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Thermodynamic and structural properties of high temperature solid and liquid $EuBr_2$

L. Rycerz [a], S. Gadzuric [b,d], E. Ingier-Stocka [a], R.W. Berg [c], M. Gaune-Escard [d,*]

[a] *Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland*

[b] *Faculty of Natural Science, Department of Chemistry, University of Novi Sad, Trg. D. Obradovica 3, 21000 Novi Sad, Serbia and Montenegro*

[c] *Department of Chemistry, DTU (Technical University of Denmark), Kemitorvet, Building 207, DK-2800 Lyngby, Denmark*

[d] *Ecole Polytechnique, CNRS UMR 6595, Technopole de Chateau-Gombert, 5 rue Enrico Fermi, 13453 Marseille cedex 13, France*

Abstract

Heat capacity of solid and liquid $EuBr_2$ was measured by differential scanning calorimetry 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, $S^0_m(EuBr_2, s, 298.15\ K)$, and the standard molar enthalpy of formation, $\Delta_{form}H^0_m(EuBr_2, s, 298.15\ K)$, the thermodynamic functions of europium dibromide were calculated up to $T = 1300$ K. Preliminary structural investigations were conducted both by reflectometry and Raman spectroscopy.

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1. Introduction

Lanthanides are a product of nuclear fission in nuclear reactors. Thus spent nuclear fuel contains lanthanides, which must be removed during its reprocessing. Molten salt technology is a promising route for this reprocessing, which involves rare earth halides and their mixtures with alkali halides. Such an application requires the characterisation of the basic physicochemical properties of both pure lanthanide halides and their mixtures with alkali halides. However, this knowledge is scarce. In addition, when experimental data are available from different sources, they are often in poor agreement. Thus a general and systematic research program focused on lanthanide halides and their systems with alkali halides has been started.

A substantial amount of thermochemical data has been reported for lanthanide dichlorides, but as with the trihalides, only estimated values are available for lanthanide dibromides [1–3]. Thermodynamic data on europium(II) bromide, i.e. temperature and enthalpy of fusion [1,2,4], entropy at 298 K and enthalpy of formation of solid $EuBr_2$ at 298 K [5,6] as well as heat capacity of solid and liquid europium(II) bromide [6] are estimated values. Thus, the experimental determination of these thermodynamic properties is of considerable importance and was performed in the present work.

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[*] Corresponding author. Tel.: +33 (0)4 91 10 6887; fax: +33 (0)4 91 11 7439.

E-mail address: mge@polytech.univ-mrs.fr (M. Gaune-Escard).

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2. Experimental

2.1. Chemicals

Europium(II) bromide was synthesized from the oxide Eu_2O_3 (Aldrich 99.9%) by a modified Haschke and Eick method [7]. Its 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).

All manipulations with $EuBr_2$, being extremely hygroscopic, were performed in an argon glove box with a measured volume fraction of water of about 2×10^{-6} and continuous gas purification by forced recirculation through external molecular sieves.

2.2. Measurements

Temperature, enthalpy of fusion and heat capacity of $EuBr_2$ 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. The apparatus and the procedure for enthalpy measurements were described in detail in [8,9].

The so-called 'step method' used for C_p measurements was already described [10,11]. In this method, small heating steps are followed by isothermal delays, when thermal equilibrium of the sample is achieved. In our experiments each heating step of 5 K was followed by 400 s of isothermal delay. The heating rate was 1.5 K min^{-1}. All experiments were started at 300 K and were performed up to 1100 K. The mass difference of the quartz cells in a particular experiment did not exceed 1 mg (mass: 400–500 mg). The mass of the samples was 300–500 mg.

The fusion temperature and enthalpy of $EuBr_2$ were also determined from DSC experiments conducted at heating and cooling rates ranging 1–5 K min^{-1}.

Electronic reflectance spectra of powdered samples were measured with a Cary 500 Scan UV–Vis–NIR spectrophotometer (Varian) in the 10 000–50 000 cm^{-1} range. The scan rate was 3614 cm^{-1} min^{-1}, with a data interval of 1 nm, and a slit width of 2 nm.

