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NEW PHASE OF VARIABLE COMPOSITION IN THE Tl_9TbTe_6 - Tl_9BiTe_6 SYSTEM

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The phase equilibria in the Tl_9TbTe_6 - Tl_9BiTe_6 system were investigated by using differential thermal analysis (DTA), X-ray diffraction (XRD), microhardness measurements and its phase diagram was constructed. It is shown that the system is not quasi-binary due to the peritectic melting of Tl_9TbTe_6 , but stable below the solidus. In the system found a new quaternary phase of variable composition $\text{Tl}_9\text{Bi}_{1-x}\text{Tb}_x\text{Te}_6$ ($0 < x < 1$) with Tl_5Te_3 structure.

Keywords: thallium-terbium tellurides, thallium-bismuth tellurides, phase equilibria, solid solutions, crystal structure

Introduction

Heavy metal chalcogenides attracted increased interest due to their interesting functionalities, in particular, semiconductor, thermoelectric properties [1,2]. Moreover, some of them are also found to be topological insulators [3].

Ternary thallium chalcogenides, $\text{Tl}_4\text{A}^{\text{IV}}\text{Te}_3$ [Sn, Pb] and $\text{Tl}_9\text{B}^{\text{V}}\text{Te}_6$ [Sb, Bi] obtained in respective systems are structural analogs of Tl_5Te_3 and form an important class of thermoelectric materials with anomaly low thermal conductivity [4-7]. Particularly, Tl_9BiTe_6 shows high ZT value comparable to the state-of-the-art thermoelectric materials [8].

New ternary compounds Tl_9LnTe_6 (Ln-Ce, Nd, Sm, Gd) were presented for the first time by Babanly M. group [9, 10]. These compounds are ternary derivatives of Tl_5Te_3 structure type (Sp.gr. $I4/mcm$).

Phase equilibria in the Tl_5Te_3 - Tl_9NdTe_6 - Tl_9BiTe_6 (I) and Tl_2Te - Tl_9NdTe_6 - Tl_9BiTe_6 (II) systems were investigated to obtain solid solutions with Tl_5Te_3 structure [11]. The systems are characterized by formation of continuous (I) or wide (II) areas of solid solutions with Tl_5Te_3 structure.

Later, a series of tellurides $\text{Tl}_{10-x}\text{Ln}_x\text{Te}_6$ was synthesized, structurally characterized and the thermoelectric properties determined by Kleinke H. group [12-14]. The authors confirmed the results of above mentioned works [9-11] that these compounds are substitution variants of Tl_5Te_3 .

The highest ZT value of ~ 0.20 was obtained for cold-pressing and sintering $\text{Tl}_{8.98}\text{Nd}_{1.02(6)}\text{Te}_6$ and $\text{Tl}_{8.99}\text{Sm}_{1.01(7)}\text{Te}_6$ at ~ 550 K [13] and 0.21 at 581 K for Tl_9LaTe_6 [12].

The Tl_9CeTe_6 , Tl_9PrTe_6 and Tl_9TbTe_6 compounds also were found to be paramagnetic due to the presence of unpaired electrons [14].

In this work, the phase equilibria in the Tl_9TbTe_6 - Tl_9BiTe_6 system for obtaining of solid solutions with Tl_5Te_3 structure have been studied. It was assumed, that incorporation of lanthanide to the crystal structure can improve the thermoelectric properties and give the magnetic properties for obtained phases.

Experimental

Materials and syntheses. Tl_9BiTe_6 and Tl_9TbTe_6 were synthesized from elements (Tl granules, 99.99%; Tb powder, -40 mesh, 99.9%; Bi foil, -99.999 mass%, Te broken ingots, 99.99%), all purchased from Alfa Aesar. To prevent a reaction between the ampoules and the terbium, the syntheses were carried out in graphitized ampoules. The elements were weighed in the respective stoichiometric ratio and then placed into silica tubes in that glove box. The total mass of one ingot was 1 g. The tubes were closed with a vacuum valve, and then moved out of the box to a vacuum line, where they were sealed under a pressure of approximately 10^{-3} mbar. The reactions were carried out in these fused silica tubes by heating in a re-

sistance furnace at 900K (Tl_9BiTe_6) and 1200K (Tl_9TbTe_6) for 3h, followed by cooling in the switched-off furnace.

The Tl_9LnTe_6 compounds form by peritectic reactions and it is difficult to achieve equilibrium [10-12]. To accelerate the interaction on interfaces, the obtained intermediate ingot of Tl_9TbTe_6 was crushed to fine powders using agate mortar and pestle, pressed into pellets and again annealed at 700K. This process was repeated until homogeneous compound was obtained. The total annealing time of tablet was $\sim 1000\text{h}$.

