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Note

QUANTITATIVE DTA MEASUREMENTS OF THE ENTHALPIES OF MIXING OF TERNARY GERMANIUM SYSTEMS

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The enthalpies of formation of melts in the ternary systems Ge–Ga–Te, Ge–In–Te, Ge–Pb–Te, Ge–Sb–Te as well as mixing enthalpies in quasi-binary systems based on germanium telluride and gallium, indium, lead and antimony tellurides were measured by quantitative differential thermal analysis in a purified argon atmosphere. The enthalpies of formation of tellurium with gallium [1], indium [2], lead [3] and antimony [2] are already known. The quantitative DTA method developed by us allows the formation enthalpies of multicomponent melts to be rapidly determined.

EXPERIMENTAL

The measurements were conducted on a modified apparatus of original design [4]. The determination of mixing enthalpies was conducted according to ref. 5 by direct mixing of liquid components in special quartz cells which were evacuated prior to argon inlet. The samples (0.3 g) were heated at 10 K min^{-1}. A calcined aluminium oxide sample was used as a reference. A differential chromel–alumel thermocouple with 0.2 mm diameter in a quartz jacket was placed in the centre of the sample and reference. Enthalpy calculation was carried out according to the equation $m\Delta H = KA$, where m is the sample mass, ΔH is the enthalpy of transition or mixing, K is a calibration constant, and A is the curve peak area. The calibration constant, K, was determined by the melting enthalpies of highest-purity indium, tin, bismuth, tellurium, antimony, germanium and silver. Since K strongly depends on cell size, and cells were not identical, they were calibrated.

The tellurides GeTe, Ga_2Te_3, In_2Te_3, PbTe and Sb_2Te_3 necessary for the mixing enthalpy determinations were obtained by direct alloyage of components taken in a stoichiometric proportion in evacuated (up to 10^{-1} Pa) quartz ampoules. The samples were kept in a melted state for 12 h and were then annealed at temperatures below the melting temperatures of the compounds for 200–250 h. Identification of the samples obtained was done by X-ray and thermal analyses methods.

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TABLE 1

Mixing enthalpies of germanium with the gallium–tellurium melt (Ge–GaTe sample)

Sample composition (g)			Ge (atom%)	A (cm^2)	K (J cm^{-2})	$\Delta H^{\mathrm{mix}}_{\mathrm{Ge+GaTe}}$ (kJ mol^{-1})	$\Delta H^{\mathrm{liq}}_{\mathrm{Ge-Ga-Te}}$ (kJ mol^{-1})
Ge	Ga	Te					
0.0248	0.0972	0.1788	10.92	5.4	1.55	2.7	−24.9
0.0491	0.0883	0.1617	21.07	8.0	1.55	3.9	−20.6
0.0758	0.0795	0.1455	31.41	10.3	1.55	4.8	−16.5
0.0826	0.0776	0.1421	33.20	25.8	0.73	5.7	−15.0
0.1000	0.0707	0.1293	40.46	13.4	1.55	6.1	−12.3
0.1245	0.0620	0.1136	49.08	32.7	0.73	6.9	−8.9
0.1369	0.0576	0.1055	53.29	32.2	0.73	6.7	−7.8
0.1427	0.0555	0.1017	55.20	31.5	0.73	6.5	−7.4
0.1445	0.0545	0.0998	56.00	29.2	0.73	6.0	−7.6
0.1605	0.0495	0.0905	60.91	12.7	1.55	5.4	−6.7
0.1744	0.0445	0.0816	65.28	26.0	0.73	5.2	−5.6
0.1895	0.0392	0.0718	70.07	10.0	1.55	4.2	−5.1
0.2248	0.0266	0.0489	80.29	7.6	1.55	3.1	−3.1
0.2510	0.0124	0.0317	89.02	10.1	0.73	1.9	−1.5

RESULTS AND DISCUSSION

In the germanium–gallium–tellurium system, mixing enthalpies of germanium with gallium–tellurium melts for four samples with Ga : Te ratios of 3 : 1, 1 : 1, 2 : 3 and 1 : 3 were determined at 1270 K. Experimental data and enthalpies of formation of ternary melts calculated from liquid components (ΔH^{liq}) are given in Table 1. Mixing of germanium telluride and gallium telluride was conducted at 1095 K. The enthalpies of formation of melts obtained from the above tellurides are given in Table 2. Mixing of germanium and gallium tellurides is accompanied by a considerable increase