Raman spectra were measured with a DILOR-XY 800 mm focal length multichannel spectrometer with both macro- and microscope entrances, horizontal Ar^+-ion laser excitation (514.5 nm, 300 mW, vertically polarized), and liquid N_2-cooled CCD light detection. Rayleigh scattered light was filtered off with a double pre-monochromator (slits 200 μm). The Raman spectral resolution was about 4 cm^{-1} and the precision about 1–2 cm^{-1}, obtained by calibration with Raman lines from crystalline S_8.

All experimental procedures are detailed in [12]. The low temperature spectra were achieved by recording directly from the capillary ampoule immersed into boiling N_2 in an unsilvered Dewar jar, avoiding ice formation by a lid and outside condensation of moisture by blowing a stream of heated air around the jar.

3. Results and discussion

Only one endothermic peak, corresponding to melting, was observed in each thermogram. The melting temperature was determined as the average value of the onset temperature, T_{ons}, obtained from several runs on eight samples. Fusion of $EuBr_2$ was found to occur at 941 K with a corresponding enthalpy change of 22.2 ± 0.4 kJ mol^{-1}. To the best of our knowledge these data are new and constitute the first experimental direct determination of the melting point and ΔH^0_{m} for $EuBr_2$. The found experimental temperature validates the early estimate, 940 K, given by Brewer [4] more reliably than other literature estimations [1,2] reporting 950 and 975 K, respectively. Brewer [4] also gave an estimate of the melting enthalpy ΔH^0_{m} (25.1 kJ mol^{-1}). This value is also reported in several compilations [1,2] and fits well in the range of the experimental enthalpy.

Experimental heat capacity results also constitute original data sets on $EuBr_2$, and these data are plotted against temperature in Fig. 1. In the solid range, they are well represented by the first order polynomial (1) in J mol^{-1} K^{-1}:

$$C^0_{p,\text{m}} = 73.79 + 8.31 \cdot 10^{-3} T \qquad (1)$$

with a standard deviation ±2.25 J mol^{-1} K^{-1}.

On the liquid range, experimental heat capacity data were averaged to the constant value $C^0_{p,\text{m}} = 105.39 \pm 3.32$ J mol^{-1} K^{-1}. The only literature source reporting heat capacity of solid $EuBr_2$ [6] was based on an estimate and was also plotted in Fig. 1 (dashed line). These estimated data are systematically larger in the whole temperature range (for example: 8% at 300 K, 13% at 870 K).

The thermodynamic functions of $EuBr_2$ were calculated up to 1300 K using our experimental melting temperature and enthalpy together with heat capacity data. The value $C^0_{p,\text{m}}(EuBr_2, \text{s}, 298.15\ \text{K})$ was determined by

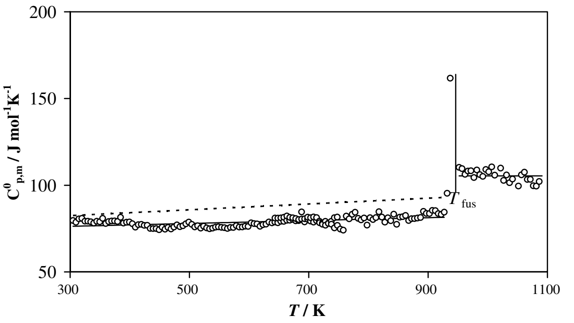

Fig. 1. Molar heat capacity of $EuBr_2$: open circles – experimental results, solid line – polynomial fitting of experimental results, dashed line – literature estimations.

extrapolation of our results to 298.15 K. The estimated value of standard entropy $S^0_m(EuBr_2, s, 298.15\ K) = 136.92\ J\ mol^{-1}\ K^{-1}$ was taken from literature [5].

The $C^0_{p,m} = f(T)$ equation (1) was then used to calculate enthalpy increments $H^0_m(T) - H^0_m(298.15\ K)$ in kJ mol^{-1}, entropy $S^0_m(T)$ and Gibbs energy functions $(G^0_m(T) - H^0_m(298.15))/T$ in J K^{-1} mol^{-1} both for solid as well as liquid $EuBr_2$. The values of these functions at selected temperatures are presented in Table 1.

