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Equilibrium Diagram Calculation of Zn-Te, Cd-Te and Zn-Cd-Te Semiconductors

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Abstract: In this research, the thermodynamic and phase diagrams of binary semiconductors compounds ZnTe and CdTe and also the ternary compound Zn-Cd-Te were established. For this purpose, the regular associated solution theory was used in all cases except the one of the solid phase of the ternary compound, where we have used the pseudo-regular associated solution model. The equilibrium diagrams are calculated by the numerical resolution of the free enthalpy equations for different phases.

Key words: Zn-Te, Cd-Te, Zn- Cd-Te regular associated solution, pseudo-regular associated solution

INTRODUCTION

The equilibrium diagrams calculation requires, generally, the use of theoretical thermodynamic models for the liquid and solid phases. These allow us to express the free enthalpy equations in the best way.

Since, the phase diagrams of this kind of materials present at nearly x = 0.5 the compound for all temperatures, the liquid phase can be described by the sub-regular associated model. To express the free enthalpy ΔG the redlich-kistler polynomial has been used.

The used variables are the concentrations y_i and the interaction parameters between different species α_H, α, β_H, β. The associated parameters ΔH, ΔS are calculated at the congruent melting point of each associated species. The ternary solid phase is described using the Pseudo-Regular Associated Solution model (PRAS). The value of various parameters between the species is calculated, on one hand, by the numerical resolution of the free enthalpy equations, corresponding to the equality between the activities of the compounds in the gas phase and the activities of the same compounds in the liquid phase and in the other hand, the equality between the chemical potentials of the compounds in the liquid phase and those in the solid phase.

Thermodynamic analysis

Solid phase description: The solid phase consist in the pseudo binary compound $(AC)_x(BC)_{1-x}$. The free enthalpy of the mixture is given by the sum of the ideal free enthalpy $\Delta^{id}{}_sG^S{}_S$ and the free enthalpy of the excess, $\Delta^{ex}{}_sG^S{}_S$ expressed in the pseudo-regular associated solution model as follows:

$$\Delta^m G_s^S = RT[x\log x + (1-x)\log(1-x)] + \alpha x(1-x) \tag{1}$$

The final relationship of the free enthalpy of the solid, compared to the pure solid elements, will be then deduced and given by:

$$\Delta^m G_e^S = RT[x\log x + (1-x)\log(1-x)] + \alpha x(1-x) + x\Delta^0 G_{AC} + (1-x)\Delta^0 G_{BC} \tag{2}$$

where,

α = The interaction parameter between AC and BC ($\alpha = \alpha_H$-$T\alpha_S$ (Marbeuf *et al*., 1985, 1992; Tuang *et al*., 1982)).

Δ^0G_{AC}, Δ^0G_{BC} = The free enthalpy of the formation of AC and BC compounds.

Considering the Gibbs-Duhem relation permits us to deduce the chemical potential from each species in the solid, as given in Eq. 3/4:

$$\mu_{AC}^S = RT\log a_{AC}^S = \alpha_S(1-x)^2 + RT\log x + \Delta^0 G_{AC} \tag{3}$$

$$\mu_{BC}^S = RT\log a_{BC}^S = \alpha_S(1-x)^2 + RT\log x + \Delta^0 G_{BC} \tag{4}$$

Liquid phase description: The description of the liquid phase is well made by applying the sub regular associated model. In this study, x_i(i = 1, 2, 3) are the molar fractions of the pure elements and y_i(i = 1, 2, 3, 4, 5) the molar fractions of the species.

The free enthalpy of the mixture compared to the pure liquid species can be written by:

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$$\Delta_S^m G_S^1 = \Delta_s^{id} G_S^1 + \Delta_S^{ex} G_S^1 \tag{5}$$

where, $\Delta^{id}{}_s G^l{}_S$ is the ideal free enthalpy

$$\Delta_s^{id} G_S^1 = RT \sum_{i=1}^{5} y_i \log y_i$$

and $\Delta^{ex}{}_s G^l{}_S$ is the free enthalpy of the excess, written in the 2nd order of the Redlich-Kistler polynom as:

$$\Delta_S^{ex} G_S^L = \sum_{i=i}^{4} \sum_{j=2}^{5} y_i y_j [\alpha_{i-j} - \beta_{i-j}(y_i y_j)] - \eta y_1 y_2 y_3$$

