Phase Equilibria in the Tl₄PbTe₃-Tl₉SmTe₆-Tl₉BiTe₆ Section of the Tl-Pb-Bi-Sm-Te System

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Abstract
Phase equilibria in the section Tl₄PbTe₃-Tl₉SmTe₆-Tl₉BiTe₆ of the Tl-Pb-Bi-Sm-Te system were determined by combination of differential thermal analysis, powder X-ray diffraction methods as well as microhardness measurements. The phase diagrams of the boundary systems Tl₄PbTe₃-Tl₉SmTe₆, Tl₉SmTe₆-Tl₉BiTe₆, isothermal section at 820 and 840 K, some isopleth sections and as well as liquidus and solidus surfaces projections, were plotted. Unlimited solid solutions, which crystallize in Tl₅Te₃ structure type were found in the system at the solidus temperatures and below.

Keywords: Thallium-lead telluride; thallium-samarium tellurides; thallium-bismuth tellurides; phase equilibria; liquidus and solidus surfaces; solid solutions

1. Introduction

Complex chalcogenides based materials of great interest for many years due to their functional properties such as optic, photoelectric, magnet, thermoelectric et al.¹⁻³ Some of these materials exhibit properties of topological insulators and can use in spintronic devices.⁴⁻⁶ Furthermore, a number of papers present the results of the study of interactions of the rare-earth elements with heavy elements chalcogenides.⁷⁻⁹

Tl₅Te₃ compound crystallizes in tetragonal structure (Sp.gr.I₄/mcm, a = 8.930; c = 12.598 Å), ¹⁰,¹¹ and has a number of ternary substitutional analogs of Tl₄AIVTe₃ and Tl₉BVTe₆ -type (AIV-Sn, Pb; BV-Sb, Bi),¹²⁻¹⁴ which also possess a good thermoelectric performance.¹⁵,¹⁶ Moreover, authors¹⁷ found the Dirac-like surface states in the [Tl₁Ⅲ][Tlavage₂]₃ (Tl₅Te₃) and its non-superconducting tin-doped derivative [Tl₁Ⅲ][Tl₁Ⅱ-SnP]₃Te₃.

A new thallium lanthanide tellurides of Tl₉LnTe₆ -type (Ln- Ce, Nd, Sm, Gd, Tb, Tm) were found to be a new structural analog of Tl₅Te₃,¹⁸,¹⁹ H. Kleinke and co-workers ²⁰⁻²² confirmed the results of the studies,¹⁸,¹⁹ and determined the thermoelectric and magnetic properties for a number Tl₅LnTe₆-type compounds.

The development of the novel preparative methods for direct synthesis of functional materials requires to provide an accurate study of phase relations and plot the phase diagram.

Early, we presented the results of a study of phase relations for a number of systems including the Tl₅Te₃ compound or its structural analogs.²³⁻²⁵ The formation of unlimited solid solutions was shown for these systems.

In this paper, we continue to study similar systems and present the experimental results on phase equilibria in the Tl₄PbTe₃-Tl₉SmTe₆-Tl₉BiTe₆ section of the Tl-Pb-Bi-Sm-Te system.

The initial compounds of above-mentioned system have been studied in a number of papers. Tl₄PbTe₃ and Tl₉BiTe₆ melt congruently at 893 K,²⁶ and 830 K,¹⁴ respectively, while Tl₉SmTe₆ is formed incongruently at 755 K.²⁵ The tetragonal lattice constants of Tl₄PbTe₃, Tl₉SmTe₆, and Tl₉BiTe₆ are following: a = 8.841, c =
According to Ref. 26, the boundary system Tl₄PbTe₃-Tl₉BiTe₆ is quasi binary and characterized by the formation of unlimited solid solutions (δ) with Tl₂Te₃-structure.

2. Experimental

2.1. Materials and Syntheses

The following reagents were used as starting components: thallium (granules, 99.999%), lead (ingot, 99.99%), samarium (powder, 99.9%), bismuth (granules, 99.999%), and tellurium (broken ingots 99.99%).

We used protective gloves at all times when working with thallium because thallium and its compounds are highly toxic and contact with skin is dangerous.

