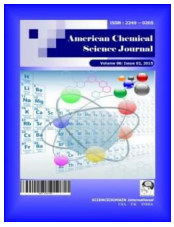

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Phase Relations in the Tl_9TbTe_6-Tl_9BiTe_6 System and Some Properties of Solid Solutions

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Authors' contributions

This work was carried out in collaboration between all authors. Author SZI managed the literature searches and wrote the first draft of the manuscript. Author TMG synthesized the samples and carried out DTA analysis. Author MAM managed the XRD analysis. Author MBB managed the analyses of the study and plotted the phase diagrams. All authors read and approved the final manuscript.

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ABSTRACT

By using X-ray powder diffraction and differential thermal analyses, scanning electron microscopy technique and microhardness measurements the phase equilibria in the Tl_9TbTe_6-Tl_9BiTe_6 system were investigated. According to the obtained experimental results the T-x diagram and concentration dependence of the cell parameters and microhardness of alloys of the Tl_9TbTe_6-Tl_9BiTe_6 system were 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, it is found to be continuous solid solutions with Tl_5Te_3 structure. These phases may be of interest to thermoelectric and magnetic materials.

Keywords: Thallium-terbium telluride; thallium-bismuth telluride; phase equilibria; solid solutions; crystal structure.

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1. 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 [3,4].

Ternary thallium chalcogenides, $Tl_4A^{IV}Te_3$ [A^{IV}-Sn, Pb] and $Tl_9B^{V}Te_6$ [B^{V}-Sb, Bi] obtained in respective systems are structural analogs of Tl_5Te_3 (Sp.gr. *I*4/*mcm*) and promising thermoelectric materials [5-8]. For example, Tl_9BiTe_6 has an extremely low thermal conductivity [9].

The existence of new ternary compounds Tl_9LnTe_6 (Ln-Ce, Nd, Sm, Gd, Tm) structural analogs of Tl_5Te_3 was first reported by M.Babanly et al. [10-12]. As shown in [13], ytterbium does not form compound of Tl_9LnTe_6 type in contrast to other lanthanide [10-12].

One of the ways for improving thermoelectric properties of previously known compounds is the complexification of their composition and structure, which leads to reduction in the thermal conductivity and the increase of the thermoelectric figure of merit [14].

For this purpose, phase equilibria in the Tl_2Te-Tl_9NdTe_6-Tl_9BiTe_6 (I), Tl_5Te_3-Tl_9NdTe_6-Tl_9BiTe_6 (II) [15], Tl_5Te_3-Tl_4PbTe_3-Tl_9NdTe_6 (III) [16] and Tl_5Te_3-Tl_9NdTe_6-Tl_9SbTe_6 (IV) [17] systems were investigated. The systems are characterized by formation of wide (I) or continuous (II-IV) areas of solid solutions with Tl_5Te_3 structure.

Later, a series of tellurides $Tl_{10-x}Ln_xTe_6$ was synthesized, structurally characterized and the thermoelectric properties determined by H.Kleinke et al. [18-20]. The authors confirmed the results of [10-12] these compounds are substitution variants of Tl_5Te_3 (Fig. 1).

Moreover, the Tl_9CeTe_6, Tl_9PrTe_6 and Tl_9TbTe_6 also were found to be paramagnetic due to the presence of unpaired electrons [20].

In this work, the phase relations in the Tl_9TbTe_6-Tl_9BiTe_6 system were studied. We assumed that incorporation of lanthanide atoms to the crystal lattice may give the magnetic properties and improve the thermoelectric properties of obtained phases.

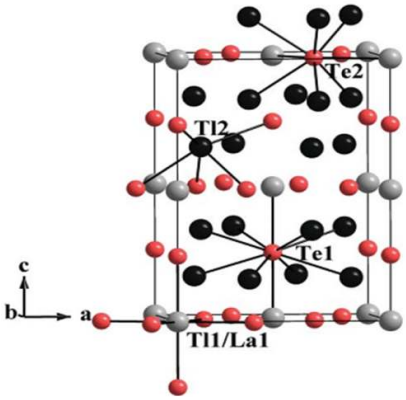


Fig. 1. Crystal structure of Tl_9LaTe_6 [18]

