

# Measurement and Calculation of the $\text{YbI}_2\text{-Al}$ ( $A = \text{Na, K, Rb, Cs}$ ) Phase Diagrams<sup>1</sup>

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The phase diagrams of the  $\text{YbI}_2\text{-Al}$  ( $A = \text{Na, K, Rb, Cs}$ ) systems have been measured by differential thermal analysis and X-ray powder diffraction. A set of thermodynamic functions have been optimized based on an interactive computer-assisted analysis. The optimized phase diagrams and thermodynamical data are self-consistent. © 1995 Academic Press, Inc.

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## 1. INTRODUCTION

It has been reported that some compounds of rare earth and alkali halides (such as  $\text{NaScI}_4$ ,  $\text{CsCeI}_4$ ,  $\text{CsNdI}_4$ , and  $\text{CsLaI}_4$ ) and the divalent samarium compounds  $\text{NaSmI}_3$  and  $\text{CsSmI}_3$  (1–6) show higher vapor pressures than those of the rare earth salts alone. This has been confirmed by the observation of an increase in vapor pressure over a molten mixture of cerium iodide and sodium iodide in high-intensity discharge lamps (5). It is believed that the complexes of rare earth and alkali halides would be potentially useful as new filling materials for discharge lamps. Therefore, it is very important to study the phase diagrams and thermodynamic properties of the systems containing rare earth and alkali halides.

A few phase diagrams for divalent rare earth (*RE*) halides and alkali (*A*) halides have been published (7–11). The compounds  $\text{AEuCl}_3$  ( $A = \text{Cs, Rb}$ ),  $\text{AEu}_2\text{Cl}_3$  ( $A = \text{Na, K, Rb, Cs, Tl}$ ), and  $\text{K}_2\text{EuCl}_4$  have been reported in the  $\text{EuCl}_2\text{-AlCl}_3$  binary systems (8). In the  $\text{SmI}_2\text{-Al}$  systems (11), the compounds  $\text{ASm}_2\text{I}_5$  ( $A = \text{K, Rb, Cs}$ ),  $\text{ASmI}_3$  ( $A = \text{Rb, Cs}$ ),  $\text{A}_2\text{SmI}_4$  ( $A = \text{Rb, Cs}$ ), and  $\text{A}_3\text{SmI}_5$  ( $A = \text{Rb, Cs}$ ) have also been reported. To ascertain the general pattern of the phase relationships of binary  $\text{REX}_2\text{-AX}$

systems and to search for new luminous materials for discharge lamps, the phase diagrams of  $\text{YbI}_2\text{-Al}$  ( $A = \text{Na, K, Rb, Cs}$ ) systems are experimentally determined and theoretically calculated in this paper.

## 2. EXPERIMENTAL DETAILS

$\text{YbI}_2$  was prepared by reaction of ytterbium with  $\text{HgI}_2$  (12). High-purity commercial reagent grade  $\text{NaI}$ ,  $\text{KI}$ ,  $\text{RbI}$ ,  $\text{CsI}$  (melting points 661, 680, 646 and 626°C, respectively) were used without further purification. However, they were dried by heating in vacuum ( $2.7 \times 10^{-4}$  Pa) at 350°C for 3 hr before use. The purities of  $\text{SmI}_2$  and  $\text{Al}$  were checked by X-ray and thermal analyses.

