## PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

# Phase Equilibria and Some Properties of Solid Solutions in the Tl<sub>5</sub>Te<sub>3</sub>-Tl<sub>9</sub>BiTe<sub>6</sub>-Tl<sub>5</sub>Te<sub>2</sub>Cl System

D. M. Babanly, S. V. Askerova, Z. S. Aliev, and M. B. Babanly

Institute of Chemical Problems, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan Baku State University, Baku, Azerbaijan e-mail: babanly\_mb@rambler.ru

Received April 8, 2010

**Abstract**—Phase equilibria in the  $Tl_5Te_3$ — $Tl_9BiTe_6$ — $Tl_5Te_2Cl$  system were studied by differential thermal analysis (DTA), X-ray powder diffraction, and measurements of microhardness and also emf of concentration circuits with reference to a thallium electrode. A number of polythermal sections, the isothermal sections of the phase diagram at 760 and 800 K, and projections of the liquidus and solidus surfaces were constructed. It was shown that the system is characterized by the formation of unlimited solid solutions with the  $Tl_5Te_3$  structure. The concentration dependences of the crystal lattice parameters, microhardness, and emf in the solid solutions were described.

DOI: 10.1134/S0036023611110040

Tellurides of heavy metals, including thallium  $(Tl_9BiTe_6, Tl_2SnTe_5, Ag_9TITe_5, etc.)$ , are promising compounds for thermoelectric materials design [1, 2].

Thallium telluride  $Tl_5Te_3$  has thermoelectric properties and, because of the specific of its crystal lattice [3], has a number of ternary analogues produced by both cation and anion substitutions. Typical representatives of its cation-substituted structural analogues are  $Tl_4B^{IV}Te_3$  ( $B^{IV} = Sn$ , Pb) [4] and  $Tl_9B^{V}Te_6$  ( $B^{V} = Sb$ , Bi) [5, 6], and its typical anion-substituted structural analogues are  $Tl_5Te_2Hal$  (Hal = Cl, Br, I) [7].

Among structural analogues of  $Tl_5Te_3$ , the compound  $Tl_9BiTe_6$  has record-breaking high thermoelectric indexes [8, 9] and is considered a promising matrix compound for design of new similar materials. One of way to improve the applied properties of  $Tl_9BiTe_6$  is to obtain its base solid solutions. The following systems were investigated for this purpose:  $Tl_5Te_3-Tl_4PbTe_3 Tl_9BiTe_6$  [10],  $Tl_5Te_3-Tl_4SnTe_3-Tl_9BiTe_6$  [11],  $Tl_5Te_3 Tl_9NdTe_6-Tl_9BiTe_6$  [12], and  $Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2I$ [13]. Unlimited solid solutions with the  $Tl_5Te_3$  structure were found to exist in these systems.

In this work, we studied phase equilibria in the  $Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Cl$  system (A) to obtain new cation- and anion-substituted multicomponent solid solutions based on  $Tl_9BiTe_6$ .

The initial compounds of system A have been studied in detail. Tl<sub>5</sub>Te<sub>3</sub> melts congruently at 723 K [14, 15] and crystallizes in a tetragonal lattice (space group *I*4/*mcm*) with the parameters a = 8.929 Å, c = 12.620 Å, and Z = 4 [3]. Unlike other thallium tellurides, Tl<sub>5</sub>Te<sub>3</sub> is a variable-composition phase with quite a wide homogeneity range (~34.5–38 at % Te [14, 15]). The compound Tl<sub>9</sub>BiTe<sub>6</sub> melts congruently at 833 K [16] and crystallizes in a tetragonal lattice with the parameters a = 8.855 Å, c = 13.048 Å, and Z = 2 [5]. The Tl-Bi-Te system was studied in the composition range Tl<sub>2</sub>Te-Bi<sub>2</sub>Te<sub>3</sub>-Te [16]. Tl<sub>9</sub>BiTe<sub>6</sub> was found to have an extensive homogeneity region ( $\delta$  phase), which almost completely occupies the composition triangle Tl<sub>2</sub>Te-Tl<sub>5</sub>Te<sub>3</sub>-Tl<sub>9</sub>BiTe<sub>6</sub>.

