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DETERMINATION OF MELTING POINTS FOR A^2B^6 COMPOUNDS

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Abstract

A new technique of rapid heating, recording both the melting and evaporation processes in an open system was proposed to determine the melting points of A^2B^6 (A=Zn, Cd) compounds. The different melting character and temperatures were detected for the equiatomic and non-stoichiometric composition of A^2B^6. A fit of these data to previously obtained results was considered and the reasons for their discrepancy were discussed.

Keywords: A^2B^6 melting points, rapid heating, thermal analysis

Introduction

The melting points (*m.p.*) of A^2B^6 (A=Zn, Cd) compounds known from the literature [1–19] were determined by thermal analysis in open systems mainly due to their high *m.p.* (>1300°C) and vapour pressures (>5 atm). In these procedures some inert fluxes and/or high-pressure inert gases were used to minimize the sublimation of A^2B^6. Besides, in [1, 2, 11] rapid heating (30 s instead of 2 h) assisted in attaining this end. In Table 1 all known *m.p.* values of A^2B^6 compounds are summarized. Significant differences can be observed in the melting points measured at slow and rapid heating for ZnS and CdS. For other compounds a marked scatter appears in the data obtained by similar techniques. A close examination of the experimental procedures brought out that a few values of *m.p.* starred in Table 1 were somewhat uncertain. This was connected with improperly designed sample holders, interactions between A^2B^6 and container material and incorrect measurement of the melting point itself. Unfortunately, in none of these works was the effect of the evaporation of A^2B^6 on their composition considered. It is possible that the authors relied on the certain assumption of congruent sublimation of A^2B^6 over the temperature range. However, for CdTe and ZnTe a

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pseudo-congruent sublimation was detected above 700°C which led to an increase in the Te contents of only 10^{-3}–10^{-2} at.%. It was enough to change the corresponding melting point to an extent exceeding the experimental errors [20–22]. The observed high sensitivity of the melting point to minor variations in composition may be responsible for the large errors as well as the marked scatter in *m.p.* values for the remaining A^2B^6. It follows that precise composition characteristics are necessary especially for the open systems. But such minor variations in the composition can be determined by very specific analytical techniques or static vapour pressure measurements [21]. In earlier works the required characteristics of the compositions were missing. Therefore it was difficult to understand how the composition is related to the measured temperature and to estimate the actual effect of variations in composition on the solidus (T_S) and liquidus (T_L) temperatures of A^2B^6.

Table 1 Melting points of A^2B^6 according to [1–19]

Compounds	Temperature and error ( )°C		
	closed system	open system	
		rapid heating	slow heating
ZnS		1800–1900, 1830(20)	1718(10), 1650(20)
ZnSe	1520(20)		1526(10), 1515(20)
ZnTe	1300(10), 1295(20), 1357		1305(10), 1239
CdS		1750, 1485(20)	1405(10), 1500
CdSe	1258(3), 1268(2)		1264(10), 1239
CdTe	1098(3), 1090(2), 1092(2) 1092(3), 1092(1), 1106, 1100		1100(10)

To obtain reliable values for the composition/*m.p.* relationship we attempted a new experiment. It included the precise characterization of the initial sample and the thermal procedure to preserve the initial composition up to the melting or its change due to pseudo-congruent sublimation. A new high-temperature thermomicroscopic apparatus operating in a wide range of heating rates was used for this purpose. The design and operation of the apparatus have been described in detail [23]. Its principle is based on the measurement by a suitable IR photodiode of variations in the radiation coefficient of heating in the solids in an open holder. These variations are connected with solid–liquid, solid–vapour or liquid–vapour transitions. In addition to the melting peak, in the heating curves evaporation manifested itself as a peak when the vapour pressure of the substance attained the pressure in the apparatus or as a slight deviation from the zero position of the baseline when evaporation was weak. Therefore, by the very form of the heating curves one can estimate the gaseous phase production is appreciablly or not. The permitted intervals of gas pressure 1–3 atm and heating rates 2, 5, 17, 50°C s^{-1} were crucial factors in determining the kinetics and/or mechanism of the sublimation process and the mass losses during heating.

