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Phase studies on the quasi-binary thallium(I) telluride–gallium(III) telluride system

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ABSTRACT

The phase diagram for the quasi-binary Tl_2Te–Ga_2Te_3 system was constructed based on 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 listed. The diagram was compared with another diagram for the same system published earlier by other authors. The study produced substantial evidence corroborating the formation of two new chemical compounds.

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1. Introduction

The thallium(I) telluride–gallium(III) telluride system was formerly examined by Babanly and Kuliyev [1]. In their studies they employed differential thermal analysis (DTA) as the main experimental method, while X-ray diffraction (XRD) and microhardness measurement were used as auxiliary ones. The authors published phase diagram for this system presented in Fig. 1. It followed from the diagram that the system components formed two chemical compounds: at 25 mol% Ga_2Te_3 (i.e. $3Tl_2Te{\cdot}Ga_2Te_3$ or Tl_3GaTe_3) incongruently melting at 691 K, and at 50 mol% Ga_2Te_3 (i.e. $Tl_2Te{\cdot}Ga_2Te_3$ or $TlGaTe_2$) melting congruently at 1048 K. The latter was rather a phase of variable composition (γ). Both the compounds formed terminal solid solutions α with Tl_2Te 5 mol% wide and β with Ga_2Te_3 20 mol% wide, respectively.

The paper [1] was published more than thirty years ago when the level of the experimental technique was certainly lower compared with the present state. Consequently, the results reported earlier might be of lower accuracy as it was many times showed by us, e.g. [2,3], while only reliable phase diagrams may serve as a base of searching for new materials with favorable physico-chemical properties.

On the other hand, we studied earlier the Tl_2Te–In_2Te_3 system [2,3], analogous to the system $Tl_2Te{\cdot}Ga_2Te_3$, accordingly, the phase diagram of the latter should resemble that of the former. The components of the system thallium(I) telluride–indium(III) telluride form two ternary compounds [2,3]: at 42.9 mol% In_2Te_3 (i.e. $4Tl_2Te{\cdot}3In_2Te_3$) melting incongruently at 1021.4 K and 54.5 mol% In_2Te_3 (i.e. $5Tl_2Te{\cdot}6In_2Te_3$) melting congruently at 1044.9 K. From the comparison of the data [1] and [3] it may be seen that the analogy is rather poor, unless the data [1] are precisely determined.

These were reasons why we decided to reexamine the Tl_2Te–Ga_2Te_3 system by common thermal analysis (TA), a method that appeared [4] to be more accurate than others. X-ray diffraction was also employed to obtain complementary information.

2. Experimental

2.1. Materials

The components of the system examined, i.e. thallium telluride and gallium telluride, were prepared from high-purity elements: thallium 99.9 mass%, gallium 99.9 mass% and tellurium 99.99 mass% (all from Aldrich Chemical Co.). The metal tellurides were synthesized by simple fusion of 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 stirred for 15 min at a temperature about 100 K higher than the melting point of the respective metal telluride.

2.2. Apparatus and measurements

The phase studies on the Tl_2Te–Ga_2Te_3 system were made by TA method, employing a quartz apparatus designed for phase and

