

Tl₄PbTe₃–Tl₉SmTe₆ SYSTEM

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Abstract. The aim of the present study was to determine the phase relations in the Tl–Pb–Sm–Te quaternary system on the Tl₄PbTe₃–Tl₉SmTe₆ composition area. According to the results obtained by the differential thermal analysis, powder X-ray diffraction technique and microhardness measurements, the system is characterized by the formation of unlimited areas of solid solutions which crystallize in the tetragonal Tl₅Te₃ structure type. Receive experimental data can be used for choosing the composition of solution-melt for the growth of high-quality crystals of δ- phase which are of interest like thermoelectric materials.

Keywords: thallium-lead telluride, thallium-samarium tellurides, phase equilibria, solid solutions, crystal structure.

1. INTRODUCTION

Heavy *p*-elements chalcogenides are prospective functional materials with optic, photoelectric, magnet, thermoelectric et al properties [1, 2]. Furthermore, some of these materials possess properties of topological insulators and can use in spintronic devices [3].

Tl₅Te₃ compound due to features of crystal structure (Sp.gr.I4/mcm, *a* = 8.930; *c* = 12.598 Å) [4] has a number of ternary substitutional analogs such as of Tl₄A^{IV}Te₃ and Tl₉B^VTe₆ (A^{IV}–Sn, Pb; B^V–Sb, Bi) [5–7] which also possess a good thermoelectric performance [8, 9].

A new thallium lanthanide tellurides with composition Tl₉LnTe₆ (Ln–Ce, Nd, Sm, Gd, Tb, Tm) founded by authors of [10, 11] are also ternary analogs of Tl₅Te₃ [10, 11]. Authors of [12, 13] determined the thermoelectric and magnetic properties for a number Tl₉LnTe₆-type compounds.

In order to develop modern preparative methods for controlled synthesis of novel functional materials, it is necessary to investigate phase relationships in the respective systems.

Early, the results of phase equilibria investigations for a number of systems including the Tl₅Te₃ compound or its structural analogs showed the formation of continuous series of solid solutions these systems [14–16].

In this paper, we present the experimental results on phase equilibria in the Tl₄PbTe₃–Tl₉SmTe₆ of the Tl–Pb–Sm–Te system.

Tl₄PbTe₃ melts congruently at 893 K [17], while Tl₉SmTe₆ decomposes peritectically at 755 K [15]. The tetragonal lattice constants of Tl₄PbTe₃ and Tl₉SmTe₆ are following: *a* = 8.841, *c* = 13.056 Å, *z* = 4 [18]; *a* = 8.855, *c* = 13.048 Å, *z* = 2 [15].

According to Ref. [17], the boundary system Tl₄PbTe₃–Tl₉BiTe₆ is quasi-binary and characterized by the formation of unlimited solid solutions (δ) with Tl₅Te₃-structure.

2. EXPERIMENTAL

2.1. Materials and syntheses

Thallium (granules, 99.999%), lead (ingot, 99.99%), samarium (powder, 99.9%), and tellurium (broken ingots 99.999%) were used as the starting elements

We used protective gloves at all times when working with thallium because thallium and its compounds are highly toxic and contact with skin is dangerous.

Stoichiometric amounts of the starting elements were weighed and put into silica tubes of about 20 cm in length and diameter about 1.5 cm. Then these tubes were sealed under a vacuum of 10^{–2} Pa. Tl₄PbTe₃ were synthesized by heating in a resistance furnace at 920 K followed by cooling in the switched-off furnace. In the case of Tl₉SmTe₆, the ampoule was graphitized using pyrolysis of toluene in order to prevent the reaction of samarium with quartz. Taking into ac-

count the results of the [15], the intermediate ingot of Tl₉SmTe₆ was powdered in an agate mortar, carefully mixed, pressed into a pellet and annealed at 700 K within ~700 h.

All of the synthesized compounds were identified by differential thermal analysis (DTA) and X-ray diffraction

The alloys of the Tl₄PbTe₃-Tl₉SmTe₆ system were prepared by melting of previously synthesized compounds. After synthesis, the samples containing > 60 % Tl₉SmTe₆ were powdered, mixed, pressed into pellets and annealed at 700 K during ~ 800 h in order to complete the homogenization. The total mass of each ingot is about 1 g.

2.2. Methods

DTA and XRD analyses, as well as microhardness measurements, were used to analyze the samples of the investigated system.

