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PHASE DIAGRAM OF THE $SnSb_4Te_7$-$SnBi_4Te_7$ SYSTEM

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Abstract. Phase equilibria in the $SnSb_4Te_7$-$SnBi_4Te_7$ system were experimentally investigated by means of the differential thermal analysis and powder X-ray diffraction technique. It was be shown that the studied system is non-quasibinary due to the incongruent melting of the starting compounds, but stable in the subsolidus. The system is characterized by the formation of a continuous series of solid solutions with tetradimite-like hexagonal structure. The crystal lattice parameters of solid solutions are the linear function of the composition.

Keywords: *$SnSb_4Te_7$-$SnBi_4Te_7$ system, phase equilibria, solid solutions, tetradimite-like structure, tin-bismuth-antimony tellurides.*

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1. Introduction

Development of the using of the effective thermoelectric materials for thermal energy conversion into electricity is one of the most important problems of modern materials science. Those materials should possess three important characteristics: high electrical conductivity, low thermal conductivity, and high Seebeck coefficient (Kanatzidis, 2001; Shevelkov, 2008; Gayner *et al.*, 2016). The best ratio of these values is found in the bismuth telluride-based alloys with the tetradimite-like structure, particularly, in compounds with the general formulas $SnB^{IV}_2Te_4$ and $SnB^{IV}_4Te_7$ (X = Sb and Bi) (Tesfaye *et al.*, 2018; Kanatzidis, 2017; Ahluwalia, 2016; Gao *et al.*, 2013).

Recent studies have shown that single crystals of these layered compounds have unusual properties due to the realization on their surface a special quantum state called topological insulator (TI). Thanks to these properties, TIs are promising for use in quantum computers and spintronics (Pacile *et. al.*, 2018; Okuda *et al.*, 2013; Vergniory *et al.*, 2015; Eremeev *et al.*, 2012; Niesner *et. al.*, 2014).

Search and development of the physicochemical methods of preparation of new multi-component compounds and phases based on them require studying the phase equilibria and thermodynamic properties of the corresponding systems (Babanly *et al.*, 2017a; Imamaliyeva *et al.*, 2018). On the other hand, systems composed by formuleanaloges are of particular interest, owing probability of the formation of wide areas of solid solutions in them. Solid-phase equilibria and thermodynamic properties of the $SnTe – Bi_2Te_3$ (Sb_2Te_3) –Te, $PbTe – Bi_2Te_3$ – Te systems using EMF measurements were studied in (Babanly *et al.*, 2011a; Babanly *et al.*, 2011b; Guseinov *et al.*, 2017).

In present work, the phase equilibria of the $SnSb_4Te_7$-$SnBi_4Te_7$ system were investigated and constructed, in order to obtain solid solutions.

According to (Elagina *et al.*,1959), the SnTe-Sb_2Te_3 system forms only one ternary compound $SnSb_2Te_4$, which melts incongruently at 603°C. However, in other works (Vergniory *et al.,* 2015; Popescu & Chalcogenides, 2001) it was suggested that the SnTe-Sb_2Te_3 system formed $SnSb_4Te_7$ compound in addition to the $SnSb_2Te_4$. Theoretical calculations on the crystal structure of the $SnSb_4Te_7$ compound were also given: Sp. gr: P-3m1, a = 4.37 Å, c = 23.79 Å.

Re-investigation of the SnTe -Sb_2Te_3 system by RFA (Seidzade *et al.,* 2018) confirmed the existence of $SnSb_2Te_4$ and $SnSb_4Te_7$ compounds.

In the SnTe-Bi_2Te_3 system, three ternary compounds $SnBi_2Te_4$, $SnBi_4Te_7$ and $SnBi_6Te_{10}$ with incongruent melting by peritectic reactions at 600, 589 and 582°C, respectively, were revealed (Karpinski *et al.,* 2003). The parameters of the hexagonal lattice of $SnBi_4Te_7$ are: Sp. gr. P-3m1, a = 4.39 Å, c = 23.98 Å (Kuznetsov *et al.,* 2001).

