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New phase of variable composition in the Tl_9GdTe_6-Tl_9BiTe_6 system

[1]Samira Z. Imamaliyeva, [2]Turan M.Gasanly, [3]Imamaddin R. Amiraslanov, [1*]Mahammad B.Babanly

[1]*Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev, National Academy of Science of Azerbaijan, H.Javid, 113, Az1143, Baku, Azerbaijan*
[2]*Baku State University, Z.Khalilov, 23, Az1148, Baku, Azerbaijan*
[3]*Institute of Physics, National Academy of Science of Azerbaijan, H.Javid, 131, Az1143, Baku, Azerbaijan*

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ABSTRACT

In the present study, the phase equilibria in the Tl_9GdTe_6-Tl_9BiTe_6 system were investigated by using differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDS) technique. Phase diagram and concentration dependence of the unit cell parameters of the Tl_9GdTe_6-Tl_9BiTe_6 system were constructed. It was established, that system is characterized by formation of continuous solid solutions with Tl_5Te_3-type structure. However, the system is non quasi-binary due to the peritectic melting of the Tl_9GdTe_6 compound. The Tl_9GdTe_6 compound is substitution variant of Tl_5Te_3, crystallizing in space group *I*4/*mcm*. Unit cell lattice parameters of Tl_9GdTe_6 were determined from a least-squares refinement a = 8.870(3)Å and c = 13.027(10) Å, z = 2.

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INTRODUCTION

Rare earth chalcogenides have attracted attention for their applications in technology due to their wide range of properties, such as optical, electric, magnetic, and thermal. Some rare earth tellurides are widely used in technics (as high-temperature thermoelectric materials, operated magnetic elements, laser materials), design and development of micro- and nanotechnology devices (Ghamri *et al*., 2015; Jha, 2014; Magliocchi *et al*., 2004). In addition, the $LaBiTe_3$ was found to be topological insulator (Yan *et al*., 2010).

First time the new ternary rare earth tellurides Tl_9LnTe_6 (where Ln-Ce, Nd, Sm, Gd, Tm), were revealed by Babanly's group (Babanly *et al*, 2009a, b; Imamaliyeva *et al*., 2008a, b; 2009). These compounds are ternary derivatives of Tl_5Te_3 (Sp.gr. *I*4/*mcm*). Their calculated lattice parameters were within expected body centered tetragonal Bravais lattice.

Later, the tellurides $Tl_{10-x}La_xTe_6$ ($0.2 \le x \le 1.15$) were synthesized, as well as structurally characterized and their thermoelectric properties determined by Kleinke's group (Bangarigadu-Sanasy *et al*, 2011). The authors confirmed the results of Babanly *et al*. (2009a,b) and Imamaliyeva *et al*. (2008,a,b; 2009) that these compounds are substitution variants of Tl_5Te_3 with lattice parameters a = 8.9220(4)Å, c = 13.156(1)Å, V = 1047.2(1)Å^3, for x=1 (Z = 2) (Fig.1).

Moreover, the investigations have shown that thallium lanthanide tellurides $Tl_{10-x}Ln_xTe_6$ (Ln=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er) also possess thermoelectric properties (Bangarigadu-Sanasy *et al*., 2011; Bangarigadu-Sanasy *et al*., 2013; Sankar *et al*., 2012). The highest ZT value of about ~0.20 was obtained for cold-pressing and sintering phases $Tl_{8.98}Nd_{1.02(6)}Te_6$ and $Tl_{8.99}Sm_{1.01(7)}Te_6$ at ~550 K (Bangarigadu-Sanasy *et al*, 2013) and about 0.21 for Tl_9LaTe_6 at 581 K (Bangarigadu-Sanasy *et al*., 2011).

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 (Bangarigadu-Sanasy *et al*., 2014).

Quansheng and Kleinke (2015) reported the formation of Tl_9LnTe_6 (Ln=La, Ce, Pr, Na, Sm, Gd, Tb) series, which were obtained by hot-pressing technique. Their crystal structure and thermoelectric properties were measured and analyzed in order to get the highest ZT values.

Corresponding Author: Mahammad B.Babanly, Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev, National Academy of Science of Azerbaijan, Az1143, Baku, Azerbaijan
Tel.: +994 518378621; E-mail: babanlymb@gmail.com, deputy_directors@kqki.science.az.

