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Phase diagram of the YbTe–Sb_2Te_3–Bi_2Te_3 quasi-ternary system

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ABSTRACT

The phase equilibria in the YbTe–Sb_2Te_3–Bi_2Te_3 quasi-ternary system were investigated by means of differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscope with energy dispersive analysis (SEM-EDS) techniques. Two isothermal sections of the system at 300 and 850 K, the projection of the liquidus surface as well as several isopleth sections were experimentally carried out. The boundary quasi-binary sections YbTe–Bi_2Te_3 and YbTe–Sb_2Te_3 restudied and existence of the four ternary compounds $YbSb_2Te_4$, $YbSb_4Te_7$, $YbBi_2Te_4$ and $YbBi_4Te_7$ reported earlier were not confirmed. Along the boundary Sb_2Te_3–Bi_2Te_3 system the existence of continuous solid solubility field with the tetradymite type crystal structure was revealed at 300 and 850 K.

1. Introduction

Numbers of binary and ternary chalcogenides of heavy *p*- and rare-earth elements have been extensively studied in the former years. Due to their physical properties they form a good base for design of novel high-performance materials, including thermoelectrics and topological insulators [1–4]. Among these systems tellurides of rare-earth as well as antimony or bismuth ones takes important place [3–5]. Recently, $YbSb_2Te_4$ have been proposed as a new member of thermoelectric materials [5].

The purpose of the present work is to determine phase equilibria in the YbTe–Sb_2Te_3–Bi_2Te_3 quasi-ternary system in order to obtain phase relationships and to provide more accurate experimental data for the preparing pure and high quality materials.

Initial binary compounds of this system are very well studied. YbTe melts congruently at ~2000 K and crystallizes in the NaCl type cubic crystal structure, (space group *Fm*-3*m* with the unit cell parameters $a = 6.345$ Å [6,7]). Both Sb_2Te_3 and Bi_2Te_3 melt congruently at 893 and 858 K, and crystallize in the rhombohedral tetradymite structure type with the unit cell parameters: $a = 4.264$; $c = 30.458$ Å, $z = 9$ and $a = 4.395$; $c = 30.44$ Å, $z = 9$, respectively [8,9].

Also the boundary quasi-binary sections of the system were studied in detail.

The phase diagram of the Sb_2Te_3–Bi_2Te_3 system belongs to type I within the Roseboom's classification and characterized by formation of a continuous solid solution with the tetradymite structure type [8].

Some investigations on the phase diagram of the Yb–Sb–Te system have been reported in Refs. [10,11]. Maksudova et al. [10] claimed that the YbTe–Sb_2Te_3 is a quasi-binary system includes two ternary compounds $YbSb_2Te_4$ and $YbSb_4Te_7$; the former melts peritectally at 923 K, whereas the latter melts congruently at 943 K. Both compounds reported in the Th_3P_4 type cubic structure with the following lattice parameters: $a = 10.4$ Å and $a = 10.625$ Å, respectively [10]. A more detailed investigation of the Yb–Sb–Te ternary system was later carried out by Aliev and co-authors [11]. Both $YbSb_2Te_4$ and $YbSb_4Te_7$ ternary compounds were also confirmed.

More recently, Guloy and co-authors [5] synthesized the $YbSb_2Te_4$ by high energy ball milling and for this compound they suggested layered rhombohedral structure similar to the structure of $PbSb_2Te_4$, which is a 21-layer derivative of the tetradymite structure [3]. However, this structure was not confirmed by any kind of structural investigation and crystallographic data were not reported. In addition, it was revealed that $YbSb_2Te_4$ is perspective thermoelectric material; the dimensionless thermoelectric figure of merit almost reaches 0.5 at 510 K [5].

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In our previous work [12] we report the fragment of the phase diagram of YbTe–Sb_2Te_3 system for 0–25 mol% YbTe. It is shown that the solubility limit for YbTe in Sb_2Te_3 is achieved at 15 mol% YbTe at 300 K and at 17.5 mol% YbTe at 855 K.

