Thermochimica Acta, 78 (1984) 129–134
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HEATS AND ENTROPIES OF FUSION OF ABC_2 CHALCOPYRITE SEMICONDUCTORS

G. KÜHN, W. MÖLLER and W. ENGEL

Sektion Chemie der Karl-Marx-Universität, WB Kristallographie, Leipzig (DDR)

(Received 1 February 1984)

ABSTRACT

Using quantitative DTA the melting temperatures and the enthalpies of fusion of some $A(I)B(III)C(VI)_2$ and $A(II)B(IV)C(V)_2$ compounds are measured. The entropies of fusion are calculated and discussed in terms of the dielectric theory, and with regard to the structure of the liquid phase.

INTRODUCTION

Ternary compounds crystallizing in a diamond-like chalcopyrite structure have long been of interest for their semiconductive characteristics and their electro-optical properties [1]. In order to grow single crystals of these materials the knowledge of the respective thermodynamic data is desirable. The entropies of fusion are of particular importance for the quantitative description of solid–liquid equilibria. They also provide useful information about changes in the structural and binding states during the melting process. In this communication the results of quantitative DTA measurements of the ABC_2 semiconductors are reported and discussed (cf. ref. 2).

EXPERIMENTAL

The $A(I)B(III)C(VI)_2$ compounds used in the experiments were prepared by the following general method. A stoichiometric mixture of the pure elements (99.999% or better) was sealed in a quartz glass ampoule evacuated to a pressure of less than 10^{-2} Pa. To minimize the risk of explosion and to guarantee complete reaction to the ternary compound a stepwise heating procedure was employed [3,4]. The ingots prepared by this technique were polycrystalline. X-ray diffraction analysis was used to confirm the structure and the lattice constants of these compounds. The latter were found to be in good agreement with published data [1]. No other phase occurred besides chalcopyrite.

0040-6031/84/$03.00

To determine the enthalpies of fusion DTA measurements were made using a Setaram microthermoanalyser. For this, evacuated quartz glass ampoules were used (height, 10 mm; OD, 4 mm). These were placed in 100-μl Al_2O_3 crucibles. To obtain maximum thermal contact these ampoules were ground on their longitudinal sides and on their bases. The same base and wall thicknesses were used throughout (microscopic control). Platinum was used as reference material. A linearity was found between the weighed portion and the peak area up to 25 mg. The influence of the heating rate on the area of the peak was negligible. The measurements were made under the following standard working conditions:

Thermocouples	Pt–6% Rh/Pt–30% Rh
Heating rate	3, 6 and 9 K $\min^{-1}$
DTA amplification	$\pm 25\ \mu$V
Paper feed rate	90 cm h^{-1}

The enthalpy of fusion, ΔH^F, was found from the equation

$$\Delta H^F = K \int_0^t \Delta T \, dt$$

where the integral is the area of the peak from time zero to t and K is the coefficient of the heat transfer of the system. To determine K substances of 99.999% purity were used (Fig. 1). The following expression was obtained

$$K(T) = 2.27 \times 10^{-4}\, T + 4.06 \times 10^{-2} \text{ J cm}^{-2}$$

The error in the enthalpy measurements was $\pm 12\%$. For the calibration of the temperature (T_{onset}) the same substances presented in Fig. 1 were used. The accuracy was $\pm 3\%$. This gives a maximum total error for the melting entropies of about $\pm 15\%$.

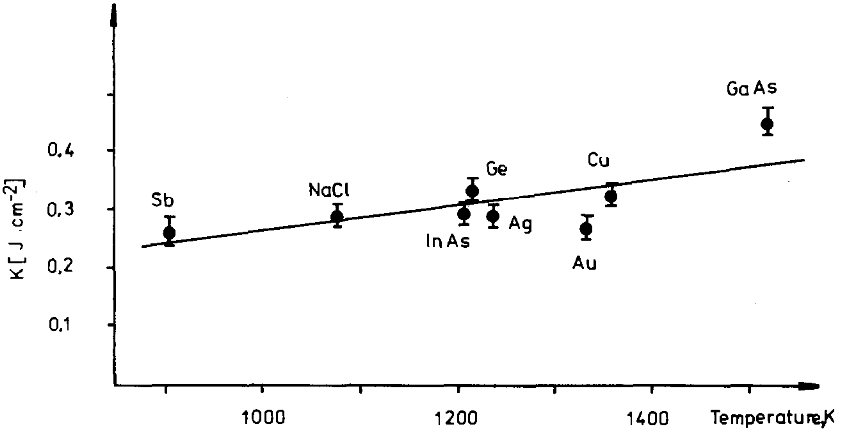

Fig. 1. The heat transfer coefficient, K vs. temperature.

