ELSEVIER

Journal of Alloys and Compounds 228 (1995) 13–15

Journal of
ALLOYS
AND COMPOUNDS

Thermodynamic properties of the solid solutions ZnTe–CdTe, ZnTe–HgTe and CdTe–HgTe

V.R. Sidorko, L.V. Goncharuk*

Institute of Problems of Materials Science, Krzyzanovsky St. 3, 252180 Kiev, Ukraine

Received 9 January 1995; in final form 25 April 1995

Abstract

The Gibbs free energy, enthalpy and entropy of formation of the ZnTe–CdTe, ZnTe–HgTe and CdTe–HgTe solid solutions were determined by measuring the e.m.f. of high temperature galvanic cells. All solid solutions investigated exhibit positive deviations from Raoult's law. Thermodynamic stability of all solid solutions decreases with decreasing temperature and the energetics of formation depends on the interaction of components of the metallic sublattice.

Keywords: Thermodynamic stability; Solid solutions

1. Introduction

The pseudobinary systems ZnTe–CdTe, ZnTe–HgTe and CdTe–HgTe form a complete series of solid solutions and attract wide attention primarily because of their promising character for optoelectronic devices. A precise knowledge of the thermodynamic properties as well as the phase diagram of the alloy system is very important for the production processes. In spite of the importance of the thermodynamic values experimental thermodynamic studies of these ternary systems are scarce.

2. Experimental details

Thermodynamic properties of the pseudobinary solid solutions formed by the semiconducting zinc, cadmium and mercury tellurides were studied by means of e.m.f. measurements with the following galvanic cells:

$$[\mathrm{ZnTe}+\mathrm{Te}]|\mathrm{Zn}^{2+} \text{ in a eutectic melt}| \quad [\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Te}+\mathrm{Te}] \qquad (1)$$

in the temperature range 673–793 K,

$$[\mathrm{ZnTe}+\mathrm{Te}]|\mathrm{Zn}^{2+} \text{ in a eutectic melt}| \quad [\mathrm{Zn}_x\mathrm{Hg}_{1-x}\mathrm{Te}+\mathrm{Te}] \qquad (2)$$

in the temperature range 618–693 K and

$$[\mathrm{CdTe}+\mathrm{Te}]|\mathrm{Cd}^{2+} \text{ in a eutectic melt}| \quad [\mathrm{Cd}_x\mathrm{Hg}_{1-x}\mathrm{Te}+\mathrm{Te}] \qquad (3)$$

in the temperature range 600–683 K.

The samples were prepared from zinc, cadmium and mercury tellurides as starting materials in evacuated quartz ampoules. Total contents of impurities were less than 10^{-3} mass%. The polycrystalline tellurides were ground to fine powders, mixed and pressed into pellets. The heat treatment was performed in evacuated (10^{-5} mmHg) quartz ampoules at 1223 K for 100 h (ZnTe–CdTe) and 923 K for 760 h (ZnTe–HgTe and CdTe–HgTe). Then the pellets were ground again to fine powder and mixed with pure tellurium to such an extent that the composition of samples corresponded to the isoconcentrate 90 at.% Te. To be used as electrodes in the galvanic cells, the mixtures prepared were pressed into pellets and heat treated at 655 K for 380 h. A eutectic mixture KCl–LiCl–BaCl_2 ($T_{\mathrm{fus}} = 593$ K [1]) was used as an electrolyte. The reversibility of operation of the galvanic cell was controlled to the equilibrium [ZnTe + Te[or [CdTe + Te] relative to the zinc or cadmium electrodes (the latter being used for comparison). The method em-

---

* Corresponding author.

SSDI 0925-8388(95)01703-8

ployed and the treatment of experimental values have been described elsewhere [2].

3. Results and discussion

The results of the present research are given in Tables 1, 2 and 3. According to the data obtained all solid solutions investigated are characterized by positive deviations of the activities of the components from Raoult's law (Fig. 1). This is in agreement with the results described in the literature [5,7,8]. Only Zabdyr observed insignificant negative deviations of a_{ZnTe} from the ideal behaviour in the system ZnTe–CdTe (Fig. 1(a)). According to our results the thermodynamic stability of the solid solutions studied decreases with decreasing temperature. The excess Gibbs energy and enthalpy of formation of the solid solutions are positive in the entire concentration range (Fig. 2). This fact agrees well with a tendency of solid solutions to decompose at decreasing temperature. In Ref. [9] the existence of a miscibility gap in the system CdTe–HgTe in the solid state was established (critical point at $x_{CdTe} = 0.55$ and T = 455 K). A definite similarity of the thermodynamic behaviour of the ZnTe–CdTe and Zn–Cd solid solutions as well as the ZnTe–HgTe and Zn–Hg solutions could be observed, characterized by positive deviations of the activities from Raoult's law (Fig. 3) and positive values of enthalpy of mixing ($\Delta_f H^{extr} \leq 2.0$ kJ mol^{-1} for the Zn–Cd system and $\Delta_f H^{extr} \leq 0.4$ kJ mol^{-1} for the Zn–Hg system [11]). Although cadmium–mercury melts exhibit insignificant negative deviation from ideal behaviour (Fig. 2(b)) (that fact agrees with the presence of the intermediate phases formed at low temperatures by a peritectic reaction), CdTe–HgTe solid solutions are characterized by positive deviations from Raoult's law. It may be expected (at least, for the ZnTe–CdTe and ZnTe–HgTe systems) that the energetics of formation of the pseudobinary solid solutions of the zinc, cad-