The thermodynamic functions of $EuBr_2$ formation can be calculated as a function of temperature from the above thermodynamic functions. The formation of $EuBr_2$ from the elements is described by the reaction:

$$Eu(s,l) + Br_2(l,g) = EuBr_2(s,l) \qquad (2)$$

relating the thermodynamic functions of $EuBr_2$ formation to thermodynamic functions of metallic Eu and bromine Br_2. These functions for Eu(s,l) and Br_2(l,g) were calculated using literature data for $C^0_{p,m}$ and $S^0_m(298.15\ K)$ [13]. The enthalpy of $EuBr_2$ formation at 298.15 K, $\Delta_{form}H^0_m(EuBr_2, s, 298.15\ K) = -843.50$ kJ mol^{-1}, also required in this calculation, was taken from literature [5].

Different phase changes occur in this system described by reaction (2): boiling of bromine at 331 K (enthalpy of 29.56 kJ mol^{-1}), melting of $EuBr_2$ at 941 K, solid–solid phase transition of europium at 765 K (enthalpy of 0.2 kJ mol^{-1}) and fusion of Eu at 1096 K with enthalpy of 9.2 kJ mol^{-1}. These changes were taken into account in calculation of formation enthalpy $\Delta_{form}H^0_m$ (kJ mol^{-1}) and Gibbs formation energy $\Delta_{form}G^0_m$ (kJ mol^{-1}). The values of thermodynamic functions of $EuBr_2$ formation at selected temperatures are collected in Table 1.

To document the purity, electronic reflectance spectra were recorded for $EuBr_2$ samples that have been previously melted, homogenised and solidified. The band positions observed may correspond to sixfold or eightfold coordination of bromide ions around Eu^{2+}

Table 1
Thermodynamic functions of $EuBr_2$ at selected temperatures from 298.15 to 1300 K

T/K	$C^0_{p,m}(T)$/ J K^{-1} mol^{-1}	$S^0_m(T)$/ J K^{-1} mol^{-1}	$-(G^0_m(T) - H^0_m(298.15))$/ T/J K^{-1} mol^{-1}	$H^0_m(T) - H^0_m(298.15)$/ kJ mol^{-1}	$\Delta_{form}H^0_m(T)$/ kJ mol^{-1}	$\Delta_{form}G^0_m(T)$/ kJ mol^{-1}
298.15	76.27	136.91	136.91	0.00	−753.7	−725.8
300	76.28	137.39	136.92	0.14	−753.7	−725.6
331	76.54	144.90	137.32	2.51	−754.6	−722.7
331	76.54	144.90	137.32	2.51	−784.1	−722.7
400	77.12	159.45	139.92	7.81	−783.3	−710.0
500	77.95	176.74	145.61	15.56	−782.1	−691.8
600	78.78	191.03	152.03	23.40	−781.0	−673.8
700	79.61	203.23	158.49	31.32	−779.9	−656.1
765	80.15	210.33	162.60	36.51	−779.2	−644.6
765	80.15	210.33	162.60	36.51	−779.4	−644.6
800	80.44	213.92	164.77	39.32	−779.0	−638.5
900	81.27	223.44	170.77	47.41	−778.1	−621.0
941	81.61	227.07	173.14	50.75	−777.8	−613.8
941	105.39	250.69	173.14	72.97	−755.6	−613.8
1000	105.39	257.10	177.91	79.19	−753.8	−605.0
1096	105.39	266.76	185.27	89.30	−751.1	−590.8
1096	105.39	266.76	185.27	89.30	−760.3	−590.8
1100	105.39	267.14	185.57	89.72	−760.2	−590.2
1200	105.39	276.31	192.75	100.26	−757.2	−574.9
1300	105.39	284.75	199.51	110.80	−754.3	−559.8