DTA heating curves were obtained in the range from room temperature to ~1400 K at a heating rate of 10 K/min using a Netzsch 404 F1 Pegasus differential scanning calorimeter system. The crystal structure was studied by X-ray diffraction at room temperature on a Bruker D8 powder diffractometer (CuK α radiation) in the range $2\theta = 10-70^\circ$. Microhardness measurements were performed on a PMT-3 microhardness tester and an indenter load of 0.2 N.

3. RESULTS AND DISCUSSION

The results of DTA and microhardness measurements, as well as the parameters of the crystal lattices for some intermediate alloys of the Tl₄PbTe₃-Tl₉SmTe₆ section, are given in the Table. Based on these data, phase diagram and the composition dependences of properties are plotted (Fig. 1). This section is characterized by the formation of continuous solid solutions (δ) with Tl₅Te₃-structure. However, this system is non-quasi-binary section of the Tl-Pb-Sm-Te quaternary system due to peritectic melting of Tl₉SmTe₆. This leads to crystallization TlSmTe₂ compound in a wide composition interval and formation L+TlSmTe₂ two-phase and L+TlSmTe₂+ δ three-phase areas. The L+TlSmTe₂+ δ area is shown by a dotted line because not fixed experimentally due to narrow temperature interval.

Polished surfaces of the intermediate alloys were visually observed under the microscope of microhardness meter, in order to determine the phase constituents. Microhardness measurements (Fig. 1b) are in good agreement with phase diagram: curves have a flat maximum that is typical for systems with continuous solid solutions [19].

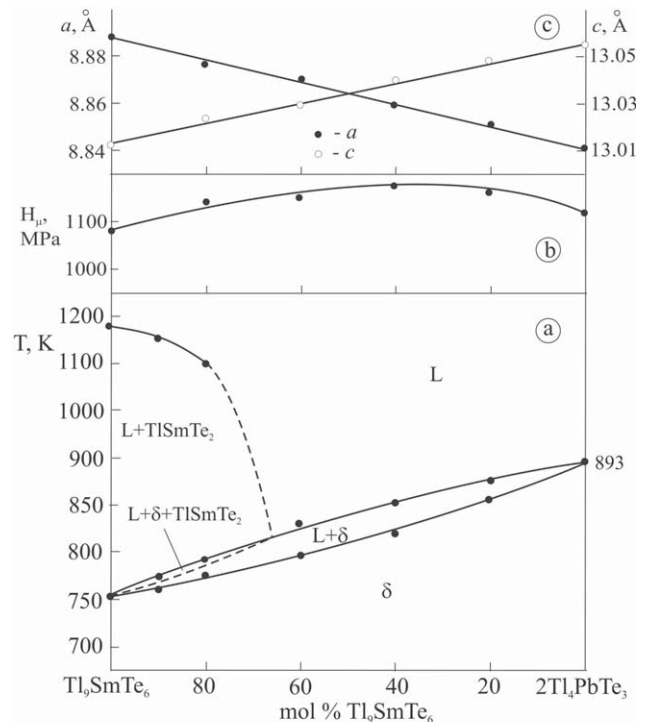


Fig. 1. Phase diagram (a), concentration relations of microhardness (b), and lattice parameters (c) for the Tl₄PbTe₃-Tl₉SmTe₆ system

The XRD powder patterns for some alloys of the Tl₄PbTe₃-Tl₉SmTe₆ section are presented in Fig. 2. As can be seen, powder diffraction patterns of starting compounds as well as intermediate alloys are single-phase and have the diffraction patterns qualitatively similar to Tl₅Te₃ with slight reflections displacement from one compound to another. For example, we present the powder diffraction pattern of alloy with composition 30, 50 and 70 mol.% Tl₉SmTe₆. The lattice parameters of solid solutions obey the Vegard's law, i.e. depend linearly on composition (Table, Fig. 1c).

4. CONCLUSION

The phase diagram of the Tl₄PbTe₃-Tl₉SmTe₆ section is constructed. This section is characterized by an unlimited solubility of components in the solid state. Obtained experimental data can be used for choosing the composition of solution-melt and to evaluate technologically parameters necessary for the growth of crystals of δ - phase of high quality which are of interest like thermoelectric materials.

