Scientific paper

Phase Equilibria and some Properties of Solid Solutions in The Tl₅Te₃-Tl₉SbTe₆-Tl₉GdTe₆ System

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Abstract

Phase equilibria in the Tl_5Te_3 - Tl_9SbTe_6 - Tl_9GdTe_6 system were experimentally studied by thermal analysis, X-ray diffraction and microhardness measurements applied to equilibrated alloys. Some isopleth sections, isothermal section at 760 K, and also projections of the liquidus and solidus surfaces, were constructed. A continuous series of solid solutions was found in this system. Solid solutions crystallize in the tetragonal Tl_5Te_3 structure type.

Keywords: Thallium-antimony tellurides; thallium-gadolinium tellurides; phase equilibria; projections of the liquidus and solidus; solid solutions; crystal structure

1. Introduction

A number of works have illustrated the continuing interests in new multinary chalcogenides of heavy p-elements, including rare earth elements. Due to their important functional properties, they find applications in a wide range of devices such as ion-selective sensors, microbatteries, modern day solar cells, and thermoelectric energy conversion. ^{1–3} Moreover; some of them have attracted interest as topological insulators. ^{4,5}

Thallium subtelluride, Tl_5Te_3 , thanks to features of crystal structure (Sp.gr.I4/mcm, a=8.930; c=12.598 Å) has a number of ternary derivatives of $Tl_4A^{IV}Te_3$ and $Tl_9B^VTe_6$ -type (A^{IV} -Sn, Pb; B^V -Sb, Bi). $^{6-9}$ These compounds exhibit good thermoelectric properties, and Tl_9Bi-Te_6 has reported a $ZT\sim1.2$ at 500 K. $^{10-12}$ Furthermore, the Dirac-like surface states were observed in $[Tl_4]TlTe_3$ (Tl_5Te_3) and its tin-doped derivative $[Tl_4](Tl_{1-x}Sn_x)Te_3$. 13

The new ternary compounds of Tl₉LnTe₆- type (Ln-Ce, Nd, Sm, Gd, Tm, Tb) which are a new of substitution derivatives of Tl₅Te₃ were reported in some wo-krs. ^{14–16} Later, H.Kleinke and co-workers have reported the crystal structure as well as magnetic and thermoelectric properties for a number of Tl₉LnTe₆-type compounds. ^{17–19}

Further studies of phase equilibria in the systems including the $\mathrm{Tl_5Te_3}$ compound or its structural analogs showed that these systems are characterized by the formation of unlimited solid solutions. ^{20–22}

This study reports a detailed investigation of phase equilibria in the Tl_5Te_3 - Tl_9SbTe_6 - Tl_9GdTe_6 system.

Tl₅Te₃ and Tl₉SbTe₆ melt congruently at 723 and 790 K while Tl₉GdTe₆ melts with decomposition by the peritectic reaction at 800 K.^{7, 23, 24} The lattice parameters of Tl₉SbTe₆ and Tl₉GdTe₆ are following: a = 8.829, c = 13.001 Å, z = 2; a = 8.870; c = 13.027 Å, $z = 2.^{24, 25}$

The ${\rm Tl_5Te_3}$ - ${\rm Tl_9SbTe_6}$ system is characterized by the formation of continuous solid solutions areas based on ${\rm Tl_5Te_3}$.

2. Experimental

2. 1. Materials and Syntheses

For the synthesis, we used the high purity thallium, antimony, gadolinium, and tellurium (the purity of the ingredient was better than 99.99 mass. %).

The surface of thallium was coated by a thin oxide film, which was removed before use.

It should be noted that, thallium and its compounds are extremely toxic, and should be handled with great care. Thallium is readily absorbed through the skin and care should be taken to avoid this route of exposure. Therefore, we used protective gloves at all times when working with thallium. However, no respiratory tract covers are required since thallium is not volatile.

The elements were weighed to be about 10 g in total according to the molar ratio of the corresponding binary and ternary compound, were placed in silica tubes of about 20 cm in length and then were sealed under a vacuum of 10^{-2} Pa.

Taking into account the congruent melting of $\mathrm{Tl_5Te_3}$ and $\mathrm{Tl_9SbTe_6}$, their synthesis was carried out by heating of elements in one zone electric furnace at the 750 and 830 K, respectively followed by cooling in the switched-off furnace.

The obtained intermediate ingot of Tl₉GdTe₆ was carefully ground in an agate mortar, pressed into the circular pellet of about 10 mm diameter and annealed at 770 K within ~1000 h as it was done in previous work.²⁴ The weight losses during the pellet preparation were less than 0.5 mass. %. In order to prevent a reaction between the gadolinium and the quartz during high temperature reactions, quartz tubes coated internally with a thin layer of carbon were used.

