PHASE RELATIONS IN Tl₉GdTe₆-Tl₉SbTe₆ AND Tl₉TbTe₆-Tl₉SbTe₆ SYSTEMS

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Phase equilibriums in the Tl₉GdTe₆-Tl₉SbTe₆ and Tl₉TbTe₆-Tl₉SbTe₆ systems have been examined by means of differential thermal analysis, X-ray diffraction and microhardness measurements over equilibrium alloys. Phase diagram and concentration dependence of the unit cell parameters and microhardness of both systems plotted. It found that the systems are non-quasi-binary due to incongruent melting of Tl₉Gd (Tb) Te₆ compositions but proved to be stable below the solidus. Systems are characterized by formation of continuous solid solutions with Tl₅Te₃ structure. Solid solutions obtained may be of interest as thermoelectric and magnetic materials.

Keywords: thallium-terbium telluride, thallium-gadolinium telluride, thallium-antimony telluride, phase equilibriums, solid solutions, crystal structure.

1. INTRODUCTION

A number of works are illustrative of the growing interest in new multinary chalcogenide materials. This is due to their specific functional properties, such as thermal, electrical and optical [1-3]. Furthermore, recent studies have shown that some of them exhibit topological insulator properties [4,5]. Doping by rare-earth elements may improve their properties to provide them with additional functionality [6-8].

Thallium subtelluride, Tl₅Te₃ is suitable "matrix" for production of novel complex materials. This composition is crystallized in tetragonal structure (Sp.gr. I₄/mcm) [9, 10] and has a number of ternary cation- [11-14] and anion-substituted [15-18] ternary structural analogs. Cation-substituted compositions of Tl₄⁺IVTe₃ [A⁻IVSn, Pb] and Tl₉⁺B⁻VTe₆ [B⁻V-Sb, Bi] types form an important class of thermoelectric materials with anomalous low thermal conductivity [19-21]. Particularly, Tl₉BiTe₆ shows high ZT value comparable to the state-of-the-art thermoelectric materials [21]. On the other hand, according to recent investigations, anion-substituted Tl₅Se₂I composition is a prospective material for efficient X-ray and γ-ray detection [22].

A new substitution variant of Tl₅Te₃, thallium lanthanide tellurides, Tl₉LnTe₆ (Ln-Ce, Nd, Gd, Tb) has been obtained first by authors [23-25] to ensure their melting property and crystal lattice parameters. Moreover, according to [25, 26], ytterbium does not form the composition Tl₉YbTe₆. Later, a number of tellurides, Tl₁₀-xLnₓTe₆, were synthesized, structurally characterized and their thermoelectric properties identified by authors [27-29].

Earlier, with the purpose of obtaining a solid solution with Tl₅Te₃ structure the phase relations in the Tl₉NdTe₆-Tl₉BiTe₆, Tl₉TbTe₆-Tl₉BiTe₆ and Tl₉GdTe₆-Tl₉BiTe₆ systems had been studied in [30-32]. Authors showed the formation of continuous areas of solid solutions with Tl₅Te₃ structure.

The goal of the present work is to determine phase equilibria in the Tl₉GdTe₆-Tl₉SbTe₆ and Tl₉TbTe₆-Tl₉SbTe₆ systems and thus obtain phase relationships and provide more accurate experimental data for preparation of pure and high quality materials.

Tl₉SbTe₆ melts congruently at 798 K [11] and has a low symmetry crystal structure of Tl₅Te₃ (Sp.gr. I₄/m), a = 8.829 Å and c = 13.001 Å, Z = 2 [33]. Tl₉GdTe₆ and Tl₉TbTe₆ melt with decomposition by peritectic reactions at 800
2. EXPERIMENTAL

2.1. Materials and syntheses

Thallium (granules, 99.999 mass%), antimony (granules, 99.999 mass%), gadolinium (powder, 99.9%), terbium (powder, 99.9%), and tellurium (broken ingots 99.999 mass%) were used as starting materials. The elements were weighed to total about 20 g (Tl$_9$SbTe$_6$) and 10 g (Tl$_9$GdTe$_6$, Tl$_9$TbTe$_6$) as per the molar ratio of the corresponding ternary composition, and placed in silica tubes, 20 cm long, and then sealed under a vacuum of $10^{-3}$ Pa. The synthesis was carried out by heating in one zone an electric furnace at 850 K (Tl$_9$SbTe$_6$) and 1200 K (Tl$_9$GdTe$_6$, Tl$_9$TbTe$_6$), followed by cooling in the switched-off furnace. To prevent a reaction between rare-earth elements and tubes, the silica tubes were coated with a carbon film via the decomposition of ethanol.