According to the literature [13–15], the YbTe–Bi_2Te_3 sub-system also contains two ternary compounds, namely $YbBi_2Te_4$ and $YbBi_4Te_7$. The former decomposes by a peritectic reaction at 873 K, whereas the latter melts congruently at 918 K [14]. Both compounds are reported to have a Th_3P_4 type cubic structure with the following lattice parameters: $a = 10.48$ Å and $a = 10.62$ Å, respectively [14].

2. Experimental

Antimony (99.999 mass%), bismuth (99.999 mass%), ytterbium (99.99 mass%) and tellurium (99.999 mass%) were used as starting materials. The binary compounds Sb_2Te_3 and Bi_2Te_3 were synthesized by melting stoichiometric amounts of the pure elements in sealed silica ampoules. The synthesis of YbTe was carried out in niobium tubes at 1400 K for 10–12 h. Then temperature of furnace cooled down to 750–800 K and annealed for about 500 h to achieve equilibrium. The purity of the synthesized compounds was checked by the differential thermal analysis (DTA) and X-ray diffraction analysis (XRD).

In order to verify the existence of the ternary compounds $YbSb_2Te_4$, $YbBi_2Te_4$, $YbSb_4Te_7$ and $YbBi_4Te_7$ we have synthesized them from elementary components and from pre-synthesized binary YbTe and Sb_2Te_3 or Bi_2Te_3 compounds according to the literature procedures [5,10,13]. But, unfortunately we could not identify these alloys as single phase. Even after annealing for about 1500 h, we observed two-phase in all samples.

Taking into account this problem we undertook the complete reinvestigation of the binary YbTe–Sb_2Te_3 and YbTe–Bi_2Te_3 sub-systems, as well as several isopleth sections in order to construct the complete phase diagram of the YbTe–Sb_2Te_3–Bi_2Te_3 system.

All alloys were prepared by melting the stoichiometric quantities of the pre-synthesized binary compounds in sealed niobium tubes under vacuum ($\sim 10^{-2}$ Pa) which were placed in evacuated fused-silica jackets. Most alloys heated up to 1200 K for about 10–12 h., and then the resulting melts were cooled down to 800–820 K and held at this temperature for ~1500 h in order to complete homogenization.

Differential thermal analysis (DTA), X-ray powder diffraction (XRD) and scanning electron microscope with energy dispersive analysis (SEM-EDS) were employed to analyze the samples. DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter. XRD analysis was done with the Bruker D8 ADVANCE diffractometer (Cu $K\alpha_1$ radiation). The microstructure and equilibrium compositions of the phases were determined by FEI Quanta™ 250 scanning electron microscope with Oxford Instruments energy dispersive X-ray spectrometer.

3. Results and discussion

The combined analysis of all our experimental data and the results found in the literature on the phase equilibria in the Sb_2Te_3–Bi_2Te_3 [8,9] system enabled us to build a self-consistent phase diagram of the YbTe–Sb_2Te_3–Bi_2Te_3 quasi-ternary system.

3.1. Quasi-binary border sub-systems

The phase diagrams of the both quasi-binary border subsystems YbTe–Sb_2Te_3 and YbTe–Bi_2Te_3 were constructed using the results of differential thermal analysis, X-ray diffraction technique and scanning electron microscopy with energy dispersive analysis (Fig. 1a and b). Apparently, the phase diagrams of these systems completely differentiate from those of reported in [10,13]. Both phase diagrams belong to eutectic type (type *V* within the Roseboom's classification) with the invariant points lying at 78 mol% Sb_2Te_3 and 860 K (e_1) and 85 mol% Bi_2Te_3 and 848 K (e_2), respectively. At the eutectic temperatures the solubility limit of YbTe in Sb_2Te_3 and Bi_2Te_3 (β-phase) are achieved at 18 and 13 mol%, respectively. The observed solubility of Sb_2Te_3 and Bi_2Te_3 in YbTe (α-phase) is extremely small (no more than ~1 mol%) in the both sub-system.

