Chemistry of
Metals and Alloys

Chem. Met. Alloys 5 (2012) 37-41
Ivan Franko National University of Lviv
www.chemetal-journal.org

Phase equilibria in the Tl_2S–PbS–GeS_2 system and crystal structure of $Tl_{0.5}Pb_{1.75}GeS_4$

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Received February 20, 2012; accepted June 27, 2012; available on-line November 5, 2012

The phase equilibria in the quasi-ternary system Tl_2S–PbS–GeS_2 at 520 K were investigated by XRD methods. Three intermediate quaternary phases were discovered, Tl_2PbGeS_4, ~$Tl_2PbGe_3S_8$ and $Tl_{0.5}Pb_{1.75}GeS_4$. The crystal structure of the quaternary phase $Tl_{0.5}Pb_{1.75}GeS_4$ was determined by powder XRD in the non-centrosymmetric space group *I*-43*d*, *Z* = 16 and *a* = 1.420082(6) nm ($Ag_{0.5}Pb_{1.75}GeS_4$ structure type). Atomic parameters were refined in the isotropic approximation ($R_I = 0.0496$, $R_p = 0.0944$). The phase diagram of the Tl_2GeS_3–PbS section was investigated. The section is quasi-binary, of the eutectic type, with formation of the equimolar compound Tl_2PbGeS_4, which melts incongruently at 781 K and undergoes a polymorphous transformation at 688 K. The HT-modification crystallizes with a monoclinic structure (S.G. *P*12/*a*1, *a* = 0.89079(7), *b* = 0.90951(7), *c* = 1.04772(7) nm, β = 94.116(7)°).

Thallium chalcogenides / Crystal structure / Phase diagram / Isothermal section

Introduction

Interest in the quasi-ternary systems $A^I{}_2X$–$B^{II}X$–$D^{IV}X_2$, where A^I = Cu, Ag; B^{II} = Zn, Cd, Hg; D^{IV} = Si, Ge, Sn, and *X* = S, Se, Te [1], is caused by the formation of quaternary compounds $A^I{}_2B^{II}D^{IV}X_4$, of which there are over 40 representatives and which crystallize with acentric orthorhombic (S.G. *Pmn*2_1 or *Cmc*2_1) or tetragonal (S.G. *I*-42*m* or *I*-4) structures. These structures are derived from wurtzite or sphalerite and are characterized by tetrahedral coordination of the atoms. Their sets of properties make them of interest for infrared and non-linear optics and semiconductor technology. Two compounds were also found for B^{II} = Pb; Cu_2PbSiS_4 crystallizes in the trigonal S.G. *P*$3_2$21 with the lattice parameters *a* = 0.60565, *c* = 1.51841 nm [2], and Ag_2PbGeS_4 has an orthorhombic structure (S.G. *Ama*2 with the lattice parameters *a* = 1.02390, *b* = 1.02587, *c* = 0.67701 nm) [3]. The Ag_2S–PbS–GeS_2 system also features the existence of $Ag_{0.5}Pb_{1.75}GeS_4$, which crystallizes in the non-centrosymmetric cubic S.G. *I*-43*d*, *a* = 1.40277 nm [4]. The authors of [4] also report a series of isostructural compounds $A_{0.5}M_{1.75}GeX_4$ (*A* = Ag, Cu, Li, Na; *M* = Pb, Eu; *X* = S, Se). The substitution of Tl for Cu or Ag is of interest for the search for new compounds. Thallium-containing systems are little studied, though the formation of the equimolar compounds Tl_2PbGeS_4 [5] and $Tl_2B^{II}C^{IV}Te_4$ (B^{II} = Cd, Hg, Mn; D^{IV} = Ge, Sn) [6] has been reported.

Here we report the results of a study of the phase equilibria in the Tl_2S–PbS–GeS_2 system and a description of the crystal structure of $Tl_{0.5}Pb_{1.75}GeS_4$.

Experimental

The alloys were synthesized from elementary Tl, Pb, Ge, and S (of at least 99.99 wt.% purity) by the single-temperature method in evacuated quartz ampoules. The alloys were first heated to 670 K at the rate of 30 K/h, held for a day (for the bonding of sulfur), and then heated to 1270 K. The melts were kept at this temperature for 6 h with periodic vibration and then cooled to 520 K at 20 K/h. The alloys were annealed at this temperature for 250 h. The synthesis ended in quenching the ampoules into cold water. A series of alloys in the region of existence of the $Tl_{0.5}Pb_{1.75}GeS_4$ phase were synthesized and annealed at 670 K.

