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Phase studies on the quasi-binary thallium(I) telluride-bismuth(III) selenide system

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ABSTRACT

The phase diagram for the quasi-binary Tl₂Te–Bi₂Se₃ system was delineated from the results of phase studies by both common thermal analysis and X-ray diffraction. Numerical values of the phase transition temperatures at different alloy compositions within the whole concentration range, were obtained. They have been listed in a table that can be used by other authors in any computational treatment of the system. The diagram was compared with that published earlier by other authors employing differential thermal analysis as a main experimental method. As a result of the present study, three new chemical compounds have been found.

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1. Introduction

The thallium-containing chalcogenides (thallium-based ternary chalcogenides) that are formed in the quasi-binary $Tl_2X-Bi_2X_3$ (X = S, Se, Te) systems, belong to the materials with interesting semiconductor properties. The investigation of the quasi-binary chalcogenide sections $Tl_2Se-Bi_2Se_3$ and $Tl_2Te-Bi_2Te_3$ showed that the formation of ternary compounds is quite common [1,2]. The compounds involve promising set of physical properties, this giving a push to the search for new materials with interesting electrical characteristics.

For instance, the newest result unambiguously established that the compound TlBiSe₂ was a strong topological insulator with a single Dirac cone at the Brillouin-zone center. The large bulk gap (~0.20 eV) made TlBiSe₂ a topological insulator with better mechanical properties than the previous binary 3D topological insulator family. For TlBiTe₂, the observed negative bulk gap indicated it as a semimetal, instead of a narrow-gap semiconductor as commonly believed. This semimetality naturally explains its mysteriously small thermoelectric figure of merit comparing to other compounds in the family. The unique band structures of TlBiTe₂ and the band gap of 0.35 eV (the largest among known topological insulators) also suggest it as a candidate for topological superconductors [3,4]. It was confirmed that Tl₉BiTe₆ may be of potential for thermoelectric applications in the temperature range from 400 to 600 K. The thermal conductivity of Tl₉BiTe₆ is extremely low as compared to those of state-of-the-art thermoelectric materials [5].

The system under consideration is of the type $A^{III}B^{VI}-C^VD^{VI}$, where A and C are metals and B, D are chalcogens neighboring in the same group of the Periodic Table. The thallium(1) telluride–bismuth(III) selenide system was studied formerly once [6]. From the phase diagram published in the paper [6] (Fig. 1), it does not follow clearly whether any chemical compound is formed in the system or not. However, comparison of two analogous systems Tl₂Se–Bi₂Se₃ [1] and Tl₂Te–Bi₂Te₃ [2] show existence at least two compounds in each. Because of a very small difference in the radius of selenium and tellurium, it may be supposed that in Tl₂Te–Bi₂Se₃ system also chemical compounds should be formed. This is the reason why we decided to re-investigate the title system by thermal analysis (TA) and XRD methods.

2. Experimental

2.1. Materials

The components of the system examined, i.e. thallium telluride and bismuth selenide, were prepared from pure elements: thallium 99.9 mass%, bismuth 99.9 mass%, selenium 99.9 mass% and tellurium 99.99 mass% (all from Aldrich Chemical Co.). The metal chalcogenides were synthesized by simple fusing stoichiometric quantities of the elements, weighed with an accuracy of ± 0.0001 g, in quartz tubes in a purified argon atmosphere (5 N pure, BOC Gazy, Poznan) and then mixed for 15 min at temperature about 100 K higher than the melting point of the respective metal chalcogenide.

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Fig. 1. Phase diagram for the system Tl₂Te-Bi₂Se₃ (according to [6]).

2.2. Apparatus and measurements

The phase studies on the Tl₂Te–Bi₂Se₃ system were performed by making use of the TA method (cooling curve technique) in a quartz apparatus designed for phase and cryometric investigations at high temperatures [7]. The phase transition temperatures of the examined samples were determined by using a thermopile Pt/Pt,Rh calibrated at the freezing points of standards (lead, zinc, aluminium, potassium chloride and silver). The molten samples (no less than 25 g) were vigorously stirred throughout the experiments with a quartz stirrer to maintain equilibrium conditions of crystallization of the melts. The cooling rate was 0.8-1.2 K/min, the accuracy of measurements was ± 0.5 K. The thermopile was connected to a dual display multimeter Fluke 45 which was joined to a computer for the processing and display of the experimental data.

