ELSEVIER

Thermochimica Acta 338 (1999) 135–138

thermochimica acta

www.elsevier.com/locate/tca

The phase diagram of the system $NdBr_3(s)$–$NdI_3(s)$

E.H.P. Cordfunke[a], G.D. Elzinga[b], M.E. Huntelaar[b,*], P. van Vlaanderen[b]

[a]*University of Amsterdam, Institute of Molecular Chemistry, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

[b]*NRG, P.O. Box 25, 1755 ZG Petten, The Netherlands*

Received 14 June 1999; accepted 9 July 1999

Abstract

The system $NdBr_3(s)$–$NdI_3(s)$ has been studied by differential thermal analysis (DTA) and X-ray diffraction analysis. At room temperature, $NdBr_3(s)$ and $NdI_3(s)$ have an orthorhombic structure (space group Cmcm). For the lattice parameters, the values $a = 0.4131$ nm, $b = 1.2765$ nm, and $c = 0.9192$ nm, and $a = 0.4296$ nm, $b = 1.4060$ nm, and $c = 0.9971$ nm are found, respectively. A phase transition in $NdI_3(s)$ at (859.3 ± 0.6) K was observed, resulting in a complex phase diagram of a eutectic system and two solid-solubility regions.

Keywords: Neodymium triiodide; Neodymium tribromide; Phase diagram; X-ray powder diffraction; DTA; $NdBr_3(s)$; $NdI_3(s)$

1. Introduction

Rare earth metal trihalides have found several important applications in the chemical industry. For instance, they are used in combination with an alkali metal halide in discharge lamps to obtain the desired colour of the light produced. Often, combinations of an alkali metal halide and a mixture of a rare earth tribromide and triiodide are applied, and a knowledge of the phase relationships in these systems is required to model the chemical equilibria in these lamps. Unfortunately, most of the phase relationships in these systems have not been investigated, and, as a consequence, assumptions have to be made in this respect. In a previous paper, we reported a study of the system $DyBr_3(s)$–$DyI_3(s)$, which showed an almost ideal solution behaviour [1]. In the present paper, the system $NdBr_3(s)$–$NdI_3(s)$ is dealt with, showing a much more complex behaviour.

2. Experimental

The $NdBr_3(s)$ and $NdI_3(s)$ samples were provided by Philips Lighting BV (Eindhoven, The Netherlands). At room temperature, both $NdBr_3(s)$ and $NdI_3(s)$ have an orthorhombic structure, space group Cmcm. X-ray diffraction powder analysis (Guinier de Wolff, Cu-K$\alpha_{1,2}$, Enraf-Nonius, type FR 552) of both samples contained in sealed polythene envelopes, showed no crystalline impurities. Since there were no data available on the crystal structure of $NdBr_3(s)$, lattice parameters were determined by X-ray diffraction, using Cu-Kα_1 radiation, and a mixture of Si–W

*Corresponding author. Tel.: +31-224-56-4052; fax: +31-224-56-188

E-mail address: huntelaar@nrg-nl.com (M.E. Huntelaar)

0040-6031/99/$ – see front matter
PII: S0040-6031(99)00218-X

Table 1
Unit cell parameters of $NdBr_3$(s) and NdI_3(s) at room temperature

Compound	Unit cell axis (nm)	Space group	Density (g cm^{-3})
$NdBr_3$(s)	$a = 0.4131$ $b = 1.2765$ $c = 0.9192$	Cmcm	5.327
NdI_3(s)	$a = 0.4296$ $b = 1.4060$ $c = 0.9971$	Cmcm	5.807

as an internal standard. The 4Θ values were measured at least three times, using a Nonius Guinier viewer coupled to a Sony Magnoscope which determines the 4Θ at 0.001 mm. The results are listed in Table 1.

Differential thermal analysis (DTA) was performed using a Mettler TA13 apparatus. The handling procedures of the very hygroscopic halide samples were done in a glove box filled with recirculating, purified argon with an average mass fraction of water and oxygen of $<5 \times 10^{-6}$. Previously outgassed (12 h at 1273 K in 5% H_2–95% Ar atmosphere) quartz ampoules were used as sample containers. After the containers had been loaded, they were evacuated and sealed. 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 using the same sample, in order to study the reproducibility of the processes. The temperatures were read as extrapolated onset temperatures (the solid state transition and the solidus), according to the ICTA convention [2], the liquidus temperatures were read as extrapolated peak temperatures [3]. Both the temperature and the calorimetric sensitivity of the DTA apparatus were calibrated using certified reference materials of ICTA and high purity metals (Sn, Cd, Pb, Zn, Te, Al, and Ag).

