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The system $DyBr_3$–DyI_3

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Abstract

The system $DyBr_3$–DyI_3 has been studied by differential thermal analysis (DTA), and a regular solution behaviour has been observed. For the enthalpies of fusion of $DyBr_3$ and DyI_3 the values 46.4 ± 1.5 and 56.5 ± 1.5 kJ mol^{-1}, respectively, have been found. © 1997 Elsevier Science B.V.

Keywords: Dysprosium tribromide; Dysprosium triiodide; Enthalpy of fusion; Phase diagram

1. Introduction

Metal halide lamps are widely used for their high luminous efficiency and colour quality. To improve life time and colour stability in new generations of this type of lamps, thermodynamic modelling of the chemical processes in the lamp is helpful, since it gives information about the gaseous species present in the arc tube over the condensed phase, and about the activities of the molten halides in equilibrium with the vapour [1,2]. To that purpose the thermodynamic properties of the pure phases, and the phase relations in the relevant systems have to be known.

The present work is part of a programme to provide accurate thermodynamic properties of the rare earth halides. In a previous paper [3], a determination of the enthalpies of formation of $DyBr_3(s)$ and $DyI_3(s)$ has been described. The present paper deals with the phase relations in the binary system composed of these compounds.

2. Experimental

High-purity samples of $DyBr_3$ and DyI_3 were provided by Philips Lighting (Eindhoven, The Netherlands); the compounds have a faint yellow colour. Both $DyBr_3$ and DyI_3 have the BiI_3 structure at room temperature (rhombohedral; space group $R\bar{3}$); X-ray diffraction powder analysis of the samples showed no crystalline impurities. Chemical analyses of dysprosium were performed by complexometric titration with a standard EDTA solution and photometric detection; its precision is believed to be better than 0.1%. Bromide and iodide were determined by an argentometric titration with a standard $AgNO_3$ solution. The results of the analyses are given in Table 1.

Differential thermal analysis (DTA) was performed using a Bähr Thermoanalyse DTA 701 and a Mettler TA 13 apparatus. The very hygroscopic samples were weighed in proper compositions in an argon-filled glove box in which the H_2O content was less than about 1 ppm. Two different types of cups were used as the sample containers: one of molybdenum metal with

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Table 1
Analytical results: molar mass M, and mass fraction w

Compound	M (g mol^{-1})	$10^2 \cdot w$(Dy)		$10^2 \cdot w$(X) [a]	
		Found	Calculated	Found	Calculated
$DyBr_3$	402.2120	40.43±0.02	40.40	59.56±0.02	59.60
DyI_3	543.2134	29.93±0.02	29.91	69.84±0.07	70.09

[a] X - Br, I.

a screw cap and a gold ring as a seal (in Bähr apparatus), the other made of quartz with a thin, flattened bottom which was sealed after being filled with an argon pressure of about 13.3 kPa (in Mettler apparatus). Calibrations of temperature and calorimetric sensitivity were done with high-purity samples of Zn, Sb, Ag, and Au at the same heating rate. The DTA curves were taken at a rate of 10 K min^{-1} both by heating and cooling; several cycles (at least 3) were taken (after cooling), using the same sample in order to study the reproducibility of the processes. The temperatures were read as extrapolated onset temperatures, according to the ICTA convention [4], and (for the second peak of the solid solution) as extrapolated peak temperature [5].

3. Results

3.1. The phase diagram

The results of the measurements are given in Table 2. For the fusion temperatures of $DyBr_3$ and DyI_3 the values 1151.0 ± 1.5 and 1251.5 ± 1.5 K, respectively, were found. These temperatures have to be compared with the values 1154 ± 5 and 1228 ± 5 K from literature [6]. The solidus and the liquidus temperatures of the solid solutions were determined during heating of the samples; the temperatures obtained by cooling were about 10 K lower due to undercooling. At some temperatures resolution of the liquidus and solidus was difficult to judge, and again onset and peak temperatures were read.

Table 2
Solidus and liquidus temperatures of $DyBr_3$–DyI_3 solid solutions

DyI_3 (mol%)	Solidus temperature (K)	Liquidus temperature (K)
0	—	1151.1
10	1151	1160
35	1156	1171
50.0	1167	1183
59.5	1174	1190.5
70.0	1195	1213
80.0 [a]	1213	1225.5
90.0	1229	1242
100	—	1251.5

[a] In quartz.

3.2. Thermodynamic properties

$DyBr_3$(s) and DyI_3(s) are mutual soluble in all ratios. The measurements indicate a slight deviation of the ideal solution behaviour, and can be described by a regular solution model. Indeed, enthalpy of solution measurements in 0.1 mol dm^{-3} HCl(aq) of solid solutions with compositions 50, 65, and 85 mol% DyI_3, as described for the pure phases in a previous paper [3], do not show any deviation from

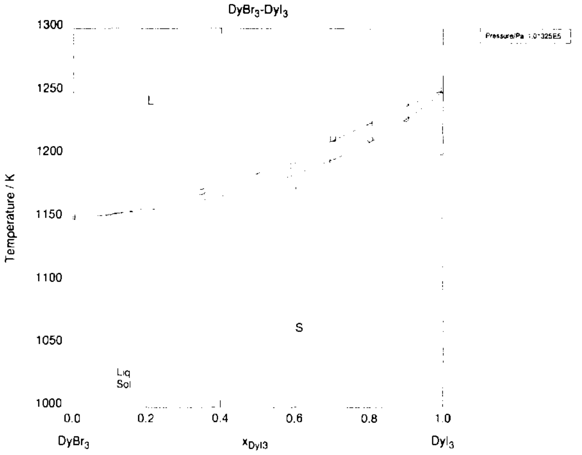

Fig. 1. The phase diagram of the $DyBr_3$–DyI_3 system; experimental points and calculated curve.

the values obtained with mixtures of the same composition within the accuracy of the measurements ($100\,\mathrm{J\,mol^{-1}}$). We thus assume no deviation of ideality in the solid state, and attribute the deviation entirely to that of the liquid solution. The regular behaviour can now be described with

$$\Delta_{\mathrm{mix}}H^0(\mathrm{liq}) = -4375x(1-x)\,\mathrm{J\,mol^{-1}}$$

The phase diagram calculated with the MTDATA programme [7], is shown in Fig. 1. Binary systems of rare earth halides with which this result could be compared, have not been found in the literature.

The enthalpies of fusion of $DyBr_3$ (rhombohedral) and DyI_3 have been obtained from the DTA-peaks (at least five determinations), after correction for the calorimetric sensitivity. The values obtained for $DyBr_3$ and DyI_3 were $\Delta_{\mathrm{fus}}H^0 = 46.4 \pm 1.5$ and $56.5 \pm 1.5\,\mathrm{kJ\,mol^{-1}}$, respectively. No data have been found in the literature with which these values can be compared.

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