The compound Tl<sub>5</sub>Te<sub>2</sub>Cl was detected while studying the system Tl–Te–Cl along the section Tl<sub>2</sub>Te–TlCl [7]. The intermediate  $\delta$  phase based on this compound was shown to melt with decomposition by a syntectic reaction at 708 K. At this temperature, the phase separation region extends from ~7 to 83 mol % Tl<sub>2</sub>Te. The parameters of the tetragonal unit cell of Tl<sub>5</sub>Te<sub>2</sub>Cl (space group *I*4/*mcm*) are *a* = 8.920 Å, *c* = 12.691 Å, and *Z* = 4 [7].

#### **EXPERIMENTAL**

For preparing alloys in system A, we synthesized the initial compounds  $Tl_5Te_3$ ,  $Tl_9BiTe_6$ , and  $Tl_5Te_2Cl$ . The first two compounds, which melt congruently, were synthesized by alloying stoichiometric amounts of high-purity constituent elements in evacuated (~10<sup>-2</sup> Pa) quartz ampoules at temperatures somewhat (by 30–50 K) exceeding their melting points with subsequent slow cooling of the melt.

The compound  $Tl_5Te_2Cl$  was synthesized in two stages. Initially, TlCl was synthesized according to a published procedure [17]. Metallic thallium was dissolved at ~350 K in dilute (5%)  $H_2SO_4$  to obtain a  $Tl_2SO_4$  solution. To a boiling 2%  $Tl_2SO_4$  solution, dilute HCl was added until the precipitation was com-



Fig. 1. (a) Phase diagram of the  $Tl_9BiTe_6-Tl_5Te_2Cl$  system and (b) unit cell parameters, (c) microhardness, and (d) emf of concentration circuits (1) versus composition.

pleted. After cooling the mother solution, TlCl was withdrawn, washed with distilled water, and dried for a long time in a drying cabinet at 380–390 K.

Then,  $Tl_5Te_2Cl$  was synthesized by alloying thallium monochloride with required amounts of Tl and Te in an evacuated quartz ampoule. The alloying temperature was ~850 K. This compound melts syntactically [7]; the melt consists of two separating liquid phases. For this reason, heterogeneous mixtures containing TiCl and the phases based on  $Tl_5Te_2Cl$  and TlCl crystallize from the melt even on slow cooling. Therefore, to ensure the completeness of the interaction, the ampoules were slowly (for ~5 h) cooled to 700 K while being continuously shaken and kept at this temperature for ~300 h.

The synthesized compounds were identified by differential thermal analysis (DTA) and X-ray powder diffraction.

Samples of system A with compositions lying along three mutually perpendicular radial sections were prepared by vacuum alloying of the preliminarily synthesized initial compounds with subsequent homogenizing annealing at  $\sim$ 700 K for 800–1000 h.

The samples were investigated by DTA (NTR-72 pyrometer, Chromel/Alumel thermocouples, and x-y recorder), X-ray powder diffraction (Philips X'Pert MPD diffractometer, Cu $K_{\alpha 1}$  radiation), and measurements of microhardness (PMT-3 microhardness meter, 20-g load) and the emf of concentration circuits of the type

$$(-)Tl (solid)/glycerol + KCl + TlCl/[Tl-Bi-Te-Cl] (solid) (+).$$
(1)

The assembly of the electrochemical cell and emf measurements were described in detail previously [18]. The emf of circuits (1) was measured by a compensation method with a V7-43A digital voltmeter within the temperature range 300–400 K.

#### **RESULTS AND DISCUSSION**

The boundary quasi-binary constituents  $Tl_5Te_3$ - $Tl_9BiTe_6$  and  $Tl_5Te_3$ - $Tl_5Te_2Cl$  in the  $Tl_5Te_3$ - $Tl_9BiTe_6$ - $Tl_5Te_2Cl$  system are characterized by unlimited mutual solubility of components and are described by T-x diagrams without extreme points [16, 19].

