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REFINEMENT OF THE PHASE DIAGRAM OF THE SnSe - Sb_2Se_3 SYSTEM

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Abstract: *Considering the inconsistency of the available literature data on phase equilibria in the SnSe - Sb_2Se_3 system, the issue was re-examined by differential thermal analysis and X-ray diffraction technique. A new, refined version of the phase diagram was constructed. It was found that the ternary compound $Sn_2Sb_2Se_5$ and the intermediate γ-phase with a homogeneity region of 48-60 mol% Sb_2Se_3 are formed in the system, which melting with decomposition by peritectic reactions at 598°C ($Sn_2Sb_2Se_5$) and 560°C (γ-phase). This area includes stoichiometric compositions of ternary compounds $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$. A comparative analysis of the results obtained with literature data was carried out.*

Keywords: *SnSe - Sb_2Se_3 system, phase diagram, eutectic, tin and antimony selenides.*
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Introduction

Compounds formed in the $A^{IV}X - B^{V}_2X_3$ (A^{IV}- Sn, Pb; B^{V}-Sb, Bi; X-Se, Te) quasi-binary systems are promising functional materials. In particular, compounds of the $A^{IV}B^{V}_2Te_4$, $A^{IV}B^{V}_4Te_7$, $A^{IV}B^{V}_6Te_{10}$ types with tetradimite-like layered structure had higher thermoelectric parameters as compared to $A^{IV}Te$ and B_2Te_3 binary compounds [1-5]. In addition, recent studies show that most of these compounds are three-dimensional topological insulators and can be used in spintronics [6-9]. Alloys of the Sn – Sb – Se system are of interest in thermoelectric materials in both crystalline and glass formed states [10–12].

The development of methods for synthesis of new complex phases was based on phase equilibriia data in the corresponding systems [13-16].

The development of methods for synthesis of new complex phases is based on data on phase equilibria in the corresponding systems [13-16An analysis of the literature data [17-19] on the phase equilibria in the SnSe - Sb_2Se_3 quasi-binary system shows that they are of controversial nature. According to [17], it was characterized by the formation of one congruently melting ternary compound $Sn_2Sb_6Se_{11}$ (563°C). Two eutectics were detected in the system which crystallized at 553° C and 550° C and had compositions of 54.5 and 61.5 mol % Sb_2 Se_3, respectively. According to [18], two compounds were formed in the system: $Sn_2Sb_6Se_{11}$ with congruent melting at 561°C, and $Sn_2Sb_2Se_5$ – with incongruent melting at 563°C. Solid solutions based on both crystal modifications of SnSe were detected. The authors of [19] showed a formation of a single ternary compound, $SnSb_2Se_4$ in the SnSe - Sb_2Se_3 system. This compound crystallized in an orthorhombic structure (Sp.Gr. Pnnm) with lattice parameters a = 26.610 Å, b = 21.066 Å and s = 4.0423 Å [20]. According to [21], the $Sn_2Sb_2Se_5$ compound also had an orthorhombic structure (Sp.Gr. Pnnm, a = 35.16 Å, b = 25.96 Å, c = 4.14 Å). We have not found data on the crystal structure of a compound with the composition $Sn_2Sb_6Se_{11}$.

In this paper, we present a new refined variant of the T - x diagram of the SnSe - Sb_2Se_3 quasi-binary system and the comparative analysis with literature data attached.

The starting compounds of the reviewed system were explored in detail. The SnSe compound melts congruently at 880°C [22] and crystallizes in an orthorhombic structure (Sp.Gr. Pcmn) with lattice parameters a = 4.44175, b = 4.15096, c = 11.49417 [23]. The Sb_2Se_3 compound also melts congruently at 600°C [22] and crystallizes in an orthorhombic structure (Sp.Gr. Pnma, a = 11.7808 Å, b = 3.9767 Å and c = 11.6311 Å [24].

Experimental part

Materials and synthesis

Compounds SnSe and Sb_2Se_3 were synthesized using high-purity antimony (Sb-00002, 99.999%), tin (Sn-00005, 99.999%), selenium (Se-00002, 99.999%) purchased from Evochem Advanced Materials GMBH (Germany). Stoichiometric mixtures of elementary components were placed in a quartz ampoule which was evacuated to a residual pressure of ~ 10^{-2} Pa. The synthesis of SnSe was carried out in a dual-zone inclined furnace. The temperature of the lower "hot" zone was 930 °C, and that of the upper "cold" zone was up to 630 °C which was somewhat lower than the boiling point of selenium (685 °C) [25]. Sb_2Se_3 was synthesized in a one-zone furnace at 650°C.