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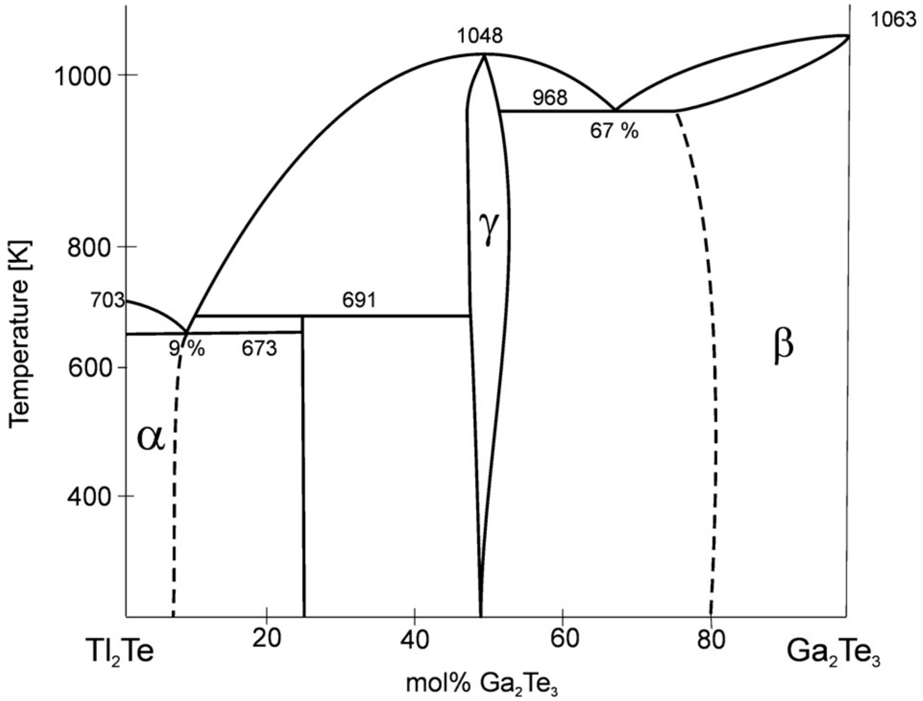

Fig. 1. Phase diagram for the system Tl_2Te–Ga_2Te_3.

According to [1].

cryometric studies at high temperatures, described in detail in [5]. The vessel was filled with the pure argon to prevent sample oxidation. The phase transition temperatures of the samples were determined using a Pt/Pt, Rh thermopile calibrated at the freezing points of standards (lead, zinc, aluminium, potassium chloride and silver). The molten samples (no less than 28 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, and the accuracy of measurement was ±0.5 K. The thermopile was connected to a Fluke 45 dual display multimeter, which was connected to a computer for the processing and display of the experimental data.

To confirm the results obtained by TA, use was also made of the XRD method. Alloy samples with compositions 2, 8, 25, 35, 47, 54.5, 65 and 85 mol% Ga_2Te_3 were prepared by melting and mixing appropriate quantities of components in quartz tubes in a pure argon atmosphere. 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 the pure components (Tl_2Te and Ga_2Te_3) were performed using a Siemens D5000 diffractometer.

3. Results

The experimental results, i.e. the temperatures of crystallization of different alloys, obtained by TA are summarized in Table 1. These data enabled the precise phase equilibrium diagram to be delineated for the thallium(I) telluride–gallium(III) telluride system (Fig. 2). The constructed phase diagram was checked by the XRD examination aimed at identifying phase compositions of different $Tl_2Te + Ga_2Te_3$ alloys.

Both the TA and the XRD data evidenced two new chemical compounds $Tl_{19}GaTe_{11}$ and $Tl_{10}Ga_{12}Te_{23}$ (not found earlier [1])

Table 1

The phase transition temperatures at different alloy compositions within the whole concentration range of the system Tl_2Te–Ga_2Te_3.