#### PHASE EQUILIBRIA AND SOME PROPERTIES

Section	Phase	T <sub>melt</sub> , K	Unit cell parameters, Å		M MDa	E mV
			а	С	<i>w</i> , wra	<i>L</i> , IIIV
Tl <sub>9</sub> BiTe <sub>6</sub> -Tl <sub>10</sub> Te <sub>4</sub> Cl <sub>2</sub>	Tl <sub>9</sub> BiTe <sub>6</sub>	830	8.855(5)	13.048(8)	980	446
	Tl <sub>9.2</sub> Bi <sub>0.8</sub> Te <sub>5.6</sub> Cl <sub>0.4</sub>	755-815	8.870(6)	12.975(7)	1280	
	$Tl_{9.4}Bi_{0.6}Te_{5.2}Cl_{0.8}$	730-805	8.883(7)	12.900(8)	1320	438
	$Tl_{9.6}Bi_{0.4}Te_{4.8}Cl_{1.2}$	720-790	8.900(7)	12.840(7)	1340	
	$Tl_{9.8}Bi_{0.2}Te_{4.4}Cl_{1.6}$	715-740-768	8.916(6)	12.758(7)	1335	427
	$Tl_{10}Te_4Cl_2$	708	8.920(7)	12.691(8)	1340	424
$Tl_9BiTe_6-[Tl_{10}Te_5Cl]$	Tl <sub>9.2</sub> Bi <sub>0.8</sub> Te <sub>5.8</sub> Cl <sub>0.2</sub>	775-825	8.868(5)	12.969(8)	1180	440
	Tl <sub>9.4</sub> Bi <sub>0.6</sub> Te <sub>5.6</sub> Cl <sub>0.4</sub>	750-813	8.884(6)	12.893(8)	1280	435
	Tl <sub>9.6</sub> Bi <sub>0.4</sub> Te <sub>5.4</sub> Cl <sub>0.6</sub>	730–795	8.896(7)	12.814(8)	1300	
	$Tl_{9.8}Bi_{0.2}Te_{5.2}Cl_{0.8}$	715-758	8.910(6)	12.735(8)	1340	425
	Tl <sub>10</sub> Te <sub>5</sub> Cl	710-718	8.924(7)	12.655(7)	1350	420
$[Tl_{9.5}Bi_{0.5}Te_6] - Tl_{10}Te_4Cl_2$	Tl <sub>9.5</sub> Bi <sub>0.5</sub> Te <sub>6</sub>	760-808	8.892(6)	12.840(9)	1170	432
	Tl <sub>9.6</sub> Bi <sub>0.4</sub> Te <sub>5.6</sub> Cl <sub>0.4</sub>	735-800	8.898(7)	12.809(8)	1270	430
	Tl <sub>9.7</sub> Bi <sub>0.3</sub> Te <sub>5.2</sub> Cl <sub>0.8</sub>	722–783	8.904(6)	12.783(8)	1330	
	$Tl_{9.8}Bi_{0.2}Te_{4.8}Cl_{1.2}$	715-765	8.909(7)	12.754(8)	1380	427
	$Tl_{9.9}Bi_{0.1}Te_{4.4}Cl_{1.6}$	710-735-745	8.915(7)	12.722(7)	1390	

Some properties of the initial compounds and solid solutions in the  $Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Cl$  system

**The Tl<sub>9</sub>BiTe<sub>6</sub>–Tl<sub>5</sub>Te<sub>2</sub>Cl system** (Fig. 1), which forms a continuous solid solution series ( $\delta$  phase), is, as a whole, non-quasi-binary because of the incongruence of melting of the compound Tl<sub>5</sub>Te<sub>2</sub>Cl [7]. Within the composition range ~53–100 mol % Tl<sub>9</sub>BiTe<sub>6</sub>, the  $\delta$ phase primarily crystallizes from a homogeneous melt; near the composition Tl<sub>5</sub>Te<sub>2</sub>Cl (0–53 mol % Tl<sub>9</sub>BiTe<sub>6</sub>), the  $\delta$  phase crystallizes by the syntectic reaction liquid + liquid<sub>1</sub>  $\implies \delta$ ; and the compositions of the separating phases leave the *T*–*x* plane of this system.

