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BRIEF COMMUNICATION

Phase Diagram of EuI_2–KI Binary System

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The phase diagram of the EuI_2–KI binary system was studied by differential thermal analysis (DTA) and X-ray powder diffraction (XRD). The phase diagram of the EuI_2–KI system shows the existence of one congruently melting compound, KEu_2I_5, and one incongruently melting compound, K_4EuI_6. There are two eutectic points located at 465°C, 20 mol% KI and 439°C, 60 mol% KI, respectively.

***Key Words*: binary system; phase diagram; EuI_2–KI; X-ray powder diffraction.**

1. INTRODUCTION

A bountiful amount of work has been carried out on the phase diagrams of binary systems containing trivalent rare earth halides and alkali halides (1, 2). Only a few phase diagrams of the systems, however, containing divalent rare earth (*RE*) halides and alkali (*A*) halides have been presented in the literature (3, 4). Through a series of studies of phase diagrams, the compounds $A\mathrm{EuCl_3}$ (A = Cs and Rb), $A\mathrm{Eu_2Cl_5}$ (A = Cs, K, Rb, Na, and Tl), and $\mathrm{K_2EuCl_4}$ have been found in the phase diagrams of the $\mathrm{EuCl_2}$–ACl binary systems. In the $\mathrm{YbI_2}$–AI systems (A = Na, K, Rb, and Cs) (5), the compounds $\mathrm{NaYb_2I_5}$ (monoclinic), $\mathrm{KYbI_3}$, $\mathrm{RbYbI_3}$, $\mathrm{CsYbI_3}$ (orthorhombic), $\mathrm{Rb_4YbI_6}$, $\mathrm{Cs_2YbI_4}$, and $\mathrm{Cs_6YbI_8}$ have also been found. It was reported that $A\mathrm{Sm_2I_5}$ (A = K, Rb, and Cs), $A\mathrm{SmI_3}$ (A = Rb and Cs), $A_2\mathrm{SmI_4}$ (A = Rb and Cs), and $A_3\mathrm{SmI_5}$ (A = Rb and Cs) exist in the $\mathrm{SmI_2}$–AI system (6, 7).

Some investigations pointed out that a number of complexes of rare earth and alkali metal halides (such as $\mathrm{NaScI_4}$, $\mathrm{CsCeI_4}$, $\mathrm{CsNdI_4}$, and $\mathrm{CsLaI_4}$) and the divalent Samarium compounds $\mathrm{NaSmI_3}$ and $\mathrm{CsSmI_3}$ (8, 9) show higher vapor pressures than those of the rare earth salts alone. The divalent rare earth iodides have been developed in the laboratory as effective luminescent materials used in discharge lamps, and the technique has been patented in China.

Therefore it is of interest to ascertain the general pattern of the phase relationships of binary $RE\mathrm{X_2}$–AX systems and to search for new luminous materials for discharge lamps. The studies of the phase diagrams of $\mathrm{EuI_2}$–AI (A = Li (10), Na (10), Rb (11), and Cs (12)) systems have been experimentally determined in recent years. The work in this paper is to complete the phase diagrams of $\mathrm{EuI_2}$–AI series.

2. EXPERIMENTAL DETAILS

$\mathrm{EuI_2}$ was synthesized by reacting Europium (purity 99.9%) with $\mathrm{HgI_2}$ (13). The sample was sealed under vacuum (2.8×10^{-4} Pa) and heated first at 300°C for 24 h and then at 500°C for 120 h. To refine KI for $\mathrm{EuI_2}$–KI samples, an analytically pure agent was recrystalized twice, dried at 150°C under vacuum, and stored in a glove box under an argon atmosphere for later use. The melting temperature of KI tested is 682°C. The purity of both $\mathrm{EuI_2}$ and KI were checked by DTA and XRD.

$\mathrm{EuI_2}$–KI samples with different molar ratios were prepared by weighing and mixing $\mathrm{EuI_2}$ and KI in the glove box under argon. Oxygen concentration was less than 0.5%, and the water was removed by condensation with liquid nitrogen since $\mathrm{EuI_2}$ easily absorbs water and oxidizes. Each sample was sealed in a quartz ampoule (diameter 5 mm) under vacuum (2.8×10^{-4} Pa) and each one weighed about 120 mg. A total of 37 samples were prepared, and each was heated to 790°C for 10 min and then held at 550°C for more than 72 h. To make each sample in a good equilibrium and to get a better thermal effect in DTA, the samples were annealed for more than 10 days at different temperatures.

DTA curves of the samples were recorded with a differential thermal analyzer (Model LCT-1). The heating rate was ± 5°C min^{-1} for heating and cooling procedures. The span of DTA was ± 50 μV, the speed of record paper was 2 mm min^{-1}, and temperature accuracy was ± 1°C. All DTA data measured were calibrated against temperatures using standard materials which were high-grade In, Sn, Pb,

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TABLE 1
Parameters of Crystal Structure of KEu_2I_5

Name	KEu_2I_5
Parameters of cell	
a (nm)	0.9936
b (nm)	0.8929
c (nm)	1.4226
β (°)	90.02
Space group	$P2_1/c$
Density (g/cm^3)	5.14
Z	4
Coordination number of Eu^{2+}	7, 8
Molar volume (cm^3/mol)	190.5

Ag_2SO_4, SiO_2, K_2CrO_4, and $BaCO_3$. The DTA data from heating and cooling procedures were almost the same, the difference between them being no more than 2%.