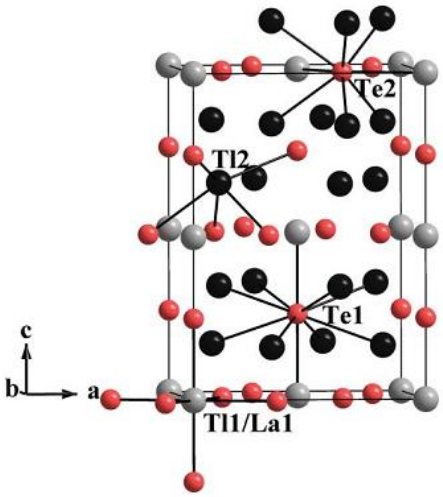


Fig. 1: Crystal structure of $Tl_{9.72}La_{0.28}Te_6$ (Bangarigadu-Sanasy *et al*., 2011).

These compounds complement the class of ternary structural analogues of Tl_5Te_3. Thus, other known ternary thallium chalcogenides, especially, $Tl_4A^{IV}Te_3$ [A^{IV}-Sn, Pb] and $Tl_9B^{V}Te_6$ [B^{V}-Sb, Bi] compounds form an important class of thermoelectric materials (Babanly *et al*., 1979; Babanly *et al*., 1985a,b; Gotuk *et al*., 1979). Particularly, Tl_9BiTe_6 shows high ZT value comparable to the state-of-the-art thermoelectric materials (Gou *et al*., 2013; Kurosaki *et al*., 2007; Wolfing *et al*., 2001).

It is known that one of the ways for improving thermoelectric properties of previously known compounds is the complexification their composition, because incorporation of heavy atoms into crystal lattice may significantly reduce the lattice contribution to the total thermal conductivity, which leads to an increase of the thermoelectric figure of merit (Ioffe, 1957).

For this purpose, phase equilibria in a number of systems, such as Tl_5Te_3-Tl_4SnTe_3-Tl_4PbTe_3 (Babanly *et al*., 1979), $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$ (Jafarov *et al*., 2013), $3Tl_2Se+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2Se_3$ (Veisova *et al*., 2003) have been studied and multicomponent phases with the Tl_5Te_3 structure were obtained.

Similar solid solutions are formed in the system with ternary thallium-neodymium telluride (Babanly *et al*, 2010; Imamaliyeva *et al*., 2008, a,b; 2009).

In present work, the phase equilibria in the Tl_9GdTe_6-Tl_9BiTe_6 system have been studied for obtaining of solid solutions with Tl_5Te_3 structure. It was assumed, that incorporation of rare earth into the crystal structure can improve the thermoelectric properties and give the magnetic properties for obtained phases.

Experimental:

Materials

Tl_9BiTe_6 and Tl_9GdTe_6 were synthesized from elements (Tl granules, 99.99%; Gd 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 gadolinium, 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 tubes were closed with a vacuum valve and 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 resistance furnace at 900K (Tl_9BiTe_6) and 1200K (Tl_9GdTe_6) for 3h, followed by cooling in the switched-off furnace.

The Tl_9LnTe_6 compounds are formed by peritectic reactions. Therefore achieving a homogeneous mix of the reactants even after thorough grinding is not easy (Babanly *et al*.,2009, a,b, 2010; Imamaliyeva *et al*, 2008 a,b, 2010). There are extra peaks on the DTA curve (Fig.2a) of as-cast Tl_9GdTe_6 showing incomplete synthesis. To accelerate the interaction on interfaces, the obtained intermediate ingot of Tl_9GdTe_6 was crushed to fine powders using agate mortar and pestle, pressed into pellets and again annealed at 1000 K. This procedure was repeated several times until the targeted compound is obtained without any side products. The total annealing time of tablet was about ~1000 h. Retesting DTA and SEM showed its homogeneity (Fig.2b).

The samples of the Tl_9GdTe_6-Tl_9BiTe_6 system were prepared by melting of 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 700 K and kept at this temperature during 1000 h. Finally, the furnace was switched off. SEM analysis showed that mixtures containing <60 mol% Tl_9GdTe_6 were monophasic (Fig.3a), while mixtures containing >60mol% Tl_9GdTe_6 were not-homogeneous (Fig.3b) 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.

