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Tl-S phase diagram, structure and thermodynamic properties

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A new Tl-S equilibrium phase diagram has been compiled, starting from thermodynamical and structural properties.

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1. Introduction

Alloys based on $A^{III}B^{VI}$ compounds possess a wide spectrum of semiconductor properties. Chalcogenides of thallium belong to this group of alloys, and they can be applied to manufacturing high-speed optical disks DVD+RW [1,2]. Information recording is based on dot phase transition of a non-crystalline film (in vitreous state) into crystal under the influence of a laser pulse.

The detailed understanding of such a phase transition mechanism requires first of all to carry out the analysis of binary "thallium-chalcogen" phase diagrams and of polymorphic transitions in crystalline compounds of thallium with chalcogen (sulfur, selenium, tellurium). Special attention should be given to those areas of the phase diagram where vitreous state can be obtained under given conditions.

In this paper, we focus on eliminating a number of debatable problems concerning the thallium-sulfur phase diagram by means of the critical analysis of literature data.

2. Phase diagram of the system Tl-S

Variants of the thallium-sulfur phase diagram are presented in compilations [3-5]. According to Hansen and Anderko [3], the Tl-S system contains 4 phases (Fig.1). The diagram in [4] is accepted according to [3]. During the years 1967-1971 electromotive forces (EMF) and X-ray diffraction (XRD) methods [6-8] helped to understand the Tl-S system. Five intermediate phases were identified: Tl_2S, Tl_4S_3, TlS, TlS_2 and Tl_2S_5. Last phase Tl_2S_5 shows two modifications (black and red).

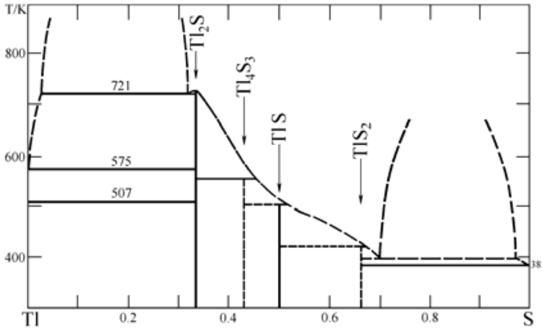

Fig. 1. Tl-S phase diagram [3].

A narrow domain of homogeneity was found in Tl_4S_3. The hypothesis of TlS congruent fusion is raised on the basis of the thermodynamic analysis of thallium-sulfur system.

The partial thallium-sulfur phase diagram in the field of 33 – 50 at. % S was investigated in [9], and the congruent fusion of thallium monosulfide was also established.

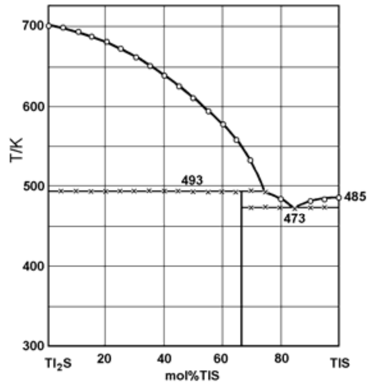

Fig. 2. Partial Tl-S phase diagram with experimental data points [9].

Kabré et al [10] proposed the stoichiometry Tl_2S_3 instead of TlS_2. Thus the left part of the liquid miscibility gap (I) is shifted towards sulfur (Fig. 3) and it arrives to the monotectic line with composition 74 at. % S.

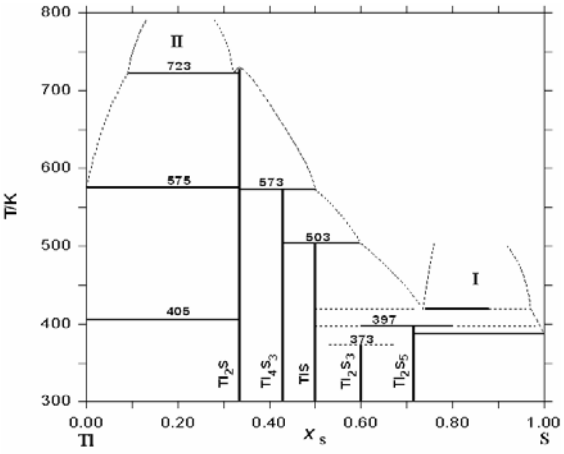

Fig. 3. Tl-S phase diagram [10].