The identity of both synthesized compounds was controlled by DTA and XRD. The obtained melting points and crystal lattice parameters within deviation (± 2 °C and ± 0.0003 Å) were in good agreement with the literature data.

Alloys of the studied system were prepared by fusion of the starting compounds at various ratios in evacuated quartz ampoules followed by homogenizing annealing at 450 °C for ~ 500 h and quenching into cold water.

Analysis

For the analysis of samples, differential thermal analysis (DTA) and X-ray powder diffraction (XRD) were used. DTA was performed using the NETZSCH 404 F1 Pegasus system with the heating rate reaching 10 °C min^{-1}. Temperatures of thermal effects were taken mainly from heating curves. Accuracy of temperature measurement was ± 2°C.

Powder X-ray diffraction patterns were obtained on Bruker D2 Phaser diffractometer (Cu $K\alpha_1$ radiation) at a room temperature. The X-ray images were indexed using Topas V3.0 software Bruker.

Results and its discussion

Results of XRD of annealed samples are shown in Fig. 1. As can be seen, samples containing 33.3; 50 and 60 mol. % Sb_2Se_3 had diffraction patterns that differed from original components. On the other hand, samples containing 50 and 60 mol.% Sb_2Se_3 had the same qualitatively diffraction patterns. This confirms the existence of individual phases with compositions $Sn_2Sb_2Se_5$ $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$ and shows that the latter two are isostructural to be within the homogeneity region of some intermediate phase of variable composition.

The diffraction patterns of samples containing 20 and 80 mol.% Sb_2Se_3 were two-phase mixtures of SnSe + $Sn_2Sb_2Se_5$ and $Sn_2Sb_6Se_{11}$ + Sb_2Se_3, respectively. A comparison of diffraction patterns with published data [18, 20, 21] shows that they were identical to the known $Sn_2Sb_2Se_5$ and $SnSb_2Se_4$ compounds. Types and parameters of crystal lattices of intermediate phases were determined on the basis of the powder diffractograms:

$Sn_2Sb_2Se_5$: Sp.Gr. Pbnm a = 35.08(28) Å, b = 25.87(22) Å, c = 4.09 (6) Å.
$SnSb_2Se_4$: Sp.Gr..Pnnm a =26.605 (25) Å, b =21.049 (20) Å, c = 4.0385 (5) Å.

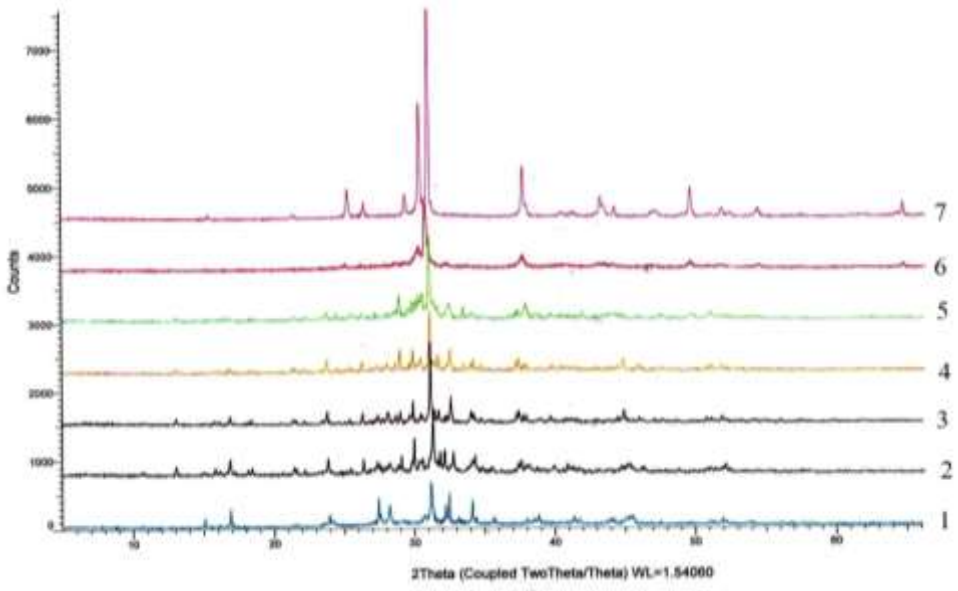

Fig. 1. X-ray powder diffraction patterns for alloys of the SnSe - Sb_2Se_3 system.1- Sb_2Se_3; 2- 80 mol% Sb_2Se_3; 3- 60 mol% Sb_2Se_3; 4- 50 mol% Sb_2Se_3; 5- 33.3 mol% Sb_2Se_3; 6- 20mol% Sb_2Se_3; 7-SnSe

The powder diffraction pattern (Fig. 2) of a sample with a composition of 60 mol% Sb_2Se_3 ($Sn_2Sb_6Se_{11}$) was also completely indexed based on the crystallographic data of $SnSb_2Se_4$: a = 26.604 (25), b = 21.068 (25), c = 3.8265 (5).