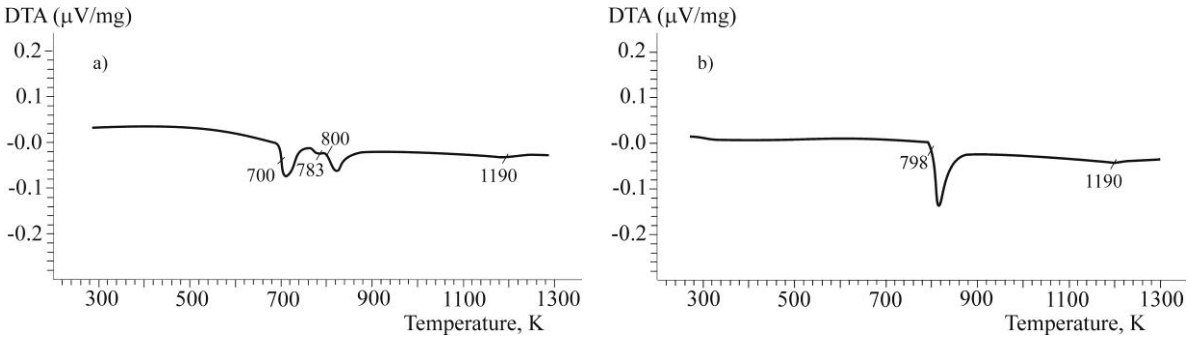
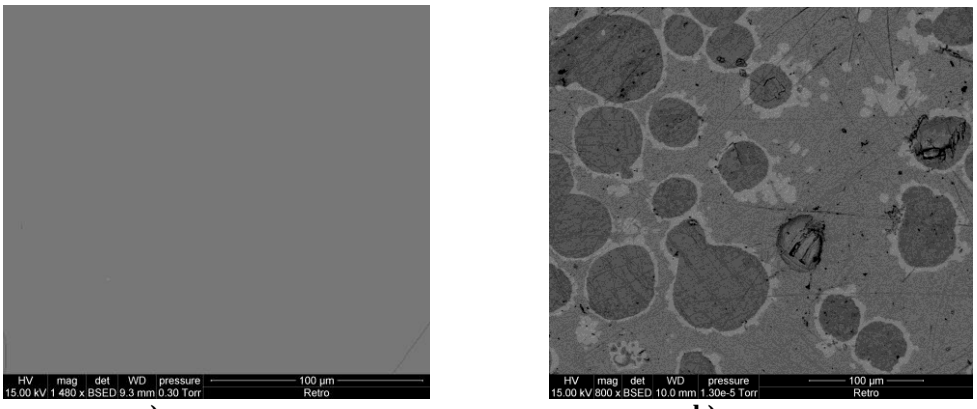


Fig. 2: The heating curve of the as-cast (a) and annealed (b) Tl_9GdTe_6



a) **b)**

Fig. 3: SEM images of some alloys in the Tl_9GdTe_6–Tl_9BiTe_6 system: 40 mol% Tl_9GdTe_6 (a) and 70 mol% Tl_9GdTe_6 (b)

Methods:

Differential thermal analysis (DTA), X-ray powder diffraction (XRD) and scanning electron microscope with energy dispersive analysis (SEM-EDS) were used 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 some cases the 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.

The microstructure and equilibrium compositions of the phases were determined by FEI Quanta™ 250 scanning electron microscope with Oxford Instruments energy dispersive X-ray spectrometer (SEM–EDS).

RESULTS AND DISCUSSION

DTA showed that Tl_9BiTe_6 melts congruently at 830 K. Comparison of Tl_9TbTe_6 thermograms with previously obtained ones for other lanthanides are performed by Imamalieva *et al*. (2008a,b), Babanly *et al*. (2009a,b), Babanly *et al*. (2010), and Imamaliyeva *et al*. (2009). It 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.2b).

Powder XRD patterns of the Tl_9BiTe_6 and Tl_9TbTe_6 compounds were identical to that of Tl_5Te_3. Unit cell lattice parameters were determined from a least-squares refinement: a = 8.854(5), c = 13.047(6) Å, z = 2 (Tl_9BiTe_6) and a = 8.870(3)Å and c = 13.027(10) Å, z = 2 (Tl_9GdTe_6). These values are practically equal with the data (Doert and Böttcher, 1988) for Tl_9BiTe_6 and slightly differ from data (Sankar *et al*., 2012) for Tl_9TbTe_6. The lattice parameters evaluated from the X-ray diffraction patterns are listed in Table.