The thallium-sulfur phase diagram, proposed by Vorob'ev et al [11], practically coincides with that of [10]. Phase Tl_2S_3 is quoted in [11] with reference [10]. In Massalski handbook [6], thallium-sulfur diagram is accepted according to [10].

The narrow area of the thallium-sulfur phase diagram in the range of 48.8 - 52.0 at. % S was investigated in [12] by differential thermal analysis (DTA) on cooling. (Fig.4). According to [12], TlS is formed peritectically at 469K and undergoes polymorphic transformations at 352 and 290K.

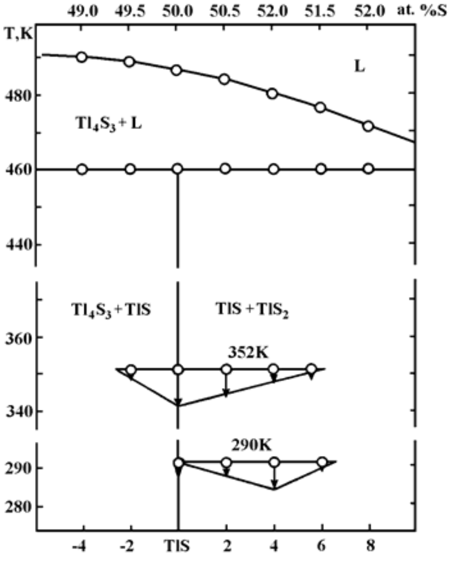

Fig. 4. Partial Tl-S phase diagram with experimental data points [12].

The temperatures of phase transitions for thallium sulfides: Tl_2S, Tl_4S_3, TlS and Tl_2S, are shown in Table1: crystal ∅ liquid, crystal ∅ liquid + crystal ′, crystal ∅ crystal ′ + crystal ″ under various references.

3. About some features of thallium - sulfur alloys in liquid and solid conditions.

In this paragraph, some particularities of Tl-S alloys syntheses both in liquid and solid states are considered. They were partially described in [6-8] and are quoted here with some new understanding. A series of alloys of Tl-S with concentrations from 30.0 to 90.0 at. % S was studied by EMF and XRD methods [6-8]. It was established, that reaction between Tl and S are violent, with bright flashes at thallium fusion temperature, 575K. As a result of such interaction, dark liquid alloys formed. They are homogeneous for concentrations from 34.0 to 66.7 at. % S and from 30.0 to 32.9 while from 68.0 to 90 at. % S a distinct separation into two liquid layers takes place. This aliquation does not change with time both in liquid, and in solid states.

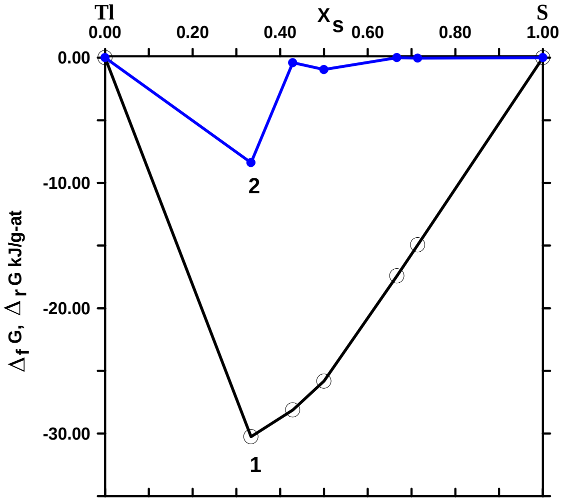

Fig. 5. Dependence of Gibbs energy formation $\Delta_f G$ (1) of thallium sulfides (Tl_2S, Tl_4S_3, TlS, TlS_2 and Tl_2S_5) versus the pure components (Tl and S) and on the proximate phases $\Delta_r G$ (2) for 298K.

