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Phase Equilibria in the Quasi-Binary Thallium(I) Selenide – Bismuth(III) Selenide System

by Z. Sztuba, I. Mucha and W. Gaweł

Department of Analytical Chemistry, Wrocław Medical University, Faculty of Pharmacy,
Szewska 38, 50-139 Wrocław, Poland

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The phase equilibrium diagram for the system $Tl_2Se – Bi_2Se_3$ has been constructed from the results of thermal analysis. The diagram has been compared with that for the analogous system $Tl_2Te – Bi_2Te_3$, as well as with that published earlier for the same $Tl_2Se – Bi_2Se_3$ system, delineated from the data obtained by other methods.

Key words: phase diagram, binary metal selenide system, thermal analysis

Over the last three decades, one of the most important fields of searching for the new semiconductor materials are binary metal chalcogenide systems of the type $M_mX_n – M'_zX_u$ (common anion), $M_mX_n – M'_zY_u$ (different anions) and $M_mX_n – M'$ (compound – metal), where M and M' are any metals, and X and Y are elements of 15 and 16 group of Periodic Table. Such systems are called "binary", "quasi-binary" or "pseudo-binary". It has been shown [1], however, that there are no "pseudo-binary" systems, while "binary" are mainly those built of two elements. Accordingly, the best term for the systems of the types given above is "quasi-binary".

A system of the type $M_mX_n – M'_zX_u$ as the title one, is a polythermal section of the ternary system M – M' – X (as *e.g.* Tl – Bi – Se). The probability of chemical compounds formation in the system is the higher, the stronger ionic interactions between the components of the side binary systems: M – M', M – X, M' – X. Such a case is when X is an electronegative element as selenium or tellurium ($Tl_2Se – Bi_2Se_3$ and $Tl_2Te – Bi_2Te_3$).

The $Tl_2Te – Bi_2Te_3$ system was studied formerly several times [2–5]. Its final phase diagram was published in [5], while that of the system $Tl_2Se – Bi_2Se_3$ [6–8] seemed still incomplete. Accordingly, it was necessary to undertake a study aimed at refining data on this system. This is the reason why we decided to re-examine the phase equilibria in the $Tl_2Se – Bi_2Se_3$ system.

The studies on the phase equilibria in this system were performed thrice:

1. Zbigli and Raevskii [6] (1984) examined the system by differential thermal analysis (DTA), X-ray diffraction, microstructure and microhardness methods, and published first phase diagram thereof (Fig. 1). They stated that the system components form two chemical compounds: Tl_9BiSe_6 and $TlBiSe_2$, both congruently melting at temperatures 795 K and 995 K, respectively. The former of them formed terminal solid solution (γ) with Tl_2Se, the latter being rather a phase of variable composition (β).

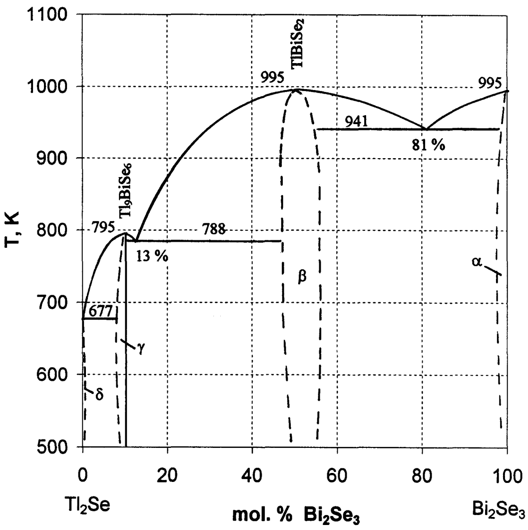

Figure 1. Phase diagram for the system Tl_2Se – Bi_2Se_3 reconstructed from the data [6].