2. Experimental

2.1. Materials

The initial binary compounds SnTe, Sb_2Te_3, and Bi_2Te_3 were synthesized by the fusion of elementary components of high purity. Synthesis was carried out in evacuated (~ 10^{-2}Pa) quartz ampoules at 700-800 ° C, followed by slow cooling in the off-furnace mode. Bismuth, antimony, tin, tellurium (99.995%) were purchased from Alfa Aesar. The identification of the synthesized compounds was controlled by differential thermal analysis (DTA) and X-ray phase analysis (XRD). Obtained values of peritectic decomposition temperatures and crystal lattice parameters (Table) are in good agreement with data of (Vergniory *et al.,* 2015; Kuznetsov *et al.,* 2001).

By melting of stoichiometric amounts of binary compounds at 700 ° C the ternary compounds $SnSb_4Te_7$ and $SnBi_4Te_7$, as well as intermediate alloys of the studied systems were synthesized. The received alloys (0.5 g each) were quenched by ejecting ampoules from the furnace (700°C) into cold water and then annealed at 450°C (500 h) to achieve the state closest to equilibrium.

2.2. Methods

Heating curves were recorded on NETZSCH 404 F1 Pegasus differential scanning calorimeter. The DTA measurement was performed between room temperature and 700°C with a heating and cooling rate of 10°C·min^{-1}. The temperatures of thermal effects were determined mainly from the heating curves. The accuracy of the temperature measurement was within ± 2°.

The data of the powder diffraction of X-rays (PXRD) were received from the Bruker D2 Phaserdiffractometer with Cu $K_{\alpha 1}$ (λ = 1.54056 Å) radiation at the room temperature. The unit cell parameters of initial compounds and intermediate alloys were calculated by indexing of powder patterns using Topas V3.0 software. The accuracy of the lattice parameters is given in parentheses (Table).

3. Results and discussion

X-ray powder diffraction patterns of the starting compounds and some intermediate alloys of the $SnSb_4Te_7$-$SnBi_4Te_7$ system are shown in Fig. 1.

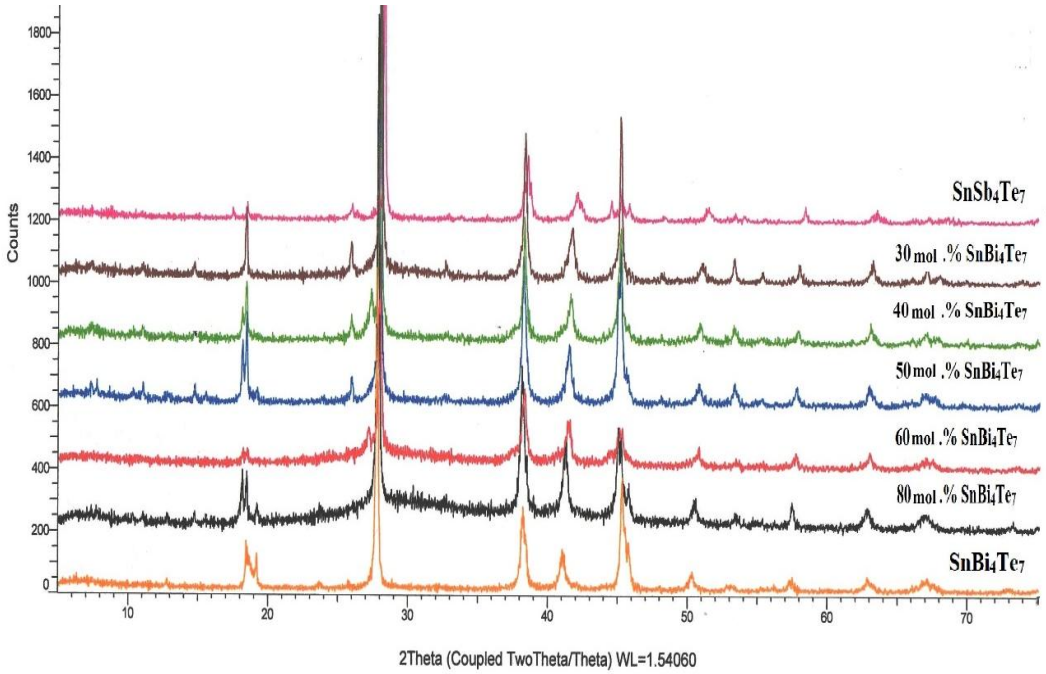

Figure 1. XRD powder patterns of some alloys of the $SnSb_4Te_7$-$SnBi_4Te_7$ system

As can be seen, all samples have qualitatively identical diffraction patterns characteristic for tetradimite-like structures with some slight shift of reflection lines shift that is typical for substitutional solid solutions

Based on the DTA data (Table), a T-x diagram of the $SnSb_4Te_7$-$SnBi_4Te_7$ system was plotted (Fig. 2).

