PHASE RELATIONS IN THE Tl₅Te₃-Tl₉SbTe₆-Tl₉TbTe₆ SYSTEM

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Abstract. Phase relations in the Tl₃Te₃-Tl₉SbTe₆-Tl₉TbTe₆ system were experimentally studied by DTA, XRD technique and microhardness measurements. Several isopleth sections and isothermal section at 760 K, as well as projections of the liquidus and solidus surfaces were constructed. It is determined that the system is characterized by an unlimited solubility of components in the solid state.

Keywords: thallium-therbium tellurides, thallium-antimony tellurides, phase relations, projections of the liquidus, solid solutions, crystal structure.

1. Introduction

Chalcogenides of heavy p-elements are essential due to their important properties like thermoelectric, optical, etc. [1-3]. Moreover, some of such compounds have attracted scientific and technological interest as topological insulators [4, 5].

Rare earth elements tellurides are important materials for the fabrication of microbatteries, multilayer high-efficiency solar cells, etc. [6]. Moreover, ab-initio calculations [7] shown that LaBiTe₃ is a topological insulator and exhibits thermoelectric properties [8].

Thallium telluride, Tl₃Te₃, due to features of its crystal structure is suitable “matrix” for fabrication of novel complex materials. This compound crystallizes in tetragonal structure [9] (Sp.gr. I4/mcm, a = 8.930; c = 12.598 Å) with four formula units per unit cell (Fig. 1). The basic structural component of Tl₃Te₃ compound is octahedron with a thallium atom, Tl(2), in its center. These octahedra connected by vertices form a frame Tl₄Te₁₂, or (TlTe)₄. The other 16 thallium atoms, Tl(1) link octahedra along the c axis and form a unit cell Tl₁₆(TlTe)₄. B⁺⁺ (B²⁺-Sb, Bi) substitution for half of the Tl(2) atoms, resulting in the compounds Tl₉BTe₆ or Tl₁₆(Th₁⁺B²⁺₅ Te)₁₄ (I), while the replacement of all these thallium atoms by cations A⁺⁺ (A²⁺-Sn, Pb) is leading to formation of Tl₉ATe₃ or Tl₁₆(A²⁺Te)₁₄ (II).

Compounds of type (I) and (II) were detected during the experimental phase relations investigations of respective ternary systems [10-13]. These materials have good thermoelectric performance, whereas Tl₉BiTe₆ was found to have the highest ZT value (ZT =1.2 at 500 K) [14-16]. Furthermore, authors [17] report the discovery of Dirac-like surface states in Tl₉(Tl₁₋ₓSnₓ)Te₃ and Tl₉Te₃.

Earlier we presented new thallium lanthanide tellurides with composition Tl₉LnTe₆ (Ln-Ce, Nd, Sm, Gd, Tm, Tb), which were found to be ternary substitution variant of Tl₉Te₃ [18-20]. Moreover, it was shown that ytterbium does not form the compound Tl₉YbTe₆ [20, 21]. Latter, H. Kleinke et al. determined the crystal structure as well as magnetic and thermoelectric properties for a number of Tl₉LnTe₆-type compounds [22-25].

In order to obtain solid solutions based on Tl₅Te₃-potential thermoelectric material, we investigated phase equilibria of a number of systems including Tl₅Te₃ compound or its structural analogues [26-28]. We found that these systems are characterized by formation of continuous solid solutions.

The investigation performed in the present paper is aimed to study phase relations in the Tl₅Te₃-Tl₉SbTe₆-Tl₉TbTe₆ system.

Starting compounds are well known materials. Tl₅Te₃ and Tl₉SbTe₆ melt congruently at 723 K [29] and 800 K [10] while Tl₉TbTe₆ melts with decomposition by the peritectic reaction at 780 K [30]. The lattice parameters of Tl₉TbTe₆ and Tl₉SbTe₆ are the following: a = 8.871, c = 12.973, z = 2 [30]; a = 8.829, c = 13.001 Å, z = 2 [31].