The composition of the eutectics was determined by a graphical method, i.e. by simple extrapolation of the liquidus curves up to their intersection with the solidus line, accordingly, the compositions were given with an accuracy of $\pm 1 \mod \%$.

To confirm the results of the TA, use was also made of the XRD method. Alloy samples with compositions 5, 10, 20, 40, 50, 60, 68, 70, 80 and 90 mol% Bi₂Se₃ were prepared in the same way as metal chalcogenides (Section 2.1). The solidified samples were powdered in an Analysette 3 Spartan pulverisette 0 vibration mill (Fritsch) and homogenized for 7 days under vacuum at 650 K, then quenched in a cooling bath (ice + methanol). The XRD examinations of the alloys as well as of pure components (Tl₂Te and Bi₂Se₃) were performed using a Siemens D 5000 diffractometer, employing Cu_{Kα,Kβ} radiation (20 mA, 35 kV). The measurements were made in 2 θ angle range of 15°–60° with a 0.04° step and at least 2 s per step.

3. Results

The measurements of phase transformation temperatures in the system thallium(I) telluride–bismuth(III) selenide were effected by common thermal analysis within the whole concentration range. Results of these measurements have been listed in Table 1 to enable other authors to employ them in future computational treatment of the system. From these data, the phase equilibrium diagram for the system has been delineated – Fig. 2. The constructed phase diagram was checked by the XRD examination aimed at identifying phase compositions of different $Tl_2Te+Bi_2Se_3$ alloys. It appeared that in the system $Tl_2Te-Bi_2Se_3$ three quaternary compounds were formed.

The first of the compounds found in this study, was formed with a component molar ratio $Tl_2Te:Bi_2Se_3 = 9:1$ to which the formula $Tl_{18}Bi_2Te_9Se_3$ may be ascribed. This compound composition



Fig. 2. Phase diagram for the system Tl₂Te–Bi₂Se₃ (this work).

was evidenced by both the maximum (at $10.0 \text{ mol}\% \text{ Bi}_2\text{Se}_3$ and 794.7 K) on the liquidus line and the arrangement of the experimental points corresponding to the eutectic at $26.9 \text{ mol}\% \text{ Bi}_2\text{Se}_3$, melting at 749.7 K. The points may be observed only at compositions higher than $10.0 \text{ mol}\% \text{ Bi}_2\text{Se}_3$.

The other compound was formed at 70.0 mol% Bi_2Se_3 , its component molar ratio being $Tl_2Te:Bi_2Se_3 = 3:7$ to which a formula $Tl_6Bi_{14}Te_3Se_{21}$ may be ascribed. Rather sharp maximum on the liquidus line at 946.7 K lies at 70.00 mol% Bi_2Se_3 . Moreover, the experimental points corresponding to the next eutectic (at 84.8 mol% Bi_2Se_3) melting at 913.9 K, appear just above the compound composition. These facts unequivocally determine the congruently melting compound composition.

At the component molar ratio $Tl_2Te:Bi_2Se_3 = 1:1$, a compound of composition $Tl_2Bi_2TeSe_3$ is formed according to a peritectic reaction $L+Tl_6Bi_{14}Te_3Se_{21} \leftrightarrow Tl_2Bi_2TeSe_3$ at 895.0 K. At 749.7 K this compound with $Tl_{18}Bi_2Te_3Se_3$ (9:1) forms the eutectic containing 26.9 mol% Bi_2Se_3. The points corresponding to the eutectic temperature may be observed only at compositions lower than 50.0 mol% Bi_2Se_3.

Both the TA and the XRD data evidenced three new chemical compounds $9Tl_2Te\cdotBi_2Se_3$ ($Tl_{18}Bi_2Te_9Se_3$), $Tl_2Te\cdotBi_2Se_3$ ($Tl_2Bi_2TeSe_3$) and $3Tl_2Te\cdot7Bi_2Se_3$ ($Tl_6Bi_{14}Te_3Se_{21}$) (not found earlier [6]) and confirmed the existence of terminal solid solutions α and β reported in [6].