Stoichiometric amounts of the starting components were weighed with accuracy ±0.0001 g. Then they were put into silica tubes of about 20 cm in length and diameter about 1.5 cm and sealed under a vacuum of 10⁻² Pa. Tl₄PbTe₃ and Tl₉BiTe₆ were synthesized by heating in a resistance furnace at 920 K followed by cooling in the switched-off furnace.

In the case of Tl₉SmTe₆, the ampoule was graphitized using pyrolysis of toluene in order to prevent the reaction of samarium with quartz. Taking into account the results of the work26, the intermediate ingot of Tl₉SmTe₆ was powdered in an agate mortar, carefully mixed, pressed into a pellet and annealed at 700 K within ~700 h.

The resulting ingots were homogeneous polycrystals alloys that were established by the differential thermal analysis (DTA) and X-ray diffraction (XRD).

2.2. Methods

DTA and XRD analyses, as well as microhardness measurements, were used to analyze the samples of the investigated system.

The phase transformation temperatures were determined using a NETZSCH 404 F1 Pegasus differential scanning calorimeter within room temperature and ~1400 K at a heating rate of 10 K·min⁻¹ and accuracy about ±2 K. The phase identification was performed using a Bruker D8 diffractometer utilizing CuKα radiation. The powder diagrams of the ground samples were collected at room temperature in the 2θ range of 6–75°. The unit cell parameters of intermediate alloys were calculated by indexing of powder patterns using Topas V3.0 software. An accuracy of the crystal lattice parameters is shown in parentheses (Table). Microhardness measurements were done with a microhardness tester PMT-3, the typical loading being 20 g and accuracy about 20 MPa.

3. Results and Discussion

The Tl₄PbTe₃-Tl₉SmTe₆-Tl₉BiTe₆ section was plotted based on combined analysis of experimental results and literature data on boundary system Tl₄PbTe₃-Tl₉BiTe₆26 (Fig. 1–6).

Table 1. Experimental data of the DTA, microhardness measurements and parameters of tetragonal lattice for the alloys of the Tl₄PbTe₃-Tl₉SmTe₆ and Tl₉BiTe₆-Tl₉SmTe₆ sections of the Tl-Pb-Bi-Sm-Te system

| Solid phase compositions | Thermal effects, K | Microhardness, MPa | Tetragonal lattice parameters, Å |
|-------------------------|--------------------|--------------------|----------------------------------|
| Tl₄PbTe₃                | 893                | 1120               | 8.8409(5) 13.0556(6) |
| Tl₈.₂Pb₁.₆Sm₀.₂Te₆      | 845–875           | 1160               | 8.8504(4) 13.0482(9) |
| Tl₈.₄Pb₁.₂Sm₀.₄Te₆      | 820–850           | 1180               | 8.8602(5) 13.0387(8) |
| Tl₈.₆Pb₁.₀Sm₀.₅Te₆      | 817–845           | 1180               | 8.8645(6) 13.0343(9) |
| Tl₈.₈Pb₀.₈Sm₀.₂Te₆      | 790–830           | 1150               | 8.8702(6) 13.0298(9) |
| Tl₈.₄Pb₀.₄Sm₀.₈Te₆      | 775–800; 1190     | 1140               | 8.8788(5) 13.0280(9) |
| Tl₈.₈Pb₀.₅Sm₀.₅Te₆      | 760–775; 1155     | –                  | –                  |
| Tl₉SmTe₆                | 755; 1180         | 1080               | 8.8882(5) 13.0132(7) |
| Tl₉Bi₀.₁Sm₀.₉Te₆        | 760; 1150         | –                  | –                  |
| Tl₉Bi₀.₅Sm₀.₅Te₆        | 765–775; 1095     | 1120               | 8.8810(4) 13.0201(7) |
| Tl₉Bi₀.₆Sm₀.₄Te₆        | 770–790           | 1140               | 8.8741(5) 13.0279(8) |
| Tl₉Bi₀.₅Sm₀.₅Te₆        | 780–800           | –                  | 8.8710(5) 13.0301(8) |
| Tl₉Bi₀.₆Sm₀.₄Te₆        | 785–810           | 1110               | 8.8673(5) 13.0340(9) |
| Tl₉Bi₀.₅Sm₀.₂Te₆        | 810–820           | 1070               | 8.8614(5) 13.0410(8) |
| Tl₉BiTe₆                | 830               | 980                | 8.8545(4) 13.0476(7) |

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The Table presents the results of DTA, microhardness measurements, and parameters of the tetragonal lattice for starting compounds and some intermediate alloys.