The results of X-ray powder diffraction analysis and microhardness and emf measurements (table; Figs. 1b–1d) confirm the DTA data.

X-ray powder diffraction analysis showed that all samples are comprised of a single phase and have a tetragonal structure of the  $Tl_5Te_3$  type. The unit cell parameters of the  $\delta$  phase vary virtually linearly from those for pure  $Tl_9BiTe_6$  to those for  $Tl_5Te_2Cl$  (a = 8.859-8.920 Å, c = 13.051-12.691 Å; Fig. 1b).

We also found that the microhardness and emf in alloys in the  $Tl_9BiTe_6-Tl_5Te_2Cl$  system are continuous functions of composition: their values vary continuously between the *H* and *E* values of the initial compounds (Figs. 1c, 1d). The fact the each of the samples comprises a single phase was confirmed by microhardness measurements (which gave a single value). The continuous change in the emf of circuits (1) is indicative [18] of a continuous change in the activity of the potential-forming component (thallium) in alloys, which indirectly proves the formation of unlimited solid solutions in the system.

The results obtained from analyzing some polythermal sections of the phase diagram of system A (table; Figs. 2, 3) indicate the formation of unlimited solid solutions with the  $Tl_5Te_3$  structure in the system.

Along  $Tl_9BiTe_6$ -[ $Tl_{10}Te_5Cl$ ] and [ $Tl_{9.5}Bi_{0.5}Te_6$ ]- $Tl_{10}Te_4Cl_2$  sections (hereafter, within the square brackets are the initial "components" of the sections that are not chemical compounds), there are continuous



**Fig. 2.** (a)  $Tl_9BiTe_6-[Tl_{10}Te_5Cl]$  polythermal section of system A and (b) microhardness and (c) emf of concentration circuits (1) versus composition.

changes in onset and end temperatures of crystallization (Figs. 2a, 3a) and in the microhardness, emf (Figs. 2b, 2c, 3b, 3c), and unit cell parameters (table). Such composition—property diagrams are characteristic of systems with unlimited solid solutions.

The  $[Tl_{9.5}Bi_{0.5}Te_6]-Tl_{10}Te_4Cl_2$  polythermal section (Fig. 3a) passes through the phase separation region (liquid + liquid\_1) caused by the syntectic nature of  $Tl_5Te_2Cl$  melting. Within the corresponding composition range (~40–100 mol %  $Tl_{10}Te_4Cl_2$ ), the  $\delta$  phase crystallizes by the liquid + liquid\_1  $\implies \delta$  monovariant syntectic reaction, and the phase diagram contains the liquid + liquid\_1 +  $\delta$  three-phase region. Notably, the tie lines in the liquid + liquid\_1 two-phase regions in Figs. 2a and 3a do not lie insie the T-x plane and vary continuously with varying temperature.

Figure 4 presents **liquidus and solidus surface projections of the Tl<sub>5</sub>Te<sub>3</sub>–Tl<sub>9</sub>BiTe<sub>6</sub>–Tl<sub>5</sub>Te<sub>2</sub>Cl system,** where the isotherms on these surfaces are indicated by solid and dashed lines, respectively. The liquidus consists of two fields that describe the primary crystallization of the  $\delta$  phase from a single-phase melt and from two separating liquid phases. The curve *ab* separating these fields represents monovariant syntectic equilibrium: L +  $\delta$ . The solidus of the system consists of only one surface (shown in dashed lines) that characterizes the end of crystallization of  $\delta$  solid solutions.



**Fig. 3.** (a)  $[Tl_{9.5}Bi_{0.5}Te_6]-Tl_{10}Te_4Cl_2$  polythermal section of system A and (b) microhardness and (c) emf of concentration circuits (1) versus composition.



**Fig. 4.** Projections of liquidus (solid lines) and solidus (dashed lines) surfaces in the  $Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Cl$  system (A).