TABLE 2

Mixing enthalpies of germanium and gallium tellurides at 1095 K

Component mass (g)		GeTe composition (atom%)	A (cm^2)	K (J cm^{-2})	ΔH^{mix} (kJ mol^{-1})
GeTe	Ga_2Te_3				
0.0281	0.2718	21.2	2.0	0.59	1.8
0.0359	0.2700	25.7	2.0	0.77	2.2
0.0485	0.2508	33.5	5.6	0.59	4.5
0.0752	0.2250	46.5	6.9	0.77	6.6
0.0934	0.2063	54.1	9.4	0.59	6.4
0.0984	0.2019	56.0	8.8	0.59	5.9
0.1296	0.1705	66.5	3.7	1.34	5.1
0.1492	0.1511	72.0	3.3	1.34	4.3
0.1617	0.1385	75.3	2.4	1.34	3.0

in enthalpy. The results of our experiments allowed the enthalpies of formation of germanium–gallium–tellurium melts to be determined over the whole concentration range. They were found to be negative and the mixing enthalpy surface appeared as a recess with a minimum at the Ga_2Te_3 compound.

The determination of enthalpies of mixing of germanium– and indium–tellurium melts was done at 1250 K for three samples with indium : tellurium ratios of 2 : 3, 1 : 1 and 3 : 2. Germanium and indium tellurides were mixed at 1025 K (Table 3). The enthalpies of formation of melts in the germanium–indium–tellurium system are of a sign-variable character and have a narrow region of positive values near the boundary of the germanium–indium binary system. They form a recess with a minimum at the In_2Te_3 compound.

The enthalpies of formation of melts in the germanium–lead–tellurium system were determined at 1300 K by means of mixing liquid germanium with lead–tellurium melts for five samples with lead : tellurium ratios of 4 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 4. A mathematical treatment of the results showed that a composition-dependent enthalpy of formation of melts from liquid components in this system, $\Delta H^{\mathrm{liq}}_{\mathrm{Ge-Pb-Te}}$ (kJ mol^{-1}), was adequately described by the following polynomial

$$\begin{aligned}\Delta H^{\mathrm{liq}}_{\mathrm{Ge-Pb-Te}} &= -50.0x_1x_2 - 105.8x_1x_3 + 15.0x_2x_3 - 21.3x_1x_2(x_1 - x_2)\\ &-19.5x_1x_3(x_1 - x_3) - 0.9x_2x_3(x_2 - x_3) + 65.6x_1x_2(x_1 - x_2)^2\\ &+98.4x_1x_3(x_1 - x_3)^2 - 3.9x_2x_3(x_2 - x_3)^2 + 24.3x_1^2x_2x_3 - 54.6x_1x_2^2x_3\\ &+214.1x_1x_2x_3^2\end{aligned}$$

where x_1, x_2 and x_3 are the atomic fractions of Te, Ge and Pb, respectively.

TABLE 3

Mixing enthalpies of GeTe–In_2Te_3 melts at 1025 K ($K = 0.67$ J cm^{-2})

Component mass (g)		GeTe composition (atom%)	A (cm^2)	ΔH^{mix} ($\pm$4%) (kJ mol^{-1})
GeTe	In_2Te_3			
0.0249	0.2751	10.0	3.5	0.92
0.0509	0.2491	20.0	4.7	1.26
0.0778	0.2222	30.0	5.3	1.34
0.1058	0.1942	40.0	6.4	1.59
0.1349	0.1651	50.0	8.5	2.10
0.1652	0.1358	60.0	6.5	1.59
0.1968	0.1032	70.0	4.6	1.13
0.2298	0.0702	80.0	3.4	0.79
0.2641	0.0359	90.0	2.3	0.54

The enthalpies of formation of melts in the Ge–Sb–Te system, $\Delta H^{\text{liq}}_{\text{Ge-Sb-Te}}$ (kJ mol^{-1}), were determined at 1250 K when mixing liquid germanium with antimony–tellurium melts for three samples with Sb : Te ratios of 3 : 2, 1 : 1 and 2 : 3. The dependence of the enthalpy of formation on composition is adequately described by the following polynomial

$$\Delta H^{\text{liq}}_{\text{Ge-Sb-Te}} = -50.0x_1x_2 - 35.2x_1x_3 + 2.2x_2x_3 - 21.3x_1x_2(x_1 - x_2)$$
$$-10.7x_1x_3(x_1 - x_3) + 65.6x_1x_2(x_1 - x_2)^2 + 21.3x_1x_3(x_1 - x_3)^2$$
$$+0.8x_2x_3(x_2 - x_3)^2 + 98.1x_1^2x_2x_3 + 54.1x_1x_2^2x_3 + 61.1x_1x_2x_3^2$$

where x_1, x_2 and x_3 are the atomic fractions of Te, Ge and Sb, respectively.

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