According to the phase diagram of the Tl₅Te₃-Tl₉SbTe₆ system, this system is characterized by formation of continuous solid solution field with Tl₅Te₃-type structure [10].
2. Experimental

2.1. Materials and Syntheses

Thallium (granules, 99.999 %), antimony (granules, 99.999 %), terbium (powder, 99.9 %), and tellurium (broken ingots 99.999 %) were used as starting components. The surface of thallium was covered by oxide film, which was removed before use. These starting materials were weighed in proper molar ratio of the corresponding compound and put into silica tubes of about 20 cm in length and then were sealed under a vacuum of $10^{-2}$ Pa.

The synthesis of $\text{Tl}_5\text{Te}_3$ and $\text{Tl}_9\text{SbTe}_6$ compounds was carried out by heating in one-zone electric furnace at the 30–50°C above the melting point of the compounds followed by cooling in the switched-off furnace. Taking into account the results of [30, 32], the obtained intermediate ingot of $\text{Tl}_9\text{TbTe}_6$ was carefully powdered in agate mortar, pressed into pellet and annealed at 750 K within $\sim 1000$ h. In order to avoid reaction between the terbium and the silica ampoule, a thin layer of carbon was deposited on the inner side of quartz tube by the pyrolysis of acetone.

The purity of the synthesized starting compounds was checked by the differential thermal analysis (DTA) and X-ray diffraction (XRD).

Powder XRD pattern of the $\text{Tl}_5\text{SbTe}_6$ and $\text{Tl}_9\text{TbTe}_6$ were same as that of $\text{Tl}_5\text{Te}_3$. Their unit cell lattice parameters were practically equal with the [30, 31] (see Table).

The alloys of the $\text{Tl}_5\text{Te}_3$-$\text{Tl}_9\text{SbTe}_6$-$\text{Tl}_9\text{TbTe}_6$ system were prepared by melting from pre-synthesized compounds in evacuated silica ampoules. Taking into account the fact that an equilibrium state could not be obtained even after the long-time (1000 h) annealing [30, 32], after synthesis the samples were powdered, mixed, pressed into pellets and annealed at 700 K for $\sim 800$ h.

2.2. Methods

The samples were analyzed by X-ray diffraction and differential thermal analysis as well as microhardness measurements.

The XRD measurements of powdered specimen were recorded using a Bruker D8 diffractometer utilizing CuKα radiation within 2θ = 10–70°. DTA was performed using a NETZSCH 404 F1 Fegaus differential scanning calorimeter within room temperature and −1400 K at the heating rate of 10 K·min$^{-1}$. Microhardness measurements were done with a microhardnesmeter PMT-3, the typical loading being 20 g.

3. Results and Discussion

The combined analysis of experimental and literature data [10, 29, 30] enabled to construct the self-consistent diagram of the phase relations in the $\text{Tl}_5\text{Te}_3$-$\text{Tl}_9\text{BiTe}_6$-$\text{Tl}_9\text{TbTe}_6$ system (Table, Figs. 2-7).

The equilibrium phase diagrams of the $2\text{Tl}_5\text{Te}_3$-$\text{Tl}_9\text{BiTe}_6$ and $\text{Tl}_9\text{SbTe}_6$-$\text{Tl}_9\text{TbTe}_6$ system (Figs. 2a and 3a) are characterized by the formation of a continuous solid solutions ($d$) with $\text{Tl}_5\text{Te}_3$-type structure. However, these systems are non-quasi-binary due to peritectic melting of $\text{Tl}_9\text{TbTe}_6$. This leads to crystallization of unknown infusible X phase (presumably $\text{TlTbTe}_2$) in a wide composition range and formation of $L^+X$ and $L^+X+\delta$ phase areas. However, these areas are not experimentally fixed due to narrow temperature interval and shown by dashed line.

Microhardness measurements are in good agreement with $T$-$x$ phase diagram (Figs. 2b and 3b): curves have a flat maximum (Figs. 2b and 3b), which is typical for systems with continuous solid solutions.