α and β are the binary interaction parameters, η the ternary interaction parameter, where:

$$\alpha = \alpha_H - T\alpha_S,\ \beta = \beta_H - T\beta_S \text{ and } \eta = \eta_H - T\eta_S$$

Using the Gibbs-Duhem relation, we obtained for the species (K) the following relation

$$\begin{aligned} \mu_{sk} &= \Delta^m G_S^L + \frac{\partial(\Delta^m G_s^1)}{\partial y_k}, \\ \Delta^m G_s^1 &= \Delta_s^m G_s^1 - y_4 \Delta^d G_{AC} - y_5 \Delta^d G_{BC} \end{aligned} \tag{6}$$

$\Delta^d G_{AC}$ and $\Delta^d G_{BC}$ are the dissociation free enthalpies of AC and BC species.

In addition there are two relations expressing the chemical potential according to the activity:

$$\mu_{sk} = RT\log a_{sk},\ a_{sk} = y_k \gamma_{sk} \tag{7}$$

Combining Eq. 6 and 7 we obtain:

$$\begin{aligned} RT\log\gamma_{Sk} = &\left[\sum_{i=1}^{4} \sum_{j=2}^{5} \lambda_{i,j}(k) + \varepsilon_{i,j}(k) \right] \\ &- \delta_{4,k} \Delta^d G_{AC} - \delta_{5,k} \Delta^d G_{BC} \end{aligned} \tag{8}$$

where:

$$\begin{aligned} \lambda_{i,j}(k) = {} & \alpha_{i-j} \left[x_i \delta_{k-j} + x_j \delta_{k-i} - x_i x_j \right] \\ & + \beta_{i-j} \begin{bmatrix} \delta_{k-i}(2x_i x_j - x_j^2) + \delta_{k-j}(x_j^2 - 2x_i x_j) \\ +2x_i x_j (x_j - x_i) \end{bmatrix} \\ \varepsilon_{i,j}(k) = {} & -\eta [2x_A x_B x_C + x_B x_C \delta_{k-A} + x_A x_C \delta_{k-B} + x_A x_B \delta_{k-C}] \end{aligned}$$

Dissociation values: In each binary compound such as ZnTe, the free enthalpy of the solid combined species AC is the same free enthalpy of the formation of the compound started from liquid elements A and C. The congruent fusion of the compound AC (S) is made without variation of the free enthalpy (Farah, 1985; Tung *et al.*, 1982. This consideration allows us to write the relations as follows:

$$\Delta^m H^{el} = \frac{1}{2}(\Delta H_{AC}^0 + T_{AC}^f \Delta S_{AC}^0) \tag{9}$$

$$\Delta^m S^{el} = \frac{1}{2}(\Delta S_{AC}^0 + \Delta S_{AC}^f) \tag{10}$$

where, $\Delta H^0{}_{AC}$, $\Delta S^0{}_{AC}$, $\Delta s^f{}_{AC}$ are the experimental thermodynamics values of formation.

The dissociation parameters do not vary with the temperature; consequently we can calculate them at the melting point ($T = T^f{}_{AC}, T^f{}_{BC}$).

According to the relation Eq. 7, for example for AC (ZnTe), we obtain:

$$\Delta^d H_{AC} = \left. \begin{matrix} [y_3^2 \alpha_{HA-C} + 2\alpha_{Hass} y_3 y_4 \\ +2\beta_{Hass} y_3 y_4 (y_3 - y_4) \\ -(1+y_4)\Delta^m H^{el}] \end{matrix} \middle/ (1+y_4) \right. \tag{11}$$

$$\Delta^d S_{AC} = \left. \begin{matrix} [y_3^2 \alpha_{SA-C} + 2\alpha_{Sass} y_3 y_4 \\ +2\beta_{Sass} y_3 y_4 (y_3 - y_4) - y_4 \Delta^m H^{el} \\ -(1+y_3)\Delta^m S^{el} - 2R\log y_3 - R\log y_4] \end{matrix} \middle/ (1+y_4) \right. \tag{12}$$

$$\begin{aligned} \alpha_{ass} &= \frac{1}{2}(\alpha_{1-4} + \alpha_{3-4}) = \alpha_{Hass} - T_{AC}^F \alpha_{Sass}, \\ \beta_{ass} &= \frac{1}{2}(\beta_{1-4} + \beta_{3-4}) = \beta_{Hass} - T_{AC}^F \beta_{Sass} \end{aligned}$$

Using the same approach, we deduce the dissociation values for BC (CdTe).