The melts from 68.0 to 90.0 at. % S have a liquid top yellow layer corresponding to practically pure sulfur with disappears only at concentrations near 68.0 at. %. The melts from 30.0 to 33.0 at. % S above 722K also consist in two liquids. Inside a glass ampoule one find:

i) liquid Tl_2S at the top, black,

ii) liquid thallium at the bottom, silvery.

Thallium rich alloys rich with thallium above 70 at. % Tl were not investigated.

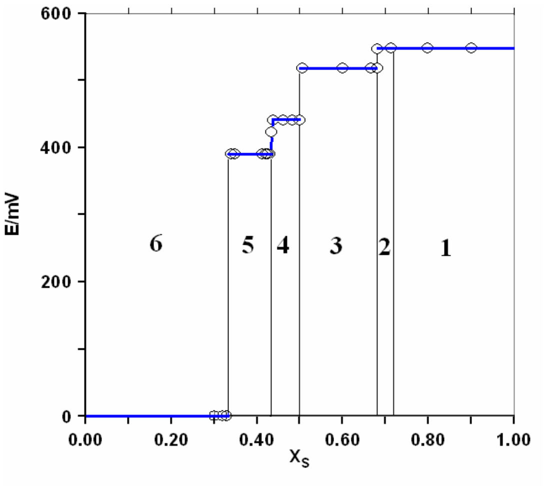

Fig. 6. Isotherm E (x) for 370K in system thallium-sulfur. Phase areas: 1) S-T_2S_5, 2) T_2S_5 - βa-phase (TlS_2), 3) βa-phase (TlS_2) - TlS, 4) TlS - γa-phase (Tl_4S_3), 5) γa-phase (Tl_4S_3) - Tl_2S, 6) Tl_2S - Tl.

After extraction from ampoules, freshly prepared alloys with 66.7 and 68.0 at. % S have shown darkening with metal shine. After alloy cooling in air, they were plastic. Then, plasticity completely disappeared after 2-3 hours. Other alloys have been prepared and solidified in ampoules. They were directly cast in the form of ingots, without integrity alteration of ampoules, then subjected to annealing. For thallium contents up to 50 at. % alloys were heat treated at 370-380K for ten days, and thallium richer alloys at 420-440K for 10-15 days. The obtained ingots were easily grounded into a powder which could be formed into pellets by compression. Then, these pellets were annealed again at the same temperatures during one to four weeks. Some alloys in the field of 49 - 90.0 at. % S have been annealed only in ingot form. All alloys with sulfur concentrations from 33.3 to 68 at. % S kept black color irrespective of storage time, while alloys near Tl_2S_5 (71.43 at. % S) stored for one year in the form of powder or pellets became red-brown.

4. Intermediate phases in system thallium – sulfur, their structure and polymorphic modifications

There have been numerous works on thallium-sulfur devoted to determining structure and polymorphic transformations in intermediate phases. According to [6 - 22] in the field 30 - 50 at. % S with all definiteness only three intermediate phases were identified with concentrations: Tl_2S, Tl_4S_3 and TlS. Above 50 at. % S, except TlS and free sulfur, two more intermediate phases were found: red Tl_2S_5 (71.4 at. % S) [15] and TlS_2 [6-8]. The last two compounds were present simultaneously in all alloys with 60-90 at. % S that were annealed only in ingot form. It has been noticed that after crushing into powder these ingots and after additional annealing at 360-370K within three months TlS_2 completely disappeared. According to XRD, the alloys of compositions 80 and 90 at. % S showed only reflections of Tl_2S_5 and sulfur, and the alloys 68.0, 66.7, and 59.9 at. % S were twophased: Tl_2S_5 and TlS were present [6-8]. Long storage (over one year) at room temperature of the alloys containing TlS_2, also led to disappearance of this phase. These observations led to a conclusion about TlS_2 thermodynamic instability, which eventually breaks up to red Tl_2S_5 and TlS either at room temperature or during annealing to 370K.