2. Barchii *et al.* [7] (1988) studied the systems $Tl_2X – Bi_2X_3$, where X = S, Se and Te, employing the same methods as the authors of [6]. They showed that in these systems the compounds of general formulas Tl_9BiX_6 and $TlBiX_2$ were formed. The results confirmed the data [6].
3. Babanly *et al.* [8] (1990) examined several sections of the ternary system Tl – Bi – Se (employing DTA, X-ray diffraction, microhardness and concentration cell EMF measurements). As regards the section Tl_2Se – Bi_2Se_3, results obtained by them generally did not differ from those presented in [6] and [7], excepting continuous solid solutions formed by Tl_2Se and Tl_9BiSe_6.

EXPERIMENTAL

Both the thallium selenide and the bismuth selenide were prepared in the same way each, *i.e.* by simple synthesis. Stoichiometric amounts of appropriate elements (thallium, bismuth and selenium 99.9% pure; Aldrich Chem. Co.) weighted with an accuracy of ± 0.0001 g were melted in a sealed quartz tube under pure argon (BOC-gazy, Poznań) atmosphere and then stirred several minutes at temperatures by *ca.* 100 K higher than the melting point of respective metal selenide.

The phase equilibria in the title system were studied by common thermal analysis (TA), not to use the same method (DTA) that had been employed by the authors of [6–8]. The TA method enables one to determine the phase transition temperatures with a better accuracy [1] than the DTA does, namely ± 0.2 K. In the present work, however, the experimental points were rather dispersed, consequently the phase transition temperatures could be determined with an accuracy of only ± 0.4 K.

The measurements were performed by using the same technique as in our earlier works, *e.g.* [5], *i.e.* by cooling curve determination in a quartz apparatus designed for phase and cryometric investigations, described in details in [1]. The temperatures were measured by means of thermopile consisting of three thermocouples Pt/Pt,Rh connected in series, calibrated at freezing points of standards (tin, lead, zinc, aluminium, potassium chloride and silver). Throughout the measurements, liquid samples placed in an alumina crucible (20 mm in diameter) were vigorously stirred with a quartz stirrer making vertical strokes, the temperature decreasing rate being 0.8–1.2 K/min. The sample mass was from 30 to 45 g. The thermopile was connected to dual display multimeter (Fluke 45); the latter being combined with a computer that displayed the cooling curve after the experimental data having been treated.

The compositions of examined alloys were calculated from the masses of the components taken. Taking into account the error in the graphical determination of co-ordinates for characteristic points of the phase diagram, the compositions are given with an accuracy of not less than ± 0.5 mol. % Bi_2Se_3.

RESULTS AND DISCUSSION

Based on the results obtained by TA method, the phase diagram for the Tl_2Se – Bi_2Se_3 system was established within the whole concentration range (Fig. 2). It followed from the diagram that in the system three chemical compounds were formed:

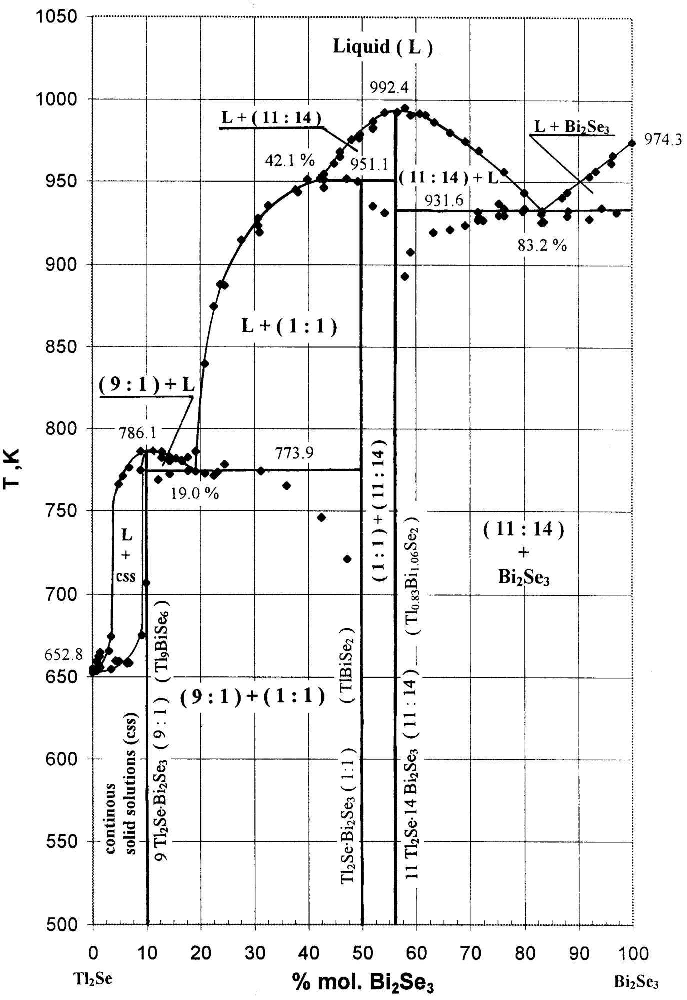

Figure 2. Phase diagram for the system Tl_2Se – Bi_2Se_3.

Tl_9BiSe_6, $TlBiSe_2$ and $Tl_{0.83}Bi_{1.06}Se_2$. The first and the last of the compounds are congruently melting at temperatures 786.1 ± 0.4 K and 992.4 ± 0.4 K, respectively, while $TlBiSe_2$ undergoes a decomposition (peritectic transformation) at 951.1 ± 0.4 K, peritectic point being at 42.1 ± 0.5 mol. % Bi_2Se_3. The co-ordinates of two eutectics are: 19.0 ± 0.5 mol. % Bi_2Se_3, 773.9 ± 0.4 K and 83.2 ± 0.5 mol. % Bi_2Se_3, 931.6 ± 0.4 K. All the temperatures are mean values of several determinations of each in several measurement series.

The thallium selenide and the next compound Tl_9BiSe_6 form a subsystem that exhibits unlimited miscibility in both solid and liquid phases (continuous solid solutions), the solidus and liquidus lines forming fair-sized two-phase area. The point of co-ordinates 10 mol. % Bi_2Se_3 and 706.8 K belongs also to the solidus line, its particular position being a result of a natural dispersion of experimental points. Accordingly, it cannot be considered as an indication of any phase transformation of the compound Tl_9BiSe_6.

It should be noted that the phase diagram for the system $Tl_2Se - Bi_2Se_3$ resembles that for the $Tl_2Te - Bi_2Te_3$ system presented in Fig. 3 [5]. The good similarity of the phase diagrams might be expected because the systems are analogous. In either system three compounds are formed of general formulae $TlBiX_2$, Tl_9BiX_6 and $Tl_{0.83}Bi_{1.06}X_2$, the first of them being incongruently melting, as well as continuous solid solutions covering the range Tl_2X - Tl_9BiX_6. The only difference is that in the system $Tl_2Te - Bi_2Te_3$ an additional (fourth) compound is formed ($TlBi_7Te_{11}$) decomposing in the subsolidus region. Undoubtedly, replacing anion (Se) by its heavier homologue (Te) results in increasing number of compounds.

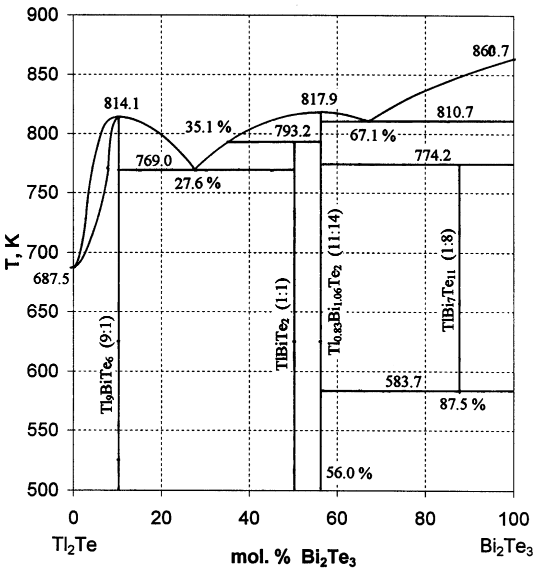

Figure 3. Phase diagram for the system $Tl_2Te - Bi_2Te_3$ according to [5].