3. Results

The results of the DTA measurements are given in Table 2. For the temperatures of fusion of $NdBr_3$(s) and NdI_3(s), the values (953.2 ± 0.3) K and (1058.7 ± 0.6) K were found, respectively. These temperatures have to be compared with the values 955 K, for $NdBr_3$(s) [4]; and 1057 K [5], 1060 K [6], and 1058 K [7] for NdI_3(s). For NdI_3(s), a reversible phase transition was found at (859.3 ± 0.6) K, in fair agreement with the value 847 K found previously [8].

At room temperature, NdI_3(s) is orthorhombic (space group Cmcm), and isostructural with $NdBr_3$(s). The unit cell parameters of both compounds, as determined in the present study, are given in Table 1. The results for NdI_3(s) are in good agreement with the literature [9,10], whereas for $NdBr_3$(s), no data have been found. The high-temperature phase of NdI_3(s), which is stable from 859.3 K up to the fusion temperature, is rhombohedral (space group R-3), with $a = 0.7610$ nm and $c = 2.089$ nm [11].

The tentative phase diagram of the system $NdBr_3$(s)–NdI_3(s), based on the results in Table 2,

Table 2
Transition temperatures of the $NdBr_3$(s)–NdI_3(s) system

Mole fraction NdI_3(s)	Phase transition temperature/K	Solidus temperature/K	Liquidus temperature/K
0.0000	–	–	953.2 ± 0.3
0.0517	–	921.4 ± 1.1	949.2 ± 0.3
0.1334	–	898.4 ± 0.0	929.5 ± 0.7
0.1814	–	–	921.2 ± 0.3
0.2461	–	–	–
0.3528	–	893.4 ± 0.0	–
0.4713	–	891.7 ± 0.7	–
0.5290	885.0 ± 0.7	892.5 ± 0.9	933.0 ± 0.9
0.5914	872.4 ± 1.4	888.9 ± 2.6	947.2 ± 0.6
0.6710	863.2 ± 0.5	883.8 ± 2.6	977.9 ± 0.2
0.7169	857.5 ± 1.0	–	989.0 ± 2.4
0.7998	855.2 ± 0.3	–	1015.4 ± 0.0
0.9080	851.1 ± 1.3	–	1037.7 ± 0.7
1.0000	859.3 ± 0.6	–	1058.7 ± 0.6

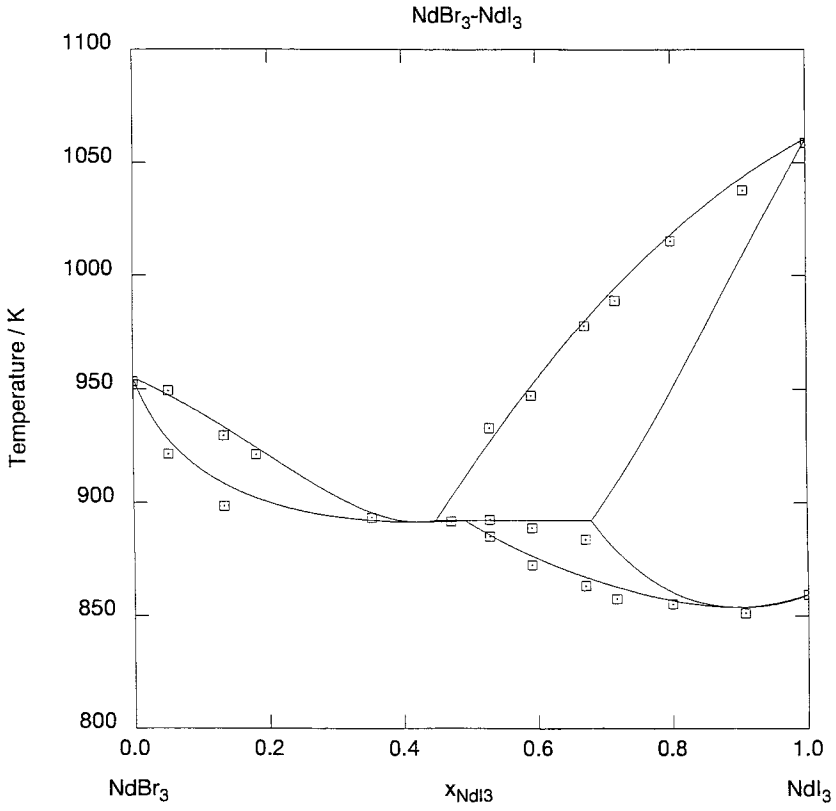

Fig. 1. Tentative phase diagram of the system $NdBr_3$(s)–NdI_3(s). The experimental points are shown as open squares.