RESULTS AND DISCUSSION

The experimentally determined melting temperatures and heats of fusion are shown in Table 1.

More information about the melting process can be obtained from the analysis of the entropies of fusion. We can divide the entropy of fusion of an arbitrary semiconductor into four parts [18]

$$\Delta S^{\mathrm{F}} = \Delta S^{\mathrm{F}}_{\mathrm{m}} + S_{\mathrm{b}} + S_{\mathrm{l}} + \left.\frac{\partial E}{\partial T}\right|_{\mathrm{v}} \tag{1}$$

where $\Delta S^{\mathrm{F}}_{\mathrm{m}}$, S_{b} and S_{l} represent the entropy of fusion of the solid metallic phase of the same material, the entropy of the dehybridization of the covalent bond which results when the semiconductor transforms to a metallic melt, and the entropy of mixing in the liquid phase, respectively. The fourth term denotes the contribution of the specific heat. S_{l} is assumed to be the entropy of mixing of an ideal solution: for an elemental semiconductor, $S_{\mathrm{l}} = 0$; for a binary compound AB, $S_{\mathrm{l}} = 5.8$; and for a ternary compound ABC_2, $S_{\mathrm{l}} = 8.65$ J K^{-1} g-atom^{-1}. The two terms $\Delta S^{\mathrm{F}}_{\mathrm{m}}$ and S_{b} represent a contribution to the entropy of fusion of an arbitrary tetrahedral semiconductor independent of its chemical composition. After Van Vechten [18] results for $S_{\mathrm{b}} = 23.1$ J K^{-1} g-atom^{-1} and $\Delta S^{\mathrm{F}}_{\mathrm{m}} = 9.7$ J K^{-1} g-atom^{-1}. Neglecting the last term in eqn. (1) we obtain the maximum entropy of fusion of a semiconductor

$$\Delta S^{\mathrm{F}}_{\mathrm{max}}(\mathrm{A(IV)}) = 32.8 \text{ J K}^{-1} \text{ g-atom}^{-1}$$

$$\Delta S^{\mathrm{F}}_{\mathrm{max}}(\mathrm{A(I)B(VII), A(II)B(VI), A(III)B(V)}) = 38.6 \text{ J K}^{-1} \text{ g-atom}^{-1}$$

$$\Delta S^{\mathrm{F}}_{\mathrm{max}}(\mathrm{A(I)B(III)C(VI)_2, A(II)B(IV)C(V)_2}) = 41.4 \text{ J K}^{-1} \text{ g-atom}^{-1}$$

TABLE 1

Melting temperatures and heats of fusion compared to literature values

Substance	T^{F} (K)		ΔH^{F} (kJ mol^{-1})	
	This work	Lit.	This work	Lit.
$CuGaS_2$	1513	1513[5], 1514[6]	50.6 ± 10.1	
$CuGaTe_2$	1140	1143[7], 1143[8]	72.9 ± 10.9	
$CuInS_2$	1362	1363[9], 1368[10]	44.8 ± 6.7	40.0 ± 8.0[17]
$CuInSe_2$	1262	1258[10], 1259[11]	49.3 ± 9.9	
$CuInTe_2$	1062	1053[8], 1062[12]	65.0 ± 9.7	
$CuFeS_2$	1206	1155[13], 1150[14]	20.7 ± 3.1	47.3 ± 2.1[13]
$AgGaSe_2$	1113	1120[14], 1123[8]	17.4 ± 2.6	
$ZnSiAs_2$	1356	1357[14]	113.3 ± 15.3	
$ZnSnAs_2$	1050	1048[15]	111.7 ± 19.0	
$CdSiP_2$	1422	1470[14]	92.7 ± 13.9	
$CdGeP_2$	1065	1073[16]	46.7 ± 7.0	