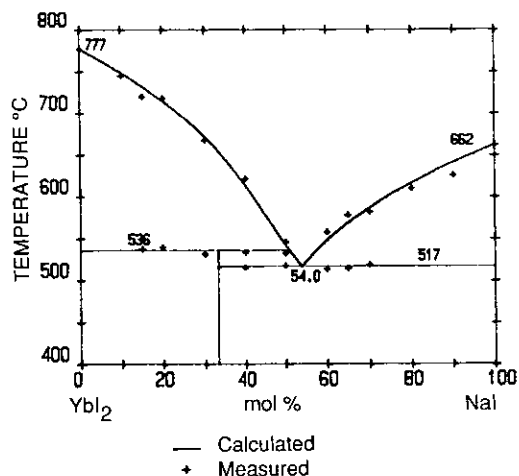
$\text{YbI}_2\text{-Al}$  samples (13–15) with different molar ratios were prepared by weighing and mixing  $\text{YbI}_2$  and  $\text{Al}$  in a dry box under an argon atmosphere in which the oxygen concentration was less than 0.5%. Water was removed by condensation with liquid nitrogen as well. Each sample was sealed in a quartz ampoule in vacuum ( $2.7 \times 10^{-4}$  Pa). To reach equilibrium, the  $\text{YbI}_2\text{-Al}$  samples were heated at 400–500°C for 240 hr. Differential thermal curves of the samples were recorded with a differential thermal analyzer (homemade, model 4-1; heating rate, 5°C  $\text{min}^{-1}$ ; temperature accuracy,  $\pm 1\%$ ). A phase analysis was performed on the basis of X-ray powder diffraction data, obtained with a 114.6- or 57.3-mm Debye-Scherrer Camera and nickel-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154178$  nm).

## 3. EXPERIMENTAL RESULTS

The experimental results are shown in Figs. 1–4. The phase diagram of the  $\text{YbI}_2\text{-NaI}$  system (Fig. 1) shows that

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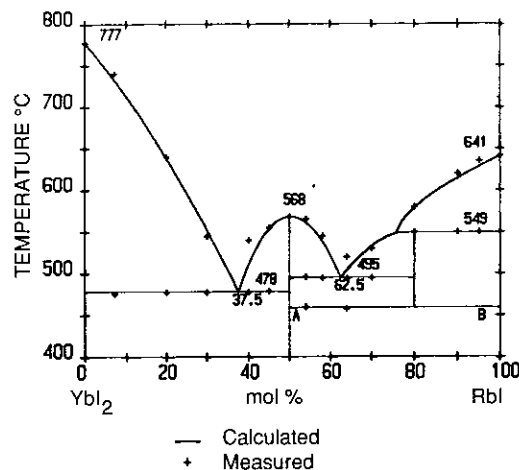
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FIG. 1. YbI<sub>2</sub>-NaI phase diagram.

this system involves one incongruently melting compound NaYb<sub>2</sub>I<sub>5</sub> with a peritectic temperature of 536°C; the eutectic point is located at 54.0 mole% NaI and 517°C. In the YbI<sub>2</sub>-KI system (Fig. 2), there is also one incongruently melting compound KYbI<sub>3</sub>, which has the peritectic temperature 504°C, and a eutectic point located at 455°C, at 64.0 mole% KI.

The congruently melting compound RbYbI<sub>3</sub>, with a melting temperature of 568°C, and the incongruently melting compound Rb<sub>4</sub>YbI<sub>6</sub>, with a peritectic temperature of 549°C, are presented in Fig. 3. There are also two eutectic points measured at 478 and 495°C at 37.5 and 62.5 mole% RbI in the YbI<sub>2</sub>-RbI system.

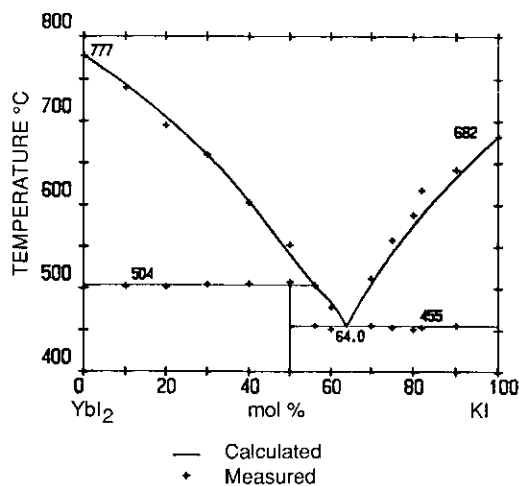
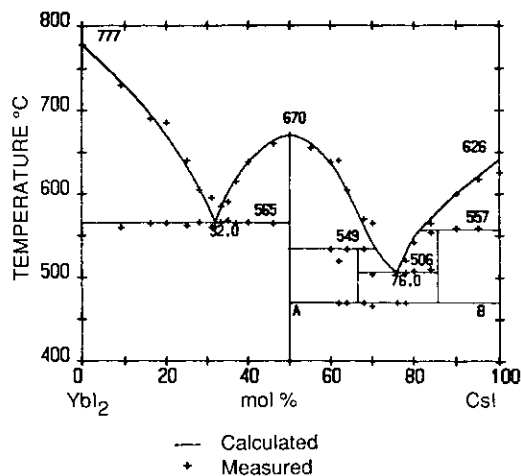
Figure 4 shows that the melting point of the congruently melting compound CsYbI<sub>3</sub> is 670°C; the peritectic temperatures of the two incongruently melting compounds