In considering that the equilibrium state could not be obtained even after a long-time (1000 h.) annealing [30-32], intermediate ingots of Tl$_9$GdTe$_6$ and Tl$_9$TbTe$_6$ were powdered in agate mortar, pressed into pellets and annealed at 730 K within $\sim$700 h.

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

Just one endothermic effect was revealed for Tl$_9$SbTe$_6$ (790 K), and two effects for Tl$_9$GdTe$_6$ (800 and 1190 K) and Tl$_9$TbTe$_6$ (780 and 1110 K) showed the completion of the synthesis.

Powder XRD pattern for the Tl$_9$SbTe$_6$, Tl$_9$GdTe$_6$ and Tl$_9$TbTe$_6$ were similar to that of Tl$_7$Te$_3$. The lattice parameters were refined using the Topas V3.0 software (Table 1). They are practically equal to those shown in [34] for Tl$_9$SbTe$_6$, and slightly differ from [28] for Tl$_9$TbTe$_6$.

2.2. Methods

Differential thermal analysis (DTA), X-ray powder diffraction (XRD), and microhardness measurements were made to analyze the samples. DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter. Measurements were carried out at room temperature and $\sim$1400 K. Temperatures of thermal effects were read mainly from the heating curves. But in some samples thermal effects were read from cooling curves in order to establish the onset of crystallization.

X-ray powder diffraction (XRD) data were collected at room temperature in reflection mode using a Bruker D8 ADVANCE powder diffractometer and CuK$_\alpha$ radiation within 20 $\text{=}$10 to 70$^\circ$.

Microhardness measurements were performed with a microhardness meter PMT-3 with typical loading reaching 20 g.
3. RESULTS AND DISCUSSION

The Tl₉GdTe₆-Tl₉SbTe₆ and Tl₉TbTe₆-Tl₉SbTe₆ systems (Table 1, Fig.1) are non-quasi-binary section of the Tl–Gd(Tb)–Sb–Te quaternary system due to peritectic melting of Tl₉Gd(Tb)Te₆ compositions. However, they are characterized by the formation of continuous solid solutions (δ).

Note that the δ-solid solutions are primarily crystallized in 0-63 mol% Tl₉GdTe₆ composition area. Primary crystallization of X-phase occurs in the range of >63 mol% Tl₉GdTe₆. The mono-variant peritectic L+X ↔ δ reaction takes place below 800K and leads to the formation of three-phase area L+X+δ. This area is not experimentally fixed due to narrow temperature interval and shown by dotted line (Fig.1).

We have assumed that the X phase has a composition of TlGdTe₂. This assumption is confirmed by the presence of the most intense reflection peaks of TlGdTe₂ [34] on diffractograms of cast alloys from an area exceeding 63 mol% Tl₉GdTe₆.

Note that the nature of phase equilibriums in the Tl₉TbTe₆-Tl₉SbTe₆ system is qualitatively identical.

It should be noted that irrespective of the very close melting temperature of Tl₉SbTe₆ (790K) and peritectic decomposition of Tl₉GdTe₆ (800 K) and Tl₉TbTe₆ (780 K) compositions, the liquids and solidus curves of both studied systems have no extremum points.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature of melting, K</th>
<th>Microhardness, MPa</th>
<th>Parameters of tetragonal lattice, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Tl₉TbTe₆</td>
<td>780; 1100</td>
<td>1100</td>
<td>8.8713</td>
</tr>
<tr>
<td>Tl₉Sb₀.₁Tb₀.₉Te₆</td>
<td>781; 1080</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tl₉Sb₀.₂Tb₀.₈Te₆</td>
<td>782; 1030</td>
<td>1160</td>
<td>8.8626</td>
</tr>
<tr>
<td>Tl₉Sb₀.₄Tb₀.₆Te₆</td>
<td>784</td>
<td>1140</td>
<td>8.8542</td>
</tr>
<tr>
<td>Tl₉Sb₀.₆Tb₀.₄Te₆</td>
<td>786; 1030</td>
<td>1130</td>
<td>8.8458</td>
</tr>
<tr>
<td>Tl₉Sb₀.₈Tb₀.₂Te₆</td>
<td>788</td>
<td>1080</td>
<td>8.8374</td>
</tr>
<tr>
<td>Tl₉SbTe₆</td>
<td>790</td>
<td>1000</td>
<td>8.8312</td>
</tr>
<tr>
<td>Tl₉Sb₀.₈Gd₀.₂Te₆</td>
<td>791</td>
<td>1050</td>
<td>8.8412</td>
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<tr>
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<td>793</td>
<td>1120</td>
<td>8.8482</td>
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<tr>
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<td>1140</td>
<td>8.8563</td>
</tr>
<tr>
<td>Tl₉Sb₀.₂Gd₀.₈Te₆</td>
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<td>1160</td>
<td>8.8631</td>
</tr>
<tr>
<td>Tl₉Sb₀.₁Gd₀.₉Te₆</td>
<td>798; 1160</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tl₉GdTe₆</td>
<td>800; 1190</td>
<td>1100</td>
<td>8.8703</td>
</tr>
</tbody>
</table>
Both examined systems go to show that the temperature interval of the crystallization of the $\delta$-phase is less than 3 K. The fact makes it possible to characterize the $\delta$-solid solutions as quasi-ideal solution.

