SOME RECENT RESULTS ON THE EuBr₂-MBr BINARY SYSTEMS
(M= Li, Na, K, Rb)

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ABSTRACT

DSC was used to study phase equilibrium in the EuBr₂-MBr binary systems (M=Li, Na, K, Rb). The results obtained provided a basis for constructing the corresponding phase diagrams. The electrical conductivity of the same EuBr₂-MBr liquid mixtures was measured on an extended composition and temperature range.

INTRODUCTION

By opposition to most lanthanide compounds [1] which correspond to the valence state (III), europium is one of the few rare earth metal that forms stable compounds in the valence state (II). A substantial amount of thermochemical data has been reported on lanthanide (III) halides in literature but they are mostly estimations based on approximations of thermodynamic values. Also this lesser information on lanthanide dihalides indicated the lack of experimental data, for both dichlorides and dibromides. Following previous investigations on the thermodynamic [2,3] and transport properties [4] of EuCl₂-based melts, the present work focuses on europium(II) bromide–alkali bromide melts.

Experimental investigations were conducted very recently on EuBr₂ in order to assess the reliability of estimated temperature and enthalpy of fusion [5–8], entropy at 298 K and formation enthalpy of solid EuBr₂ at 298 K [9,10] as well as heat capacity of solid and liquid europium(II) bromide [10]. Therefore, we have determined experimentally the heat capacity of solid and liquid EuBr₂ in the temperature range 300–1100 K. The temperature and enthalpy of fusion were also determined experimentally. By combination of these results with the literature data on the entropy at 298.15 K, Δ⁰ s (EuBr₂, s, 298.15 K) and the standard molar enthalpy of formation, Δ⁰ f m (EuBr₂, s, 298.15 K), the thermodynamic functions of europium dibromide were calculated up to T = 1300 K [11].
The present work reports recent results on phase diagrams and electrical conductivity of the EuBr₂-LiBr, EuBr₂-NaBr, EuBr₂-KBr and EuBr₂-RbBr binary systems.

**EXPERIMENTAL**

**Materials**

Europium(II) bromide was synthesized from the oxide Eu₂O₃ (Aldrich 99.9%) by a modified Haschke and Eick method [12]. Its chemical analysis was performed by mercurimetric (bromine) and complexometric methods (europium). The results are as follow: Eu, 48.74 % found, 48.75 % calc.; Br, 51.26 % found, 51.25 % calc.

Alkali metal bromides (LiBr, NaBr, KBr and RbBr) were Merck Suprapur reagent (min. 99.9%). Before use, they were progressively heated up to fusion under gaseous HBr atmosphere. Excess of HBr was then removed from the melt by argon bubbling.

**Preparation of the EuBr₂-MBr binary mixtures.** The appropriate amounts of EuBr₂ and MBr were melted in vacuum-sealed quartz ampoules. The melts were homogenised and solidified. Homogenous mixtures of different composition were prepared in this way and used in phase diagram and electrical conductivity measurements.

**Chemicals handling.** All chemicals were handled inside a high purity atmosphere argon glove box with a water content less than 2 ppm. Continuous gas purification is ensured by forced circulation through external molecular sieves.

**Measurements**

**Fusion temperature and enthalpy.** Fusion temperature and enthalpy of all EuBr₂-MBr binary mixtures were determined from DSC experiments conducted at heating and cooling rates ranging 1–5 K min⁻¹. The apparatus and the measurement procedure were described in details in [13].