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

Only one thermal effect was observed for Tl_5Te_3 (723 K) and Tl_9SbTe_6 (790 K); whereas two peaks for Tl_9GdTe_6 which were relevant the peritectic reaction at 800 K and its liquidus at 1190 K. These data are in good agreement with the literature references.^{7,23,24}

XRD confirmed that synthesized compounds were phase-pure. Powder XRD pattern of the Tl_9SbTe_6 and Tl_9GdTe_6 were similar to that of Tl_5Te_3 . The unit cell parameters were practically equal to literature data (Table 1). ^{24,25}

Synthesized binary and ternary compounds were used for the fabrication of the alloys of the Tl₅Te₃-Tl₉Sb-Te₆-Tl₉GdTe₆ system. The alloys weighing 1 g were synthesized in quartz tube evacuated to 10⁻² Pa. Taking into account the fact that an equilibrium state could not be obtained even after the long-time (1000 h) annealing, after synthesis the samples containing more than 60 mol% Tl₉GdTe₆ were powdered, mixed, pressed into circular pellets of about 10 mm diameter and annealed at 700 K for 1 month.

2. 2. Methods

X-ray powder diffraction (XRD), differential thermal analysis (DTA) and also microhardness measurements were employed to check the purity of the synthesized starting compounds and analyze the samples in order to plot the phase diagrams.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter within room temperature and ~1400 K depending on the composition of the alloys at a heating rate of 10 K min⁻¹ and accuracy about ±3°. Temperatures of thermal effects were taken mainly from the heating curves.

The XRD measurements of the powdered specimen were recorded using a Bruker D8 diffractometer utilizing CuK_{α} radiation within $2\theta = 10 \div 70^{\circ}$. The unit cell parameters 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 microhardnesmeter PMT-3, the typical loading being 20 g and accuracy about 20 MPa.

3. Results and Discussion

The combined analysis of obtained experimental and literature data [7, 24, 25] allowed us to construct the diagram of the phase equilibria in the Tl₅Te₃-Tl₉SbTe₆-Tl₉GdTe₆ system (Table, Fig.1-6).

The $2Tl_5Te_3$ - Tl_9SbTe_6 system is quasi-binary and characterized by the formation of unlimited solid solutions (δ) with Tl_5Te_3 -structure.⁷

The $2Tl_5Te_3$ - Tl_9GdTe_6 and Tl_9SbTe_6 - Tl_9GdTe_6 systems (Table 1, Figs. 1a, 2a) are characterized by the formation of continuous solid solutions (δ) with Tl_5Te_3 -structure. However, they are non-quasi-binary sections of the Tl_-Gd_-Te ternary and $Tl_-Sb_-Gd_-Te$ quaternary systems due to the peritectic melting of the Tl_9GdTe_6 compound. This leads to crystallization infusible X phase in a wide composition interval and formation two-phase L + X and three-phase $L + X + \delta$ areas. These areas are not experimentally fixed due to narrow temperature interval and shown by dotted line.

We have assumed that the X phase has a composition TlGdTe₂. This assumption is confirmed by the presence of the most intense reflection peaks of TlGdTe₂ on diffractograms of the as-cast alloys from the region more than 63 mol% Tl₉GdTe₆.²⁶

It should be noted that regardless a very close melting temperature of Tl_9SbTe_6 (790K) and peritectic decomposition of Tl_9GdTe_6 (800 K) compounds, the liquidus and solidus curves have not extremum points and temperature interval of the crystallization of the δ -phase is less than 3 K. Such phenomenon is realized when the enthalpy of mixing during the formation of solid and liquid solutions from starting compounds is practically equal to zero. In other words, in the studied system the Sb \rightarrow Gd replacement in the solid and liquid states are not accompanied by a significant thermal effect. This fact allows us to characterize the δ -solid solutions as quasi-ideal solution.