No.	Comp. (mol% Ga_2Te_3)	Temp. (K)	No.	Comp. (mol% Ga_2Te_3)	Temp. (K)
1	0.00	687.5	43	36.00	961.5
2	0.98	705.4	44	38.77	987.6
3	1.99	707.5	45	44.37	1005.0
4	2.76	709.1	46	46.80	1018.4
5	5.00	710.9	47	46.80	1013.4
6	6.07	710.2	48	52.20	1029.6
7	6.07	677.6	49	54.45	1034.5
8	8.02	704.9	50	56.61	972.1
9	8.02	680.0	51	56.91	1029.0
10	9.74	698.6	52	59.09	973.4
11	9.74	680.8	53	59.35	1020.2
12	10.78	694.7	54	60.13	1008.0
13	10.78	680.9	55	61.65	973.4
14	12.58	691.6	56	62.15	1001.2
15	12.58	684.0	57	64.02	975.4
16	14.35	685.4	58	64.40	999.1
17	15.54	682.1	59	64.87	1010.5
18	16.10	772.1	60	66.72	987.7
19	16.55	686.7	61	66.95	973.8
20	17.46	890.0	62	68.23	997.7
21	17.46	826.1	63	68.23	984.3
22	17.89	678.2	64	68.95	979.7
23	18.60	687.0	65	69.10	979.5
24	19.62	869.0	66	71.06	975.3
25	20.82	928.5	67	71.06	965.3
26	20.82	688.6	68	71.84	965.5
27	22.92	902.3	69	73.95	974.7
28	22.92	686.4	70	74.22	987.2
29	23.12	895.0	71	74.22	968.2
30	25.70	926.5	72	75.45	1004.3
31	25.70	683.4	73	75.45	996.3
32	25.73	953.7	74	77.55	1011.7
33	27.20	964.8	75	77.55	975.3
34	27.20	685.4	76	80.36	1020.5
35	29.82	937.5	77	80.36	973.8
36	29.82	930.3	78	83.40	1029.7

Table 1 (*Continued*)

No.	Comp. (mol% Ga_2Te_3)	Temp. (K)	No.	Comp. (mol% Ga_2Te_3)	Temp. (K)
37	31.62	969.2	79	85.58	1036.8
38	31.62	965.2	80	85.58	973.7
39	31.62	943.4	81	88.12	1045.6
40	31.89	970.9	82	90.83	1052.0
41	31.89	676.7	83	98.18	1059.5
42	33.69	968.9	84	100.00	1065.0

and confirmed the existence of terminal solid solutions α and β reported in [1]. Thereby it was shown, that the compounds Tl_3GaTe_3 and $TlGaTe_2$ [1] had not been formed in the system under consideration.

4. Discussion

4.1. New ternary compounds found in the system Tl_2Te–Ga_2Te_3

The first of the compounds found by us, was formed with a component molar ratio Tl_2Te:Ga_2Te_3 = 19:1 (or $19Tl_2Te \cdot Ga_2Te_3$), to which the formula $Tl_{19}GaTe_{11}$ may be ascribed. This compound composition was evidenced by both the maximum (at 5.0 mol% Ga_2Te_3) on the liquidus line corresponding to congruent melting of the compound at 710.9 K and the arrangement of the experimental points corresponding to the eutectic at 14.4 mol% Ga_2Te_3, melting at 684.0 K. The points may be observed only at compositions higher than 5.0 mol% Ga_2Te_3.

The other compound was formed at 54.5 mol% Ga_2Te_3, its component molar ratio being Tl_2Te:Ga_2Te_3 = 5:6 ($5Tl_2Te \cdot 6Ga_2Te_3$), to which a formula $Tl_{10}Ga_{12}Te_{23}$ may be ascribed. Rather sharp max-

