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**POLYTHERMAL SECTION SnSe–CuSbSe₂
OF PHASE DIAGRAM OF THE Cu₂Se–SnSe–Sb₂Se₃ SYSTEM**

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Phase equilibria in the Cu₂Se–SnSe–Sb₂Se₃ system were studied along the SnSe–CuSbSe₂ section by means of differential-thermal analysis and X-ray diffraction technique and its phase diagram was constructed. It was found that the SnSe–CuSbSe₂ section is quasibinary and refers to an eutectic type with limited solid solutions based on the starting compounds. The solubility based on SnSe and CuSbSe₂ is maximal at the eutectic temperature (700 K) and reaches 25 and 5 mol%, respectively.

Keywords: *Cu₂Se–SnSe–Sb₂Se₃ system, SnSe–CuSbSe₂ section, phase diagram.*

Introduction

Complex copper chalcogenides have attracted much attention thanks to their outstanding photoelectric, thermoelectric, non-linear optic and etc. properties [1–3]. On the other hand, these materials exhibit excellent mixed ionic conductivity with Cu⁺ ions which make them prospective candidates for elaborate ion-selective electrodes or solid-state electrolytes for different kind of electric batteries, sensors, displays, etc. [4, 5]. In particular, the Cu–Sb–Sn–X (X=S, Se) systems are of great interest for the development of new ecologically safe thermoelectric materials [6–8].

Taking this into account, we undertook a complex study of these systems on concentration planes Cu₂X–SnX–Sb₂X₃. This work presents the results of the study of the polythermal section SnSe–CuSbSe₂ of the quaternary Cu–Sb–Sn–Se system.

Tin monoselenide SnSe melts congruently at 1134 K [9] and crystallizes in the orthorhombic system, space group *Pcmn*, with following lattice parameters: $a = 4.46$, $b = 4.19$, $c = 11.57$; $Z = 4$ [10].

The CuSbSe₂ compound melts congruently at 750 K [11]. This compound has the diamond-like structure with Cu atoms occupied in the center of Se-formed tetrahedrons and crystallizes in the orthorhombic system, with space

group *Pnma* and lattice parameters at room temperature: $a = 6.467$, $b = 4.045$ and $c = 15.048$ Å; $Z = 4$ [12]. Recent studies have shown that ternary selenostibite CuSbSe₂ has the better photo-electrical conversion performance and appears to be a promising absorber material for thin-film solar cells due to its attractive optical and electrical properties, as well as earth-abundant, low-cost, and low-toxic constituent elements [13–15], as well as the compound SnSe exhibits exceptionally good thermoelectric properties at high temperatures above ~800 K, including a very low thermal conductivity [16, 17].

Experimental part

Materials and syntheses

The initial compounds SnSe and CuSbSe₂ were synthesized by melting of elementary components of high purity (99.999 %) in vacuumed ($\sim 10^{-2}$ Pa) quartz ampoules. The synthesis was carried out at temperatures 50°C higher than the melting points of the synthesized compounds. Further ampoules with tin selenide and ternary selenostibite were slowly cooled to room temperature. Differential thermal analysis and powder X-ray diffraction technique were employed to probe the phase-purity of the synthesized starting compounds SnSe and CuSbSe₂.

A series of SnSe–CuSbSe₂ alloys with compositions of 10, 20, 30, 40, 50, 60, 70, 80 and 90 mol% CuSbSe₂ 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 0.8–1 g, and then annealed at 675 K for 500 hours.

Methods

Studies of samples carried out by differential-thermal analysis (DTA) and powder X-ray diffraction (XRD) method.

The differential-thermal analysis was carried out in the temperature range from room temperature to 1200 K with a heating rate of 10 K/min 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 _{α 1}-radiation. The X-ray images were indexed using Topas V3.0 software Bruker.

Results and discussion

The phase diagram of the SnSe–CuSbSe₂ system was constructed based on DTA and XRD data (Table, Figure 1).