**800-K** isothermal section of the phase diagram of system A (Fig. 5a) comprises four fields. The liquid +  $\delta$  two-phase region is located between the corresponding single-phase fields (liquid and  $\delta$ ) and allows one to determine their coupled mutually saturated compositions. By comparing Fig. 5a and Figs. 2a, 3a, it is easy



Fig. 5. Isothermal sections of the phase diagram of system A at (a) 800 and (b) 760 K.

to show that the tie lines in the liquid +  $\delta$  two-phase regions of the above polythermal sections lie outside their *T*-*x* planes. Figure 5a also demonstrates the liquid + liquid<sub>1</sub> phase separation region, which occupies a considerable part of the concentration triangle from the side of Tl<sub>5</sub>Te<sub>2</sub>Br. Obviously, the tie lines liquid + liquid<sub>1</sub> in this region are also outside the plane of this isothermal section.

In **760 K isothermal section** (Fig. 5b), phase equilibria are somewhat different. In the region liquid +  $\delta$  (field S'L'L"S"), the tie lines connect the conjugated curves of liquidus (L'L") and solidus (S'S"); and in the other two two-phase regions (liquid<sub>1</sub> +  $\delta$  and liquid + liquid<sub>1</sub>), the tie lines lie outside the plane of the isothermal section. The compositions of the coexisting

phases in the liquid + liquid<sub>1</sub> +  $\delta$  three-phase region are also represented by points located outside this plane and, in Fig. 5a, they are separated conditionally according to the phase rule requirements.

The data obtained on phase equilibria in the  $Tl_5Te_3-Tl_9BiTe_6-Tl_5Te_2Cl$  system can be used for choosing the compositions of melts and their crystallization temperature in growing single crystals of  $\delta$ -solid solutions of given compositions.

### REFERENCES

- 1. A. V. Shevel'kov, Usp. Khim. 77 (1), 3 (2008).
- 2. L. E. Shelimova, O. G. Karpinskii, and V. S. Zemskov, Persp. Mater., No. 5, 23 (2000).

- 3. I. Schewe, P. Bottcher, and H. G. Schnering, Z. Kristallogr. **188**, 287 (1989).
- S. Bradtmöller and P. Böttcher, Z. Anorg. Allg. Chem. 619, 1155 (1993).
- 5. T. Doert and P. Bottcher, Z. Kristallogr. 24, 1479 (1988).
- 6. T. Doert and P. Böttcher, Z. Kristallogr. 209, 96 (1994).
- D. M. Babanly, A. A. Nadzhafova, M. I. Chiragov, and M. B. Babanly, Khim. Problems (Baku), No. 2, 149, (2005),
- B. Wolfing, K. Kloc, J. Teubner, and E. Bucher, Phys. Rev. Lett. 35 (19), 4350 (2001).
- S. Yamanaka, A. Kosuka, and K. Korosaki, J. Alloys Compd. 352, 275 (2003).
- 10. G. B. Dashdieva, F. N. Guseinov, and M. B. Babanly, Azerb. Khim. Zh., No. 2, 14 (2008).
- 11. G. B. Dashdieva, F. N. Guseinov, and D. M. Babanly, in *Khim. Problemy (Baku)* No. 4, 704 (2006).

- 12. M. B. Babanly, J.-C. Tedenac, S. Z. Imamaliyeva, et al., J. Alloys Compd. **491** (1–2), 230 (2010).
- 13. D. M. Babanly, S. V. Askerova, I. M. Babanly, and Yu. A. Yusibov, Neorg. Mater. **46** (1), 23 (2010).
- M. M. Asadov, M. B. Babanly, and A. A. Kuliev, Izv. Akad. Nauk SSSR, Neorg. Mater. 13 (8), 1407 (1977).
- 15. H. Okamoto, J. Phase Equil. 21 (5), 501 (2001).
- 16. M. B. Babanly, A. Akhmad'yar, and A. A. Kuliev, Zhurn. Neorgan. Khimii **30** (9), 2356 (1985).
- 18. M. B. Babanly, Yu. A. Yusibov, and V. T. Abishev, *EMF Measurements in the Theromdynamics of Compound Semiconductors* (BGU, Baku, 1992) [in Russian].
- D. M. Babanly, I. I. Aliev, Yu. A. Yusibov, and M. I. Chiragov, Azerb. Khim. Zh., No. 1, 151 (2007).