X-ray diffraction spectra were recorded at a DRON 4-13 diffractometer using Cu K_α radiation ($10° \leq 2\theta \leq 80°$ range, 0.05° scan step, 2 s exposure at each point for the phase analysis, and

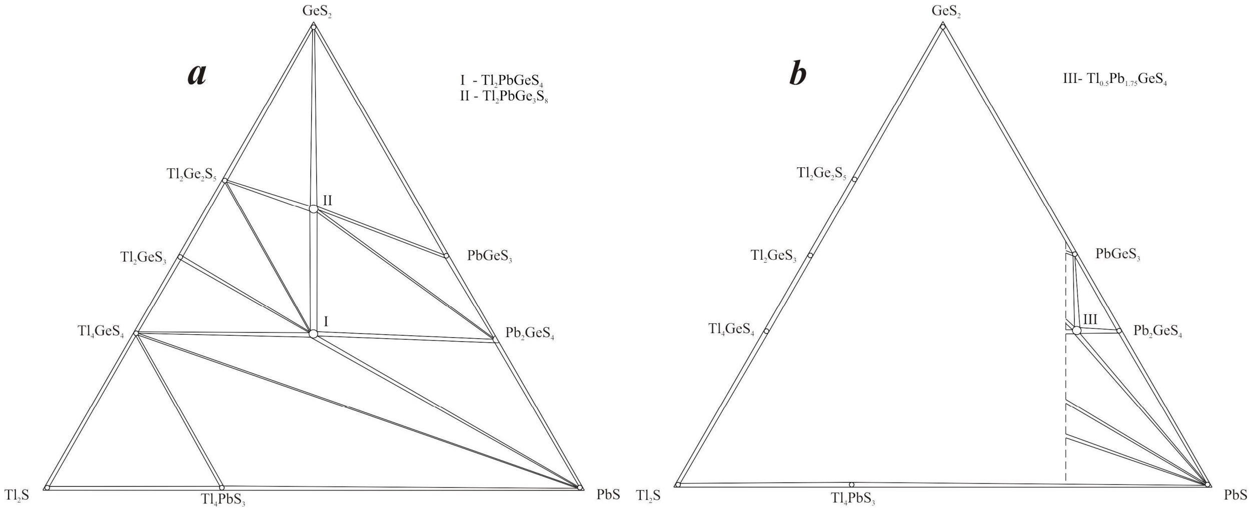

Fig. 1 Isothermal sections of the Tl_2S–PbS–GeS_2 system at 520 K (*a*) and 670 K (*b*).

$10° \le 2\theta \le 100°$ range, 0.02° scan step, 20 s exposure at each point for the refinement of the structure parameters). The structure refinement was performed using the full-profile Rietveld method included in the CSD software package [7].

The alloys of the quasi-binary system Tl_2GeS_3–PbS were investigated by DTA using a Paulik-Paulik-Erdey derivatograph with a Pt/Pt-Rh thermocouple. Uniform heating of the furnace at a rate of 10 K/min was computer-controlled, and the cooling was inertial.

Results and discussion

The results of the study of the phase equilibria in the Tl_2S–PbS–GeS_2 system are presented in the isothermal section at 520 K shown in Fig. 1,*a*. Two quaternary phases were found at this temperature, among which Tl_2PbGeS_4 that forms in the quasi-binary section Tl_2GeS_3–PbS with an equimolar ratio of the binary selenides of the quasi-ternary system. Its diffraction pattern was indexed in the monoclinic space group *P*12/*a*1 with the lattice parameters a = 0.89079(7), b = 0.90951(7), c = 1.04772(7) nm, β = 94.116(7)°, which agree well with literature data [5].

The phase diagram of the Tl_2GeS_3–PbS section investigated by DTA and XRD of 13 alloys is presented in Fig. 2. The system liquidus consists of three fields of primary crystallization, of PbS, Tl_2GeS_3 and Tl_2PbGeS_4, with the incongruent type of melting. The peritectic interaction is depicted by the reaction L+PbS↔Tl_2PbGeS_4 (coordinates of the invariant point 48 mol.% PbS and 781 K). The quaternary phase forms a eutectic with Tl_2GeS_3 with the coordinates 18 mol.% PbS and 694 K. The existence of a polymorphous transformation of the intermediate compound yields a horizontal line in the sub-solidus part at 668 K.