Experimental

The equiatomic compositions of A^2B^6 were the object of our study. Their strict stoichiometry could be achieved by the very conditions of preparation. Large crystals were obtained in the sublimation process at low temperature when incongruent sublimation was absent. Their colour, the transparency without any colloidal inclusions visible with an optical microscope as well as the measured densities and lattice parameters (Table 2) served as an experimental evidence of the desired stoichiometry. Additionally a specific chemical method named in [25] differential dissolving was used only for the CdS and ZnS crystals. It showed that the molar Zn(Cd)/S relation was kept constant within the accuracy of analysis, about 0.01 at.%, in all 300 portions of the solution formed during dissolving the crystals in HCl with increasing concentration. It was a good indicator of real stoichiometry without any excess components in the tested crystals.

Table 2 Characteristics of equiatomic A^2B^6 crystals

A^2B^6	Lattice parameters/Å		d_{calc}	d_{exp}±0.01g/sm³
	our±0.01	known		
ZnS (S)	a=5.40	5.406	4.14	4.13
ZnSe (S)	a=5.67	5.669		
ZnTe (S)	a=6.10	6.103		
CdS (W)	a=4.13	4.136	4.84	4.84
	b=6.71	6.713		
CdSe (W)	a=4.30	4.30	5.81	5.80
	b=7.02	7.01		
CdTe (S)	a=6.47	6.478	5.86	5.89

W – wurtzite; S – sphalerite forms

Contrary to the crystals, a commercial ZnS powder was identified as the non-stoichiometric, Zn-rich compound due to its blue fluorescence as shown in [18]. We could not go beyond the qualitative characterization of the ZnS powder as neither the lattice parameters not densities are sensitive to the non-stoichiometry in the case of powders. The thermal behaviour of the non-stoichiometric powder was quite different from that of ZnS crystals: it began to sublimate at reduced temperatures more readily (Fig. 1).

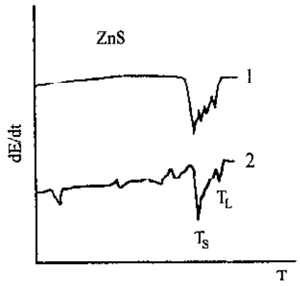

Fig. 1 Heating curves of equiatomic ZnS crystals (1) and Zn-rich powder (2) obtained under similar conditions: mass – 3 mg, rate – 17°C s^{-1}, gas pressure – 1 atm

A set of samples of each compound was melted at different heating rates: $\varphi=2$, 5, 17 and 50°C s^{-1}. At least 8–10 runs were made at each rate where the gas pressure was varied from $P=3$ to 1 atm in steps of about 0.3 atm. The procedure was necessary to find the conditions where the melting composition was exactly like the initial one and where it was not. Such information was extracted from the $m.p.=f(\varphi, P)$ dependences obtained. If neither the character nor the melting point varied over the studied range of φ and P values, this was taken as evidence of the composition constancy. If they both varied, it meant that the initial composition was shifted to x_1, x_2, x_3... values, i.e. the compound was enriched in one of the components. We could arrange these values in the corresponding $x_3>x_2>x_1>x$ series, but we had no analytical technique to determine these compositions in the small weights remainding after the runs.

It is known from [23] that large samples do not give true *m.p.* owing to the large temperature gradient within the sample. To avoid this, the maximum sample mass (thicknesses) were calculated from the expression in [23]. However, the experimental mass were 20 or 30% above the calculated ones (about 4 mg) to preserve a portion of the substances taken up to the melting point.

The temperature of the melting peak was taken as the melting point. To eliminate the possible overlapping of the melting peak with the boiling peak, i.e. intensive sublimation of the solid, the pressure in the apparatus was chosen so as to shift the boiling peak to a temperature below or above the melting temperature. For each gas pressure the temperature of the boiling peak was calculated from the known temperature dependences of the vapour pressures of A^2B^6 compounds [26] and compared with the expected *m.p.* If it was impossible to differentiate these peaks based on their positions, forms, and intensities, quenching procedures were performed at each characteristic point of the close peaks. Then the properties of the samples were examined, namely the state, shape, colour and transparency. Neither the negative-positive positions of the peaks on the temperature scale nor their areas were used to clarify the origin of transitions starting from considerations in [23].