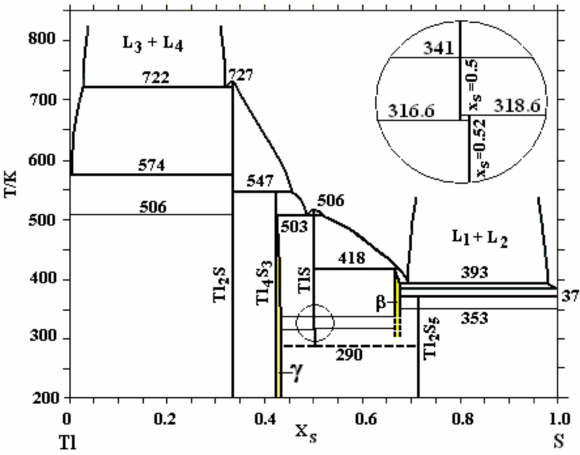

Fig. 7. Tl-S compiled phase diagram.

All sulfur rich liquids (more than 66 at. % S) consist of two layers [6-8]. The liquid miscibility gap disappears only at a composition nearby 67 at. % S, i.e. the left branch of miscibility gap ((L_1+L_2) see Fig. 8)) adjoin the composition of TlS_2. After crystallization of the two phase liquids, the upper yellow layer remained distinct. XRD of this layer corresponded to pure sulfur. This induced the second conclusion, the phase coexisting with free sulfur, at temperatures close to 385K, is TlS_2. From that, it follows, that Tl_2S_5 (71.4 at. % S) can be formed only peritectoidally from TlS_2 and sulfur at 372K. Such concept removes Hansen's objection [3] concerning the impossibility of existence of Tl_2S_5 as it is under the liquid miscibility gap. Tl_2S_5 was found by [14] and confirmed by our research. Tl_2S_3, according to Kabré [10] and accepted in Massalski compilation [5], until now is not confirmed.

Table 1. Temperatures of phase transitions in the alloys Tl-S system.

Reference Phase	[9]	[8]	[10]	[11]	[5]	[12]
Tl_2S_5	-	373 (3)	396 (2)	403 (3)	397 (3)	-
β-phase (TlS_2)	-	418 (2)	-	-	-	-
Tl_2S_3 (?)	-	-	373 (3)	-	373 (3)	-
TlS	484 (1)	506 (1)	503 (2)	503 (2)	503 (2)	460 (2)
Tl_4S_3	491 (2)	547 (2)	573 (2)	588 (2)	573 (2)	-
Tl_2S	700 (1)	727 (1)	727 (1)	727 (1)	733 (1)	-
1- congruent fusion (crystal ∅ liquid)						
2 - incongruent melting (crystal ∅ liquid + crystal ′)						
3 - peritectoid transformation (crystal ∅ crystal ′ + crystal ″)						

For TlS_2, the diffraction lines quoted in [7] were obtained on freshly prepared alloy with 66.7 at. % S, after elimination of reflections of red Tl_2S_5 and TlS. The XRD data of this alloy TlS_2 (66.7 at. % S) have shown that it contained about 50 % of TlS_2, approximately the same quantity of phase Tl_2S_5 and only a small amount of thallium monosulfide.

Table 2. Crystal structures of thallium sulfides.