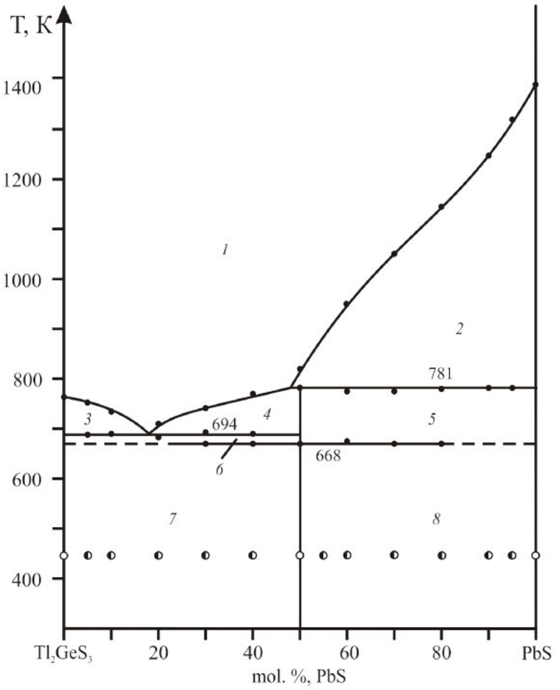

Fig. 2. Phase diagram of the quasi-binary system Tl_2GeS_3–PbS:
1 – L, 2 – L + PbS, 3 – L + Tl_2GeS_3, 4 – L + γ-Tl_2PbGeS_4, 5 – γ-Tl_2PbGeS_4 + PbS, 6 – γ-Tl_2PbGeS_4 + Tl_2GeS_3, 7 – γ'-Tl_2PbGeS_4 + Tl_2GeS_3, 8 – γ'-Tl_2PbGeS_4 + PbS.

Another quaternary phase was found in the Tl_2PbGeS_4–GeS_2 section; its structure is currently being investigated. The cleanest diffraction pattern of this phase corresponds to a composition of 20 mol.% Tl_2S, 20 mol.% PbS, 60 mol.% GeS_2, with an overall formula of $Tl_2PbGe_3S_8$.

Taking into account the existence of the phase $Ag_{0.5}Pb_{1.75}GeS_4$ in the Ag-containing system, the possibility of an analogous phase in the title system was examined. The investigation confirmed the existence of the compound $Tl_{0.5}Pb_{1.75}GeS_4$, which, however, exists at higher temperatures (670 K), and is isostructural to the Ag-containing phase [4]. Phase equilibria in the region of its formation are presented in Fig. 1,*b*.

The conditions of the X-ray experiment and the crystallographic parameters of the $Tl_{0.5}Pb_{1.75}GeS_4$ structure are listed in Table 1. Indexing of the diffraction pattern of this quaternary compound showed that it has cubic symmetry. The lattice parameter is a = 1.420082(6) nm (R_I = 0.0496, R_p = 0.0944). Systematic absences in the diffraction pattern of $Tl_{0.5}Pb_{1.75}GeS_4$ indicate space group *I*-43*d* (structure type $Ag_{0.5}Pb_{1.75}GeS_4$).

Experimental and calculated diffraction patterns of $Tl_{0.5}Pb_{1.75}GeS_4$ and their difference are plotted in Fig. 3. Standardized atom coordinates and displacement parameters are listed in Table 2; the inter-atomic distances are listed in Table 3.

The first coordination environment formed by sulfur atoms around Ge atoms is tetrahedral. The Pb1 atoms have octahedral coordination; that of the Pb2 and Tl atoms is a trigonal prism with two additional atoms. The S1 and S2 atoms are characterized by tetrahedral and distorted octahedral surrounding by cations. The arrangement of metal atoms around a Ge-centered tetrahedron formed by sulfur atoms is shown in Fig. 4. The disc-like thermal ellipsoids of the chalcogen atoms indicate the strong bonds with the germanium atom. The packing of Ge-centered tetrahedra in the investigated structure in shown in Fig. 5.

Table 1 Investigation of the $Tl_{0.5}Pb_{1.75}GeS_4$ crystal structure.

Space group	*I*-43*d*
a, nm	1.420082(6)
V, nm^3	2.86379(4)
Number of atoms per cell	116
Number of formula units (Z)	16
Radiation; wavelength, nm	Cu K_α; 0.154185
Diffractometer	DRON 4-13
Refinement method	Full profile
Calculated density D_X, g/cm^3	6.1747(1)
Absorption coefficient μ, 1/cm	1149.62
Number of atoms sites	6
Number of free parameters	29
2θ and $\sin\theta/\lambda_{max}$	99.92 and 0.497
R_I and R_p	0.0496 and 0.0944