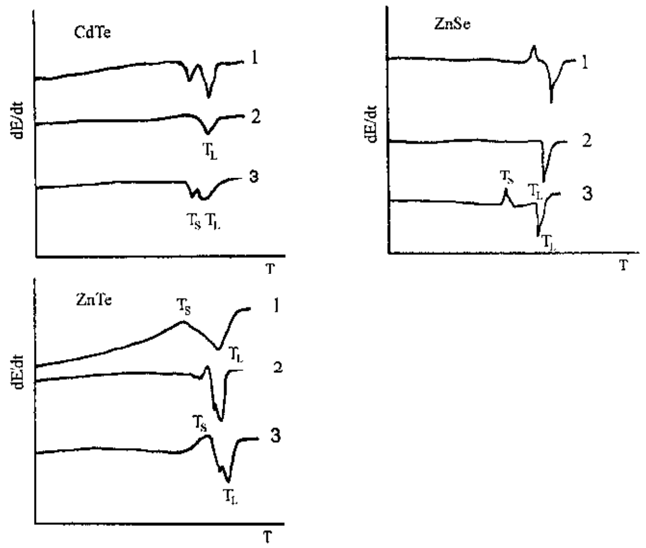

Fig. 2 Heating curves of equiatomic CdTe (a), ZnSe (b), ZnTe (c) crystals with characteristic melting points. Conditions: mass (mg), rate (°C s^{-1}), gas pressure (atm) a) 1 – 3.2, 17, 3; 2 – 3.3, 17, 2.5; 3 – 3.5, 5, 2.0; b) 1 – 2.9, 17, 3; 2 – 3.0, 17, 1.8; 3 – 3.2, 17, 1.0; c) 1 – 2.8, 50, 3; 2 – 3.0, 17, 2.0; 3 – 3.3, 17, 1.5

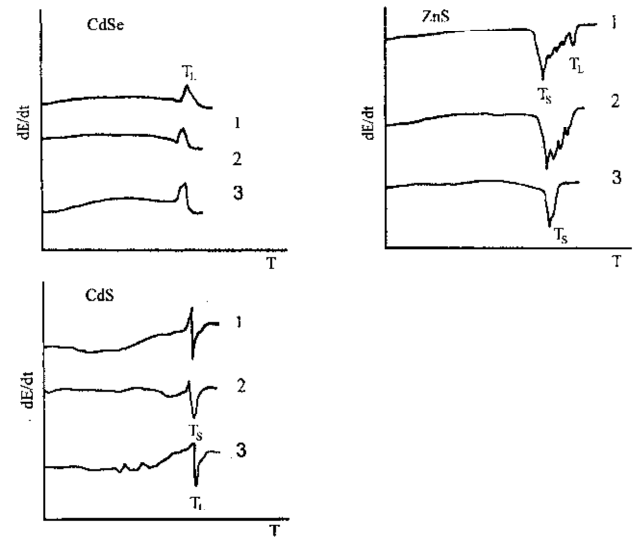

Fig. 3 Heating curves of equiatomic CdSe (a), ZnS (b), CdS (c) crystals with characteristic melting points. Conditions: mass (mg), rate (°C s^{-1}), gas pressure (atm) a) 1 – 2.5, 17, 3; 2 – 2.9, 17, 2.0; 3 – 3.1, 17, 1.5; b) 1 – 2.8, 17, 3; 2 – 3.2, 17, 2.0; 3 – 3.5, 17, 1.5; c) 1 – 3.2, 50, 3; 2 – 3.0, 17, 3.0; 3 – 4.0, 17, 1.0