Phase	Space group	Crystal system	Lattice periods, nm			P/GPa, T/K	Refer.
			a	b	c		
Tl_2S	R3	3	1.220	-	1.827	298	[6]
			1.220	-	1.817	298	[22]
			1.212		1.8175	298	[23]
			1.226		1.829	673	[18]
	HP9	3	0.61425	-	0.821	Above 723	[18]
α-Tl_4S_3	$P2_1/a$	5	0.7972	0.7757	1.303 γ=104.0°	298	[16]
β-Tl_4S_3	$P2_1/c$	5	0.7720	1.2982	0.7960 γ=103.5°	298	[9]
TlS	C2	5	1.1018	1.1039	6.016(7) γ=100.69	More low 318.6	[20]
	$P4_12_12$	2	0.78039	-	2.9552	318.6-340	[21]
	I4/mcm	2	0.77		0.679	298	[13]
			0.7787		0.6807	298	[14]
			0.7785	-	0.681	298	[6,7]
			0.7785		0.6802	Above 340	[19]
	R-3mh	3	0.3945	-	2.1788	10 GPa	[24]
	Pm-3m	1	0.32025	-	-	25 GPa	[24]
Tl_2S_5 (red)	$R2_12_12_1$	4	0.666	0.652	1.675	More low 353	[15]
			0.666	0.652	1.675	298	[6,7]
Tl_2S_5 (black)	P_{bcn}	4	2.345	0.888	1.057	Above 353	[15]
Crystal system: 1-cubic, 2-tetragonal, 3-hexagonal, 4-ortorhombic, 5-monoclinic.							

All intermediate phases in the system Tl-S, except TlS_2, possess polymorphic transformations (Tab. 2). Tl_2S has two hexagonal forms, the transformation temperature being 673K. β-Tl_4S_3 has been obtained after very slow crystallization from fusion. Grinding β-Tl_4S_3 into powder transforms it irreversibly into α-Tl_4S_3. TlS has at least three polymorphic modifications. Transformation of a tetragonal cell ($P4_12_12$) TlS in monoclinic form, most likely, occurs for a composition change from 50 to 52 at. % S (phase TlS_{1+x}).

Table 3. EMF versus temperature for different two phase alloys in the Tl-S system.

№	x_{Tl}	T_{min}- T_{max}	Phase area	E = f (T), Volt
1	0.100-0.201	342-381	S - Tl_2S_5	$(0.5161+0.87 \cdot 10^{-4})\pm 0.0074(1/55+(T-60.84)^2/7351.53)^{1/2}$
2	0.320	342-378	Tl_2S_5-Tl_8S_{17}	$(0.5117+0.95 \cdot 10^{-4}T)\pm 0.0066(1/12+(T-58.58)^2/1134.92)^{1/2}$
3	0.100-0.320	342-381	joint equation for areas S-TlS_2 and TlS_2-Tl_2S_5	$(0.5142+91 \cdot 10^{-4}T)\pm 0.0075(1/67+(T-60.43)^2/8536.45)^{1/2}$
4	0.32-0.495	327-391	TlS_2-TlS	$(0.5747-1.54 \cdot 10^{-4}T)\pm 0.0060(1/111+(T-4.23)^2/30111.50)^{1/2}$
5	0.500-0.561	317-427	TlS-solid solution 56.1 at. % Tl	$(0.4074+0.91 \cdot 10^{-4}T)\pm 0.0042(1/260+(T-67.0)^2/21678.0)^{1/2}$
6	0.566	318-420	solid solution	$(0.3306+2.51 \cdot 10^{-4}T)\pm 0.0063(1/47+(T-73.5)^2/32665.75)^{1/2}$
7	0.575-0.660	338-437	Tl_4S_3-Tl_2S	$(0.3951-0.14 \cdot 10^{-4}T)\pm 0.0043(1/99+(T-382.05)^2/67706.75)^{1/2}$

As it has been noted above, TlS_2 is not thermodynamically stable under ambient conditions. This phase decomposes during storage over one year completely into TlS and Tl_2S_5. Our XRD analysis [9] for an alloy 33.3 at. % Tl has revealed, that the set of reflections corresponds to a mixture of three phases: TlS, TlS_2 and Tl_2S_5. The indexing in [9] has led to a wrong definition for a tetragonal elementary cell with parameters a=2.317 and b=5.476 nanometers.