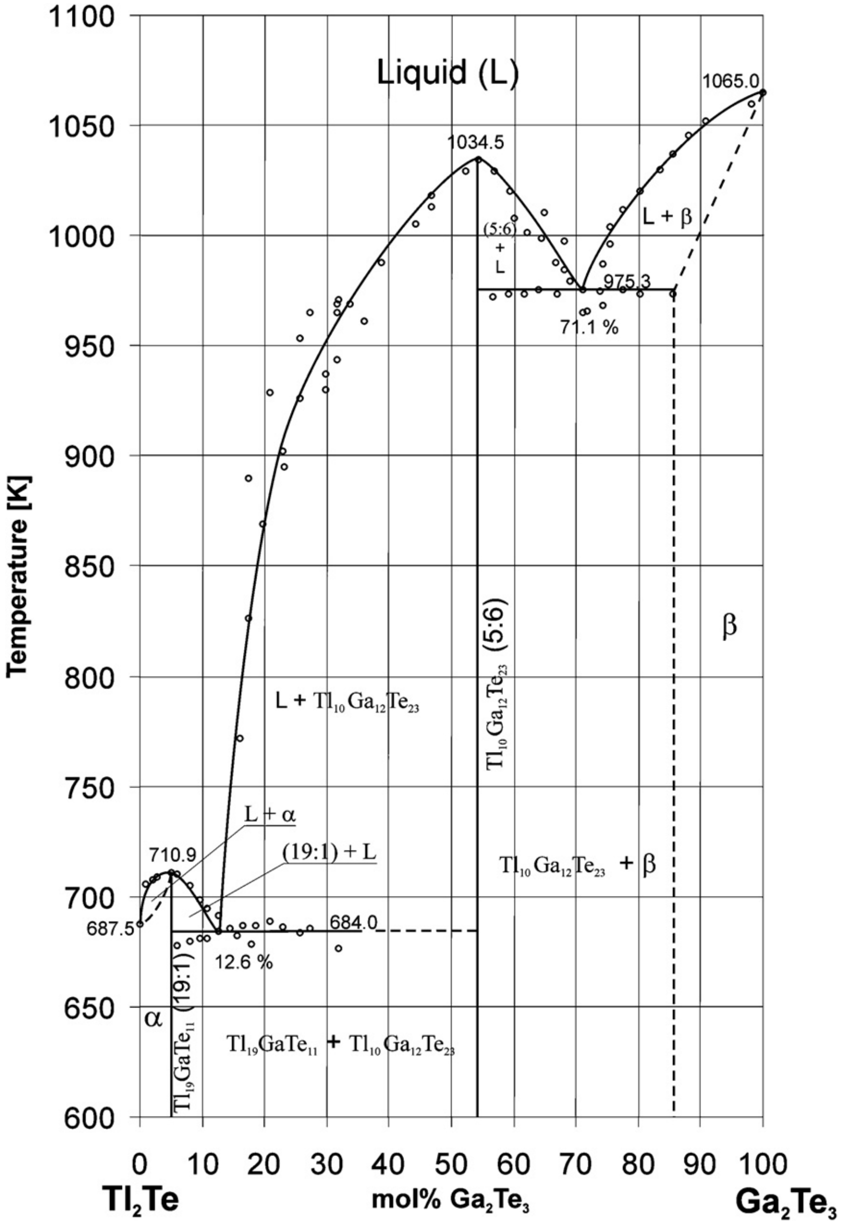

Fig. 2. Phase diagram for the system Tl_2Te–Ga_2Te_3 (this work).