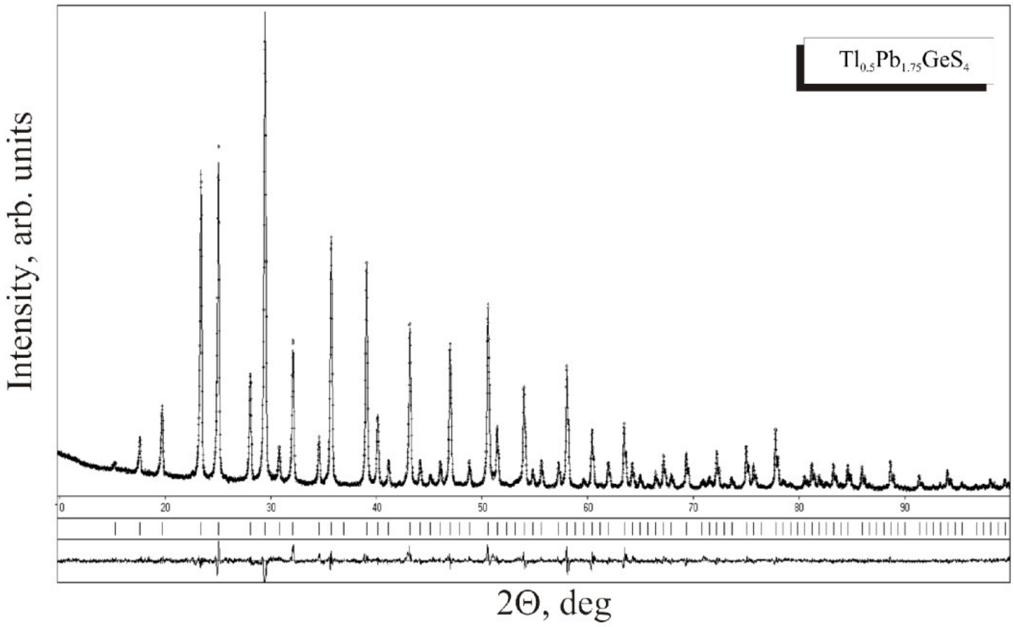

Fig. 3 Experimental and theoretical diffraction patterns of $Tl_{0.5}Pb_{1.75}GeS_4$ and their difference.

Table 2 Atom coordinates, site occupation and isotropic displacement parameters in the $Tl_{0.5}Pb_{1.75}GeS_4$ structure.

Atom	Wyckoff site	*x*	*y*	*z*	Site occupation	$B_{iso}\times10^2$, nm^2
Tl(1)	12*b*	3/8	0	1/4	0.6667	2.43(4)
Pb(1)	24*d*	0.3471(2)	0	1/4	0.1667	0.79(14)
Pb(2)	24*d*	0.01823(5)	0	1/4	1	2.36(2)
Ge(1)	16*c*	0.22378(7)	0.22378(7)	0.22378(7)	1	1.17(3)
S(1)	16*c*	0.0665(2)	0.0665(2)	0.0665(2)	1	1.20(6)
S(2)	48*e*	0.1176(2)	0.3186(2)	0.1635(2)	1	1.59(10)

Table 3 Interatomic distances in the $Tl_{0.5}Pb_{1.75}GeS_4$ structure.

Atoms	Distance, nm
Tl(1)–S(2)	0.3093(3) ×4
Pb(1)–S(2)	0.3015(3) ×2
	0.3219(3) ×2
Pb(2)–S(1)	0.2855(3) ×2
Pb(2)–S(2)	0.2828(3) ×2
	0.3444(3) ×2
	0.3566(3) ×2
Ge(1)–S(1)	0.2281(3)
Ge(1)–S(2)	0.2195(3) ×3

Regarding the second coordination sphere of sulfur atoms, the crystal structures of the compounds in the series Tl_4GeS_4 – Tl_2PbGeS_4 – $Tl_{0.5}Pb_{1.75}GeS_4$ – Pb_2GeS_4 can be presented as a packing of tetrahedra of sulfur atoms around germanium atoms at the sites of an anion sub-lattice forming rhombododecahedra (cubes with additional atoms above the faces) (Fig. 6). The structures of this series differ in the degree of distortion of the anion sub-lattice, and the number and location of the metal atoms. The right part of the figure omits the S atoms, and presents only the cations around a Ge atom for better visualization. The cations in the Tl_4GeS_4 structure form trigonal prisms with two additional atoms above one side face, which may also be described as octahedra with two extra atoms. The structure of Tl_2PbGeS_4 also contains trigonal prisms with two additional atoms above side faces; also these polyhedra can be described as octahedra with two extra atoms. The $Tl_{0.5}Pb_{1.75}GeS_4$ structure features trigonal prisms of Pb atoms and additional atoms (Tl* = 0.667Pb+0.167Tl) above the side faces. The lead atoms in the Pb_2GeS_4 structure form distorted octahedra around the anion tetrahedra.