4. Discussion

Results of X-ray examination of some $Tl_2Te + Bi_2Se_3$ alloys are presented in Fig. 3. As it will be shown later, the XRD patterns entirely corroborate the results described in the previous section. From comparison of the XRD pictures of pure Tl_2Te (Fig. 3a) and The phase transition temperatures at different alloy compositions within the whole concentration range of the system Tl₂Te-Bi₂Se₃.

No.	Comp. (mol% Bi ₂ Se ₃)	Temp. (K)	No.	Comp. (mol% Bi ₂ Se ₃)	Temp. (K)
1	0.00	691.9	31	47.99	882.0
2	2.03	698.0	32	48.86	900.7
3	2.03	721.0	33	48.86	888.0
4	7.86	760.0	34	48.86	744.6
5	7.86	790.0	35	50.51	906.2
6	10.26	794.7	36	51.80	909.3
7	13.21	743.8	37	53.06	913.9
8	13.21	793.1	38	53.31	913.7
9	15.79	787.0	39	53.31	895.0
10	18.80	740.9	40	55.41	913.9
11	18.80	779.1	41	55.41	895.8
12	21.53	750.0	42	56.12	922.5
13	21.53	763.8	43	58.74	927.3
14	26.89	751.9	44	58.74	894.9
15	30.56	792.0	45	59.98	932.8
16	30.56	747.6	46	62.52	893.0
17	33.78	808.6	47	66.60	943.4
18	33.78	749.7	48	66.60	895.0
19	36.56	822.1	49	70.00	946.7
20	36.56	748.7	50	70.79	946.4
21	39.11	845.9	51	70.79	909.1
22	39.11	749.3	52	74.43	943.0
23	41.89	864.8	53	74.43	913.0
24	41.89	745.5	54	78.44	936.3
25	43.93	749.3	55	78.44	911.0
26	43.93	873.9	56	84.84	913.9
27	45.70	887.5	57	90.38	932.2
28	45.70	877.0	58	90.38	911.0
29	47.32	746.8	59	97.00	956.1
30	47.99	900.0	60	97.00	910.7
			61	100.00	966.8



Table 1

Fig. 3. The X-ray diffraction patterns of some Tl₂Te + Bi₂Se₃ alloys.

the alloy containing 5 mol% Bi₂Se₃ (Fig. 3b) it can be seen that the peaks in the latter figure are shifted compared to the former which provides an evidence of the terminal solid solution (α) on the Tl₂Te matrix. The existence range of the solution α did not surpass 10 mol% Bi₂Se₃, i.e. up to the compound 9:1 (Fig. 3c).

Although the maximum on the liquidus line (794.7 K) at 10.0 mol% Bi₂Se₃ (Fig. 2) provides a strong and sufficient evidence for the compound $9Tl_2Te$ ·Bi₂Se₃, an additional confirmation follows from comparison of XRD diffraction patterns on either side of the compound, i.e. Fig. 3b, d and e. The patterns of the sample 5 mol% Bi₂Se₃ (Fig. 3b) shows superimposed peaks characteristic of the compound 9:1 and pure Tl_2Te , while those in Fig. 3d (20 mol% Bi₂Se₃) and in Fig. 3e (40 mol% Bi₂Se₃) – the peaks characteristic of the compound 9:1 and 1:1.

The X-ray diffraction patterns of the alloy samples of compositions of 20 mol% Bi_2Se_3 (Fig. 3d), and 40 mol% Bi_2Se_3 (Fig. 3e) show superimposed peaks characteristic of the compound $Tl_1_8Bi_2Te_9Se_3$ (9:1) together with strong peaks corresponding to the next compound $Tl_2Bi_2TeSe_3$ (1:1), which is clearly proved by the XRD pattern in Fig. 3f (50 mol% Bi_2Se_3).