**Electrical Conductivity Measurements.** Electrical conductivity measurements were carried out in a capillary quartz cell with the conductivity meter Tacussel CDM 230. The procedure was described in details elsewhere [14,15]. The cell filled with the compound or the mixture under investigation was placed into the furnace with a stainless steel block, used to achieve a uniform temperature distribution. The conductivity of the melt was measured in the course of increasing and decreasing temperature runs by platinum electrodes with the conductivity meter Tacussel CDM 230. The mean value of these two measurements was used in calculations. Experimental runs were performed at heating and cooling rates ranging from 1 to 2 K min⁻¹. Temperature and conductivity data acquisition was made with a PC computer interfaced to the conductivity meter. Temperature was measured by means of a Pt/Pt–Rh thermocouple within the accuracy 1 K. The experimental cell was calibrated with a pure NaCl melt [15]. All the measurements were carried out under static argon atmosphere. The accuracy of measurements was about ±2%.
RESULTS AND DISCUSSION

EuBr₂–MBr phase diagrams.

The EuBr₂–MBr phase diagrams (M=Li and Rb) were established for the first time. DSC investigations performed on samples with different compositions yielded both the temperature and the fusion enthalpy of the concerned mixtures. Due to supercooling effect, all temperature and enthalpy values reported in this work were determined from heating curves. To determine precisely the composition of eutectics as well as of compounds melting incongruently formed in studied systems the so-called Tamman constructions shown were used.

The phase diagram of the EuBr₂–LiBr system was found to be peritectic type (Figure 1).

![Figure 1 Phase diagram of the EuBr₂–LiBr binary system](image)

The eutectic composition \( x(\text{EuBr}_2)=0.319 \) was evaluated from the intercept of the two linear parts in Figure 2, described by the equations \( \Delta_{\text{ fus}} H_m^p = 50.417x(\text{EuBr}_2) \) and \( \Delta_{\text{ fus}} H_m^p = 30.793 - 46.194x(\text{EuBr}_2) \) in kJ mol⁻¹. In this Tamman construction it was assumed that there was no solubility in the solid state. Thus straight lines intercept the composition axis at \( x(\text{EuBr}_2)=0 \) and \( x(\text{EuBr}_2)=0.666 \). The enthalpy of fusion at the eutectic composition is \( \Delta_{\text{ fus}} H_m^p = 16.4 \) kJ mol⁻¹. The eutectic temperature determined from all the appropriate DSC curves is equal 723 K. The examination of the DSC curves in the composition range 0.55<\( x(\text{EuBr}_2)<1.00 \) suggests that in this area the stoichiometric compound exists up to \( T=781 \) K, temperature at which it melts incongruently. The experimental composition \( x(\text{EuBr}_2)=0.666 \) determined from a Tamman construction (Figure 2) argues well with the LiEu₂Br₅ stoichiometry.
The phase diagram of the EuBr$_2$–NaBr [16] system (Figure 3) was found to be of the simple eutectic type. The eutectic composition, $x$(EuBr$_2$)=0.546, was determined accurately as explained above assuming that no solid solutions were formed. The enthalpy of fusion at the eutectic composition is $\Delta H^\circ_{f, eut}$=16.5 kJ mol$^{-1}$. The eutectic temperature determined from all appropriate DSC curves is $T_{eut}$=762 K.

The EuBr$_2$–KBr phase diagram presented in Figure 4 is rather complex [17]. It exhibits two eutectics and two stoichiometric compounds. The first compound, K$_2$EuBr$_4$, decomposes peritectically at 829 K. The second one, KEu$_2$Br$_5$, melts congruently at 880 K.

844 Electrochemical Society Proceedings Volume 2004-24
The composition of the two eutectics was determined from the Tamman construction, under the assumption of no solid solubility. We obtained $x(\text{EuBr}_2)=0.427$ for the composition of the left eutectic. The eutectic temperature determined from all the appropriate DSC curves is $T_{\text{eut}}=810$ K. The enthalpy of fusion of the left eutectic is $\Delta_{\text{eu}}H_m^f=17.4$ kJ mol$^{-1}$. The composition of the right eutectic was obtained as $x(\text{EuBr}_2)=0.783$. This mixture melts at 852 K with the corresponding enthalpy 20.1 kJ mol$^{-1}$. The origin of the additional and weak thermal effect, observed in DSC thermograms at 838 K for all mixtures in the composition range 0.7<$x(\text{EuBr}_2)$<1 (black points in Figure 4) cannot be explained at the present time. Additional information is expected from projected structural investigations.