Phase diagrams and the composition dependences of properties are plotted based on these data.

$\text{Tl}_4\text{PbTe}_3$-$\text{Tl}_9\text{SmTe}_6$ and $\text{Tl}_9\text{BiTe}_6$-$\text{Tl}_9\text{SmTe}_6$ sections (Fig. 1) are characterized by the formation of unlimited solid solutions ($\delta$) with $\text{Tl}_5\text{Te}_3$-structure. But, they are non-quasi-binary sections of the $\text{Tl}$-$\text{Pb}$-$\text{Sm}$-$\text{Te}$ and $\text{Tl}$-$\text{Bi}$-$\text{Sm}$-$\text{Te}$ quaternary systems due to the peritectic character of melting of $\text{Tl}_9\text{SmTe}_6$. As the result, the crystallization of $\text{Tl}_9\text{SmTe}_6$ compound occurs in a wide composition interval which leads to the formation of two-phase $\text{L}+\text{TlSmTe}_2$ and three-phase $\text{L}+\text{TlSmTe}_2+\delta$ areas. The $\text{L}+\text{TlSmTe}_2+\delta$ area is shown by a dotted line because not fixed experimentally due to a narrow interval of temperatures.

In order to determine the phase constituents, polished surfaces of the intermediate samples were visually observed under the microscope of microhardness meter. The microhardness curves have a flat maximum which is typical for systems with unlimited solid solutions (Fig. 1b). The XRD powder patterns for some alloys of the $\text{Tl}_4\text{PbTe}_3$-$\text{Tl}_9\text{SmTe}_6$ and $\text{Tl}_9\text{BiTe}_6$-$\text{Tl}_9\text{SmTe}_6$ sections are presented in Fig. 2. Powder diffraction patterns of $\text{Tl}_4\text{PbTe}_3$, $\text{Tl}_9\text{SmTe}_6$, and $\text{Tl}_9\text{BiTe}_6$ as well as intermediate alloys are single-phase and have the diffraction patterns qualitatively similar to $\text{Tl}_5\text{Te}_3$ with slight reflections displacement from one compound to another. For example, we present the powder diffraction patterns of alloy with composition 20, 50 and 80 mol% $\text{Tl}_9\text{SmTe}_6$ for both systems. Parameters of the tetragonal lattice of solid solutions obey the Vegard's law (Table, Fig. 1c).

Isopleth sections of the $\text{Tl}_4\text{PbTe}_3$-$\text{Tl}_9\text{SmTe}_6$-$\text{Tl}_9\text{BiTe}_6$ system (Fig. 3).

In order to construct a complete $T$-$x$-$y$ diagram and to refine the boundaries of areas of primary crystallization of $\delta$-phase and $\text{TlSmTe}_2$, we constructed some isopleth sections. Figs. 3a–c present the isopleth sections $\text{Tl}_9\text{SmTe}_6$-[A], $\text{Tl}_9\text{BiTe}_6$-[B] and $\text{Tl}_4\text{PbTe}_3$-[C] of the $\text{Tl}_4\text{PbTe}_3$-$\text{Tl}_9\text{SmTe}_6$-$\text{Tl}_9\text{BiTe}_6$ system, where A, B, and C are equimolar alloys from the respective boundary system as shown in Fig. 4.

Along the $\text{Tl}_9\text{SmTe}_6$-[A] section, the $\delta$-phase crystallizes in the composition area $<60$ mol% $\text{Tl}_9\text{SmTe}_6$. In the $\text{Tl}_9\text{SmTe}_6$-rich interval the $\text{TlSmTe}_2$ primary crystallizes, then a monovariant peritectic process $\text{L}+\text{TlSmTe}_2 \leftrightarrow \delta$ takes place (Fig. 3a).

