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Note

PHYSICO-CHEMICAL STUDY OF Ge(Pb)Te–$Bi_2(Sb_2)Te_3$ SYSTEM TERNARY COMPOUNDS

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In the Ge(Pb)Te–$Bi_2(Sb_2)Te_3$ system, the interaction of binary tellurides leads to the formation of a number of ternary compounds [1–3] (given in the tables), which are characterized by a layer structure (phases of the same stoichiometry are crystallized in one structural type) and are prospective for the construction of semiconductor devices. The physico-chemical characteristics of GeTe, PbTe, Bi_2Te_3 and Sb_2Te_3 are summarized in detail in a number of publications, but the properties of ternary intermetallic compounds at high temperatures are scarcely described in the literature.

The aim of this paper is to conduct a complex thermal analysis of Ge(Pb)Te–$Bi_2(Sb_2)Te_3$ system ternary compounds.

EXPERIMENTAL

The investigations were carried out using a quantitative differential thermal analysis (DTA) and dilatometric analysis methods, by means of triple-heat-bridge and solution calorimeters and the X-ray method [4–8]. We determined the formation enthalpies of substances under standard conditions (ΔH^0_{298}) and in the liquid state ($\Delta H^{\rm liq}$), their heat capacities ($C_{\rm p}$), relative elongations ($\Delta l/l_0$), temperatures ($T^{\rm fus}$ and $T^{\rm tr}$) and heats ($\Delta H^{\rm fus}$ and $\Delta H^{\rm tr}$) of fusion and phase transitions. All measurements were carried out several times; ΔH^0_{298} and $\Delta H^{\rm liq}$ were determined by a number of methods [7,8].

The accuracy of the data obtained was evaluated by comparison with those in refs. 1–3, 9 and 10; the divergence did not exceed 2%. Tables 1 and 2 summarize errors in the reproducibility of characteristics for the 0.95 significance level.

Ternary tellurides were synthesized as in ref. 8.

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TABLE 1

Thermodynamic properties for Ge(Pb)Te–$Bi_2(Sb_2)Te_3$ system ternary compounds

Ge(Pb)Te–$Bi_2(Sb_2)Te_3$	$-\Delta H^0_{298} \pm 4$–10% (kJ mol^{-1})	$T^{tr} \pm 1\%$ (K)	$\Delta H^{tr} \pm 2\%$ (kJ mol^{-1})	$T^{fus} \pm 0.2\%$ (K)	$\Delta H^{fus} \pm 2.5\%$ (kJ mol^{-1})	$-\Delta H^{liq} \pm 5\%$ (kJ mol^{-1})
(1) $PbBi_4Te_7$	223	550–555	1	851, 861	292	130
(2) $GeBi_4Te_7$	191	650	2.1	847	263	123
(3) $GeSb_4Te_7$	140	673	-	880	240	110
(4) $PbBi_2Te_4$	150	618	-	864	154	90
(5) $GeBi_2Te_4$	114	668	0.3	860	139	71
(6) $GeSb_2Te_4$	90	678	-	888	142	70
(7) $Pb_2Bi_2Te_5$	225	630	-	858	185	150
(8) $Ge_3Bi_2Te_6$	234	650–670	2.1	858, 919	(213)	(125)
(9) $Ge_2Sb_2Te_5$	(130)	673	-	860, 877, 914	(187)	(100)

RESULTS AND DISCUSSION

The results obtained are summarized in Tables 1 and 2.

As one can see from Table 1 the formation of ternary melts with the compounds' composition is accompanied by a significant enthalpy decrease, which suggests the possibility of two- and three-component associations existing in them. X-ray analysis of the telluride samples quenched 20–30 K above the T^{fus} values (Table 1) showed that the fusion of compounds 8 and 9 had an incongruent character (a complex endothermal peak on the DTA curves with a number of T^{fus} values corresponding to this process) and phases 1–7 did not decompose during fusion. On the basis of comparing experimental and additive fusion entropies and admitting that fusion of phases 1–7 is congruent, we made an assumption that the fusion of compounds 2, 3, 5 and 6 proceeds without changes in their conductivity type, but for tellurides 1, 4 and 7 it proceeds with their partial metallization.