The EuBr$_2$-RbBr binary system is under investigation at the present time. Preliminary results (Figure 5) showed that three stoichiometric compounds exist in this system, namely Rb$_2$EuBr$_4$, RbEuBr$_3$ and RbEu$_2$Br$_5$. The 1:2 compound, Rb$_2$EuBr$_4$, decomposes peritectically at 778 K. The RbEuBr$_3$ compound, probably formed at 633 K from Rb$_2$EuBr$_4$ and RbEu$_2$Br$_5$, melts incongruently at 852 K following the solid-solid phase transition at 732 K. These provisional conclusions will be confirmed by structural studies, which are planned in the nearest future. The third compound, namely RbEu$_2$Br$_5$, melts congruently at 888 K.
The composition and temperature of the two eutectics were determined:

\[ x(\text{EuBr}_2) = 0.316; \quad T_{\text{eut}} = 776 \text{ K} \]

\[ x(\text{EuBr}_2) = 0.797; \quad T_{\text{eut}} = 859 \text{ K} \]

**Electrical conductivity of liquid EuBr\(_2\)-MBr binary mixtures.**

Electrical conductivity measurements were performed over the entire composition range (in steps of \(\sim 10\) mol\%) on EuBr\(_2\)-MBr liquid mixtures (M=Li, Na, K and Rb). The data obtained are original since neither pure EuBr\(_2\) nor the EuBr\(_2\)-MBr mixtures had been investigated previously. The specific conductivity data of the liquid phase were fitted by the second order polynomial equation [1]:

\[ \kappa = A + BT + CT^2 \]  \[1\]

The coefficients of equation are listed in Tab.1.
Table 1. Specific conductivity $\kappa = A + BT + CT^2$ (S m$^{-1}$) of EuBr$_2$–MBr melts.