Gas phase description: The gas phase is entirely described by its activity, which is related to the pressure P (vapour saturated above the liquid) for phase diagram points and given, for the monatomic case, by:

$$a_i^V = \frac{P_I}{P_I^0} \tag{13}$$

And for the diatomic gas, by:

$$a_i^V = \left(\frac{P_i}{P_i^0} \right)^{1/2} \tag{14}$$

where, indexes i, v, 0 indicate, respectively: the element, the phase and the saturation pressure.

Calculated methods

Interaction parameters calculation: The function σ, is definite by:

$$\sigma = Z_1 + Z_2 + Z_3 \tag{15}$$

where:

$$Z_1 = \sum_{n=1}^{NP}\left[\sum_{i=1}^{3}(\log\frac{a_i^L}{a_i^V})\right],\ Z_2 = \sum_{n=1}^{NP}\left[\frac{\mu_4^S - \mu_4^L}{\mu_4^S}\right],$$

$$Z_2 = \sum_{n=1}^{NP}\left[\frac{\mu_4^S - \mu_4^L}{\mu_4^S}\right]$$

NP = The number of the available experimental points.

Mathematically, the minimum of σ is 0, physically it's the equality between the activities of the various phases. The minimization of σ has been obtained by the Nelder and Mead (1965) method.

Phase equilibrium calculations:

- Solid-Liquid equilibrium.

$$\Delta G = q\Delta^m G_e^L + (1-q)\Delta^m G_e^S \tag{16}$$

- Liquid-Liquid equilibrium.

$$\Delta G = q\Delta^m G_e^{L1} + (1-q)\Delta^m G_e^{L2} \tag{17}$$

where, q represents the crystalline amount in the system, this proportion is calculated by using the Lever rule (Cahn *et al.*, 1990).

RESULTS AND DISCUSSION

This study led, at the end, to many results summarized in Table 1-4 concerning the interaction parameters between different species existing in the liquid and solid phases in both binary compounds Zn-Te, Cd-Te and the ternary one Zn-Cd-Te.

The calculated phase diagrams are shown in the Fig. 1-3 for the systems indicated above, respectively.

According to the obtained results, the values of the concentrations $y^{Tf}_{ZnTe} = 0.919$, $y^{Tf}_{ZCdTe} = 0.899$ of combined species, in the liquid at the melting point (Table 1), show a very important associated character in both systems ZnTe and CdTe.

Our results, compared to others, where the authors have used different models are nearly the same.

Table 1: Molar fraction of the combind species at the point and the dissociated values

	$\Delta^d H$(Cal mole^{-1})	$\Delta^d S$ Cal (K mol^{-1})	y^{Tf}
ZnTe	20789	4.1698	$y^{Tf}_{ZnTe} = 0.919897$
CdTe	20948.8	3.9873	$y^{Tf}_{CdTe} = 0.899978$

Table 2: The calculated parameters of the binary system Zn-Te

	Zn-Te	ZN-ZnTe	Te-ZnTe
α_H-Tα_S	-7584-T1.458	9993-T3.012	460+T0.605
β_H-Tβ_S	-13112+T7.857	0.120+T0.099	-0.099+T0.100

Table 3: The calculated parameters of the binary system Cd-Te

	Cd-Te	Cd-CdTe	Te-CdTe
α_H-Tα_S	-T6.206	27292.9-T19.98	5407+T3.027
β_H-Tβ_S	-4506+T2.458	0.299+T0.215	0