Table: Some properties of initial compounds and solid solutions of the Tl_9GdTe_6-Tl_9BiTe_6 system

Phase	Temperature of melting, K	Parameters of tetragonal lattice, Å		
		a	*c*	*V*, Å^3
Tl_9GdTe_6	798; 1190	8,870(3)	13,027(10)	1024.92
$Tl_9Bi_{0.2}Gd_{0.8}Te_6$	800-820; 1100	8.866(3)	13.031(12)	1024.31
$Tl_9Bi_{0.4}Gd_{0.6}Te_6$	805-824	8.862(5)	13.037(14)	1023.86
$Tl_9Bi_{0.6}Gd_{0.4}Te_6$	810-825	8.860(4)	13.041(10)	1023.71
$Tl_9Bi_{0.8}Gd_{0.2}Te_6$	815-826	8.856(2)	13.047(8)	1023.26
Tl_9BiTe_6	830	8,854(5)	13,048 (6)	1023.11

The phase diagram of the Tl_9GdTe_6-Tl_9BiTe_6 system (Table, Fig.4) is characterized by formation of unlimited solid solutions (δ). However, the system is non quasi-binary due to the peritectic melting of the Tl_9GdTe_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. The L+X+δ area is not experimentally fixed due to the narrow temperature interval and denoted in Fig.4 by dotted lines.

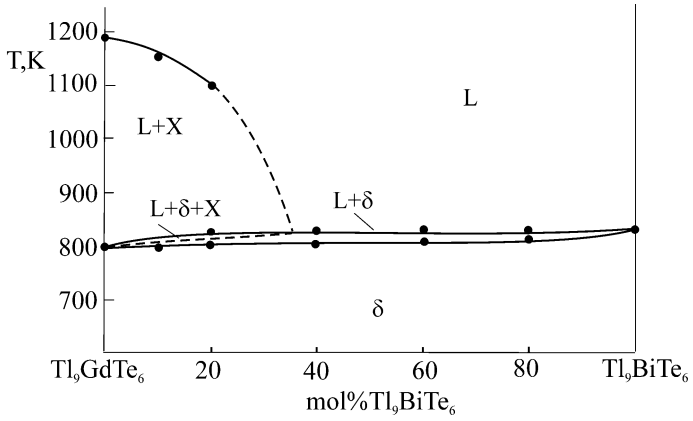


Fig. 4: Phase diagram of the Tl_9GdTe_6-Tl_9BiTe_6 system.

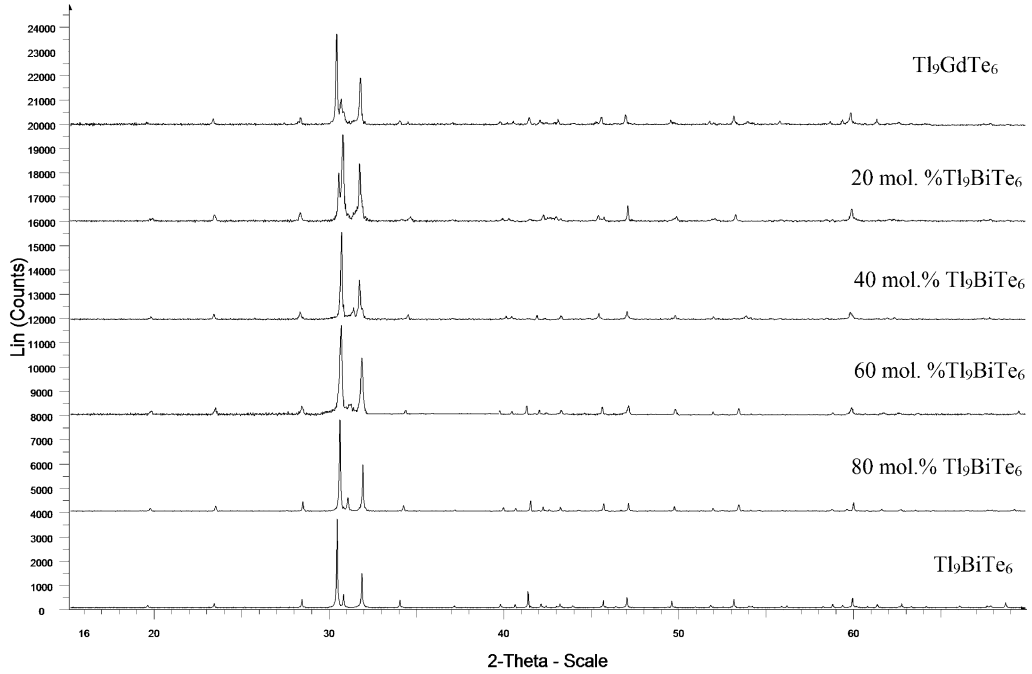


Fig. 5: XRD patterns for different compositions for the Tl_9GdTe_6–Tl_9BiTe_6 system