| x(EuBr$_2$) | $10^7 A$ S m$^{-1}$ | $10^8 B$ S m$^{-1}$ K$^{-1}$ | $10^3 C$ S m$^{-1}$ K$^{-2}$ | Temp. range K |
|------------|----------------|----------------|----------------|----------------|
| EuBr$_2$–LiBr |               |               |               |                 |
| 0.000    | -3.1513        | 14.685        | -5.8836        | 828-1115       |
| 0.109    | -3.6506        | 12.986        | -4.9449        | 830-1130       |
| 0.195    | -3.3819        | 10.089        | -3.1240        | 823-1072       |
| 0.299    | -4.5883        | 11.771        | -4.8670        | 766-1110       |
| 0.404    | -3.4951        | 8.4602        | -2.5508        | 796-1148       |
| 0.497    | -4.7800        | 10.402        | -3.5066        | 788-1109       |
| 0.584    | -3.8263        | 7.8310        | -2.3574        | 796-1109       |
| 0.667    | -4.4726        | 8.9185        | 2.8359         | 804-1090       |
| 0.689    | -3.8589        | 7.7149        | -2.3846        | 835-1138       |
| 0.801    | -4.2432        | 7.9486        | -2.3984        | 883-1105       |
| 0.868    | -2.8153        | 5.3416        | -1.2710        | 800-1071       |
| 1.00     | -3.5174        | 6.1114        | -1.6799        | 943-1173       |
| EuBr$_2$–NaBr |              |               |               |                 |
| 0.000    | -3.5543        | 10.081        | -3.6611        | 1026-1117      |
| 0.089    | -3.1295        | 9.2688        | -3.4901        | 930-1075       |
| 0.203    | -4.2595        | 9.8819        | 9.8819         | 947-1113       |
| 0.291    | -3.9937        | 9.1198        | -3.1141        | 913-1111       |
| 0.381    | -2.9119        | 6.3753        | -1.9712        | 874-1112       |
| 0.460    | -3.5105        | 7.2997        | -2.3565        | 835-1140       |
| 0.597    | -3.1073        | 6.1642        | -1.8635        | 793-1124       |
| 0.692    | -2.5922        | 4.9817        | -1.3448        | 815-1132       |
| 0.800    | -3.2803        | 6.1225        | -1.8550        | 869-1113       |
| 0.876    | -2.5445        | 4.3906        | -0.9528        | 913-1140       |
| EuBr$_2$–KBr |               |               |               |                 |
| 0.000    | -3.0507        | 6.9471        | -2.2610        | 1020-1122      |
| 0.098    | -3.4479        | 7.1720        | -2.3711        | 1015-1124      |
| 0.207    | -2.5340        | 5.2355        | -1.4941        | 902-1149       |
| 0.291    | -2.6352        | 5.2491        | -1.5371        | 862-1117       |
| 0.333    | -2.1086        | 4.1416        | -0.9614        | 903-1139       |
| 0.417    | 2.9439         | -4.6144       | 2.8077         | 1125-1159      |
| 0.448    | -2.1898        | 4.2224        | -1.0116        | 793-1130       |
| 0.498    | -2.5669        | 4.9934        | -2.5669        | 830-1127       |
| 0.587    | -2.4314        | 4.5695        | -1.2550        | 890-1114       |
| 0.599    | -2.5470        | 4.8104        | -1.3089        | 870-1134       |
| 0.667    | -2.3248        | 4.2034        | -1.1239        | 882-1118       |
| 0.687    | -2.5396        | 4.6336        | -1.2308        | 888-1112       |
| 0.731    | -4.4412        | 8.2986        | -3.0716        | 995-1088       |
| 0.781    | -2.7211        | 4.9828        | -1.3645        | 883-1152       |
| 0.907    | -3.4075        | 6.1518        | -1.9211        | 921-1111       |
| EuBr$_2$–RbBr |              |               |               |                 |
| 0.000    | -2.2863        | 5.2089        | -1.7083        | 993-1124       |
| 0.100    | -2.5677        | 5.3470        | -1.6972        | 989-1152       |
| 0.101    | -5.0148        | 9.9320        | -3.8847        | 958-1138       |
| 0.202    | -2.4242        | 4.7350        | -1.3972        | 861-1131       |
| 0.333    | -1.6979        | 3.0863        | -0.6216        | 797-1143       |
| 0.500    | -1.2988        | 2.2405        | -0.2126        | 893-1136       |
| 0.500    | -1.8838        | 3.4491        | -0.8333        | 870-1114       |
| 0.589    | -2.2661        | 4.0964        | -1.1500        | 879-1135       |
| 0.799    | -1.9450        | 3.3858        | -0.6640        | 849-1136       |
| 0.895    | -2.7123        | 4.7635        | -1.1927        | 934-1139       |
The electrical conductivity of the LiBr, NaBr, KBr and RbBr components has been measured previously and critically compared to previous literature data [18]. No data were available on EuBr₂ and original measurements were conducted very recently [11].

The experimental conductivity isotherm at 1050 K in the whole composition range is presented in Figure 6 for all the MBr–EuBr₂ systems.

The electrical conductivity decreases with increasing alkali metal cation radius, i.e. from lithium to rubidium. For all the systems, the relative changes of conductivity are significantly larger in the alkali bromide-rich region. In the europium bromide-rich region the conductivity behavior is somewhat more complicated. Its smooth decrease in the systems with LiBr and NaBr becomes smaller in the KBr system, and transforms in a broad minimum, not clearly marked, in the system with RbBr.

Figure 6. Electrical conductivity isotherms at 1050 K: open circles: EuBr₂–LiBr, black circles: EuBr₂–NaBr, open triangles: EuBr₂–KBr, black triangles: EuBr₂–RbBr

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