A comparison of crystal lattice parameters of phases with the $SnSb_2Se_4$ и $Sn_2Sb_6Se_{11}$compositions shows that increase of the Sb content led to a significant decrease in the parameter c which was due to the crystallographic radii of Sn^{2+} (1.02 Å) [26] and Sb^{3+} (0.76 Å) [27]

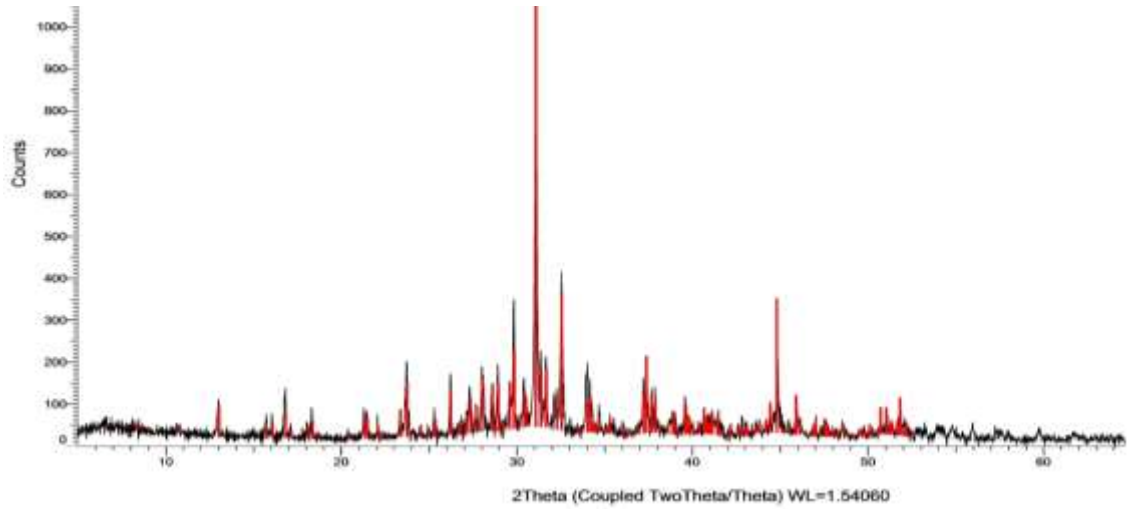

Fig. 2 Powder XRD pattern for the alloy with composition 60 mol% Sb_2Se_3 ($Sn_2Sb_6Se_{11}$). Red lines – data of [20] for the $SnSb_2Se_4$ compound.

A phase diagram of the SnSe-Sb_2Se_3 system was constructed based on the DTA results with due regard for RFA data (Fig. 3). As can be seen from the Fig.3, the system is quasibinary and has two intermediate phases that decompose according to the peritectic reaction. The compound $Sn_2Sb_2Se_5$ crystallizes at 598 °C according to the

$$L + \alpha' \leftrightarrow Sn_2Sb_2Se_5$$

reaction. (α′ is a solid solution based on a high-temperature modification of SnSe).

The second intermediate phase (γ) had a wide (48-60 mol.% Sb_2Se_3) region of homogeneity and crystallized at 560 °C by

$$L + Sn_2Sb_2Se_5 \leftrightarrow \gamma$$

Compositions of peritectic points p_1 and p_2 were 40 and 65 mol.% Sb_2Se_3, respectively.

An eutectic with coordinates 72 mol.% Sb_2Se_3 and 545 °C was found in the system. Based on both initial components, there were limited regions of solid solutions (α′, α- and β-phases).

Thermal effects reflecting the phase transition in SnSe-based solid solutions were not found on the DTA curves. Apparently, these effects overlap with more intense peaks of the peritectic reaction (598 °C).