Retesting DTA and XRD showed homogeneity of both compounds, which agrees with the data [7,11]. DTA showed that Tl_9BiTe_6 melts congruently at 830 K. Comparison with previously obtained thermograms for other lanthanides [10, 11] showed two peaks in the heating curve of Tl_9TbTe_6 , which are relevant to the peritectic reaction at 780 K and its liquidus at 1110 K (fig.1).

Powder XRD pattern of the Tl_9BiTe_6 and Tl_9TbTe_6 compound were identical to that of Tl_5Te_3 . Unit cell lattice parameters were determined from a least-squares refinement. These were $a = 8.854(5)$, $c = 13.047(6)$ Å, $z = 2$ (Tl_9BiTe_6) and $a = 8.871(3)$ Å and $c = 12.973(7)$ Å $z = 2$ (Tl_9TbTe_6). These are practically equal with the literature data [15] for Tl_9BiTe_6 and slightly differ from literature data [13] for Tl_9TbTe_6 . The lattice parameters evaluated from the X-ray diffraction pattern are shown in table.

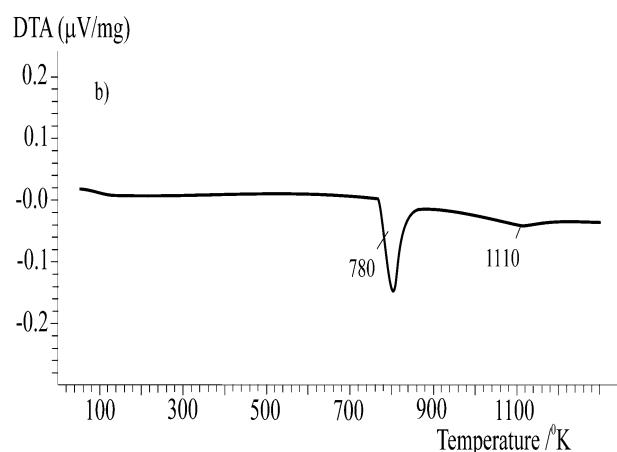


Fig. 1. The heating curve of annealed Tl_9TbTe_6

The samples of the Tl_9TbTe_6 - Tl_9BiTe_6 system were prepared by melting from pre-synthesized starting compounds in evacuated silica ampoules. The total mass of one ingot was 1 g. The synthesis was realized in a tube furnace. Ampoules were heated to maximal temperature 1270 K, kept at this temperature during 4 h and then were cooled slowly to 700K and kept at this temperature during 500 h. Finally, the furnace was switched off. DTA and XRD analyses showed that mixtures containing $>60\text{mol}\%$ Tl_9TbTe_6 were not-homogeneous after the first heating. Therefore, the samples were ground and pressed into pellets under argon, and reheated in fused silica tubes at 750 K for a 500h.

Methods. Differential thermal analysis (DTA), X-ray powder diffraction (XRD) and microhardness measurements were employed to analyze the samples. DTA was performed using a NETZSCH 404 F1 Pegasus system with two chromel-alumel thermocouples. The measurement was performed between room temperature and ~ 1400 K with a heating and cooling rate of 10 K min^{-1} . Temperatures of thermal effects were taken mainly from the heating curves. But, in the some samples thermal effects were taken from cooling curves in order to determine the onset of crystallization. The overall uncertainty of the determined phase transformation temperatures was estimated to be ± 1 K.

X-ray powder diffraction (XRD) data were collected at room temperature in reflection mode using a Bruker D8 ADVANCE powder diffractometer equipped with a Cu-target tube and a diffracted beam graphite monochromator.

Microhardness measurements were done with a microhardnesmeter ПМТ-3, the typical loading being 20 g.

Results and discussion. The phase diagram of the Tl_9TbTe_6 - Tl_9BiTe_6 system (table, fig.2) is characterized by formation of unlimited solid solutions (δ). However, the system is non quasi-binary due to the peritectic melting of the Tl_9TbTe_6 compound. This leads to a primary crystallization from the melt of other infusible phase (X) in a wide composition range (0-35

mol% Tl_9BiTe_6) and the formation on diagram the L+X and L+X+ δ phase areas. Due to the narrow temperature interval the L+X+ δ area is not experimentally fixed and denoted by dotted lines.