FIG. 3. YbI<sub>2</sub>-RbI phase diagram.

Cs<sub>2</sub>YbI<sub>4</sub> and Cs<sub>6</sub>YbI<sub>8</sub> are 534 and 557°C, respectively. Also, two eutectic points are observed at 565 and 506°C at 32.0 and 76.0 mole% CsI.

In all four YbI<sub>2</sub>-AI (A = Na, K, Rb, Cs) systems, the molar ratios at the eutectic points have been confirmed by the Tammann Trigon method, in which the endothermal curve determined by DTA is plotted against composition and the point of maximum deflection identifies the eutectic point.

The formation of the ternary ytterbium and alkali iodides, except Rb<sub>4</sub>YbI<sub>6</sub>, Cs<sub>2</sub>YbI<sub>4</sub>, and Cs<sub>6</sub>YbI<sub>8</sub> have been confirmed by X-ray diffraction measurements at room temperature. The failure to detect the three complexes by X-ray diffraction at room temperature may be due to the decomposition of this compound below 450°C. The existence of the three complexes should be

FIG. 2. YbI<sub>2</sub>-KI phase diagram.FIG. 4. YbI<sub>2</sub>-CsI phase diagram.

further confirmed by high-temperature X-ray measurements.

#### 4. OPTIMIZATION AND CALCULATION

##### 4.1. Thermodynamic Model

For many charge-asymmetric molten salt systems ( $C_m X_p - D_n X_r$ ), a better representation with fewer coefficients is obtained, if the excess thermodynamic properties of liquid solution is expressed in terms of the equivalent fraction, rather than of the mole fraction (16–18). The former is defined as

$$Z_A = \frac{pX_A}{pX_A + rX_B} \quad Z_B = \frac{rX_B}{pX_A + rX_B}, \quad [1]$$

where A and B stand for  $C_m X_p$  and  $D_n X_r$ , respectively, and  $X_A$  and  $X_B$  are mole fraction of A and B.

Obviously,  $Z_A/Z_B$  represents the charge number ratio of C and D ions. Therefore, the interaction between unit charges is considered. Then, the molar and excess molar Gibbs energy in liquid are expressed as

$$G_m^l = X_A {}^oG_A^l + X_B {}^oG_B^l + RT(X_A \ln X_A + X_B \ln X_B) + {}^E G_m^l \quad [2]$$

$${}^E G_m^l = (pX_A + rX_B) \sum_{\alpha} \sum_{\beta} (h_{\alpha\beta} - Ts_{\alpha\beta}) Z_A^{\alpha} Z_B^{\beta}, \quad [3]$$

where  ${}^oG_A$  and  ${}^oG_B$  are the standard Gibbs energy of A and B in the liquid state;  $\alpha$  and  $\beta$  are positive integral powers; and  $h_{\alpha\beta}$  and  $s_{\alpha\beta}$  are assumed to be independent of  $T$  and related to enthalpy of mixing and excess entropy of mixing.