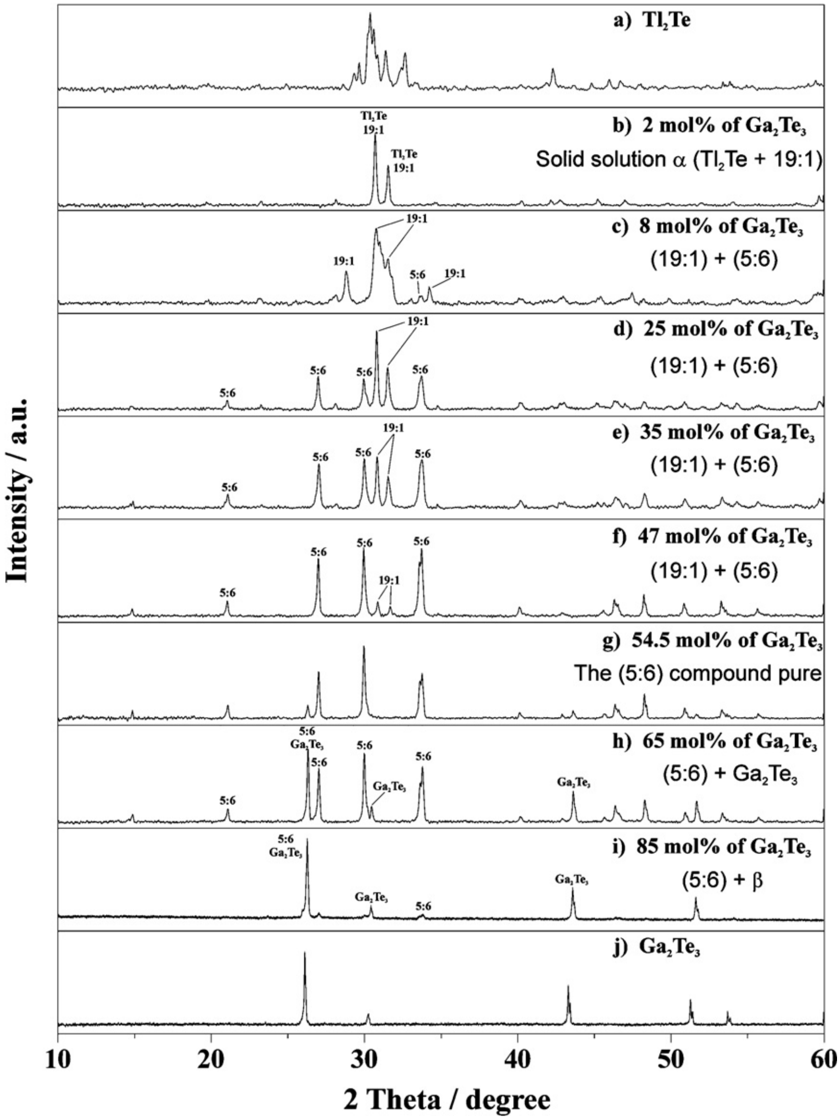

Fig. 3. The X-ray diffraction patterns of some $Tl_2Te + Ga_2Te_3$ alloys.

imum on the liquidus line corresponding to a congruent melting of the compound at 1034.5 K lies exactly (confirmed several times) at 54.5 mol% Ga_2Te_3. Moreover, the experimental points corresponding to the next eutectic (at 71.1 mol% Ga_2Te_3) melting at 975.3 K, appear just above the compound composition. These two facts unequivocally determine the compound composition. Consequently, it may be stated that the compound at 50.0 mol% Ga_2Te_3 ($TlGaTe_2$) reported in [1] does not exist.

4.2. Accuracy of measurements

The TA method (the cooling curve technique) employed in this work, enabled the melting temperatures of the compounds, eutectics and pure components to be determined with a good accuracy of ±0.5 K. The only exception is some parts of the liquidus line on either side of the compound $Tl_{10}Ga_{12}Te_{23}$ (54.5 mol% Ga_2Te_3) where the experimental points are scattered. Undoubtedly this is a result of supercooling liquid alloys even in spite of vigorous stirring. In the metal chalcogenide alloys such phenomenon may frequently appear as they easily form glasses [6,7] which results in considerable increasing viscosity of a melt.

Taking into account the maximal error in the graphical determination of the coordinates of the characteristic points of the phase diagram, the compositions of the eutectics are given with an accuracy of ±1 mol%. The eutectic coordinates were determined from intersection points of the eutectic transition line and respective two liquidus lines in the phase equilibrium diagram.

The compositions of the examined alloys were calculated from the masses of the components taken. There was no need to analyze the samples after each measurement series was completed as the mass loss due to evaporation of a more volatile component was negligible (did not exceed 0.05 mass%).

4.3. XRD examinations

The XRD patterns of the pure components and those of the alloys homogenized at 650 K are presented in Fig. 3. As it will be shown later, the XRD patterns entirely corroborate the results described above.

