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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.

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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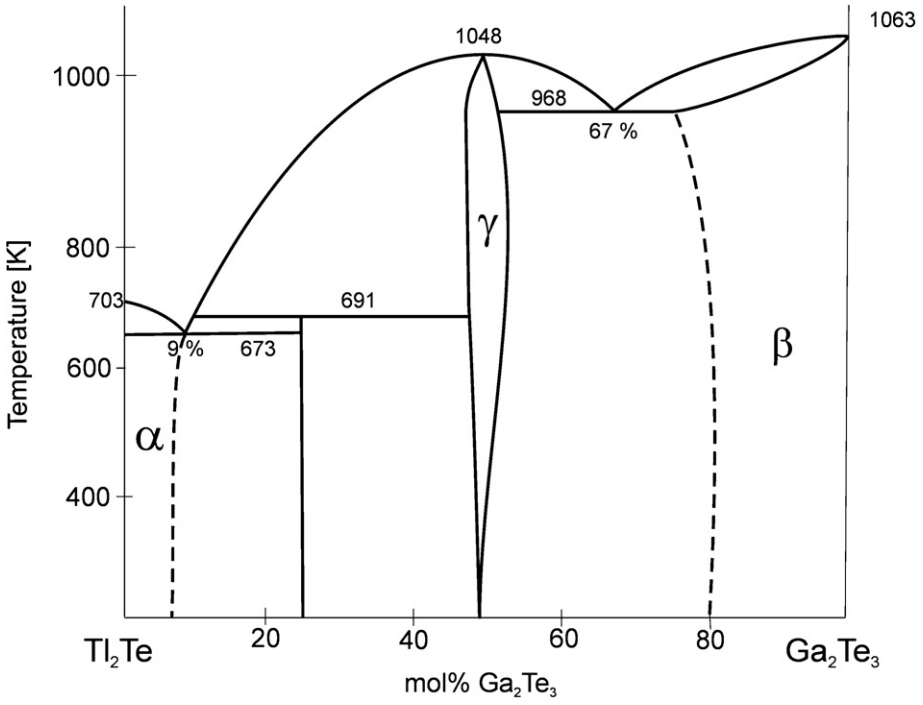

Fig. 1. Phase diagram for the system Tl_2Te–Ga_2Te_3.

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