Phase analysis was performed on the basis of X-ray powder data obtained with a 90 mm FR552 Guinier camera and Cu$K\alpha$ radiation ($\lambda = 0.154051$ nm). Its working voltage was selected as 35 kV and working current 28 mA. SiO_2 was used as an internal standard material. All data were indexed, and relative powder intensities of new compound KEu_2I_5 were calculated using the program TREOR and POWD12. The parameters of the crystal structure of KEu_2I_5 were in good accordance with the literature (14), see Table 1.

3. RESULTS AND DISCUSSION

The phase diagram of the EuI_2–KI binary system is shown in Fig. 1.

In the EuI_2–KI system there is one congruent compound, KEu_2I_5 (EuI_2 : KI = 2:1), with the melting point 487°C and one incongruent compound, K_4EuI_6 (EuI_2 : KI = 1:4), with the peritectic temperature 479°C. For the incongruently melting compound K_4EuI_6, the peritectic reaction is

$$L + KI = K_4EuI_6 \text{ (L : KI of 65 mol\%)}.$$

There are two eutectic points located at 465°C and 439°C with 20 and 60 mol% KI estimated using the Tammann Trigon method (15). The formation of compound KEu_2I_5 has been confirmed by X-ray diffraction measurements at ambient temperature. Also, according to the compound formation criterion for the REX_2–AX presented by J. Kutscher and A. Schneider (16) and successfully used on divalent iodides by Wang (17),

$$\bar{K} = \frac{K_I}{K_{II}} = \frac{(r_{RE^{2+}} + r_{X^-})^2}{2(r_{A^+} + r_{X^-})^2},$$

where K_I is the Colombian force between the A^+ (here K^+) and X^- (here I^-), K_{II} the Colombian force between the RE^{2+}(Eu) and $X^-(I^-)$, r_{A^+} ($r_{K^+} = 1.52$), $r_{RE^{2+}}$ ($r_{Eu^{2+}} = 1.31$), and r_{X^-}($r_{I^-} = 2.06$) Shannon radii (18) of ions respectively. $\bar{K}_{EuI_2-KI} = 0.4431$. When $\bar{K} = 0.359 \sim 0.425$, the compound with composition 1:1 (EuI_2:KI) will appear, and when $\bar{K} = 0.402 \sim 0.519$, the compound with composition 2:1 (EuI_2:KI) will appear. It is clear that in the EuI_2–KI system, compound KEu_2I_5 with composition 2:1 (EuI_2:KI) should appear. The phase diagram from DTA data agrees in the existence of the compound KEu_2I_5.

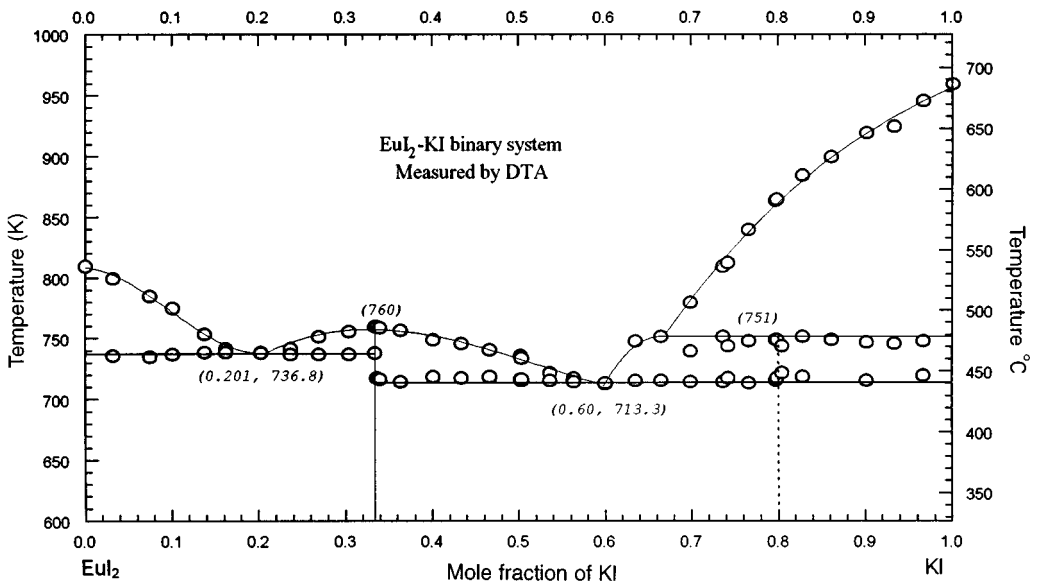

FIG. 1. Phase diagram of EuI_2–KI.

TABLE 2
Results of Phase Analysis (298 K) from X-ray Powder Diffraction

No. of sample	1	2	4	5	6	20	23	33	8
Molar ratio EuI_2:KI	9:1	4:1	2:1	3:2	1:1	2:3	5:14	1:4	1:9
Observed phases	EuI_2, KEu_2I_5	EuI_2, KEu_2I_5	KEu_2I_5	KEu_2I_5, KI	KEu_2I_5, KI	KEu_2I_5, KI	KEu_2I_5, KI	KEu_2I_5, KI	KEu_2I_5, KI

The failure to determine the compound K_4EuI_6 (1:4) by X-ray diffraction at ambient temperature may be due to the decomposition of this compound on cooling to lower temperature. Further research should be continued to confirm the existence of the compound K_4EuI_6. Here the composition of this compound was determined by means of Tammann Trigon method as well. According to the DTA and XRD results shown in Table 2, the measured phase diagram of the EuI_2–KI system shown in Fig. 1 is reasonable.

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