TABLE 2

Melting entropies of ternary semiconductors

Substance	ΔS^F (J K^{-1} g-atom^{-1})	Substance	ΔS^F (J K^{-1} g-atom^{-1})
$CuGaS_2$	8.4 ± 1.7	$AgGaSe_2$	3.9 ± 0.6
$CuGaTe_2$	15.9 ± 2.4	$ZnSiAs_2$	20.9 ± 2.8
$CuInS_2$	8.2 ± 1.2	$ZnSnAs_2$	26.6 ± 4.5
$CuInSe_2$	9.8 ± 1.9	$CdSiP_2$	16.3 ± 2.4
$CuInTe_2$	15.5 ± 2.3	$CdGeP_2$	11.0 ± 1.6
$CuFeSe_2$	4.3 ± 0.7		

Table 2 gives the experimental data. The highest values were observed for the elemental semiconductors (cf. Fig. 2). For the ternary compounds less than 50% of the ΔS^F_{max} values were observed. This behaviour may be regarded as having two causes. The crystal may already be disordered heavily below the melting temperature. This was reflected in the high specific heat capacities [19], the occurrence of phase transitions, and in a low energy of formation for point defects in these compounds [20]. On the other hand it is quite possible for structural elements to exist in the liquid phase slightly above the melting temperature having the same binding state to those observed in the solid phase. Also it can be concluded that the step of dissociation of the covalent bonds in the melt is low. This is in accord with the measurements of the specific conductivity. At 1373 K, the values are about 10^{-1} Ω^{-1} cm^{-1} for $CuInSe_2$ and 6×10^{-2} Ω^{-1} cm^{-1} for $CuInS_2$ [21]. The behaviour of the

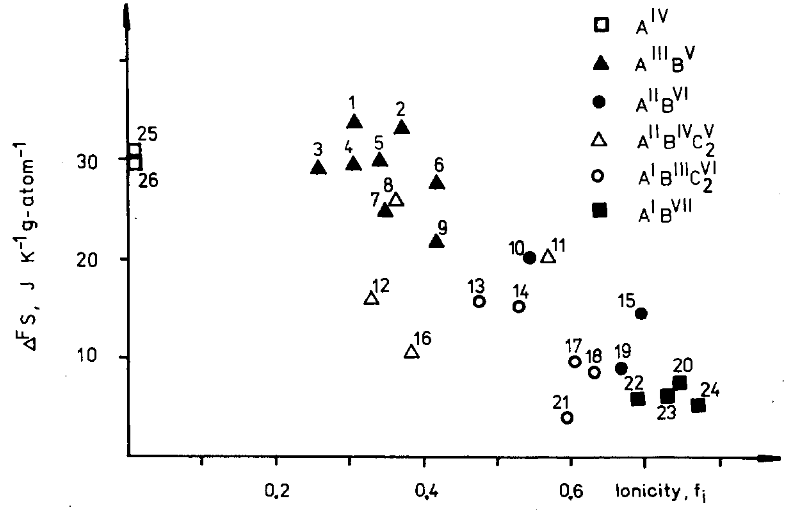

Fig. 2. Relation between the entropy of fusion and the ionicity of the chemical bonding (data used are from Tables 1 and 2 and refs. 23, 26 and 27). (1) GaAs, (2) GaP, (3) GaSb, (4) AlP, (5) InSb, (6) AlSb, (7) InAs, (8) $ZnSnAs_2$, (9) InP, (10) ZnTe, (11) $ZnSiAs_2$, (12) $CdSiP_2$, (13) $CuGaTe_2$, (14) $CuInTe_2$, (15) CdSe, (16) $CdGeP_2$, (17) $CuInSe_2$, (18) $CuInS_2$, (19) CdTe, (20) CuCl, (21) $AgGaSe_2$, (22) CuI, (23) CuBr, (24) AgI, (25) Ge, (26) Si.

viscosity and the density slightly above the melting point also suggest structure changes in the melt [22]. A similar result was found for the A(I)B(VII) compounds and the silver and copper chalcogenides. In contrast, the melts of silicon and germanium are of pure metallic character. The specific conductivity for molten germanium was found to be $1.6 \times 10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ [23]. It is also of interest to note that ΔS^F of the tetrahedral-coordinated semiconductors is a function of the ionicity f_i of the chemical bonding in the solid state [24,25] (Fig. 2). With increasing f_i a decrease of the entropy of fusion was observed.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Buhrig from the Bergakademie Freiberg/Sa. for providing the $A(II)B(IV)C(V)_2$ compounds.

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