2. MATERIALS AND METHODS

2.1 Materials and Syntheses

The starting Tl_9BiTe_6 and Tl_9TbTe_6 compounds were synthesized by melting stoichiometric amounts of the respective elements of high purity grade (Tl granules, 99.99%; Tb powder, -40 mesh, 99.9%; Bi foil, -99.999 mass%, Te broken ingots, 99.99%) in evacuated (10^{-2} Pa) sealed silica tubes. The reactions were carried out by heating in a resistance furnace at 900 K (Tl_9BiTe_6) and 1200 K (Tl_9TbTe_6) for 3 h. Then the furnace was switched off. In order to avoid the interaction between the silica tubes and the terbium, the synthesis of Tl_9TbTe_6 was carried out in graphitized ampoule.

The Tl_9LnTe_6 compounds form by peritectic reactions and it is difficult to achieve equilibrium [10-12]. The heating curve and SEM analysis of unannealed compound indicate incomplete synthesis (Figs. 2a and 3a). Therefore, after the first heating Tl_9TbTe_6 was ground, pressed into pellet and reheated for ~700 h at 730 K.

Retesting DTA (Fig. 2b), SEM (Fig. 3b) and XRD confirmed the homogeneity of both compounds, which agrees with the data [8,11]. DTA showed that Tl_9BiTe_6 melts congruently at 830 K, while there are two endothermic peaks on the heating curve of Tl_9TbTe_6 that correspond to the peritectic decomposition temperature (780 K) and to complete melting (1110 K) (Fig. 2b).

The powder X-ray diffraction patterns of the Tl_9BiTe_6 and Tl_9TbTe_6 compounds at room temperature were similar to that of Tl_5Te_3. The cell parameters were in accordance with the body centered tetragonal Bravais lattice. Unit cell lattice parameters of Tl_9BiTe_6 were practically

equal with the literature data [21], while slightly differ from [19] for Tl_9TbTe_6.

The alloys of the Tl_9TbTe_6-Tl_9BiTe_6 system were prepared by melting the stoichiometric quantities of the pre-synthesized compounds in sealed graphitized silica tubes. All alloys of the investigated system were heated up to 1200 K within 2 h followed by slowly cooling to 730 K within 300 h. Then the furnace was switched off. The total mass of the ingot was 1 g. DTA and XRD analyses showed that mixtures containing >70mol% Tl_9TbTe_6 were non-homogeneous after the first heating. Therefore, the samples were ground and pressed into pellets under argon, and reheated in fused silica tubes at 730 K for a 500 h in order to achieve the homogeneous composition.

2.2 Methods

The samples were characterized by differential thermal analysis (DTA), X-ray powder diffraction (XRD), scanning electron microscopy with energy dispersive analysis (SEM-EDS) and microhardness measurements.

DTA was performed using a NETZSCH 404 F1 Pegasus differential scanning calorimeter between room temperature and ~1400 K. Temperatures of thermal effects were taken mainly from the heating curves. In some cases in order to determine the onset of crystallization the thermal effects were taken from cooling curves.

XRD analysis was done with Bruker D8 ADVANCE diffractometer (CuK_α radiation).

FEI Quanta™ 250 scanning electron microscope with Oxford Instruments energy dispersive X-ray spectrometer was used for the determination the microstructure of the equilibrium phases.

3. RESULTS AND DISCUSSION

The combined analysis of all our experimental data enabled us to build the phase diagram of the Tl_9TbTe_6-Tl_9BiTe_6 system (Table 1, Fig. 4a). This system is characterized by formation of a continuous series of solid solutions (δ-phase). Nevertheless, the system is non-quasi-binary due to the peritectic melting of the Tl_9TbTe_6. Therefore, in a wide composition range (0-35 mol% Tl_9BiTe_6) initially crystallized other infusible phase (X-phase) and L+X and L+X+δ phase areas are formed. The L+X+δ area is not experimentally fixed due to the narrow temperature interval and depicted by dashed lines.

Microhardness measurements confirmed the phase diagram (Fig. 4b). As can be seen, the curve of microhardness has a flat maximum, which is typical for substitutional solid solutions.