The melting points of compounds $TlBiX_2$ and $Tl_{0.83}Bi_{1.06}X_2$ containing 50.0 mol. % Bi_2X_3 and 56.0 mol. % Bi_2X_3, respectively, formed in the $Tl_2Se – Bi_2Se_3$ system, are much higher than those in the $Tl_2Te – Bi_2Te_3$ by 158 K and 175 K, respectively. This is indicative of a higher stability of respective thallium selenobismuthates than that of thallium tellurobismuthates, resulted probably from more ionic character of chemical bonding in Bi_2Se_3 (melting point of which is 974.3 K) than that in Bi_2Te_3 (m.p. 860.7 K).

Instead, in case of compounds of the type Tl_9BiX_6, an opposite effect may be observed. The melting point of Tl_9BiTe_6 (containing as much as 90 mol. % Tl_2Te) is by 28 K higher than that of Tl_9BiSe_6. This is undoubtedly effect of quite substantial ionic contribution to the chemical bonding in Tl_2Te [9]. The stability of thallium telluride is higher than that of thallium selenide which results in higher melting point of the former (m.p. 687.5 K) compared with that of the latter (m.p. 652.8 K).

The results of the present study are richer than those of [6–8]. The most of differences concern the central part of the system. According to the present data within the middle concentration range two compounds are formed, while the former authors found one compound only ($TlBiSe_2$) that was regarded as phase β covering a concentration region approximately from 47 mol. % Bi_2Se_3 to 56 mol. % Bi_2Se_3. The maximum on the liquidus line presented in Fig. 2 there is exactly at 56.0 mol. % Bi_2Se_3 which excludes any doubtfulness on the composition of the compound ($Tl_{0.83}Bi_{1.06}Se_2$) congruently melting. This conclusion is clearly confirmed by the arrangement of both the experimental points corresponding to the eutectic melting at 931.6 K and the peritectic transition at 951.1 K. On the other hand, the well-marked "break" on the liquidus line at 42.1 mol. % Bi_2Se_3 and 951.1 K provides an evidence of an incongruent melting of a compound, composition of which cannot be other than 50.0 mol. % Bi_2Se_3 (*i.e.* $TlBiSe_2$) as it follows from the arrangement of the experimental points of phase transitions at 951.1 K and 773.9 K. The latter conclusion may be supported by that in the analogous system $Tl_2Te – Bi_2Te_3$, a congruently melting compound of the same general formula $TlBiX_2$ is formed.

The compositions of both the compounds $TlBiSe_2$ and $Tl_{0.83}Bi_{1.06}Se_2$ neighbour with one another (50.0 mol. % Bi_2Se_3 and 56.0 mol. % Bi_2Se_3, resp.) and this is the reason why they may be wrongly regarded as two concentration limits of any phase of variable composition as is the case with the works [6] and [7].

The only reason why the former authors did not found the compound $Tl_{0.83}Bi_{1.06}Se_2$ seemed to be shortcoming [5] of the DTA – the main experimental method employed by them. The shortcoming lies in that the little samples are not stirred throughout the measurements by using DTA apparatus (derivatograph). For that reason the supercooling and overheating very commonly occur as an effect of non-equilibrium conditions of a phase transformation, particularly in binary metal selenide systems whose components can easily form glassy alloys. On the other hand, the DTA method has also advantages such as the small mass of a sample, full automatization of measurements and especially sensitivity to enthalpy changes of a system examined. Therefore in most of works devoted to studies on phase equilibria in condensed systems, the differential thermal analysis is more readily used than the common thermal analysis.

The continuous solid solutions formed by Tl_2Se and Tl_9BiSe_6 have been found both in the present work by TA and in the work [8] by concentration cell EMF measurement. The EMF method appeared to be one of the best experimental methods [1] of studies on (quasi) binary metal systems.

The data obtained by TA studies on many systems, the phase diagrams of which had been determined formerly by DTA, resulted in verification of the diagrams, *e.g.* $Tl_2Te - Bi_2Te_3$ [5], $Tl_2Te - Ag_2Te$ [10], $Tl_2Te - HgTe$ [11], $Tl_2Te - CdTe$ [12], $Tl_2Te - Tl_2Se$ [13].

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