Microhardness measurements confirmed the phase diagram (fig.2b). As can be seen, the curve of microhardness has a flat maximum, which is typical for substitutional solid solutions.

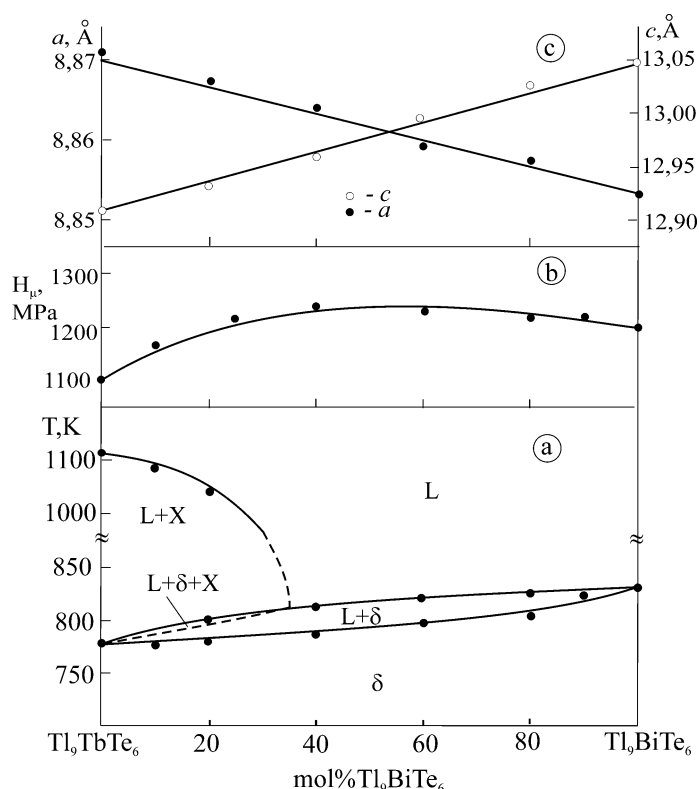
The formation of the unlimited solid solu-

tion in the Tl_9TbTe_6 - Tl_9BiTe_6 system is confirmed by XRD analysis (fig.2c). The XRD data of the alloys after annealing for about 200 h at 750 K are presented in fig.3. Apparently, all samples of this system have the same diffraction pattern typical to Tl_5Te_3 and differ from each other by some displacement of the diffraction lines. The dependence of the lattice parameters of the composition obeys the Vegard's rule within the error limits.

Table

Some properties of initial compounds and solid solutions of the Tl_9TbTe_6 - Tl_9BiTe_6 system

Phase	Temperature of melting (K)	Microhardness, MPa	Parameters of tetragonal lattice, Å	
			<i>a</i>	<i>c</i>
Tl_9TbTe_6	780; 1100	1100	8,871(3)	12,973(7)
$\text{Tl}_9\text{Bi}_{0,2}\text{Tb}_{0,8}\text{Te}_6$	783-803;1046	1215	8,867(4)	12,926(6)
$\text{Tl}_9\text{Bi}_{0,4}\text{Tb}_{0,6}\text{Te}_6$	790-815	1243	8,864(5)	12,962(8)
$\text{Tl}_9\text{Bi}_{0,6}\text{Tb}_{0,4}\text{Te}_6$	800-822	1230	8,860(4)	12,992(9)
$\text{Tl}_9\text{Bi}_{0,8}\text{Tb}_{0,2}\text{Te}_6$	805-825	1222	8,857(5)	13,025(8)
Tl_9BiTe_6	830	1200	8,854(5)	13,047(6)