XRD and SEM analyses confirmed the formation of continuous solid solutions in the Tl_9TbTe_6-Tl_9BiTe_6 system. All samples had typical to Tl_5Te_3 diffraction pattern and differ from each other by some displacement of the diffraction patterns. The dependences of the lattice constants upon composition obey the Vegard's law within the limits of error (Fig. 4c).

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

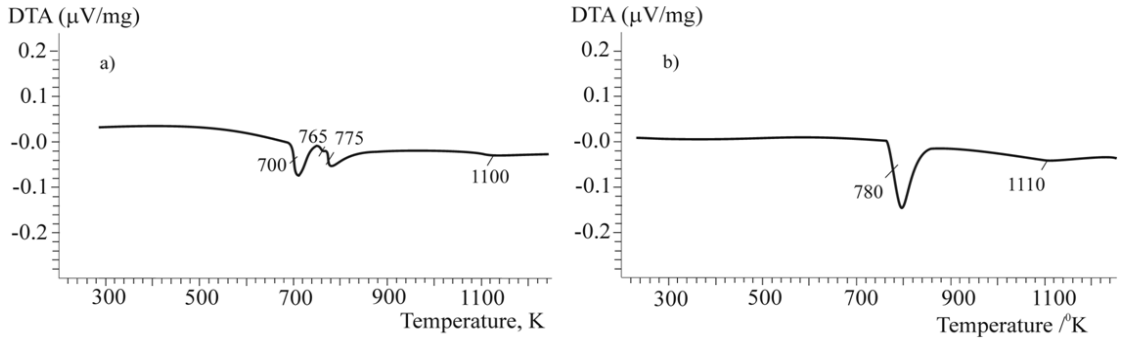
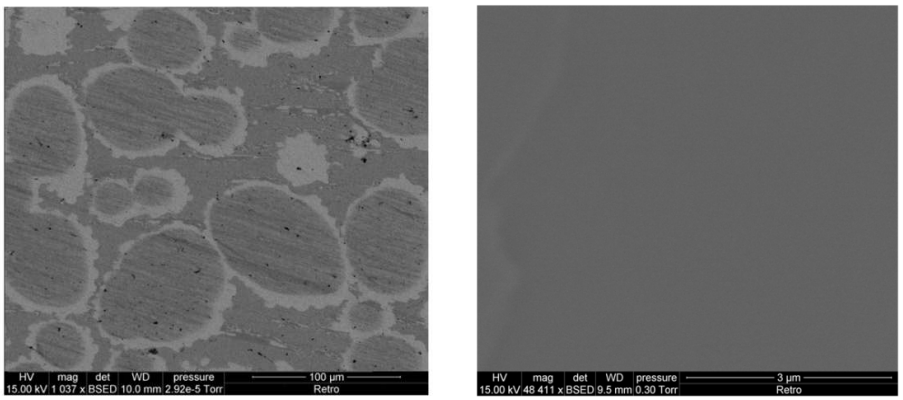


Fig. 2. The heating curves of the unannealed (a) and annealed Tl_9TbTe_6 (b).



a) b)

Fig. 3. SEM images of the unannealed (a) and annealed (b) Tl_9TbTe_6

Table 1. Results of DTA, microhardness measurements and tetragonal lattice parameters of alloys of the Tl_9TbTe_6-Tl_9BiTe_6 system

	Temperature, K	Microhardness, H_μ, MPa	Lattice parameters, Å	
			a	***c***
Tl_9TbTe_6	780; 1100	1100	8,871(3)	12,973(7)
$Tl_9Bi_{0,2}Tb_{0,8}Te_6$	783-803;1046	1215	8,867(4)	12,985(3)
$Tl_9Bi_{0,4}Tb_{0,6}Te_6$	790-815	1243	8,863(5)	13,001(8)
$Tl_9Bi_{0,6}Tb_{0,4}Te_6$	800-822	1230	8,860(4)	13,015(9)
$Tl_9Bi_{0,8}Tb_{0,2}Te_6$	805-825	1222	8,857(5)	13,031(8)
Tl_9BiTe_6	830	1200	8,854(5)	13,047(6)