Table. Some properties of the starting compounds and solid solutions in the $SnSb_4Te_7$-$SnBi_4Te_7$ system

Composition, mol. %	**Thermal effects, °C**	**Hexagonal parameters of the crystal lattice, Å (Sp.gr.: P-3m1)**
$SnSb_4Te_7$	600; 615	*a*=4,3128(4); *c*=23.796(3)
20	594-598; 614	*a*=4,3362(5); *c*=23.842(4)
40	591-596; 611	*a*=4,3408(4); *c*=23.881(4)
60	589-595; 608	*a*=4,3581(4); *c*=23.925(4)
80	587-595; 608	*a*=4,3773(5); *c*=23.951(3)
$SnBi_4Te_7$	586; 600	*a*=4,3926(4); *c*=23.982(3)

According to the XRD data of two samples with 40 and 80 mol% $SnSb_4Te_7$ quenched from 700°C (region L+γ in Fig.2), the $SnSb_2Te_4$ phase (solid solutions $SnSb_{2-x}Bi_xTe_4$) is crystallized from the melts. Analysis of powder diffractograms showed that they, in contrast with annealed alloys, contain a phase with a $SnSb_2Te_4$ structure.

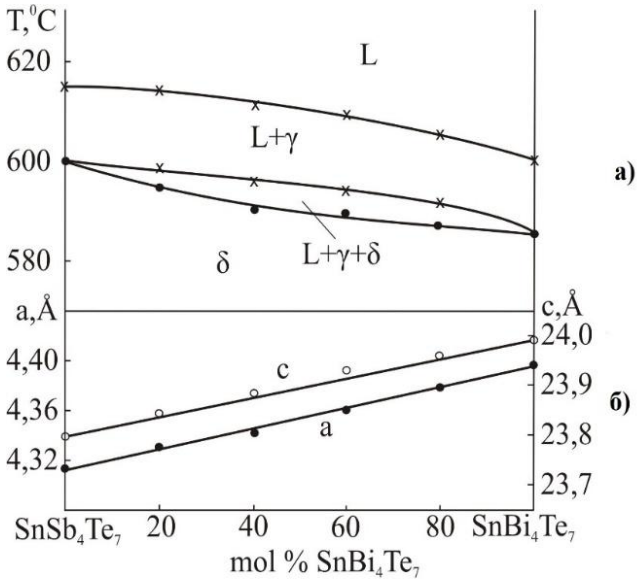

Figure 2. Phase diagram (a) and the dependence of the lattice parameters (b) on composition for the alloys of the $SnSb_4Te_7$-$SnBi_4Te_7$ system.

The two interfaced curves below the liquidus reflect the monvariant peritectic equilibrium L + γ ↔ δ. Since the total composition of all three interacting phases (L, γ, δ) is on the plane of the $SnSb_4Te_7$-$SnBi_4Te_7$ section, this peritectic reaction is completed by the simultaneous disappearance of both initial phases (L, γ) and the formation of a homogeneous δ phase.

By identifying powder diffractograms, the parameters of the crystal lattices of solid solutions were determined (Table) and graphs of the dependence of the lattice parameters on the composition were constructed (Fig. 2, b). It can be seen that the parameters of the hexagonal lattice have a linear dependence on the composition of the compounds, i.e. obey Vegard's rule.

The presented results on phase equilibria in the system can be used to obtain $SnSb_{2-x}Bi_xTe_4$ solid solutions of a given composition.

4. Conclusion

New experimental data on the phase equilibria in the $SnSb_4Te_7$-$SnBi_4Te_7$ system were obtained. It was established that the system is non-quasibinary due to the incongruent melting of the starting compounds, but stable below solidus and is characterized by the formation of a continuous series of solid solutions with tetradimite-like layered structure. The lattice parameters of solid solutions, which linearly depend on the composition, are determined.

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