Results of DTA for SnSe–CuSbSe₂ alloys

Composition, mol % CuSbSe ₂	Thermal effects, K
0 (SnSe)	1153
10	970, 1070
20	800, 1000
30	700, 720, 950
40	700, 720, 900
50	700, 720, 890
60	700
70	700, 730
80	700, 740
90	700, 750
100 (CuSbSe ₂)	760

Fig. 1. Phase diagram of the SnSe–CuSbSe₂ system.

It was found that the SnSe–CuSbSe₂ section is quasibinary and refers to a eutectic type with limited solid solutions based on the starting compounds. The solubility based on SnSe and CuSbSe₂ at the room temperature reaches ~22 and 3 mol%, respectively. Liquidus of this system consists of two branches, which characterize primary crystallization of the solid solutions based on SnSe (β -phase) and CuSbSe₂ (γ -phase). The eutectic has a composition of 65 mol% CuSbSe₂ and crystallizes at 700 K. An extension of the β -phase (25 mol %) and γ -phase (5 mol%) is maximal at the eutectic temperature. The nature of the thermal effects at 720 K for alloys with a composition of 30–50 mol% CuSbSe₂ was not established. It can be assumed that these thermal effects relate to the peritectic reaction of formation of an intermediate compound with a very narrow temperature range of existence (700–720 K).

The XRD data confirm the plotted phase diagram. As can be seen from Figure 2, the XRD data of the SnSe–CuSbSe₂ alloys 3–6 confirms their biphasic composition. The XRD patterns of these alloys consist of a set of reflection lines of the β -phase (SnSe) and γ -phase (CuSbSe₂). The XRD patterns of the alloy 2 is similar to SnSe.

Fig. 2. XRD patterns for some alloys of the SnSe-CuSbSe₂ system at room temperature: 1 – SnSe, 2 – 20 mol% CuSbSe₂, 3 – 30 mol% CuSbSe₂, 4 – 50 mol% CuSbSe₂, 5 – 60 mol% CuSbSe₂, 6 – 80 mol% CuSbSe₂, 7 – CuSbSe₂.

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Cu₂Se–SnSe–Sb₂Se₃ SİSTEMİNİN FAZA DİAQRAMININ SnSe–CuSbSe₂ POLİTERMİK KƏSİYİ**E.N.İsmayılova, G.M.Şükürova, E.R.Əliyeva, L.F.Məşədiyeva**

Cu₂Se–SnSe–Sb₂Se₃ üçlü sistemi differensial termiki və rentgen faza analizi metodları ilə SnSe–CuSbSe₂ kəsiyi üzrə tədqiq edilmiş və kəsiyin faza diaqramı qurulmuşdur. Müəyyən edilmişdir ki, SnSe–CuSbSe₂ kəsiyi kvazibinar olmaqla evtektik tipə aiddir. Sistemdə ilkin komponentlər əsasında məhdud bərk məhlul sahələri mövcuddur. SnSe və CuSbSe₂ əsasında həllolma evtektik temperaturda (700 K) maksimaldır və müvafiq olaraq 25 və 5 mol% uyğun gəlir.

Açar sözlər: Cu₂Se–SnSe–Sb₂Se₃ sistemi, SnSe–CuSbSe₂ kəsiyi, faza diaqramı.

**ПОЛИТЕРМИЧЕСКИЙ РАЗРЕЗ SnSe–CuSbSe₂ ФАЗОВОЙ ДИАГРАММЫ СИСТЕМЫ
Cu₂Se–SnSe–Sb₂Se₃****Э.Н.Исмаилова, Г.М.Шукюрова, Э.Р.Алиева, Л.Ф.Машадиева**

Фазовые равновесия в системе Cu₂Se–SnSe–Sb₂Se₃ изучены вдоль разреза SnSe–CuSbSe₂ методами дифференциально-термического и рентгенфазового анализов. Построена фазовая диаграмма разреза SnSe–CuSbSe₂ и установлено, что это сечение является квазибинарным и относится к эвтектическому типу с ограниченными твердыми растворами на основе исходных соединений. Растворимость на основе SnSe и CuSbSe₂ является максимальной при эвтектической температуре (700 К) и достигает 25 и 5 мол%, соответственно.

Ключевые слова: система Cu₂Se–SnSe–Sb₂Se₃, разрез SnSe–CuSbSe₂, фазовая диаграмма.