The formation of the unlimited solid solution in this system is confirmed by XRD analysis. The XRD data of the alloys after annealing for about 500 h at 750 K are presented in Fig.5. Apparently, all samples of this system have the same diffraction pattern typical to Tl_5Te_3 and differ from each other by small displacement of the diffraction lines. The dependence of the lattice parameters of the composition obeys the Vegard's rule within the error limits (Fig.6).

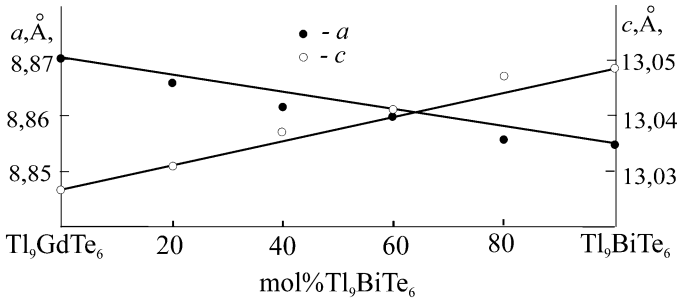


Fig. 6: Concentration dependence of unit cell parameters for the Tl_9GdTe_6-Tl_9BiTe_6 system.

Thus, in the Tl_9GdTe_6-Tl_9BiTe_6 system a new quaternary non-stoichiometric phase with a tetragonal structure was found for the first time. Based on respective characteristics of the initial ternary compounds it can be assumed that the $Tl_9Bi_{1-x}Gd_xTe_6$ ($0<x<1$) intermediate phase may have thermoelectric and magnetic properties.

Constructed T-x diagram make it possible to select the composition of alloys for growing single crystals of δ-solid solution with given composition from the melt.

Conclusions:

The phase diagram of the Tl_9GdTe_6-Tl_9BiTe_6 system has been constructed using various experimental methods. Continuous substitutional solid solutions (δ-phase) which crystallize in Tl_5Te_3 crystal structure are formed in the system. The Tl_9GdTe_6 compound is substitution variant of Tl_5Te_3, and crystallizes in *I*4/*mcm* space group. Following unit cell lattice parameters for Tl_9GdTe_6 were determined from a least-squares refinement: a = 8.870(3)Å and c = 13.027(10) Å, z = 2.

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REFERENCES

Babanly, M.B., J.-C. Tedenac, S.Z. Imamalieva, F.N. Guseynov, G.B. Dashdieva, 2010. Phase equilibria study in systems Tl-Pb(Nd)-Bi-Te new phases of variable composition on the base of Tl_9BiTe_6. J. Alloys. Compd., 491: 230-236.

Babanly, M.B., A. Akhmad'yar, A.A. Kuliev, 1985. System Tl_2Te-Bi_2Te_3-Te. J.Inorg. Chem., 30: 2356-2361.

Babanly, M.B., A. Azizulla, A.A. Kuliev, 1985. System Tl-Sb-Te. J.Inorg.Chem., 30: 1051-1059.

Babanly, M.B., A.A. Gotuk, A.A. Kuliev, 1979. Tl_5Te_3-Tl_4SnTe_3-Tl_4PbTe_3 system. Inorg.Mat., 15: 1011-1012

Babanly, M.B., S.Z. Imamalieva, F.M. Sadygov, 2009. Physico-chemical interaction of Tl and Tm(Yb) tellurides. New of Baku University. Natural Sciences Series., 4: 5-10.

Babanly, M.B., S.Z. Imamaliyeva, D.M. Babanly, 2009. Tl_9LnTe_6 (Ln-Ce, Sm, Gd) compounds – the new structural analogies of Tl_5Te_3. Azerb.Khim.Zh., 2: 121-125.

Bangarigadu-Sanasy, S., C.R. Sankar, A. Assoud, H. Kleinke, 2011. Crystal Structures and Thermoelectric Properties of the series $Tl_{10-x}La_xTe_6$ with $0.2 \leq x \leq 1.15$. Dalton Trans. ,40: 862-867.