The partial excess Gibbs energy of  $i$  ( $i = A$  or  $B$ ) in liquid ( ${}^E G_i^l$ ) can be obtained by differentiating Eq. [3] via

$${}^E G_i^l = {}^E G_m^l + (1 - X_i) \frac{d{}^E G_m^l}{dX_i} \quad [4]$$

to give

$${}^E G_A^l = p \sum_{\alpha} \sum_{\beta} (h_{\alpha\beta} - Ts_{\alpha\beta}) \times [\alpha + (1 - \alpha - \beta)Z_A] Z_A^{\alpha-1} Z_B^{\beta} \quad [5]$$

$${}^E G_B^l = r \sum_{\alpha} \sum_{\beta} (h_{\alpha\beta} - Ts_{\alpha\beta}) \times [\beta + (1 - \alpha - \beta)Z_B] Z_A^{\alpha} Z_B^{\beta-1}. \quad [6]$$

In the above formulas the coefficients  $h_{\alpha\beta}$  and  $s_{\alpha\beta}$  can be derived from a critical, self-consistent analysis of all the available diverse experimental thermodynamic and phase diagram data (19).

TABLE 1  
Thermodynamic Properties of  $\text{YbI}_2$  and AI

Comp.	$T_{\text{fus}}^{\circ}(\text{K})$	$A \times 10^{-3}$	B	$C \times 10^3$	D	$E \times 10^{-5}$
$\text{YbI}_2$	1050	30.554	-29.099	0	0	0
NaI	933	13.940	88.676	6.027	-15.975	0
KI	954	4.656	211.211	14.460	-33.547	2.46
RbI	913	0.330	120.108	5.502	-18.410	0
CsI	894	48.446	-358.448	-21.213	47.488	4.04

##### 4.2. Thermodynamic Data

The thermodynamic data of AI are selected from the literature (20); however, the thermodynamic data of  $\text{YbI}_2$  have not been reported. To optimize and calculate the phase diagrams, the heat of fusion of  $\text{YbI}_2$  is estimated from the  $\text{YbI}_2$ -AI phase diagrams. It is known (21, 22) that for a melting transition, for example, as the composition approaches a pure component  $i$ , the difference between the slopes of the liquidus and solidus curves,  $dX_i^l/dT$  and  $dX_i^s/dT$ , is thermodynamically determined by the enthalpy of fusion,  $\Delta H_{f(i)}^{\circ}$  and melting point,  $T_{f(i)}$ . That is,

$$\lim_{x_i \rightarrow 1} \left( \frac{dX_i^l}{dT} - \frac{dX_i^s}{dT} \right) = \frac{\Delta H_{f(i)}^{\circ}}{\nu RT_{f(i)}^2}, \quad [7]$$

where  $R$  is the gas constant and  $\nu$  is the number of "foreign particles" which are not present in the solvent originally, but introduced by the addition of one "molecule" of solute at infinite dilution. Equation [7] is independent of any model and can be used for estimating the enthalpy of fusion of pure component  $i$ . For  $\text{YbI}_2$ -AI systems,  $\nu = 1$ ,  $\lim_{x_i \rightarrow 1} (dX_i^s/dT) = 0$ . Therefore,  $\Delta H_{f(\text{YbI}_2)}^{\circ}$  can be calculated to be 30,554 J mole $^{-1}$  from Eq. [7].

With the aid of all these data, Gibbs energies of fusion of various iodides are given by

$$\Delta G_i^{\circ} = A + BT + CT^2 + DT \ln T + E/T \text{ J mole}^{-1}, \quad [8]$$

where the values of the coefficients are listed in Table 1.

