnSe-Sb_2Se_3 по разрезу SnSe-Cu_3SbSe_3 методами дифференциального термического (ДТА) и рентгенфазового (РФА) анализов. Результаты РФА отожженных сплавов показало, что они являются двухфазными смесями исходных соединений. Это указывает на стабильность данного разреза ниже солидуса. На основании полученных данных ДТА построена фазовая диаграмма разреза SnSe-Cu_3SbSe_3. Этот разрез является квазистабильным сечением системы Cu_2Se-SnSe-Sb_2Se_3, но в целом неквазибинарен в силу инконгруэнтного характера плавления соединения Cu_3SbSe_3. В системе наблюдается растворимость на основе SnSe (β-фаза) с протяженностью ~3 мол.%. Ликвидус системы SnSe-Cu_3SbSe_3 состоит из двух ветвей, характеризующих первичную кристаллизацию β-фазы и твердых растворов на основе высокотемпературной модификации соединения Cu_2Se (α-фазы) по разрезу Cu_2Se-Sb_2Se_3. Ниже ликвидуса в интервале составов 0-30 мол.% SnSe наблюдаются термические эффекты относящиеся моновариантной перитектической реакции $L+\alpha \leftrightarrow Cu_3SbSe_3$. В ходе реакции формируется трехфазная область $L+\alpha+Cu_3SbSe_3$. В интервале составов 30-95 мол.% SnSe происходит совместная кристаллизация α- и β-фаз. Горизонталь при 725 К отвечает нонвариантной переходной реакции: $L+\alpha \leftrightarrow Cu_3SbSe_3+\beta$. Кристаллизация завершается образованием двухфазной смеси $Cu_3SbSe_3+\beta$.

Ключевые слова: система Cu_2Se-SnSe-Sb_2Se_3, сечение SnSe-Cu_3SbSe_3, фазовая диаграмма.

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