is given in Fig. 1. Only the transition temperatures of the heating curves were used since the temperatures obtained on cooling were lower due to undercooling. At some compositions (near special points), the resolution of the transitions was difficult to judge.

X-ray analysis of two compositions (mole fractions NdI_3(s) of 0.4713 and 0.5290), after being molten and cooled down slowly, showed two phases, which means that a miscibility gap is present. The critical point of the miscibility gap was estimated by quenching in ice water the fully equilibrated samples from temperatures 843, 473 and 373 K. X-ray analysis of the quenched samples showed only one phase; therefore, the critical point of the miscibility gap is located between 298 and 373 K. The phase boundaries of the miscibility gap at room temperature were determined by measuring the unit cell volumina of the solid solutions at various compositions (Table 3).

Table 3
Unit cell volumina in $NdBr_3$(s)–NdI_3(s) system at various compositions

Mole fraction NdI_3(s)	Cell volume nm^3	Number of phases
0.0000	0.47877 ± 0.00004	1
0.0517	0.48348 ± 0.00002	1
0.1334	0.49436 ± 0.00006	1
0. 1814	0.50328 ± 0.00001	1
0.246 1	0.51543 ± 0.00002	1
0.3528	0.53008 ± 0.00001	1
0.4662	0.53333 ± 0.00024[a]	2
0.4662	0.55922 ± 0.00003[b]	2
0.6710	0.57028 ± 0.00003	1
0.7169	0.57477 ± 0.00004	1
0.7998	0.58309 ± 0.00002	1
0.9080	0.59210 ± 0.00003	1
1.0000	0.60045 ± 0.00001	1

[a] Value given for $NdBr_3$(s) phase.
[b] Value given for NdI_3(s) phase.

Extrapolation of the values from the NdI_3(s)-side to 0.55922 nm^3 results in a composition with a mole fraction NdI_3(s) of 0.546, and extrapolating the values from the $NdBr_3$(s)-side to 0.53333 nm^3 results in a composition of 0.376.

The phase diagram clearly owes its complicated character to the phase transition in NdI_3(s), resulting in partial dissolution of orthorhombic $NdBr_3$(s) into rhombohedral NdI_3(s) (solid solution with a minimum). This phase behaviour results in a complex phase diagram of a eutectic system and two solid-solubility regions.

Acknowledgements

The authors are grateful to Dr. Jos Suijker of Philips Lighting BV, Eindhoven, The Netherlands, for providing the high-purity $NdBr_3$(s) and NdI_3(s) samples.

References

[1] E.H.P. Cordfunke, R.J.H. Blacquière, Thermochim. Acta 298 (1997) 195–197.
[2] G. Lombardi, For Better Thermal Analysis, 2nd ed. ICTA Rome, 1980.
[3] M.E. Huntelaar, E.H.P. Cordfunke, A. Kok-Scheele, unpublished results.
[4] A.S. Dworkin, M.A. Bredig, J. Phys. Chem. 67 (1963) 2499–2500.
[5] F.H. Spedding, A.H. Daane, Metal. Rev. 5 (1960) 297.
[6] A.S. Dworkin, M.A. Bredig, J. Phys. Chem. 67 (1963) 697–698.
[7] L.B. Asprey, T.K. Keenan, F.H. Kruse, Inorg. Chem. 3 (1964) 1137.
[8] L.F. Druding, J.D. Corbett, J. Am. Chem. Soc. 83 (1961) 2462.
[9] JCPDS-ICDD, file 18-854 (1995).
[10] H. Bärnighausen, private communication (1977), quoted in H.P. Beck, E. Glacirow, Z. anorg. allg. Chem. 453 (1977) 79–92.
[11] R.G. Haire, J.P. Young, J. Y Bourges, Rare Earths Mod. Sci. Technol. 2 (1980) 159–164.