Results of XRD analysis for phase TlS_2 [7] do not allow to determine the parameters of this elementary cell. It is possible to suppose only, that it has either tetragonal or orthorhombic lattice. For the exact solution, it is necessary to carry out XRD analysis of phase TlS_2 at temperature 380-400K to avoid its decomposition.

The crystal structure of thallium sulfide in a range of pressure 0 - 36 GPa was studied by Demichev et al [24]. Three phase transitions of the first order were found in TlS: TlS I (type TlSe) → TlS II (type α-$NaFeO_2$) →TlS III (the deformed type α-$NaFeO_2$) → TlS IV (type CsCl) at P = 5, 10, 25 GPa accordingly. TlS II is metastable in normal conditions, and also possesses semi-conductor properties.

5. Discussion and critical analysis of the thallium-sulfur phase diagram.

The thermodynamic data (Table 3) published by [6,8] for electrochemical cells of type (I):

$$(-)Tl_{solid}\,|glycerine + CaCl_2 + \underset{(solution)}{TlCl}|(Tl_xS_{1-x})_{solid}\ (+) \quad (I)$$

(where x – mole fraction of thallium), enabled estimating intermediate phase stabilities. In Fig. 6, the Gibbs free energy of formation of Tl-S alloys referred to solid thallium and sulfur at 298K are shown (curve 1). The minimum corresponds to congruently melting Tl_2S and this is coherent with the phase diagram.

The relative stability of consecutive compounds was considered with help of G.F.Voronin technique [25]. Any compound stability depends not only on its own properties but also on those of its neighbors.

In binary systems, $A_{\tilde{1}x}B_x$ stability, relative to $A_{1-\xi'}B_{\xi'}$ ανδ $A_{1-\xi''}B_{\xi''}$, can be represented with help of equation:

$\Delta_\rho \Gamma(\xi) = \Gamma(\xi) - (1-\eta) \cdot \Gamma(\xi') - \eta \cdot \Gamma(\xi'')$,

where $x'' \geq \xi \geq \xi'$ are B component mole fractions in corresponding phases and

$\eta = (\xi - \xi') / (\xi'' - \xi')$.

At 298K, relative Gibbs free energies of formation Δ_rG of compounds Tl, Tl_2S, Tl_4S_3, TlS, TlS_2, Tl_2S_5, S referred to neighboring phases are the following: 0, –8.38, –0.40, –0.95, 0, –0.04, 0 kJ/g-at (curve 2).

At 373K, above the peritectoid decomposition of Tl_2S_5, relative Gibbs energy of formation (Δ_rG) Tl, Tl_2S, Tl_4S_3, TlS, TlS_2, S referred to surrounding phases are: 0, –8.36, –0.47, –0.73, –0.48, 0 kJ/g-at. Hence, the increase in thermodynamic stability of TlS_2 and Tl_4S_3 and its small reduction for TlS take place during heating to 373K. The stability of Tl_2S remains practically invariable.

The isothermal section E (x) at 370K (Fig. 7) represents the dependence of EMF values versus molar fraction of sulfur over the all range of composition [6-8]. The absence of significant break between areas 1 and 2 can be explain by a small variation of chemical potential for such a transformation, by a narrow temperature interval of measurements and by dispersion of the measured values E (x).

Results of the present work, reference data [3], [5], and Tables 1-3 have allowed us to propose a new phase diagram for the system Tl-S (Fig. 7).

We consider TlS_2 as a phase of variable composition. We named it β-phase. β-phase border on sulfur side varies with temperature reduction from 32.0 to 33.3 at. % Tl. The stoichiometry 66.7 at. % S corresponds to the peritectic point which temperature is close to 418K. The sulfur poor limit of β is not established at room temperature because the chemical potential of thallium varies abruptly from $Tl_2S_5 + \beta$ to $\beta + TlS$.