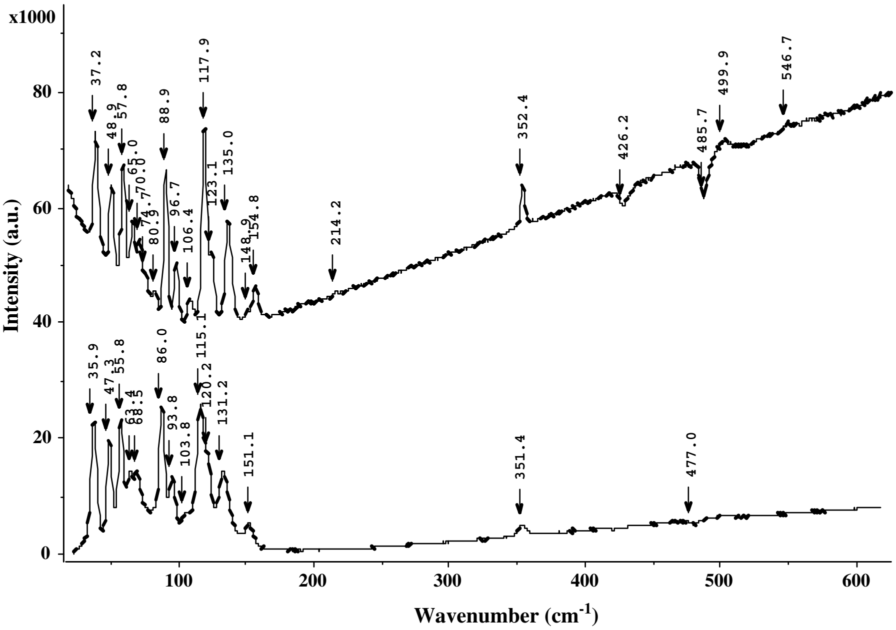

Fig. 2. Raman spectrum of polycrystalline $EuBr_2$ in capillary container, obtained at 25 °C (room temperature, below) and at −196 °C (immersed in liquid nitrogen temperature, top). Laser: 514.5 nm. Power: 300 mW. Resolution: 4 cm^{-1}. Precision: 1–2 cm^{-1}.

[14,15]. The broad, intensive bands can be related to the Laporte allowed f → d transitions of the $4f^7 \rightarrow 4f^65d^1$ origin in divalent europium ions [14–17]. No sign was observed of any IVCT (intervalence charge transfer transition) like what was found recently in the spectra of europium chlorides [16,17].

To characterise the $EuBr_2$ further, Raman spectra at room and low temperature were recorded. As seen in Fig. 2 at least 10 bands were observed below 200 cm^{-1}. According to Haschke and Eick [7], and Sanchez et al. [18], $EuBr_2$ crystallises in the tetragonal $SrBr_2$ structure belonging to space group P4/n (No. 85), with $a = 11.563 \pm 0.003$ Å, $c = 7.091 \pm 0.002$ Å and $Z = 10$. There are two crystallographically different Eu^{2+} positions in the structure that are both eightfold coordinated by Br^- ions, in a more or less regular square antiprismatic geometry [18]. This means that the primitive cell has a high number of vibrational modes (87 optic modes originating from 30 atoms with each 3 positional librations minus 3 acoustic modes), many of which are Raman active. In this way it seems understandable to observe such a high number of Raman bands. According to Giricheva et al. [19], a free $EuBr_2$ molecule has its symmetric stretching vibration at ~225 cm^{-1} and its bending vibration at ~40 cm^{-1}. In the condensed phase these modes are expected to occur at much lower frequencies due to the formation of the coordination polyhedra, thus explaining the overall appearance of the spectra in Fig. 2. In $SrBr_2$ with the same structure a similar complex of bands is found below 200 cm^{-1} [20]. This implies that the $EuBr_2$ bands above 200 cm^{-1} are non-fundamentals.

4. Conclusions

Temperature and enthalpy of fusion as well as heat capacity of solid and liquid $EuBr_2$ were determined. On the basis of these original data sets, the thermodynamic functions of europium dibromide were calculated up to 1300 K.

The reflectometry and Raman spectroscopy on the solid $EuBr_2$ samples have provided important new data for the identification. In the future we plan to complement these data with further determinations (Raman and EXAFS) over the temperature range of solid and liquid $EuBr_2$.

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