Results of microhardness measurements are in line with the plotted phase diagrams (Figs.1b). Curves have a flat maximum which is typical for systems with continuous solid solutions.

Phase diagrams of the above-mentioned systems are confirmed by powder X-ray analysis (Fig.2). Powder diffraction patterns of starting compositions and intermediate alloys are qualitatively identical with slight displacement of reflections from one composition to another. For example, we provide the powder diffraction pattern of alloy with compositions 50mol%Tl$_9$SbTe$_6$+50 mol%Tl$_9$Gd(Tb)Te$_6$. Note that the lattice parameters of the solid solutions depend linearly on composition, i.e. subject to the Vegard’s law.

Plotted T-x diagrams afford ample opportunity to select compositions for growing monocrystals of $\delta$-solid solution with given composition from the melt.
The phase diagrams of the Tl₂GdTe₆-Tl₂SbTe₆ and Tl₂TbTe₆-Tl₂SbTe₆ systems have been plotted using various experimental methods. A continuous series of the substitutional solid solutions which are crystallized in Tl₅Te₃ crystal type were found in both systems. Proceeding from respective characteristics of the starting compositions one can assume that the Tl₂Sb₁₋ₓGd(Tb)ₓTe₆ (0<ₓ<1) phases possibly have thermoelectric and magnetic properties.

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REFERENCES


PHASE RELATIONS IN Tl₉GdTe₆-Tl₉SbTe₆ AND Tl₉SbTe₆-Tl₉GdTe₆, Tl₉SbTe₆-Tl₉TbTe₆ SYSTEMS AND FAZA TARAQLIQLARI

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DTA, RFA və mikrobərkliyin ölçülməsi üsulları ilə Tl₉SbTe₆-Tl₉GdTe₆ və Tl₉SbTe₆-Tl₉TbTe₆ sistemlərində faza tarazlıqları öyrənilmiş, onların faza diagramlary, həminin kristal aşkar parametrlərinin və mikrobərkliyin tərkibində asılı əsaslıq qrafikləri qurulmuşdur. Müəyyən edilmişdir ki, hər iki sistem Tl₉Gd(Tb)Te₆ birləşmələrinin inkongruent sırası səbəbindən qeyri-kvazibinar, lakin solidusdan aşağıda onlar stabilidir və Tl₅Te₃ tipli kristal quruşa malik arası질 bolsa məhlulların xətadən daha golnəmişsi bir kristallik sırası olunurlar. Alınmış bərk məhlullar termoelektrik və maqnit materialı krəsənəkər dəyərlərdə xarakterizə olunurlar.

**Açar səçələr:** tallium–gadolinium telluridləri, tallium–terbium telluridləri, tallium–stibium telluridləri, faza tarazlıqları, bərk məhlullar, kristal quruluş.

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМАХ Tl₉SbTe₆-Tl₉GdTe₆ И Tl₉SbTe₆-Tl₉TbTe₆

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Методами ДТА и РФА, а также измерением микротвердости изучены фазовые равновесия в системах Tl₉SbTe₆-Tl₉GdTe₆ и Tl₉SbTe₆-Tl₉TbTe₆. Построены их фазовые диаграммы, а также концентрационные зависимости микротвердости и параметров кристаллической решетки. Показано, что обе системы неквазибинарны в силу инконгруэнтного плавления соединений Tl₉Gd(Tb)Te₆, однако они сольвуса стабильны и характеризуются образованием непрерывных рядов твердых растворов с тетрагональной структурой Tl₅Te₃. Полученные твердые растворы представляют интерес как термоэлектрические и магнитные материалы.

**Ключевые слова:** теллуриды таллия-гадолиния, теллуриды таллия-тербия, теллуриды таллия-сурьмы, фазовые равновесия, твердые растворы, кристаллическая структура.

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