Phase	Thermal effects, K	Microhardness, MPa,	Parameters of tetragonal lattice, Å	
	(accuracy ±3°)	(accuracy ±20 MPa)	а	\boldsymbol{c}
Tl ₅ Te ₃	723	1130	8.9303(3)	12.5987(8)
$Tl_{9.8}Gd_{0.2}Te_6$	730–744	1180	8.9184(4)	12.6848(9)
$Tl_{9.6}Gd_{0.4}Te_6$	740–763	1160	8.9064(4)	12.7707(9)
$Tl_{9.5}Gd_{0.5}Te_6$	750–770	_	_	_
$Tl_{9.4}Gd_{0.6}Te_6$	760–773	1150	8.8953(4)	12.8558(8)
$Tl_{9.2}Gd_{0.8}Te_6$	775–788; 1100	1150	8.8824(3)	12.9417(8)
$Tl_{9.1}Gd_{0.9}Te_6$	785–793; 1150	_	_	_
Ťľ ₉ GďŤe ₆	800; 1190	1100	8,8705(4)	13,0277(7)
$Tl_9Sb_{0.2}Gd_{0.8}Te_6$	798; 1100	1150	8.8616(5)	13.0218(8)
$Tl_9Sb_{0.4}Gd_{0.6}Te_6$	795	1130	8.8536(5)	13.0167(9)
$Tl_9Sb_{0.5}Gd_{0.5}Te_6$	794	_	_	_
$Tl_9Sb_{0.6}Gd_{0.4}Te_6$	793	1120	8.8454(4)	13.0115(8)
$Tl_9Sb_{0.8}Gd_{0.2}Te_6$	792	1050	8.8373(3)	13.0066(7)
Tl ₉ SbTe ₆	790	1000	8.8315(4)	13.0017(7)

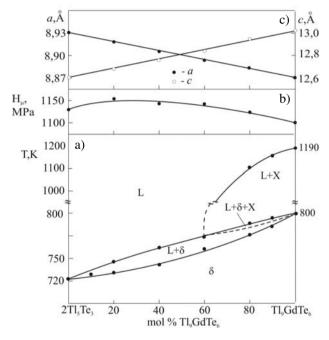


Fig. 1. Polythermal section (a), concentration relations of microhardnesses (b), and lattice parameters (c) for the system $2Tl_5Te_3$ - Tl_6GdTe_6

The curves of microhardness dependencies have a flat maximum, which is typical for systems with continuous solid solutions (Fig. 1b and 2b).

The XRD patterns obtained are presented in Fig. 3. Powder diffraction patterns of Tl₅Te₃, Tl₉SbTe₆ and Tl₉GdTe₆, and intermediate alloys were very similar to that of Tl₅Te₃ with slight reflections displacement from one compound to another. The lattice parameters of solid solutions depend linearly on the composition, i.e. obey the Vegard's rule.

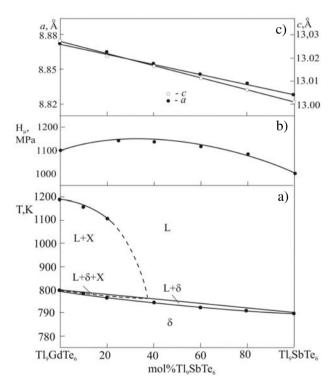


Fig. 2. Polythermal section (a), concentration relations of microhardnesses (b), and lattice parameters (c) for the system Tl_9GdTe_6 - Tl_9SbTe_6

Projections of the liquidus and solidus surfaces of the Tl_5Te_3 - Tl_9SbTe_6 - Tl_9GdTe_6 system.

Liquidus of the Tl_5Te_3 - Tl_9SbTe_6 - Tl_9GdTe_6 system consists of two fields of the primary crystallization of X-phase and δ - solid solutions, limited by the ab curve corresponds to the monovariant peritectic $L + X \leftrightarrow \delta$ equilibrium (Fig. 4).

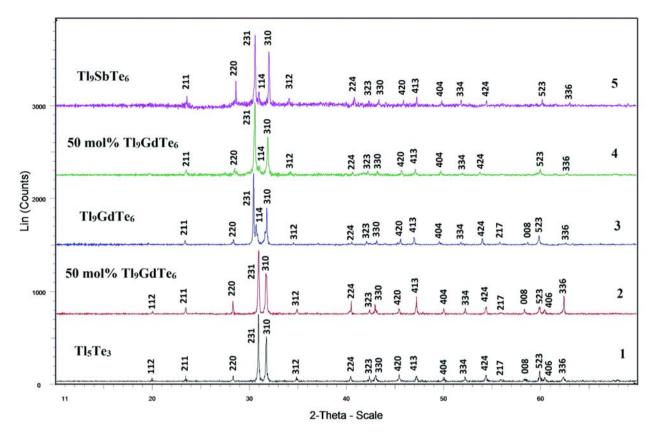


Fig. 3. XRD patterns for different compositions in the Tl_5Te_3 - Tl_9GdTe_6 (patterns 1–3) and Tl_9GdTe_6 - Tl_9SbTe_6 (patterns 3–5) systems. 1– Tl_5Te_3 ; 2–50 mol % Tl_9GdTe_6 ; 3- Tl_9GdTe_6 ; 4–50 mol % Tl_9GdTe_6 ; 5- Tl_9SbTe_6 .