As it follows from Table 2 within the range 350–650 K a slight increase or decrease in C_p takes place (for phases 1, 4 and 7 ΔC_p values are very close to zero), and for compounds 1, 2, 4, 5, 7 and 8 around T^{tr} (see Table 1) the heat capacity is of an anomalous character [6]. Around T^{tr} one can also observe a $\Delta l/l_0$ anomalous temperature dependency (including compounds 3, 6 and 9). These facts indicate that for the above substances thermostimulated first-order state transitions occur. The reproducibility of C_p and $\Delta l/l_0$

TABLE 2

Thermophysical characteristics for Ge(Pb)Te–$Bi_2(Sb_2)Te_3$ system ternary compounds

Ge(Pb)Te–$Bi_2(Sb_2)Te_3$	$\Delta l/l_0 \times 10^6 = -a + b \times 10^{-2}T$ (±5%)		ΔT (K)	$C_p = a + b \times 10^{-3}T + c \times 10^{-6}T^{-2}$ (J mol^{-1} K^{-1}) (±2.5%)			ΔT (K)
	a	*b*		*a*	*b*	*c*	
(1) $PbBi_4Te_7$	5.5	18.5	300–540	351.8	11	–	350–520
	11.4	38	550–800				
(2) $GeBi_4Te_7$	5.91	20.17	290–710	293	71.1	–	350–630
(3) $GeSb_4Te_7$	5.52	18.44	290–673	508.9	−282.5	7.47	350–630
	7.91	21.76	688–800				
(4) $PbBi_2Te_4$	5.1	16.4	290–610	–	–	–	
	–	0	630–730				
(5) $GeBi_2Te_4$	5.32	18.16	290–660	176	50.2	–	350–650
	6.43	22.44	680–780				
(6) $GeSb_2Te_4$	5.49	18.44	290–670	323.6	−195.2	5.95	350–630
	4.9	16.93	700–820				
(7) $Pb_2Bi_2Te_5$	6.5	17.3	290–620	–	–	–	–
	–	0	640–720				
(8) $Ge_3Bi_2Te_6$	4.83	16.47	290–670	270	20.9	–	350–580
	10.08	23.86	680–800				
(9) $Ge_2Sb_2Te_5$	5.79	19.4	290–670	401.66	−230.2	6.68	350–630

on the cooling and subsequent heating–cooling cycles of the samples and the results of X-ray analyses of samples quenched at temperatures 10–20 K above T^{tr} confirm the reversible character of these transitions.

Mutual recalculation (according to Hess's law) of the thermodynamic values determined for Ge(Pb)Te–$Bi_2(Sb_2)Te_3$ ternary phases agreed within the calculation error.

Using data on ΔH^{liq} from Table 1 we determined correction term values of the semiempirical models of Sharkey–Pool–Hoch and Redlich–Kister for the thermodynamic prediction of ternary solutions [11,12]. We then found the type of concentration dependence of the formation enthalpy of Ge–Bi–Te, Ge–Sb–Te and Pb–Bi–Te liquid alloys over the whole concentration triangle field, which agrees with the results of refs. 9 and 10 within calculation error. Similar evaluations may be carried out to determine ΔH_{298}^{0} values for the whole variety of Ge(Pb)–Bi(Sb)–Te ternary solid alloy compositions.

REFERENCES

1 N.H. Abrikosov and G.T. Danilova-Dorbriyakova, Sov. Inorg. Mater., 1 (1965) 204.

2 B.K. Vainshtein, R.M. Imatov and A.G. Talybov, Sov. Crystallogr., 14 (1968) 703.

3 N.H. Abrikosov and G.T. Danilova-Dorbriyakova, Sov. Inorg. Mater., 1 (1965) 57.

4 B.L. Valevsky, A.S. Skoropanov and A.A. Vecher, Sov. J. Phys. Chem., 57 (1983) 733.

5 I.A. Bulgak, A.S. Skoropanov, A.A. Vecher, G.A. Protsenko, Yu.N. Novikov and M.E. Vol'pin, Sov. Eng.-Phys. J., 46 (1984) 694.

6 B.L. Valevsky, A.A. Vecher, A.G. Gusakov, A.A. Koziro and A.S. Skoropanov, Sov. J. Phys. Chem., 57 (1983) 213.

7 A.S. Skoropanov, L.A. Mechkovsky, B.L. Valevsky and A.A. Vecher, Sov. J. Phys. Chem., 57 (1983) 1545.

8 A.A. Vecher, B.L. Valevsky, G.I. Samal and A.S. Skoropanov, Sov. Izv. Sib. Div. Acad. Sci., Chem., 14 (1982) 64.

9 P.P. Zhuk, L.A. Mechkovsky, A.S. Skoropanov and A.A. Vecher, Proc. 4th All-Union Conf. on Metal. Alloys Thermodynamics, Science Kaz. SSR, Alma-Ata, 1979, pp. 101–103.

10 S.A. Alfer, A.A. Vecher, O.A. Egorov and L.A. Mechkovsky, Sov. J. Phys. Chem., 55 (1981) 1613.

11 R.L. Sharkey, M.J. Pool and M. Hoch, Met. Trans., 2 (1971) 3039.

12 L.F. Kozin, Amalgam Pyrometallurgy, Science Kaz. SSR, Alma-Ata, 1973, p. 220.