Fig. 2. Phase diagram of the Tl_9TbTe_6 - Tl_9BiTe_6 system

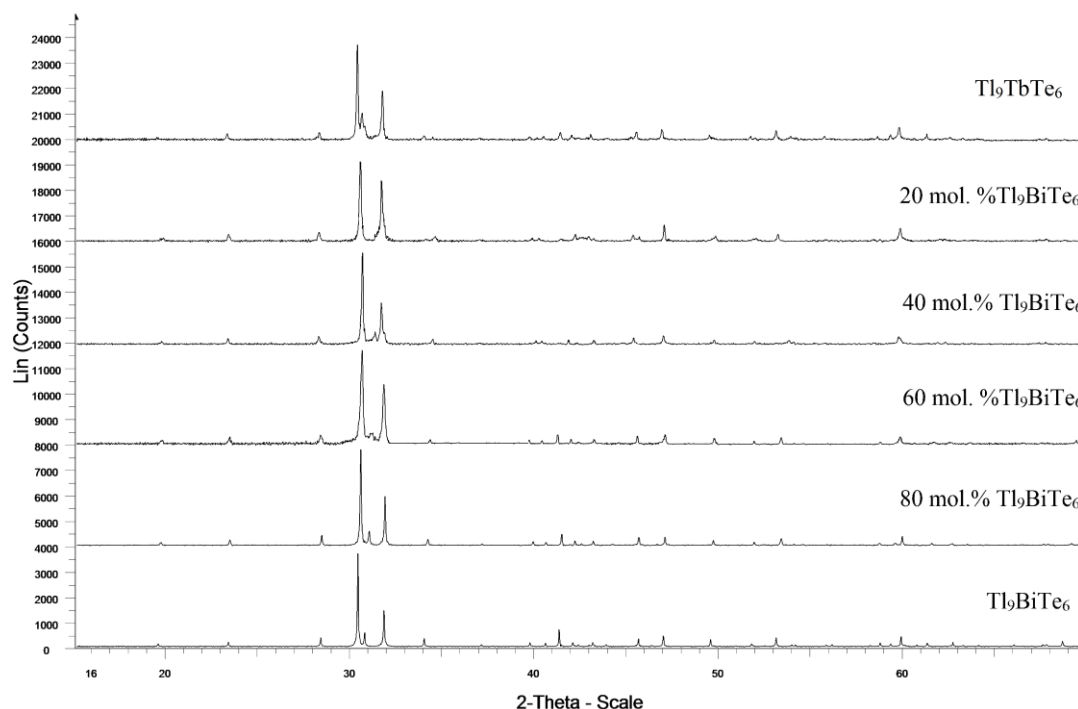


Fig. 3. XRD patterns for different compositions in the Tl_9TbTe_6 – Tl_9BiTe_6 system

Thus, for the first time, in the Tl_9TbTe_6 – Tl_9BiTe_6 system found a new quaternary non-stoichiometric phase with a tetragonal structure. Based on respective characteristics of the initial ternary compounds it can be assumed that the $\text{Tl}_9\text{Bi}_{1-x}\text{Tb}_x\text{Te}_6$ ($0 < x < 1$) intermediate phase may have thermoelectric and magnetic properties.

Constructed T-x diagram can provide great opportunities to select compositions for growing single crystals of δ -solid solution with given composition from melt.

Conclusions

The phase diagram of the Tl_9TbTe_6 – Tl_9BiTe_6 system has been constructed using various experimental methods. A wide range of the substitutional solid solutions (δ -phase) which crystallize in Tl_5Te_3 crystal type is formed in the system.

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Tl_9TbTe_6 - Tl_9BiTe_6 SİSTEMİNDƏ DƏYİŞƏN TƏRKİBLİ YENİ FAZA

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Diferensial-termiki (DTA), rentqenfaza(RFA) və mikrobərkliyin ölçülməsi üsulları ilə Tl_9TbTe_6 - Tl_9BiTe_6 sistemində faza tarazlıqları öyrənilmiş və faza diaqramı qurulmuşdur. Göstərilmişdir ki, sistem Tl_9TbTe_6 birləşməsinin peritektik ərimə xarakterinə görə qeyri-kvazibinardır, lakin solidusdan aşağıda stabildir. Sistemdə Tl_5Te_3 tipli tetraqonal quruluşa malik yeni dördkomponentli dəyişən tərkibli $Tl_9Bi_{1-x}Tb_xTe_6$ ($0 < x < 1$) fazası aşkar edilmişdir.

Açar sözlər: tallium-terbium telluridləri, tallium-bismut telluridləri, faza tarazlıqları, bərk məhlullar, kristal quruluş

НОВАЯ ФАЗА ПЕРЕМЕННОГО СОСТАВА В СИСТЕМЕ Tl_9TbTe_6 - Tl_9BiTe_6

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Методами дифференциального-термического анализа (ДТА), рентгенфазового анализа (РФА) и измерением микротвердости изучены фазовые равновесия в системе Tl_9TbTe_6 - Tl_9BiTe_6 и построена ее фазовая диаграмма. Установлено, что система неквазибинарна в силу перитектического характера плавления Tl_9TbTe_6 , но стабильна ниже солидуса. В системе обнаружена новая четверная фаза переменного состава $Tl_9Bi_{1-x}Tb_xTe_6$ ($0 < x < 1$) со структурой Tl_5Te_3 .

Ключевые слова: теллуриды таллия-тербия, теллуриды таллия-висмута, фазовые равновесия, твердые растворы, кристаллическая структура