The peritectic formation of β (418 K) is defined within ±3K. At room temperature β is unstable and decomposes into Tl_2S_5 and TlS. Nevertheless β remained in the course of four-week EMF measurements at temperatures between 342 and 381 K. Tl_4S_3 (γ-phase) possesses a homogeneity domain of about 0.5 % sulfur. Tl_2S_5 is formed by peritectoid reaction from β and solid sulfur at 373±3 K.

The temperature of formation of TlS, according to various sources, is in the interval 503-506 K (Table 1). Formation mechanism from liquid of TlS was not well established. Nevertheless from the thermodynamic analysis of intermediate phase stability (look explications above), the concept of glass-forming [26-29] and experimental data [9], TlS has certainly a congruent fusion at 503-506K. This is coherent with what was established as correlation between enthalpies and temperature of fusion of compounds A^{III}-B^{VI} and it corresponds also to the chosen temperature of TlS melting [32].

Data about glass-forming ability for this compound [30-31] support the idea of TlS congruent melting. This hypothesis is comforted by the conception of polymeric nano-heteromorphous glass and glass-forming liquid materials, depending on the individual chemical substance [26-29]. The glass structure represents a copolymer of polymorphoids that are fragments of crystals of various polymorphic modifications (PM), without translational symmetry (long-range order), but possessing short and intermediate range orders, which are characteristics of each of these PM. This position is conformed by a comparison of diffractometric and spectroscopic (Raman) data for separate glass-forming substances and their PM, and also data of differential scanning calorimetry for glass-forming substance such as SiO_2, GeO_2, H_2O, Se, $GeSe_2$, GeS_2, AsSe, $BeCl_2$, etc. [26-29]. For all these substances the formation of polymorphoids of various PM already in the liquid phase is characteristic, and fast cooling maintains nano-heteromorphous (different structure on nano-level) structures and in glassy state, increased, naturally the degree of its copolymerization.

During heating of glassy TlS at rates 3-5 K/min, a glass transition (softening) appears at 36^{o}C [30-31], because of the transformation of low-temperature PM into high-temperature forms. This effect is endothermic as it corresponds to a transformation form low-temperature PM into high-temperature PM which takes place is the crystal state at 45.4 ^{o}C (318.6 K) [19-21]. Such an effect appears in others aforementioned glass-formers at some lesser temperatures because of high-temperature polymorfoids presence in glass [26-29].

6. Conclusions

1. The interrelations of thermodynamic properties and the phase diagram of system Tl-S are discussed.

2. Compiled phase diagram of Tl-S is presented, existence of five phases is proved Tl_2S, Tl_4S_3, TlS, TlS_2 and Tl_2S_5. Phases Tl_2S and TlS melt congruently and phases Tl_4S_3, TlS_2 and Tl_2S_5 are formed by peritectic reactions.

3. All intermediate phases are thermodynamically stable at a room temperature, except TlS_2 that over time or by annealing at 370K, breaks up eventually to red Tl_2S_5 and thallium monosulfide.

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References

[1] D. Y. Adelerhof Media development for DVD+RW phase change recording // Memories of E*PCOS. European Symposium Phase Change and Ovonic Science. Balzers. Liechtenstein. 4-7 September, 2004.

[2] K. Petkov, R. Todorov, D. Kozhuharova, L. Tichi, E. Cernoskova, P. J. S.Ewen, J. Materials Sci. **39**, 961 (2004).

[3] H. Hansen, K. Anderko, Constitution of Binary Alloys. - MCGRAW-HILL. - New York. -1965.

[4] N. H.Abrikosov, V. F. Bankina, L. B Poretskaya, E. V. Skudnova, C. H Chizhevsky, Semiconductor chalcogenides and alloys on their basis. Nauka. M. 1975. 219 P .