Table 3 Melting points of A^2B^6 under different conditions

Sample		Temperature/°C			
		Composition/at.%			Result of quenching temperature and state
		50	x_1	x_2	
CdTe, cryst.	T_L	1116(10)	1114(10)	1150(10)	1108–l, 1115–l
	T_S	1075(6)	1114	1070(10)	
ZnTe, powd.	T_L	1313(3)	1320(5)	1355(5)	
	T_S	1239(5)	1285(5)	1335(5)	
CdSe, powd.	T_L	1271(15)	1250(11)	1252(10)	
	T_S	1271	1250	1252	
CdSe, cryst.	T_L	1268(8)	1258(10)	1260(5)	
	T_S	1268	1258	1260	
ZnSe, cryst.	T_L	1536(4)	1535(5)	1530(6)	
	T_S	1492(6)	1535	1490(5)	
CdS, cryst.	T_L	1590(5)	1591(10)	1590(10)	1429–s, 1496–s
	T_S	1573(5)	1575(10)	1590(10)	1566–s, 1590–l
ZnS, cryst.	T_L	1694(10)	1698(12)	1698(8)	1419–s, 1632–s+l
	T_S	1596(9)	1596(5)	1600(5)	1653–s+l, 1695–l
ZnS, powd.	T_L	1700(10)	–	1730(10)	1715–s+l, 1730–l
	T_S	1600(4)	–	1625(10)	

s – solid and; l – liquid state

The melting points of wurzite/sphalerite (W/S) structural modifications were determined to be equal in magnitude, since according to [18, 19] the W–S transition runs more rapidly than the heating in our experiments. Thus, from the point of view of the melting point, it was not essential to specify the structure of A^2B^6 compounds.

The apparatus was calibrated for each selected pair of P/φ by means of reference materials such as Au, Cu, Si, Pt, Rh, and Al_2O_3 in the range from 1000 to 2000°C. This procedure has been described in [23]. Using the calibration *m.p.* values were determined from n=5–7 parallel measurements with an accuracy of 1% or better.

Results and discussion

Figures 2 and 3 show typical heating curves obtained under different conditions for the tested compounds. They differ considerably. For CdTe, CdSe, ZnTe and ZnSe only the melting peaks appear. As expected, the boiling peaks appear only after melting, while at slow heating a weak sublimation was noticeable. For CdS the boiling peaks came before the melting and the evaporation led to some mass loss and hence to a drop of the intensity of the melting peak. For ZnS the worst variant occurred: both peaks of similar intensities overlapped. In this case we placed primary emphasis upon the quenching procedures to determine the *m.p.*

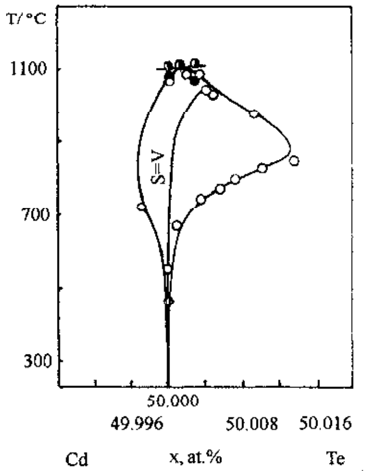

Fig. 4 The T–x projection of CdTe. Symbols are: solidus points (open circle) from [30]; solidus (solid circle) and liquidus (half-solid circle) points in this study

For CdTe, ZnTe and ZnSe both the melting character and *m.p.* did not vary in the range from 3 to 2 atm at 50 and 17°C s^{-1} rates (Fig. 2). Below these values, the evaporation became more intense resulting in a change in the measured parameters. It meant that a pseudo-congruent sublimation appeared which altered the initial equiatomic solid. As it is known from earlier experiments [20, 22, 24] the shift goes in the direction of the chalchogens. By these runs we obtained the melting characteristics of three compositions of CdTe, ZnTe and ZnSe: stoichiometric equiatomic, and two non-stoichiometric with minimum (x_1) and maximum (x_2) deviations from the equiatomic composition according to our heating conditions (Table 3). The x_1 composition melts congruently in the case of CdTe, ZnSe. For ZnTe this occurs with the composition beyond x_2. The values 1112±10, 1355±7, 1535±5°C are the maximum *m.p.* for CdTe, ZnTe and ZnSe, respectively. Only the stoichiometric CdTe, ZnTe and ZnSe melted incongruently. Due to this fact they are thermodynamically stable below 1075, 1235 and 1492°C, respectively, with an error of about 10°C.