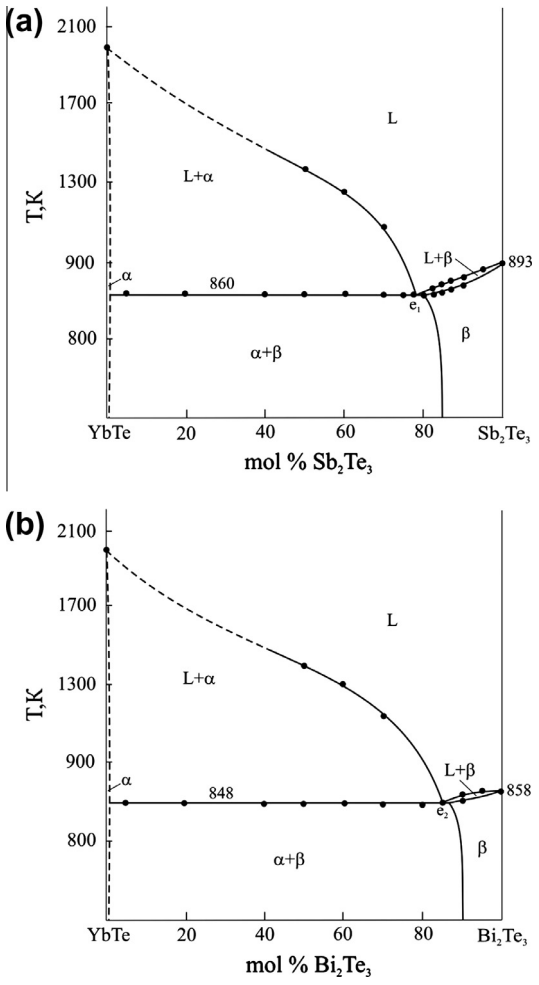

Fig. 1. Phase diagram of the quasi-binary systems YbTe–Sb_2Te_3 (a) and YbTe–Bi_2Te_3 (b).

X-ray analysis data confirm the phase diagrams of the above-mentioned systems; they are presented in Fig. 2a and b. Apparently, XRD patterns of all intermediate alloys, except those of containing more than 85 mol% Sb_2Te_3 (Fig. 2a) and 90 mol% Bi_2Te_3 (Fig. 2b), shows diffraction lines corresponding to the β-phase and α-phase. The XRD patterns for different YbTe content within the β-phase, looks like to pure phase (Sb_2Te_3 and Bi_2Te_3), but only differences are the slightly shifting of the peak positions, which showing solubility of YbTe. Upon increasing the YbTe content, the rhombohedral unit cell parameters slightly decreases.

Since in our previous work [13] we did not carry out the composition analysis of the second phase in the samples having more than 20 mol% YbTe, we labeled it δ-phase based on $YbSb_4Te_7$ according to the literature [10]. But, during the present investigation the detailed analysis of the more carefully prepared samples having more than 20 mol% YbTe showed that the composition of second phase is definitively YbTe.

The analysis of the XRD patterns of the alloys having 50 mol% and 33.3 mol% YbTe which are stoichiometric composition of the ternary samples $YbSb_2Te_4$, $YbBi_2Te_4$, $YbSb_4Te_7$ and $YbBi_4Te_7$, respectively, confirm that they are also two-phase corresponding to a α + β mixture instead of single phase. From the XRD patterns (Figs. 1 and 2), we are also did not find that any phase in this samples crystallize in the Th_3P_4 cubic structure type as it was previously reported in Refs. [10,14]. Moreover, as we shown above in Ref. [5], one of these compounds $YbSb_2Te_4$ was reported in the