[5] T. Massalski, P. R. Subramanian, H. Okamoto, L. Kacprzac, Thermodynamically Improbable Phase Diagrams. -2nd ed. ASM International. Materials Park. OH.1990.

[6] V. P. Vassiliev, A.V. Nikolskaja, Ja. I. Gerasimov, Docl. Akad. Nauk SSSR. **199**(5), 1094 (1971).

[7] V. P. Vassiliev, A.V. Nikolskaja, Ja. I. Gerasimov, Neorgan. Materials. **9**(4), 553 (1973).

[8] V. P. Vassiliev, A.V. Nikolskaja, V.V.Tchernyshov, Ja.I. Gerasimov, Neorgan. Materials. **9**(6), 900 (1973).

[9] M. Soulard, M. Tournoux, Bult. Soc. Chim. Fr.. **3**, 791 (1971).

[10] S. Kabré, M. Guittard, J. Flahaut, C. R. Acad. Sci. Serie C. **278**, 1043 (1974).

[11] J. I. Vorobev, V. V. Kirilenko, R. N. Shchelokov, Neorgan. Materials. **23**(5), 742 (1987).

[12] R. M. Sardarly, A. P. Abdulaev, G.G. Gusejnov, N. F. Nadzhafov, N. A. Eubova, Crystallography. **45**(4), 606 (2000)

[13] H. Hahn, W. Klinger, Z. Anorg. Chem. **260**(1-3), 110 (1949).

[14] V. E. Frasson, Ric. Sci. **26**, 3382 (1956).
[15] V. E. Frasson, Lettere ed Arti, Classe di scienze Matematiche e Naturali. **114**, 61 (1955).
[16] B. Leclerc, M. Bailly Acta Cryst. **29**, 2334 (1973).
[17] J. Tudo, B. Dermigny, B. Jolibois, C. R. Acad. Scien. **280**, 375 (1975).
[18] N. S. Chaus, J. I. Gornikov, Demchenko, N. M. Kompanichenko, A. G. Gritchuk, Z. Neorg. Himii. **24**(3), 622 (1979).
[19] S. Kashida, K. Nakamura, S. Katajama, Solid State Communication. **82**, 127 (1992).
[20] S. Kashida, K. Nakamura, S. Katajama, J. Condens. Matter. **5** 4243 (1993).
[21] S. Kashida, K. Nakamura, J. Solid State Chem. **110,** 264 (1994).
[22] L. I. Man, R. M. Imamov, S. A. Semiletov, Crystallography. **21**(3), 628 (2000).
[23] A. S. Radtke Carlenite, American Mineralogist. **60,** 559 (1975).
[24] G. B. Demishev, S. S. Kabalkina, T. N. Kolobbyanina, Phys. Stat. Sol. 1988.
[25] G. F. Voronin, Doct. Sci. (Chem.) Dissertation. Moscow.1970.
[26] V. S. Minaev, In: Semiconducting Chalcogenide Glass. I. Eds. Robert Fairman, Boris Ushkov. Elsevier - Academic Press. Amsterdam. Boston. London, New York. Ser. Semiconductors and Semimetals. **78**, 139 (2004).
[27] V. S. Minaev, Fiz. Khim. Stekla. **22**, 314 (1996) (Sov. J. Glass Phys. Chem. (Engl. Transl. **22**, 235).
[28] V. S. Minaev, J. Optoelectron. Adv. Mater. **3**(2), 233 (2001).
[29] V.V. Kalugin, V. S. Minaev, S. P. Timoshenkov, E. N. Markova, J. Optoelectron. Adv. Mater. **8**(6), 2086 (2006).
[30] L. Červinka, A. Hrubý, J. Non-Cryst. Solids. **30**, 191 (1978).
[31] L. Červinka, A. Hrubý, In: Amorphous semiconductors 78: Proc. Intern. Conf. Pardubice. 211, 1978
[32] V. P. Vasil’ev, Inorganic Materials. **43**(2), 115 (2007).

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