Over the entire compositions range of the $\text{Tl}_9\text{BiTe}_6$-[B] and $\text{Tl}_4\text{PbTe}_3$-[C] sections, crystallization of the $\delta$-phase occurs from the melt (Fig. 3b,c).

The XRD powder patterns for selective alloys on polythermal sections confirmed continuous solid solutions with the $\text{Tl}_5\text{Te}_3$-structure.

The liquidus and solidus surfaces projections (Fig. 4)

Projection of liquidus of $\text{Tl}_4\text{PbTe}_3$-$\text{Tl}_9\text{SmTe}_6$-$\text{Tl}_9\text{BiTe}_6$ section consists of two fields of the primary crystallization of $\text{TlSmTe}_2$ and $\delta$-solid solutions. These fields are separated by a monovariant peritectic curve $\text{L}+\text{TlSmTe}_2 \leftrightarrow \delta$ (ab curve). The solidus projection (dashed lines) con-

Fig. 1. Polythermal sections (a), concentration dependencies of microhardness (b), and lattice parameters (c) for the alloys of the $\text{Tl}_9\text{SmTe}_6$-$\text{Tl}_9\text{BiTe}_6$ and $\text{Tl}_4\text{PbTe}_3$-$\text{Tl}_9\text{SmTe}_6$ sections of the $\text{Tl}$-$\text{Pb}$-$\text{Bi}$-$\text{Sm}$-$\text{Te}$ system.
Fig. 2. XRD powder patterns for starting compounds and some alloys of the Tl₄PbTe₃-Tl₃SmTe₆ (a) and Tl₃SmTe₆-Tl₃BiTe₆ (b) systems.
sist of one surface corresponding to the completion of the crystallization of the \( \delta \)-phase.

**Isothermal sections at 820 and 840 K of the Tl\(_4\)PbTe\(_3\)-Tl\(_9\)SmTe\(_6\)-Tl\(_9\)BiTe\(_6\) section (Fig. 5)** are consists of areas of L-, Tl\(_5\)SmTe\(_2\), and \( \delta \)-phases. In alloys <60 mol% Tl\(_5\)SmTe\(_6\) in the two-phase L+\( \delta \) region the directions of the

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connodes are on the studied composition plane. It should be noted that comparison of the isopleth sections (Fig. 3) and isothermal sections (Fig. 5) shows that the directions of the connodes in the two-phase region L+δ deviate from the T–x plane and constantly vary with temperature. Isothermal sections at 820 and 840 K clearly confirm this.

4. Conclusion

A complete phase diagram of the Tl–Pb–Bi–Sm–Te system in the Tl₁₄PbTe₃–Tl₉SmTe₆–Tl₉BiTe₆ composition interval is plotted. Unlimited solubility of components in the solid state is found in the studied section. Obtained experimental results can be used for choosing the composition of solution-melt for the growth of the high-quality crystals of δ–phase which is of interest as thermoelectric material.

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Povzetek
V sistemu Tl-Pb-Bi-Sm-Te smo preučevali fazna ravnotežja dela Tl\textsubscript{4}PbTe\textsubscript{3}-Tl\textsubscript{9}SmTe\textsubscript{6}-Tl\textsubscript{9}BiTe\textsubscript{6} s termično analizo, rentgensko praškovno difrakcijo in meritvami mikrotrdote. Pripravili smo fazne diagrame sistemov Tl\textsubscript{4}PbTe\textsubscript{3}-Tl\textsubscript{9}SmTe\textsubscript{6}, Tl\textsubscript{9}SmTe\textsubscript{6}-Tl\textsubscript{9}BiTe\textsubscript{6}, izotermljene krivulje pri 820 K in 840 K, nekatere izopletne krivulje ter projekcije tekočinsko trdnih površin. Trdne raztopine kristalizirajo v Tl\textsubscript{5}Te\textsubscript{3} kristalnem sistemu pri temperaturem strjavanja in nižjih.