We would like to estimate the x_2 and x_1 values not determined in our experiment, plotting our T_L and T_S, on the corresponding T–x projections obtained by other techniques. However, this type of information was found to be reliable only for CdTe [21]. The points of our runs were plotted on the temperature axis of the T–x projection studied by the static membrane method (Fig. 4). A good correlation between these experiments permitted to determine the compositions corresponding to each pair of the T_L–T_S points.

x_1 and x_2 values different from the equiatomic composition by 10^{-3} at.% and $4\cdot10^{-1}$ at.% of Te, respectively. Hence, the tensimetric technique was by far the best to control the minor composition shifts and our technique was sensitive to temperature changes (especially T_S) associated with these shifts. There were no precise experimental T–x projections for ZnTe and ZnSe. But it is hoped that x_1 and x_2 values for these compounds must be of the same order of magnitude as those for CdTe.

We emphasize that for CdTe and ZnSe composition changes to yield x_1 and x_2 values have little effect on the magnitude of T_L resulting to only a slight scatter in their *m.p.* obtained by any method (Table 1). In contrast, for ZnTe T_L=1305±5°C, the value obtained for the stoichiometric composition differed considerably from T_L=1357±8°C obtained for x_2 next to congruent melting. A similar value of the maximum *m.p.* of ZnTe was obtained in the only work [9] under free evaporation conditions. As far as other authors (Table 1) are concerned they determined the *m.p.* only for the stoichiometric composition (about 1300°C). It is reasonable to think that both of the *m.p.* values known for ZnTe are correct but they correspond to different compositions.

Figure 3 shows that CdS, CdSe and ZnS sublimate congruently over a wide temperatures range: the character and *m.p.* were unaffected even if the mass loss was 70–80%. Besides, the equiatomic solids, CdS and CdSe, melted congruently. ZnS of stoichiometric composition was thermodynamically stable below T_S=1596±5°C and its T_L was equal to 1700±5°C. Due to the congruent character of both the melting and sublimation, *m.p.* of ZnSe as 1530±5°C was affected by the technique employed (Table 1). The same cannot be said of CdS. The T_L=1590°C measured by our technique differed from some low (1405, 1485, 1500°C) and high (1750°C) values of Table 1. Reasons for the discrepancy are not clear (maybe a different initial composition or contact with the graphite container). However, in our opinion the low values must be distinguished from the true ones. Indeed, the equiatomic crystals of CdS heated up to 1405, 1430 and 1496 °C always remained solid and unaltered in colour and transparency though diminished in size. As to the high *m.p.* value it was obviously a measurement error since the temperature of the holder rather than the sample itself was measured.

The *m.p.* (better T_L) of the equiatomic ZnS can be taken as 1705±5°C close to values obtained by other authors (Table 1). But, this value was well below 1830±20°C found in [2] and frequently cited. We have a good reason to assign this temperature to the melting of a Zn-rich composition. It was apparent from our own runs with the non-stoichiometric ZnS powder found to be enriched in Zn. Its *m.p.*=1730°C measured at a heating rate of 30°C s^{-1} was higher as compared to the equiatomic ZnS. But this temperature tended to 1700°C with decreasing heating rate when the initial composition lost the excess Zn and shifted to the equiatomic one. It was known that ZnS powder used in [2] was fluorescent (other characteristics were not reported). It means that it was the Zn-rich composition and, hence, melted at a higher temperature when heated at a very high rate. So, two melting points – 1705 and 1830°C – are justified as the values correspond to different compositions. The high difference in the temperatures *vs.* a small variation of composition means an abrupt liquidus curve for ZnS.

Conclusions

Using a new technique, a special experimental procedure was developed to determine the melting points of the equiatomic and non-stoichiometric compositions of A^2B^6 compounds. The maximum melting point corresponds to the equiatomic CdSe and CdS and shifts from the composition in the direction of the metal for ZnS or the non-metal component in the case of ZnTe, CdTe and ZnSe. A flattened liquidus curve for all A^2B^6 compounds except ZnS and ZnTe, was determined in the near-to-equiatomic composition range. Due to the abrupt liquidus curve, it was shown for ZnS and ZnTe that the evaporation effect should be properly taken into account for the reliable determination of their melting points.

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