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Journal of Nuclear Materials 344 (2005) 120–123
journal of nuclear materials
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Phase diagram and electrical conductivity of the $EuBr_2$–NaBr binary system

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Abstract

DSC was used to study phase equilibrium in the $EuBr_2$–NaBr system. It represents a typical example of simple eutectic system with the eutectic composition, $x(EuBr_2) = 0.546$, and eutectic temperature 762 K. The electrical conductivity of $EuBr_2$–NaBr liquid mixtures was measured down to temperatures of solidification. Reflectance spectra of the pure components and their solid mixtures (after homogenisation in the liquid state) with different composition were recorded in order to confirm the reliability of the constructed phase diagram.

PACS: 81.30.Dz

1. Introduction

Metallic lanthanides or their compounds are widely used in modern technologies (permanent magnets, special alloys with high mechanical, thermal and chemical resistivity, light alloys for space industry, high pressure discharge lamps, lasers, magnetic memory, etc.). Lanthanides are also product of nuclear fission in nuclear reactors. Thus spent nuclear fuel contains lanthanides, which must be removed during its reprocessing. This reprocessing can be performed with using of molten salt technology, which involves rare earth halides and their mixtures with alkali halides. Such an application requires the characterisation of basic physicochemical properties of both pure lanthanide halides and their mixtures with alkali halides. The present paper is a part of the general research program focused on lanthanide halides. It deals with the $EuBr_2$–NaBr binary system.

Europium is one of the few rare earth metals (Sm, Eu, Yb) that forms stable compounds in the divalent state. Very few investigations were carried out on divalent lanthanide-based melts or high temperature solids. Following previous results on the thermodynamic,

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doi:10.1016/j.jnucmat.2005.04.028

electrochemical and electrical properties of $EuCl_2$-based melts [1–4], the present work reports recent results on phase diagram and electrical conductivity of the europium(II) bromide–sodium bromide binary system.

2. Experimental

2.1. Chemicals

Europium(II) bromide was synthesised from the oxide Eu_2O_3 (Aldrich 99.9%) by a modified Haschke and Eick method [5]. Chemical analysis was performed by mercurimetric (bromine) and complexometric methods (europium). The results are as follows: Eu, 48.74 ± 0.13% (48.75% theoretical); Br, 51.26 ± 0.12% (51.25% theoretical).

Sodium bromide was Merck Suprapur reagent (min. 99.9%). Before use, it was progressively heated up to fusion under gaseous HBr atmosphere. Excess of HBr was then removed from the melt by argon bubbling.

The appropriate amounts of $EuBr_2$ and NaBr 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. All chemicals were handled inside a high purity argon atmosphere in glove box (water content < 1 ppm).

2.2. Measurements

Temperature and enthalpy of phase transitions were determined with a Calvet-type Setaram DSC 121 differential scanning calorimeter. The calibration of experimental temperature scale was performed with metals of minimum 5 N purity (In, Sn, Pb, Zn, Sb, Al), which temperatures of fusion cover working temperature range of apparatus. In order to avoid the possible influence of heating (cooling) rate on measured temperatures the same procedure – calibration with the above metals – was repeated at different heating rates and the correction temperature coefficients, which apply for any heating (cooling) rate, were calculated accordingly. The enthalpy calibration of the DSC 121 was obtained by Joule effect. The temperature scale and sensitivity were subsequently checked with standard materials. Deviations were found to be less than ±1 K and ±1% with respect to temperature and enthalpy, respectively.

Samples under investigation (300–500 mg) were contained in vacuum-sealed quartz ampoules. Experiments conducted at heating and cooling rates ranging 1–5 K min^{-1} on samples with 19 different compositions.

Electrical conductivity measurements were carried out in the capillary quartz cell described in details elsewhere [6], and calibrated with molten NaCl melt [7]. All measurements were carried out under static argon atmosphere. The accuracy of measurements was estimated at ±2%.

Electronic reflectance spectra of powdered samples were measured with a Carry 500 Scan UV–Vis–NIR spectrophotometer (Varian) in the 10000–50000 cm^{-1} range. The scan rate was 3614 cm^{-1} min^{-1}, data interval 1 nm, slit width 2 nm.

3. Results and discussion

3.1. Phase diagram

The $EuBr_2$–NaBr diagram was 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. The phase diagram of the $EuBr_2$–NaBr system (Fig. 1) was found to be of the simple eutectic type. The eutectic composition, $x(EuBr_2) = 0.546 \pm 0.002$, was determined accurately from the Tamman plot displayed in Fig. 2, assuming that no solid solutions were formed. The enthalpy of fusion at the eutectic composition is $\Delta_{fus}H_m = 16.5 \pm 0.7$ kJ mol^{-1}. The eutectic temperature determined from all appropriate DSC curves is $T_{eut} = 762 \pm 2$ K.

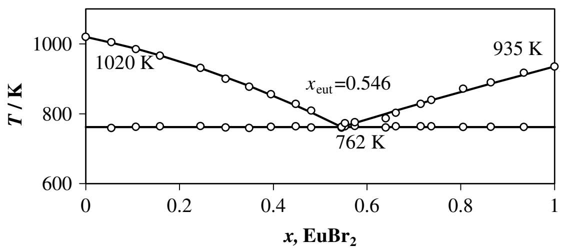

Fig. 1. Phase diagram of the $EuBr_2$–NaBr binary system.