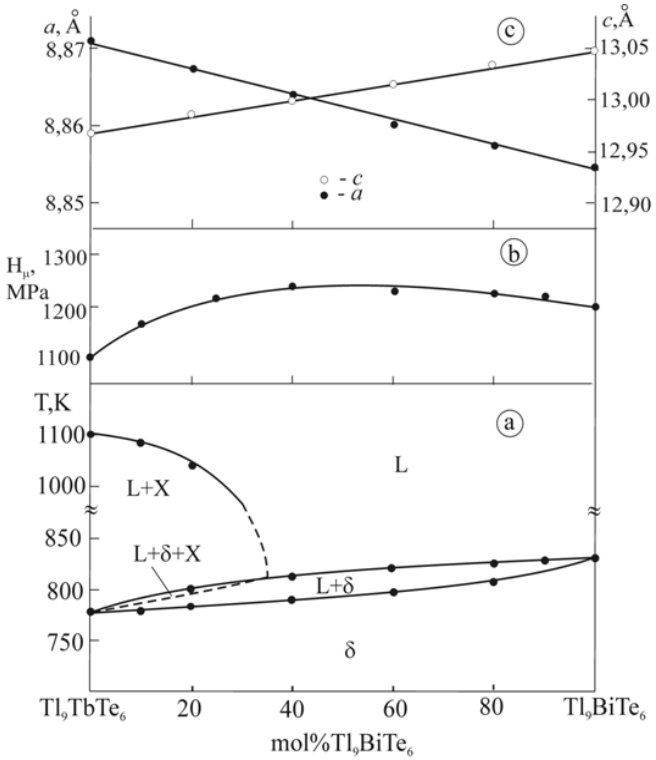


Fig. 4. Phase diagram of the Tl_9TbTe_6-Tl_9BiTe_6 system

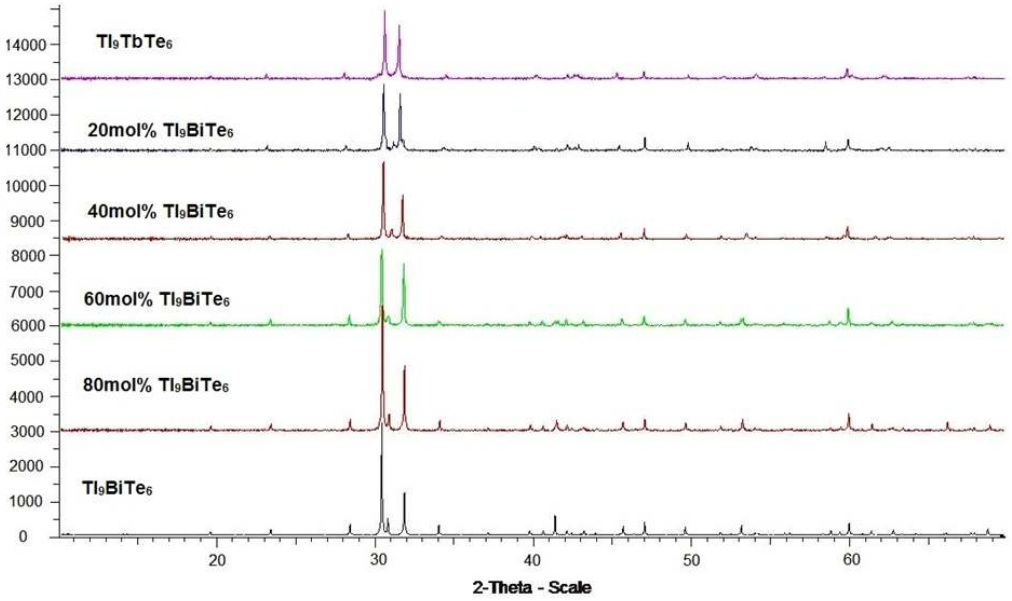


Fig. 5. XRD patterns for different compositions in the Tl_9TbTe_6–Tl_9BiTe_6 system

4. CONCLUSION

The phase diagram of the Tl_9TbTe_6-Tl_9BiTe_6 system has been constructed using various experimental methods. A continuous series of the substitutional solid solutions which crystallize in Tl_5Te_3 crystal type is formed in the system. Based on respective characteristics of the initial ternary compounds it can be assumed that the $Tl_9Bi_{1-x}Tb_xTe_6$ (0<x<1) intermediate phase may have thermoelectric and magnetic properties.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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