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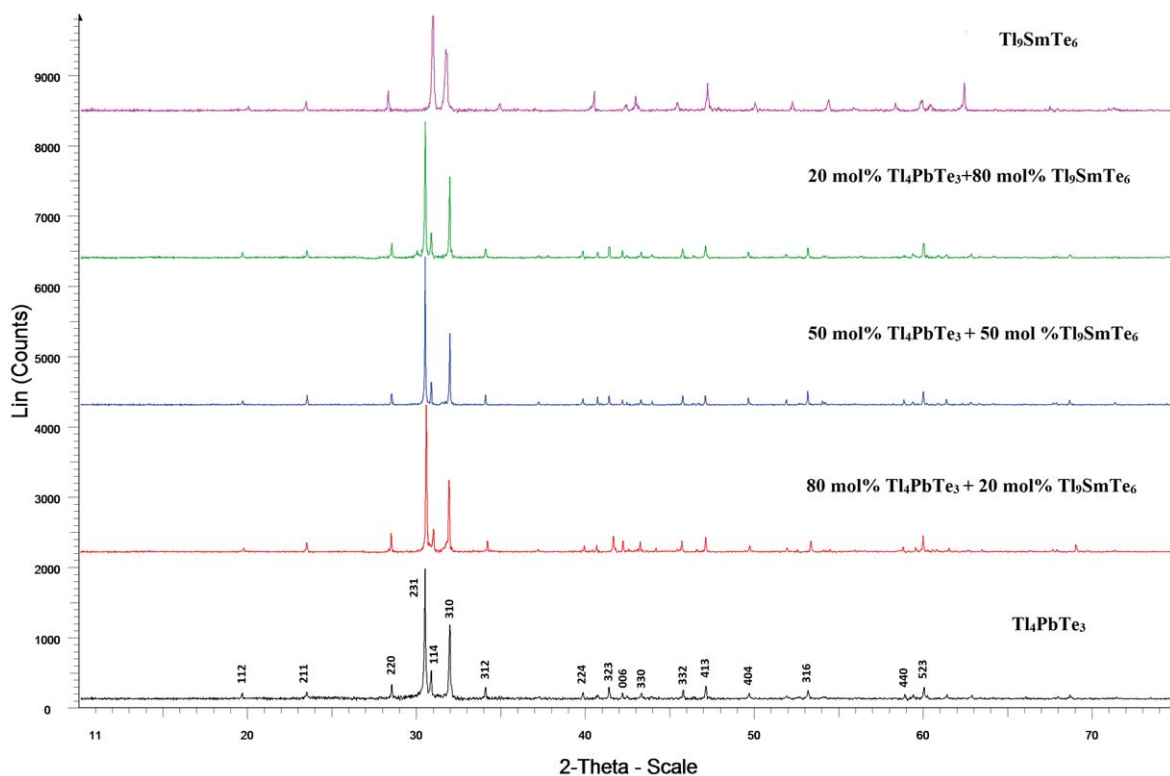


Fig. 2. XRD patterns for some alloys of the Tl_4PbTe_3 – Tl_9SmTe_6 system

Table. Composition dependence of the properties for the alloys of the Tl_4PbTe_3 – Tl_9SmTe_6 section of the Tl–Pb–Bi–Sm–Te system

Solid phase compositions	Thermal effects, K	Microhardness, MPa	Parameters of tetragonal lattice, Å	
			<i>a</i>	<i>c</i>
Tl_4PbTe_3	893	1120	8.8409(5)	13.0556(6)
$Tl_{8.2}Pb_{1.6}Sm_{0.2}Te_6$	855–875	1160	8.8504(4)	13.0482(9)
$Tl_{8.4}Pb_{1.2}Sm_{0.4}Te_6$	820–850	1180	8.8602(5)	13.0387(8)
$Tl_{8.4}Pb_{1.0}Sm_{0.5}Te_6$	810–840	–	8.8645(6)	13.0343(9)
$Tl_{8.6}Pb_{0.8}Sm_{0.6}Te_6$	790–830	1150	8.8702(6)	13.0298(9)
$Tl_{8.8}Pb_{0.4}Sm_{0.8}Te_6$	775–800; 1190	1140	8.8788(5)	13.0220(9)
$Tl_{8.9}Pb_{0.2}Sm_{0.9}Te_6$	760–775; 1155	–	–	–
Tl_9SmTe_6	755; 1180	1080	8.8882(5)	13.0132(7)

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REFERENCES

1. *Applications of Chalcogenides: S, Se, and Te*. Ed. by Gurinder Kaur Ahluwalia, Springer, 2016.
2. Singh N. and Schwingenschlogl U. *Phys. Status Solidi*, 2014, vol. 8, no. 9, pp. 805–808. DOI: 10.1002/pssr.201409110

3. Andreev O. V., Bamburov V. G., Monina L. N., Razumkova I. A., Ruseikina A. V., Mitroshin O. Yu., Andreev V. O. *Phase Equilibria in the Sulfide Systems of the 3d, 4f-Elements*. Ekaterinburg: Editorial Publication Department of the UR RAS, 2015. (in Russian)