Table 1
Thermodynamic properties of ZnTe–CdTe solid solutions at 723 K [3]

x_{ZnTe}	$-\Delta\bar{G}_{ZnTe}$ (kJ mol^{-1})	$-\Delta_f G$ (kJ mol^{-1})	ΔG^{ex} (kJ mol^{-1})	$\Delta_f H$ (kJ mol^{-1})	$\Delta_f S$ (J mol^{-1} K^{-1})	ΔS^{ex} (J mol^{-1} K^{-1})
0.1	9.475 ± 0.223	1.474	0.473	1.09	3.55	0.85
0.2	6.342 ± 0.003	2.153	0.847	1.64	5.25	1.11
0.3	4.495 ± 0.025	2.549	1.118	1.81	6.03	0.96
0.4	3.042 ± 0.063	2.713	1.328	1.85	6.31	0.72
0.5	2.058 ± 0.027	2.677	1.486	1.78	6.16	0.40
0.6	1.522 ± 0.023	2.491	1.553	1.56	5.60	0.01
0.7	1.158 ± 0.008	2.188	1.480	1.25	4.76	−0.31
0.8	0.803 ± 0.009	1.770	1.238	0.86	3.64	−0.52
0.9	0.400 ± 0.020	1.140	0.811	0.37	2.09	−0.61

Table 2
Thermodynamic properties of ZnTe–HgTe solid solutions at 653 K [4]

x_{ZnTe}	$-\Delta\bar{G}_{ZnTe}$ (kJ mol^{-1})	$-\Delta_f G$ (kJ mol^{-1})	ΔG^{ex} (kJ mol^{-1})	$\Delta_f H$ (kJ mol^{-1})	$\Delta_f S$ (J mol^{-1} K^{-1})	ΔS^{ex} (J mol^{-1} K^{-1})
0.2	4.024 ± 0.050	1.579	1.125	1.93	5.37	1.23
0.3	3.233 ± 0.034	1.817	1.501	2.62	6.80	1.72
0.4	2.679 ± 0.049	1.968	1.689	2.79	7.29	1.69
0.5	2.195 ± 0.058	1.975	1.896	2.53	6.90	0.97
0.6	1.824 ± 0.030	1.927	1.728	1.90	5.87	0.27
0.7	1.556 ± 0.089	1.887	1.435	1.34	4.94	−0.15
0.8	1.311 ± 0.015	1.722	1.144	0.81	3.88	−0.51
0.9	1.423 ± 0.039	0.914	0.826	0.27	1.81	−0.86

Table 3
Thermodynamic properties of CdTe–HgTe solid solutions at 643 K

x_{CdTe}	$-\Delta\bar{G}_{ZnTe}$ (kJ mol^{-1})	$-\Delta_f G$ (kJ mol^{-1})	ΔG^{ex} (kJ mol^{-1})	$\Delta_f H$ (kJ mol^{-1})	$\Delta_f S$ (J mol^{-1} K^{-1})	ΔS^{ex} (J mol^{-1} K^{-1})
0.1	6.728 ± 0.178	1.118	0.619	1.83	4.58	1.88
0.3	4.367 ± 0.151	1.934	1.331	3.90	9.09	4.01
0.4	3.130 ± 0.072	2.183	1.415	3.91	9.48	3.89
0.5	2.592 ± 0.028	2.286	1.420	3.40	8.84	3.07
0.6	1.754 ± 0.020	2.254	1.345	2.61	7.56	1.96
0.7	1.316 ± 0.042	2.062	1.204	1.90	6.16	1.08
0.8	0.973 ± 0.036	1.737	0.937	1.39	4.86	0.71
0.9	0.272 ± 0.019	1.142	0.596	0.72	2.90	0.20

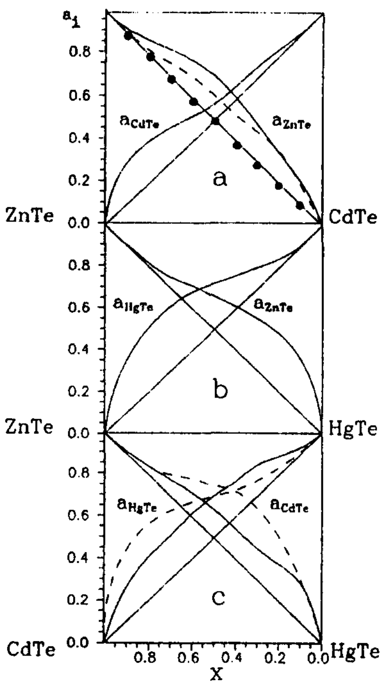

Fig. 1. Activities of components of the solid solutions. (a) ZnTe–CdTe: ——, 723 K [3]; ---, 900 K [5]; ●, 750 K [6]. (b) ZnTe–HgTe, 653 K [4]. (c) CdTe–HgTe: ——, 643 K (our data); ---, 735 K [7].