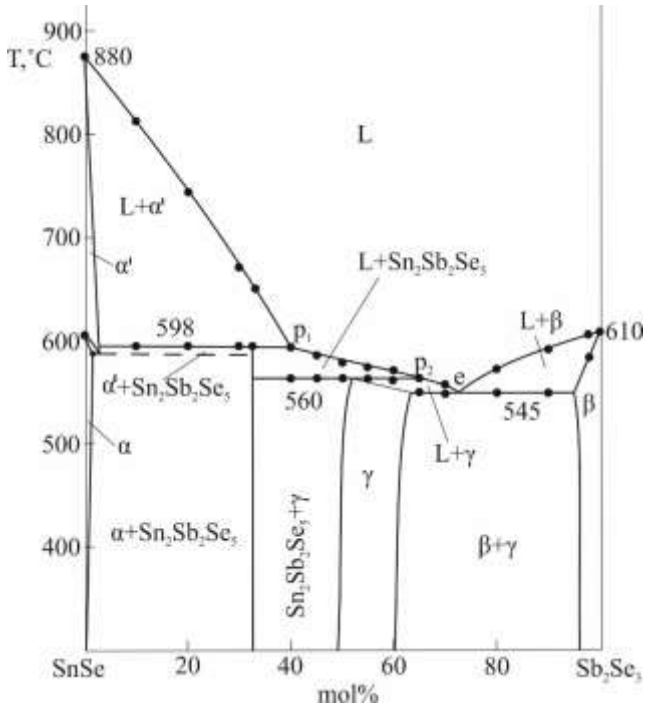

Fig. 3. Phase diagram of the SnSe- Sb_2Se_3 system

The T - x diagram differed significantly from the results of [17-19]. In contrast to the data of these works, all three compounds previously indicated in the literature are reflected in Fig. 3. We found that phases $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$ were isostructural within the homogeneity region of the γ phase which melts incongruently. The presence of a distectic point with a composition of 60 mol% Sb_2Se_3 ($Sn_2Sb_6Se_{11}$) indicated in [17, 18] was not confirmed by us. In addition, according to our data, the temperature of the peritectic reaction of the formation of the $Sn_2Sb_2Se_5$ compound is 598°C, which is 35°C higher than that indicated in [18]. There are also discrepancies in the composition of the peritectic (p_1) and eutectic (e) points.

Conclusion

A new scheme of phase equilibria in the quasi-binary SnSe - Sb_2Se_3 system was obtained to differ from those previously reported in the literature [17-19]. According to our data, this system is characterized by the formation of two intermediate phases, melting with decomposition by peritectic reactions at 598°C ($Sn_2Sb_2Se_5$) and 560°C (γ-phase). The latter has a wide homogeneity region (48-60 mol% Sb_2Se_3), which includes the ternary compounds $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$ previously mentioned in the literature.

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SnSe-Sb_2Se_3 SİSTEMİNİN FAZA DİAQRAMININ DƏQİQLƏŞDİRİLMƏSİ

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Ədəbiyyat məlumatlarının ziddiyyətli olmasını nəzərə alaraq SnSe-Sb_2Se_3 sistemində faza tarazlığı DTA və RFA üsulları ilə təkrar tədqiq edilmişdir. Müəyyən edilmişdir ki, sistemdə $Sn_2Sb_2Se_5$ birləşməsi və 48-60 mol% tərkibdə homogenlik sahəsində aralıq γ-faza əmələ gəlir və hər iki faza peritektik reaksiya üzrə parçalanmaqla əriyir. Əvvəllər ədəbiyyatda qeyd olunan $SnSb_2Se_4$ və $Sn_2Sb_6Se_{11}$ üçlü birləşmələri stexiometrik tərkibdə bu sahədə kristallaşırlar. Alınan nəticələrin ədəbiyyat məlumatları ilə müqayisəli təhlili aparılmışdır.

***Acar sözlər**: SnSe - Sb_2Se_3 sistemi, faza diaqramı, evtektika, qalay və sürmə selenidləri, bərk məhlullar*

УТОЧНЕНИЕ ФАЗОВОЙ ДИАГРАММЫ СИСТЕМЫ SnSe - Sb_2Se_3

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Учитывая противоречивость имеющихся литературных данных, фазовые равновесия в системе SnSe - Sb_2Se_3 повторно изучены методами ДТА и РФА, построен новый вариант T-x диаграммы. Установлено, что в системе образуются тройное соединение $Sn_2Sb_2Se_5$ и промежуточная γ-фаза с областью гомогенности 48-60 мол% Sb_2Se_3, плавящихся с разложением по перитектическим реакциям при 598 ℃ ($Sn_2Sb_2Se_5$) и 560 ℃ (γ-фаза). Эта область включает стехиометрические составы ранее указанных в литературе тройных соединений $SnSb_2Se_4$ и $Sn_2Sb_6Se_{11}$. Проведен сравнительный анализ полученных результатов с литературными данными.

***Ключевые слова**: система SnSe - Sb_2Se_3, фазовая диаграмма, эвтектика, селениды олова и сурьмы, твердые растворы.*