The formation of continuous solid solutions in the studied systems is confirmed by XRD (Fig. 4). Apparently, powder diffraction patterns of starting compounds and intermediate alloys were same as that of $\text{Tl}_5\text{Te}_3$ with slight reflections displacement from one compound to another. The lattice parameters of solid solutions obey the Vegard’s law, i.e. depend linearly on composition.
Some properties of phases in the Tl₅Te₃-Tl₉SbTe₆-Tl₉TbTe₆ system

<table>
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<tr>
<th>Phase</th>
<th>Temperature of melting, K</th>
<th>Microhardness, MPa</th>
<th>Parameters of tetragonal lattice, Å</th>
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<td></td>
<td></td>
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</tr>
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<td>1100</td>
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</table>

The liquidus surface projection (Fig. 5). Liquidus of Tl₅Te₃-Tl₉SbTe₆-Tl₉TbTe₆ system consists of two fields of the primary crystallization of X-phase and δ-solid solutions. These fields are separated by ab curve that corresponds to the monovariant peritectic equilibrium L+X↔δ.

Isopleth sections of the Tl₅Te₃-Tl₉SbTe₆-Tl₉TbTe₆ system (Fig. 6). Figs. 6a-c show the isopleth sections 2Tl₅Te₃-[C], Tl₉SbTe₆-[A] and Tl₉TbTe₆-[B] of the Tl₅Te₃-Tl₉SbTe₆-Tl₉TbTe₆ system, where A, B and C are alloys from the respective boundary system.

As can be seen, over the entire compositions range of the Tl₉SbTe₆-[A] and Tl₅Te₃-[C] systems only δ-phase crystallizes from the melt.

According to the phase diagram of the Tl₉TbTe₆-[B] section, in the composition area ≈60 mol % Tl₉TbTe₆ the primary crystallization of the δ-phase occurs from the liquid phase. In the Tl₉TbTe₆-rich alloys the X-phase first crystallizes, then a monovariant peritectic equilibrium L+X ↔ δ takes place.

It should be noted that conode positions in two-phase area L+δ do not correspond to the cross section planes and continuously change with temperature. The conode positions at 760 K are shown in Fig. 7.
Fig. 4. XRD patterns for different compositions in the Tl$_5$Te$_3$-Tl$_9$TbTe$_6$ (patterns 1-3) and Tl$_9$TbTe$_6$-Tl$_9$SbTe$_6$ (patterns 3-5) systems: Tl$_5$Te$_3$ (1); 50 mol % Tl$_9$TbTe$_6$ (2); Tl$_9$TbTe$_6$ (3); 50 mol % Tl$_9$TbTe$_6$ (4) and Tl$_9$SbTe$_6$ (5).

Fig. 5. Projection of the liquidus and solidus (dashed lines) surface of the Tl$_5$Te$_3$-Tl$_9$TbTe$_6$-Tl$_9$SbTe$_6$ system: δ (1) and X phase (2). Dash-dot lines show the investigated sections.

Fig. 6. Polythermal sections Tl$_{10}$Te$_6$-[C], Tl$_9$SbTe$_6$-[A] and Tl$_9$TbTe$_6$-[B] of the phase diagram of the Tl$_5$Te$_3$-Tl$_9$TbTe$_6$-Tl$_9$SbTe$_6$ system.
4. Conclusions

A complete T-x-y diagram of the Tl₃Te₃-Tl₆SbTe₆-Tl₉TbTe₉ system, including the T-x diagrams of boundary systems Tl₃Te₃-Tl₆SbTe₆ and Tl₆SbTe₆-Tl₉TbTe₉, some isopleth sections, isothermal section at 760 K, as well as the liqudus and solidus surface projections were constructed. It is found that the system is characterized by an unlimited solubility of components in the solid state. The obtained experimental data can be used for the choice of composition of solution-melt and for determining of temperature conditions for growing crystals of δ-phase with a given composition.

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References


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ФАЗОВІ ВЗАЄМОДІЇ У СИСТЕМІ Tl₅Te₉-Tl₆SbTe₆-Tl₉TbTe₉

Анотація. За допомогою ДТА та РСА аналізування мікротвердості експериментально вивчено фазові взаємодії в системі Tl₅Te₉-Tl₆SbTe₆-Tl₉TbTe₉. Побудовані ізоплетені й ізотермічні перетини за 760 K, а також проекції ліквідусу і соцідус поверхонь. Встановлено, що система характеризується необмеженою розчинністю компонентів в твердому стані.

Ключові слова: талій-тербій теллуріди, талій-сурыма теллуріди, фазова відносність, проекції ліквідуса, твердий розчин, кристалічна структура.