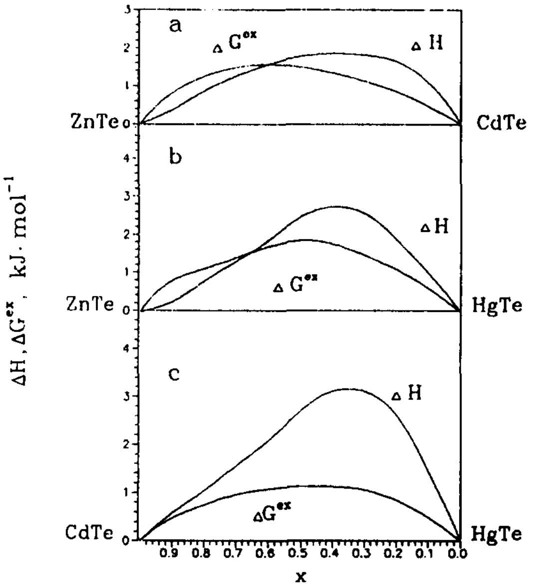

Fig. 2. The excess Gibbs energies and enthalpies of formation of the solid solutions: (a) ZnTe–CdTe (723 K); (b) ZnTe–HgTe (653 K); (c) CdTe–HgTe (643 K).

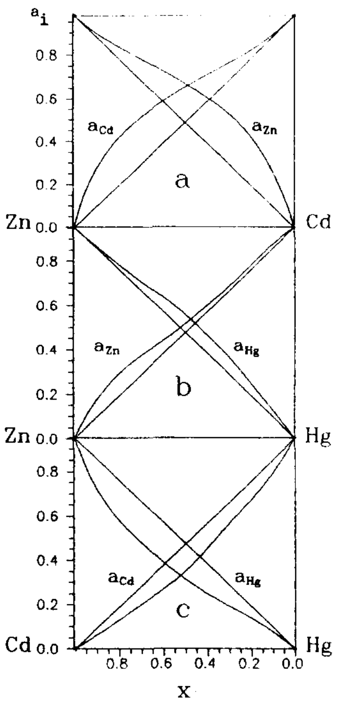

Fig. 3. Activities of components of the systems: (a) Zn–Cd (800 K) [10]; (b) Zn–Hg (598 K) [11]; (c) Cd–Hg (633 K) [11].

mium and mercury tellurides depends, to some extent, on the interaction of the components of the metallic sublattice.

References

[1] B.G. Korshunov, V.V. Safonov and D.V. Drobot, *Diagrammi Plavkosti Chloridnich Sistem*, Khimiya, Leningrad, 1972 (in Russian).

[2] G.M. Lukashenko and V.R. Sidorko, *Stabilnost' Phaz i Phazovie Ravnovesiya v Splavakh Perekhodnikh Metallov*, Naukova Dumka, Kiev, 1991, pp. 97–138 (in Russian).

[3] L.V. Goncharuk, G.M. Lukashenko, L.D. Budennaya and I.V. Dubrovin, *Zh. Fiz. Khim.*, *64* (7) (1990) 1954.

[4] G.M. Lukashenko, L.V. Goncharuk, I.V. Dubrovin and L.D. Budennaya, *Zh. Fiz. Khim.*, *65* (11) (1991) 3141.

[5] I. Katayama, T. Inomoto, Z. Kozuka and T. Iida, *Mater. Trans. Jpn. Inst. Met.*, *32* (2) (1991) 169–173.

[6] L.A. Zabdyr, *J. Electrochem. Soc.*, *131* (9) (1984) 2157.

[7] A. Nasar and M. Shamsuddin, *J. Less-Common Met.*, *171* (1991) 83.

[8] V.P. Vasiliev, M.N. Mamontov and M.A. Bykov, *Vestn. Mosk. Univ., Ser.* 2, *31* (3) (1990) 211 (*in Russian*).

[9] M. Gambino, V. Vassiliev and I.P. Broc, *J. Alloys Comp.*, *176* (1991) 13.

[10] R. Hultgren, P. Desai, D. Hawkins et al., *Selected Values of Thermodynamic Properties of Binary Alloys*, American Society for Metals, 1973.

[11] L.F. Kozin, R.Sh. Nigmetova and M.B. Dergachova, *Termodinamika Binarnikh Amalgamnikh Sistem*, Nauka, Alma-Ata, 1977 (in Russian).