From comparison of the XRD pictures of pure Tl_2Te (Fig. 3(a)) and the alloy containing 2 mol% Ga_2Te_3 (Fig. 3(b)), it can be seen that the peaks in the latter figure are shifted compared to the for-

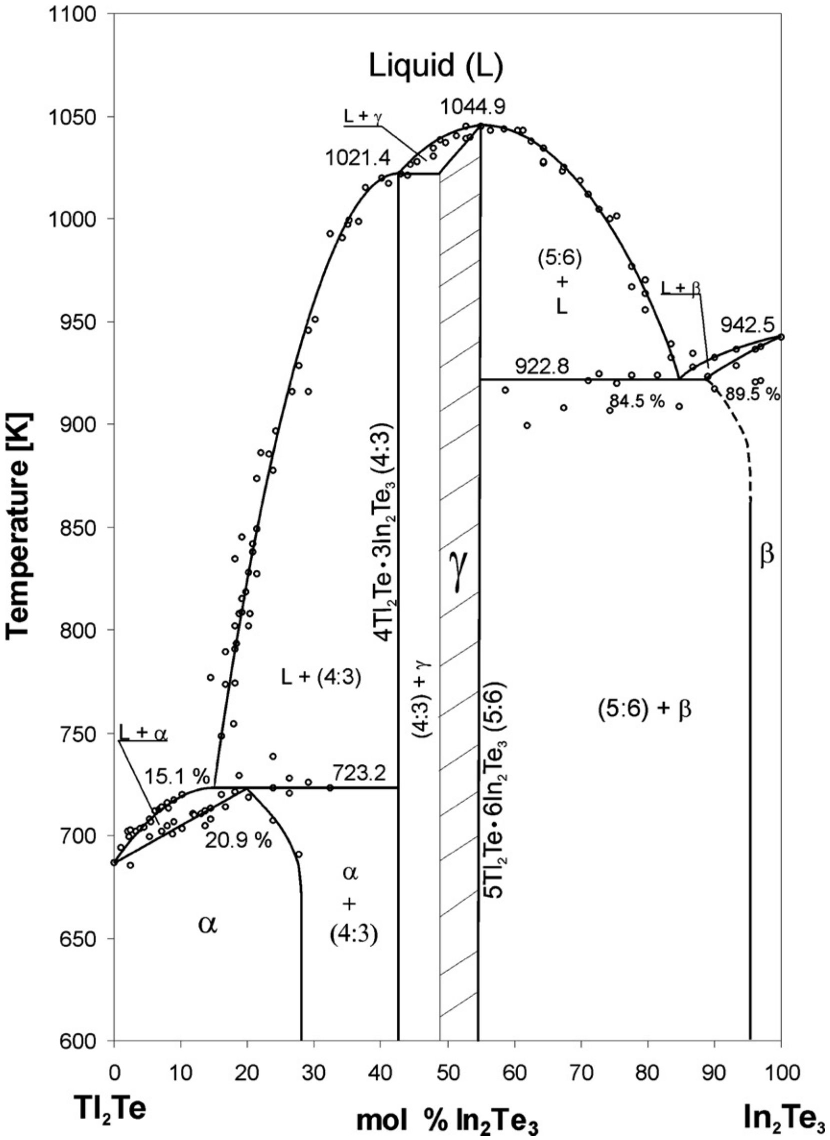

Fig. 4. Phase diagram for the system Tl_2Te–In_2Te_3 [3].

mer which provides an evidence for the terminal solid solution (α) on the Tl_2Te matrix. The region of the solid solution α covers 5 mol% Ga_2Te_3 only, i.e. up to the compound 19:1 because in Fig. 3(c) (8 mol% Ga_2Te_3) the shift is no longer observed. Fig. 3(c) almost entirely presents the XRD pattern of the compound 19:1 ($Tl_{19}GaTe_{11}$).

The X-ray diffraction patterns of the alloy samples of compositions of 25 mol% Ga_2Te_3 (Fig. 3(d)), 35 mol% Ga_2Te_3 (Fig. 3(e)) and 47 mol% Ga_2Te_3 (Fig. 3(f)) show superimposed peaks characteristic of the compound $Tl_{19}GaTe_{11}$ (19:1) together with strong peaks corresponding to the next compound $Tl_{10}Ga_{12}Te_{23}$ (5:6), which is clearly proved by the XRD pattern in Fig. 3(g) (54.5 mol% Ga_2Te_3). Accordingly, it may be inferred that no additional chemical compound is formed within the range 8–47 mol% Ga_2Te_3 (as e.g. the compound at 25 mol% Ga_2Te_3 reported in [1]). At the same time in Fig. 3(f) and (h) compared with Fig. 3(g), no shifts may be observed of the peaks characteristic of the compound 5:6, from which it follows that there is no phase of variable composition (γ) reported in [1].