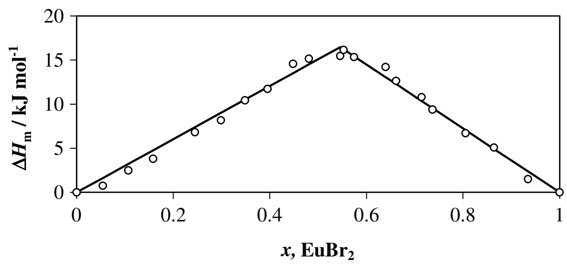

Fig. 2. Tamman construction for eutectic determination in the $EuBr_2$–NaBr system.

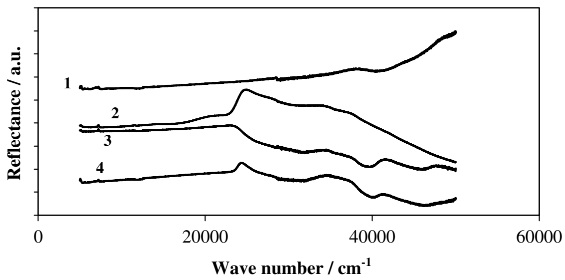

Fig. 3. Reflectance spectra of powdered samples: (1) NaBr; (2) $EuBr_2$; (3) mixture $x(EuBr_2) = 0.323$; (4) mixture $x(EuBr_2) = 0.756$.

Electronic reflectance spectra were recorded for several mixtures of $EuBr_2$ and NaBr in order to confirm the reliability of the constructed phase diagram. Fig. 3 compares the spectra of the NaBr and $EuBr_2$ components with those obtained for two $EuBr_2$–NaBr mixtures. The similar broad and intensive bands, observed both in $EuBr_2$ and the two $EuBr_2$–NaBr mixtures, can be related to the Laporte allowed $f \rightarrow d$ transitions of the $4f^7 \rightarrow 4f^65d^1$ origin in divalent europium ions [8–11]. No signs of IVCT (intervalence charge transfer) transition were detected as observed recently in europium chloride spectra [10,11]. Thus, the presence of the $EuBr_2$ characteristic bands in all mixtures confirms that the system is a simple eutectic type.

3.2. Electrical conductivity

Electrical conductivity measurements were performed over the entire composition range (in steps of ≈10 mol%) on $EuBr_2$–NaBr liquid mixtures, including the NaBr and $EuBr_2$ components.

The electrical conductivity of NaBr was found in excellent agreement with the reference value [12] critically evaluated by Janz [13] from several experimental sources [12,14–17]. At 1050 K, both values agree within 0.3%.

No experimental conductivity data were available in literature on $EuBr_2$ and separate investigations were conducted very recently [18]. The specific conductivity data of the $EuBr_2$–NaBr liquid mixtures were fitted by the polynomial equation (1):

$$\kappa = A + BT + CT^2 \tag{1}$$

the coefficients of which are listed in Table 1.

The plot in Fig. 4 shows the composition dependence of the electrical conductivity at 1050 K. This experimental isotherm indicates a smooth variation excluding the formation of any complex species in the melt, as it could be anticipated from the very simple phase diagram of the NaBr–$EuBr_2$ system.

Table 1
Specific conductivity $\kappa = A + BT + CT^2$ ($S\,m^{-1}$) of $EuBr_2$–NaBr melts

$x(EuBr_2)$	10^{-2} A ($S\,m^{-1}$)	10^1 B ($S\,m^{-1}\,K^{-1}$)	10^4 C ($S\,m^{-1}\,K^{-2}$)	Temperature range (K)
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	−3.5047	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
1.000	−3.5174	6.1114	−1.6799	943–1173

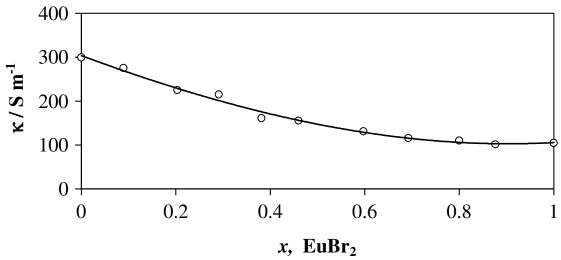

Fig. 4. Electrical conductivity isotherm of $EuBr_2$–NaBr liquid mixtures at 1050 K: open circles – experimental data, solid line – polynomial fitting.

The specific conductance decreases at increasing $EuBr_2$ concentration, with significantly larger conductivity changes in the sodium bromide-rich region.

4. Conclusions

The phase diagram of the $EuBr_2$–NaBr binary system was established from DSC investigations. It represents a typical example of simple eutectic system with the eutectic composition, $x(EuBr_2) = 0.546$, and eutectic temperature 762 K.

Electronic reflectance spectra recorded for several mixtures of $EuBr_2$ and NaBr confirmed the reliability of the constructed phase diagram. The presence of the $EuBr_2$ characteristic bands in all mixtures confirms that the system is a simple eutectic type.

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