4. Schewe I., Böttcher P., Schnering H. G. Z. *Kristallogr.*, 1989, Bd188, pp. 287–298. DOI: <https://doi.org/10.1524/zkri.1989.188.14.287>

5. Gotuk A. A., Babanly M. B., Kuliev A. A. *Inorg. Mater.*, 1979, vol. 15, pp. 1062–1067

6. Babanly M. B., Akhmadyar A., Kuliev A. A. *Russ. J. Inorg. Chem.*, 1985, vol. 30, pp. 1051–1059.

7. Babanly M. B., Akhmadyar A., Kuliev A. A. *J. Inorg. Chem.*, 1985, vol. 30, no. 9, pp. 2356–2359
8. Wolfing B., Kloc C., Teubner J., and Bucher E. *Phys. Rev. Lett.*, 2001, vol. 36, no. 19, pp. 4350–4353. DOI: 10.1103/PhysRevLett.86.4350
9. Guo Q., Chan M., Kuropatwa B. A., Kleinke H. *J. Appl. Phys.*, 2014, vol. 116, pp. 183702/1–9. DOI: <http://dx.doi.org/10.1063/1.4901460>
10. Imamalieva S. Z., Sadygov F. M., Babanly M. B. *Inorg. Mater.*, 2008, vol. 44, no. 9, pp. 935–938.
11. Babanly M. B., Imamalieva S. Z., Babanly D. M. *Azerb. Chem. J.*, 2008, no. 2, pp. 121–125. (in Russian).
12. Bangarigadu-Sanasy S., Sankar C. R., Schlender P., Kleinke H. *J. Alloys Compd.*, 2013, vol. 549, pp. 126–134. <https://doi.org/10.1016/j.jallcom.2012.09.023>
13. Bangarigadu-Sanasy S., Sankar C. R., Dube P. A., Greedan J. E., Kleinke H. *J. Alloys Compd.*, 2014, vol. 589, pp. 389–392. DOI: 10.1016/j.jallcom.2013.11.229
14. Imamalieva S. Z., Gasanly T. M., Gasymov V. A., Babanly M. B. *Acta Chim. Slov.*, 2017, vol. 64, pp. 221–226. DOI: 10.17344/acsi.2017.3207
15. Imamalieva S. Z., Gasymov V. A., Babanly M. B. *Chemist*, 2017, vol. 90, no. 1, pp. 1–6
16. Imamalieva S. Z., Gasanly T. M., Mahmudova M. A., Babanly M. B. *American Chemical Journal*, 2016, vol. 10, no. 3, pp. 1–6.
17. Babanly M. B., Dashdiyeva G. B., Guseinov F. N. *Chem. Probl.*, 2008, no. 1, pp. 69–72.
18. Bradtmöller S., Böttcher P. Z. *Anorg. Allg. Chem.*, 1993, vol. 619, pp. 1155–1160. DOI: 10.1002/zaac.19936190702
19. Glazov V. M., Vigdorovich V. N. *Microhardness of Metals and Semiconductors*. Moscow, Metallurgiya Publ., 1969. (In Russian)

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СИСТЕМА Tl_4PbTe_3 - Tl_9SmTe_6

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Аннотация. В работе приведены результаты исследования фазовых равновесий в четверной системе Tl–Pb–Sm–Te в концентрационной области Tl_4PbTe_3 - Tl_9SmTe_6 методами дифференциального термического (ДТА) и рентгенофазового (РФА) анализов, а также измерений микротвердости.

Показано, что T - x диаграмма характеризуется образованием непрерывного ряда твердых растворов (δ -фаза). В целом данный разрез является неквазибинарным вследствие инконгруэнтного характера плавления Tl_9SmTe_6 . В широком интервале составов (>35 mol.% Tl_4PbTe_3) в нем происходит первичная кристаллизация $TlSmTe_2$, что приводит к образованию на диаграмме состояния фазовых областей $L+TlSmTe_2$ и $L+TlSmTe_2+\delta$.

Кривая зависимости микротвердости от состава имеет пологий максимум, что характерно для систем с неограниченными твердыми растворами замещения.

Данные порошковых рентгенограмм показали, что все сплавы по разрезу Tl_4PbTe_3 - Tl_9SmTe_6 являются однофазными и имеют тетрагональную структуру типа Tl_5Te_3 . Параметры кристаллической решетки твердых растворов подчиняются правилу Вегарда.

Полученные экспериментальные данные могут быть использованы для выбора составов раствор-расплав для выращивания монокристаллов δ -фазы, представляющих интерес для разработки термоэлектрических преобразователей энергии.

Ключевые слова: система Tl–Pb–Sm–Te, фазовые равновесия, твердые растворы, кристаллическая структура.

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