Bangarigadu-Sanasy, S., C.R. Sankar, P.A. Dube, J.E. Greedan, H. Kleinke, 2014. Magnetic properties of Tl_9LnTe_6, Ln = Ce, Pr, Tb and Sm. J.Alloy. Compd., 589: 389-392.

Bangarigadu-Sanasy, S., C.R. Sankar, P. Schlender, H. Kleinke, 2013. Thermoelectric properties of $Tl_{10-x}Ln_xTe_6$, with Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, and $0.25 < x < 1.32$. J.Alloy.Compd., 549: 126-134.

Doert, T., P. Böttcher, 1988. Crystal structure of bismuth nonathallium hexatelluride, $BiTl_9Te_6$. Z. Kristallogr., 24: 1479-1484.

Ghamri, H., Y. Djaballah, A. Belgacem-Bouzida, 2015. Thermodynamic modeling of the Eu–Te and Te–Yb systems. J. Alloy. Compd, 643: 121-128.

Gotuk, A.A., M.B. Babanly, A.A. Kuliev, 1979. Phase equilibria in the system Tl-Sn-Te. Inorg. Mat., 15: 1062-1067.

Guo, Q., M. Chan, B.A. Kuropatwa and H. Kleinke, 2013. Enhanced Thermoelectric Properties of Variants of Tl_9SbTe_6 and Tl_9BiTe_6. Chem. Mater., 25: 4097-4104.

Imamaliyeva, S Z., F.M. Sadygov, M.B. Babanly, 2008. New thallium–neodymium tellurides. Inorg. Mater., 44: 935-938.

Imamaliyeva, S.Z., F.N. Guseinov, M.B. Babanly, 2008. Phase diagram of Tl_5Te_3-Tl_4PbTe_3-Tl_9NdTe_6 system and some properties of solid solutions, J. Chem. Probl., 4: 640-646.

Imamaliyeva, S.Z., F.N. Guseinov, M.B. Babanly, 2009. Phase equilibria in the Tl_5Te_3-

Tl_9NdTe_6-Tl_9SbTe_6 system and some properties of solid solutions. News of Baku University., Natural Sciences Series., 2: 5-11.

Ioffe, A.F., 1957. Semiconductor Thermo-elements and Thermoelectric Cooling, Infosearch Limited, London.

Jafarov, Y.I., A.V. Shevelkov, M.B. Babanly, Z.S. Aliev, 2013. Experimental investigation of the $3Tl_2Se+Sb_2Te_3 \leftrightarrow 3Tl_2Te+Sb_2Se_3$ phase diagram. J. Alloy Compd., 555: 184-192.

Jha, A.R., 2014. Rare Earth Materials: Properties and Applications, CRC Press, United States.

Kurosaki, K., R. Goto, H. Muta, S. Yamanaka, 2007. Fabrication and Thermoelectric Properties of Ag_9TlTe_x (x=5,0~6,0). Mater.Trans., 48: 2083-2087.

Magliocchi C., F.Meng, T.Hughbanks. 2004. Rare-earth-rich tellurides: Nd_4NiTe_2 and $Er_5M_2Te_2$ (M=Co, Ni). J. Solid State Chem., 177: 3896-3902.

Quansheng Guo, H. Kleinke, 2015. Thermoelectric properties of hot-pressd (Ln=La, Ce, Pr, Nd, Sm, Gd, Tb) and $Tl_{10-x}La_xTe_6$ (0,90<x<1,05). J.Alloys Compd., 630: 37-42.

Sankar, C.R., S. Bangarigadu-Sanasy, H. Kleinke, 2012. Thermoelectric Properties of $TlGdQ_2$ (Q = Se, Te) and Tl_9GdTe_6. J.Electron.Mater., 41: 1662-1666.

Veisova, S.M., Z.A. Guseinov, A. Yusibov Yu and M.B. Babanly, 2003. Reciprocal system $3Tl_2Se+Bi_2Te_3 \leftrightarrow 3Tl_2Te+Bi_2Se_3$. Russ. J. Inorg. Chem., 48: 1425-1430.

Wolfing, B., C. Kloc, J. Teubner, E. Bucher, 2001. High performance thermoelectric Tl_9BiTe_6 with an extremely low thermal conductivity. Phys. Rev. Lett., 86: 4350-4353.

Yan, B., H-J. Zhang, C-X. Liu, X-L. Qi, T. Frauenheim and S-C. Zhang, 2010. Theoretical prediction of topological insulator in ternary rare earth chalcogenides. Phys. Rev., B 82: 161108(R)