Considering a certain degree of overlap, the interatomic distances *M*–S in the $Tl_{0.5}Pb_{1.75}GeS_4$ structure (Table 3) agree well with other experimentally obtained distances.

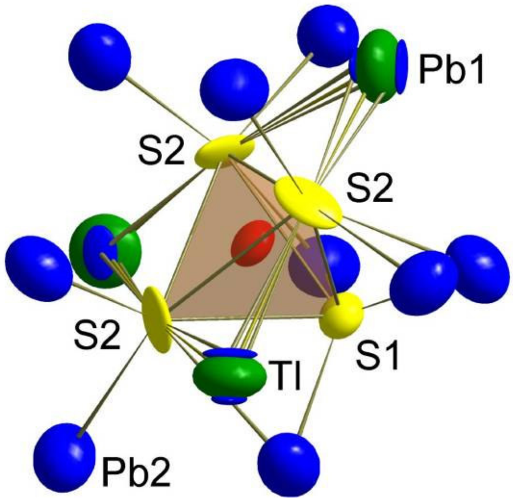

Fig. 4 Fragment of the $Tl_{0.5}Pb_{1.75}GeS_4$ structure where a Ge-centered tetrahedron is surrounded by metal atoms; the atoms are represented by their thermal ellipsoids.

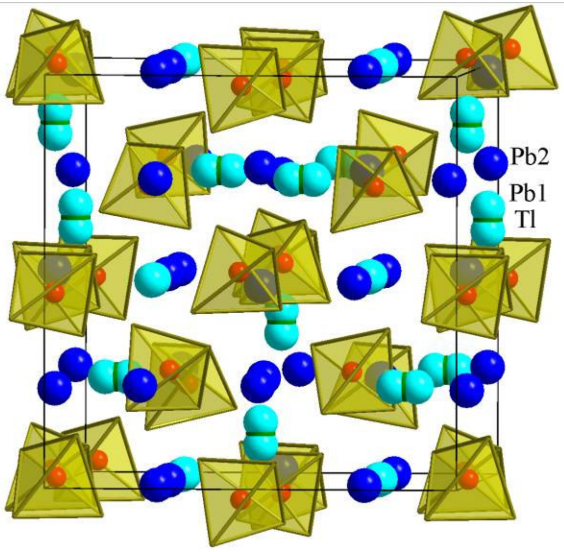

Fig. 5 Arrangement of Ge-centered tetrahedra of sulfur atoms in the $Tl_{0.5}Pb_{1.75}GeS_4$ structure.

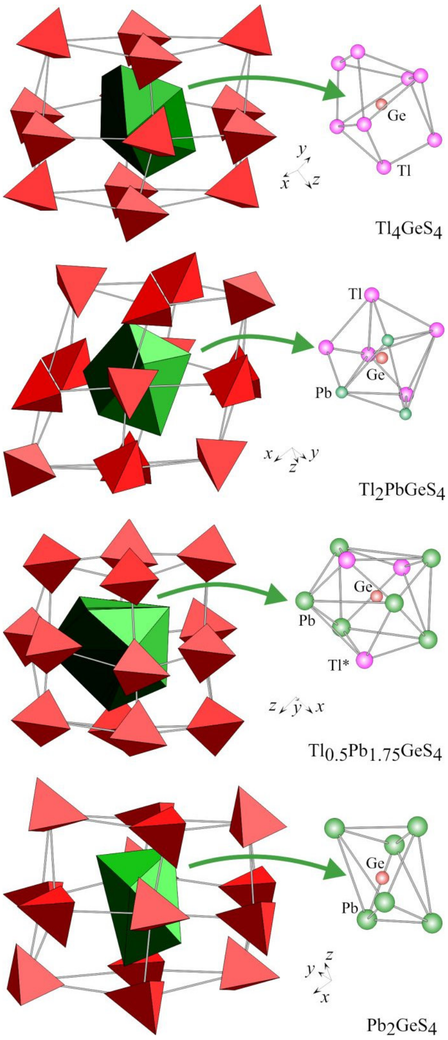

Fig. 6 Packing of cations within the frame of a similar anion sub-lattice of tetrahedra of sulfur atoms around germanium atoms, typical of the structures of compounds in the series Tl_4GeS_4 – Tl_2PbGeS_4 – $Tl_{0.5}Pb_{1.75}GeS_4$ – Pb_2GeS_4 (Tl* = 0.667Pb + 0.167Tl).

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