##### 4.3. Calculation and Discussion

For the systems of  $\text{YbI}_2(\text{A})$ -AI(B), there is no solid solubility, so the excess partial Gibbs energies of A can be calculated at points along their respective liquidus lines from the well-known expression

$$RT \ln(1 - X_B) + {}^E G_A^l = -\Delta G_{f(A)}^{\circ}. \quad [9]$$

Analogously for B, one obtains

TABLE 2  
Excess Enthalpies and Entropies of the YbI<sub>2</sub>-AI Systems

System	$h_{11} \times 10^{-3}$	$h_{12} \times 10^{-3}$	$s_{11}$	$s_{12}$
YbI <sub>2</sub> -NaI	-31.023	51.223	-30.557	50.904
YbI <sub>2</sub> -KI	-9.347	-15.236	-0.751	-19.365
YbI <sub>2</sub> -RbI	79.436	-9.819	151.826	-61.379
YbI <sub>2</sub> -CsI	-32.819	-17.893	1.407	-48.423

$$RT \ln X_B + {}^E G_B^1 = -\Delta G_{f(B)}^0 \quad [10]$$

In general, for any constituent A<sub>m</sub>B<sub>n</sub>

$$mRT \ln(1 - X_B) + nRT \ln X_B + m {}^E G_A^1 + n {}^E G_B^1 = -\Delta G_{f(A_m B_n)}^0 \quad [11]$$

At each experimental liquidus temperature and composition,  ${}^E G_A^1$  and  ${}^E G_B^1$  can be calculated via Eqs. [9] and [10]. Then, all coefficients  $h_{\alpha\beta}$  and  $s_{\alpha\beta}$  can be derived simultaneously via Eqs. [5] and [6] using the program FITBIN (18). The optimized equations

$$H_m^M = (pX_A + rX_B)(h_{11}Z_A Z_B + h_{12}Z_A Z_B^2) \text{ J mole}^{-1} \quad [12]$$

$${}^E S_m = (pX_A + rX_B)(s_{11}Z_A Z_B + s_{12}Z_A Z_B^2) \text{ J mole}^{-1} \text{ K}^{-1} \quad [13]$$

are obtained, where the coefficients  $h_{11}$ ,  $h_{12}$ ,  $s_{11}$ , and  $s_{12}$  are listed in Table 2.

Assuming that Eqs. [12] and [13] interpolate well across the central composition region between the YbI<sub>2</sub>- and AI-liquidus lines, one can then use Eq. [11] to calculate the Gibbs energies of fusion of the ternary ytterbium and alkali iodides. The resultant expressions for the Gibbs energies of fusion are obtained as

TABLE 3  
Thermodynamic Properties of Intermediate Compounds

Int. Comp.	$T_{fus}^0$ (K)	$\Delta G_f^0 = a + bT$ (J/mole)	
		$a \times 10^{-3}$	$b$
NaYb <sub>2</sub> I <sub>5</sub>	809 <sup>a</sup>	11.456	-13.318
KYbI <sub>3</sub>	777 <sup>a</sup>	6.745	-8.576
RbYbI <sub>3</sub>	841	8.615	-10.238
Rb <sub>4</sub> YbI <sub>6</sub>	822 <sup>a</sup>	18.996	-23.036
CsYbI <sub>3</sub>	943	16.021	-16.994
Cs <sub>2</sub> YbI <sub>4</sub>	807 <sup>a</sup>	10.815	-13.278
Cs <sub>6</sub> YbI <sub>8</sub>	830 <sup>a</sup>	6.885	-8.199

<sup>a</sup> Peritectic temperature.

$$\Delta G_{f(A_m B_n)}^0 = a + bT \text{ J mole}^{-1}, \quad [14]$$

where the coefficients  $a$  and  $b$  are listed in Table 3. The measured melting points or peritectic temperatures are presented in Table 3.

According to the thermodynamic data optimized above, the phase diagrams of YbI<sub>2</sub>-AI binary systems were calculated by using the program POTCOMP (18) as shown in Figs. 1-4, in which "+" denotes the experimental data. It is clear that the calculated lines agree well with the experimental data.

Comparing the four YbI<sub>2</sub>-AI phase diagrams, we observe that the larger the ionic radius of the alkali is, the larger the number is and the greater the stability of compounds contained in the system is. This observation is consistent with those of the SmI<sub>2</sub>-AI (A = Na, K, Rb, Cs) (11) and AEF<sub>2</sub>-AF (AE, alkaline earth metal; A, alkali metal) (10) systems.

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