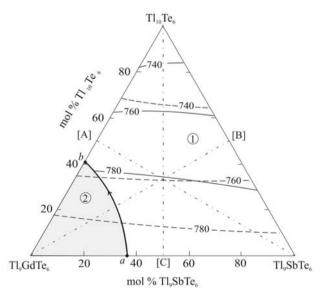


Fig.4. Projections of the liquidus and solidus (dashed lines) surfaces of the Tl_5Te_3 - Tl_9GdTe_6 - Tl_9SbTe_6 system. Dash-dot lines show the investigated sections. Primary crystallization phases: $1-\delta$; 2-X phase.

Isopleth sections of the Tl_5Te_3 - Tl_9SbTe_6 - Tl_9GdTe_6 system (Fig.5).

Figs. 5a–c show the isopleth sections $2Tl_5Te_3$ -[C], Tl_9SbTe_6 -[A] and Tl_9GdTe_6 -[B] of the Tl_5Te_3 - Tl_9SbTe_6 -

Tl₉GdTe₆ system, where A, B and C are equimolar compositions of the boundary systems as shown in Fig. 4.

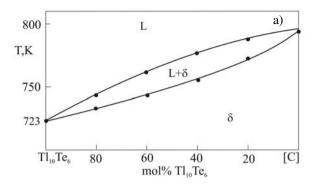
According to the phase diagram of the Tl_9GdTe_6 -[B] cut, the primary crystallization of the δ -phase occurs from the liquid phase in the composition area < 60 mol% Tl_9GdTe_6 . In the Tl_9GdTe_6 - rich alloys the X-phase first crystallizes, then a monovariant peritectic equilibrium $L + X \leftrightarrow \delta$ takes place.

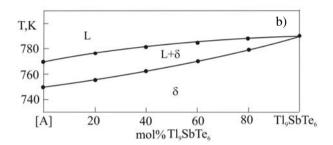
As can be seen, over the entire compositions area of the Tl_9SbTe_6 -[A] and Tl_5Te_3 -[C] cuts only δ -phase crystallizes from the melt.

Comparison between isopleth sections (Fig. 5) with the isothermal section (Fig. 6) shows, that tie-lines positions in two-phase area $L+\delta$ do not correspond to the cross section planes and continuously change with temperature. The tie-lines positions at 760 K are shown in Fig. 6.

4. Conclusion

A T-x-y diagram of the Tl₅Te₃-Tl₉SbTe₆-Tl₉GdTe₆ system, including the phase diagrams of boundary systems Tl₅Te₃-Tl₉TbTe₆ and Tl₉SbTe₆-Tl₉TbTe₆, isothermal section at 760 K, some isopleth sections and also the liquidus and solidus surfaces projections, were constructed.





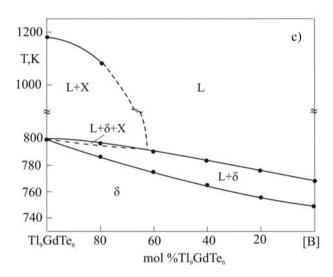


Fig. 5. Polythermal sections $Tl_{10}Te_6$ -[C], Tl_9SbTe_6 -[A], and Tl_9GdTe_6 -[B] of the phase diagram of the Tl_5Te_3 - Tl_9SbTe_6 - Tl_9GdTe_6 system.

Components of the system display unlimited solubility in the solid state. Obtained experimental data can be used for choice the composition of solution-melt and for determining of temperature conditions for growing crystals of δ -phase with a given composition.

5. Acknowledgment

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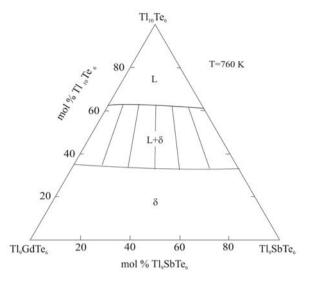


Fig.6. The isothermal section of the phase diagram at 760 K of the Tl_sTe_2 - Tl_0GdTe_6 - Tl_0SbTe_6 system.

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Povzetek

V sistemu Tl₅Te₃-Tl₉SbTe₆-Tl₉GdTe₆ smo preučevali fazna ravnotežja s termično analizo, rentgensko praškovno difrakcijo in meritvami mikrotrdote. Pripravili smo nekatere izopletne in izotermične krivulje pri 760 K ter projekcije tekočinsko trdnih površin. V tem sistemu smo našli serijo kontinuirnih trdnih raztopin. Trdne raztopine kristalizirajo v tetragonalnem Tl₅Te₃ kristalnem sistemu.