From comparison of the XRD pictures of pure Ga_2Te_3 (Fig. 3(j)) and the alloys containing 65 mol% Ga_2Te_3 (Fig. 3(h)) and 85 mol% Ga_2Te_3 (Fig. 3(i)), it can be seen that the peaks in the latter figure only, are shifted compared to the first one, which provides a good evidence for a region of the terminal solid solution (β) on the Ga_2Te_3 matrix, no more than 15 mol% wide at the (homogenization) temperature of 650 K. The last statement appears to be quite consistent with the arrangement of experimental points corresponding to the eutectic (71.1 mol% Ga_2Te_3) melting at 975.3 K. The points may be observed as far as 85.58 mol% Ga_2Te_3 (Table 1, no. 80) which corroborates the solid solution existence above this alloy composition.

5. Conclusions

The results of the present study differ considerably from those of [1] in some details, in both the composition of the chemical compounds formed in the system Tl_2Te–Ga_2Te_3 and the phase transition temperatures. It should especially be noted that the former authors did not observe the maximum on the liquidus line at 5.0 mol% Ga_2Te_3, corresponding to congruent melting of the compound at 710.9 K and determined inaccurately the composition of the other compound as being 50 mol% Ga_2Te_3, while it was exactly 54.5 mol% Ga_2Te_3.There are in the literature several reports (e.g. [8,9]) on studying properties of the compound $TlGaTe_2$ (exactly:

alloy containing 50 mol% Ga_2Te_3) since many years. The authors of the reports stated that it was a phase with wide homogeneity area. This statement indirectly confirms our results: if the compound composition is 54.5 mol% Ga_2Te_3 (5:6 or $Tl_{10}Ga_{12}Te_{23}$), and we prepare the alloy 50.0 mol% Ga_2Te_3 (because we suppose that this is $TlGaTe_2$), we will find that it is no pure $TlGaTe_2$ but some region covering the range up to 54.5 mol%. The composition 54.5 mol% will be considered as a limit of a homogeneity area. Of course, the alloy 50 mol% Ga_2Te_3 also embodies some crystal structure, thermodynamic and electrical properties that may be studied and described in publications.There are two possible reasons for the discrepancies between the present data and those of [1]. 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 formation of glasses appears very easily when the liquid sample is not stirred (as in DTA method).

It is worth comparing the phase diagrams for both the Tl_2Te–In_2Te_3 (Fig. 4) and the Tl_2Te–Ga_2Te_3 (Fig. 2) systems as analogous. There are some considerable similarities between them. The most important is that in either system one chemical compound is formed of common formula $5Tl_2Te{\cdot}6M_2Te_3$ (where M = Ga or In). Comparing melting temperatures of the compounds it may be stated that higher melting point of $5Tl_2Te{\cdot}6In_2Te_3$ (1045.0 K) is an indicative of greater tendency to compound formation in the system Tl_2Te–In_2Te_3 than in Tl_2Te–Ga_2Te_3 ($5Tl_2Te{\cdot}6Ga_2Te_3$ – 1034.5 K), since the melting temperature of a compound is a measure of a stability thereof. Another common feature of the two systems is forming terminal solid solutions α and β.

Comparison of another two analogous systems Tl_2Te–Sb_2Te_3 [10] and Tl_2Te–Bi_2Te_3 [11] shows more clearly the respective similarities and differences.

These examples are a confirmation of a rule that in such analogous systems the tendency to compound formation increases with increase in atomic weight of metal M.

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