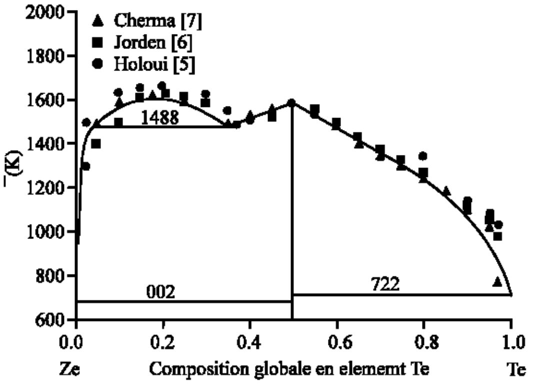

Fig. 1: The calculated phase diagram of binayr Cd-Te

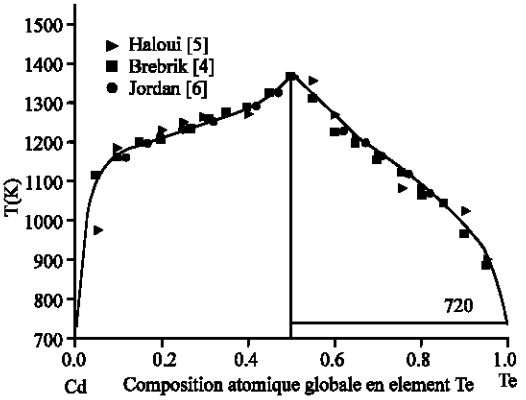

Fig. 2: The calculated phase diagram of binary system Zn-Te

The interaction parameters, of the second order β, between the associated species, in the two systems ZnTe and CdTe (Table 2 and 3), are approximately zero; which indicate a linear relation of the free enthalpy with the concentrations, there for is a quasi-regular behavior.

We can also notice that the parameters of the second order, between simple species, are important, which allow us to predict a parabolic shape of the free enthalpy.

Table 4: The calculated parameters of the ternary system Zn-Cd-Te

$\alpha_{Zn\text{-}CdTe}$	$\alpha_{Cd\text{-}ZnTe}$	$\alpha_{ZnTe\text{-}CdTe}$	$\eta_{Zn\text{-}Cd\text{-}Te}$	$\alpha_S(ZnTe)_x(CdTe)_{1-x}$
0.3-T0.1	0.1	0.9-T0.2	1587.283+T1.008	4658.88+T3.168

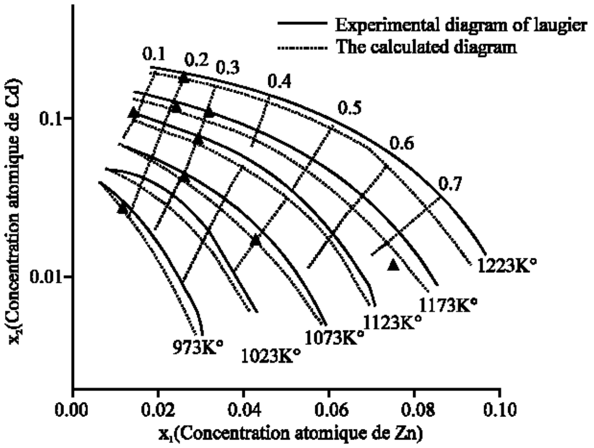

Fig. 3: The Calculated phase diagram of binary system Zn-Cd-Te

For the ternary liquid (Table 4), we found that the values of the interaction parameters Zn-CdTe, Cd-ZnTe and ZnTe-CdTe are very weak, the explanation given is that there is no interaction in the liquid, which reinforces our assumption on the negligence of the interaction between foreign species.

As for the parameters of interactions in the solid solutions, the entropic term is neglected according the enthalpy term, which proves an independent behavior of the temperature in this binary pseudo solution.

The calculated phase diagrams show a great agreement with experimental ones. The eutectic point for the Zn-Te system is laid down at temperature T = 1488 °C for a x_{TE} = 0.35 composition.

As for the ternary diagram, it takes a shape, very similar to the experimental diagram of Laugier (1973) used as reference.

CONCLUSION

The sub-regular associated model used in this research led to a well description of liquid phases of binary systems Zn-Te and Cd-Te and also the ternary one Zn-Cd-Te.

This knowledge permitted us to calculate binary Zn-Te, Cd-Te and ternary Zn-Cd-Te phase diagrams using correct thermodynamic and other parameters values.

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