The XRD picture of the compound $Tl_6Bi_{14}Te_3Se_{21}$ (70.0 mol% Bi_2Se_3) is shown in Fig. 3i. The alloy samples of compositions of 60 mol% Bi_2Se_3 (Fig. 3g), and 68 mol% Bi_2Se_3 (Fig. 3h) show superimposed peaks characteristic of the compound $Tl_2Bi_2TeSe_3$ (1:1) together with the peaks corresponding to the compound $Tl_6Bi_{14}Te_3Se_{21}$ (3:7) while those in Fig. 3j (80 mol% Bi_2Se_3) and in Fig. 3k (90 mol% Bi_2Se_3) present the peaks characteristic of the compound 3:7 and pure Bi_2Se_3 (all of them correspond to two phased regions).

From comparison of the XRD pictures of pure Bi_2Se_3 (Fig. 31) with the alloys containing 90 mol% Bi_2Se_3 (Fig. 3k) and 80 mol% Bi_2Se_3 (Fig. 3j), it can be seen that the peaks in the figures are shifted compared to the first one, which provides a good evidence for a region of the terminal solid solution (β) on the Bi_2Se_3 matrix. The last statement appears to be quite consistent with the arrangement of experimental points corresponding to eutectic at 84.8 mol% Bi_2Se_3 melting at 913.9 K. The points reach as far as to 97.00 mol% Bi_2Se_3 (Table 1, No. 59) which corroborates the solid solution existence above this alloy composition.

5. Conclusions

The results of the present study differ considerably from those of [6] in some details. The authors of [6] considered the Tl₂Te–Bi₂Se₃ system to be non-quasibinary while it appeared a quasi-binary one. They reported the presence of α , α' , β and γ phases together with two- and three-phase regions. It should especially be noted that according to the phase diagram published in [6] (Fig. 1.) no quaternary compounds were formed, however we observed two maximums on the liquidus line at 10.0 mol% Bi₂Se₃ and at 50.0 mol% Bi₂Se₃.

There are two possible reasons for these discrepancies. The first is the limitations of the differential thermal analysis employed by the former authors. In the DTA method the samples are not stirred and therefore the phase transformations occur under nonequilibrium conditions. Unlike DTA, the TA method used in this study enabled the solid and liquid phases to be in equilibrium on cooling due to efficient stirring, which resulted in precise temperature measurements of the phase transitions in the examined alloys. The other reason is that the metal chalcogenide alloys may form glasses on solidifying, which makes exact temperature measurement impossible. The glass formation appears very easily when the alloy is not stirred.

The phase diagram for the system $Tl_2Te-Bi_2Se_3$ resembled that for the $Tl_2Se-Bi_2Se_3$ [1] and $Tl_2Te-Bi_2Te_3$ [2] systems. The similarity of the phase diagrams might be expected because the systems are analogous. In all of them at least three compounds are formed, in the system $Tl_2Te-Bi_2Te_3$ one additional (fourth) compound $TlBi_7Se_{11}$ is formed. The melting points of compounds containing 50.0 mol% Bi_2X_3 increase in the direction of higher stability of respective thallium chalcogenobismuthates (793.2 K TlBiTe₂ \rightarrow 895.0 K Tl₂Bi₂TeSe₃ \rightarrow 951.1 K TlBiSe₂), resulted from more ionic character of chemical bonding in Bi₂Se₃ than in Bi₂Te₃.The same tendency can be observed for the compounds formed above 50.0 mol% Bi_2X_3 (817.9 K Tl_{0.83}Bi_{1.06}Te₂ \rightarrow 946.7 K Tl₆Bi₁₄Te₃Se₂₁ \rightarrow 992.4 K Tl_{0.83}Bi_{1.06}Se₂).

In case of compounds formed at $10.0 \text{ mol}\% \text{ Bi}_2 X_3$, an opposite effect may be observed. The melting point of $\text{Tl}_9\text{Bi}\text{Te}_6$ containing as much as $90.0 \text{ mol}\% \text{Tl}_2\text{Te}$ is by 19.4 K higher than that of $\text{Tl}_18\text{Bi}_2\text{Te}_9\text{Se}_3$ and 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 . The stability of thallium telluride is higher than that of thallium selenide which results in higher melting point of the first.

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