Short Communications

On the Homogeneity Ranges of LaB₆, EuB₆ and SmB₆

YU. B. PADERNO * and T. LUNDSTRÖM

Institute of Chemistry, Box 531,
S-751 21 Uppsala, Sweden

The width of the homogeneity ranges of the rare earth hexaborides has been determined in only a few cases.¹ For SmB₆ a relatively large decrease has been found in the cell dimension with decreasing metal content,² which has been taken to indicate the occurrence of metal vacancies in the boron-rich compositions, a conclusion supported by density measurements. For LaB₆ no cell dimension variations have been found.^{3,4} Johnson and Daane³ reported that the range of homogeneity of cubic LaB₆ extends from La_{0.99}B₆ to La_{0.82}B₆ although the *a* axis was unchanged. Storms and Mueller⁴ concluded that two phases occur, denoted LaB₆ and LaB₉, which have the same X-ray diffraction pattern (as regards intensities and cell dimensions), although the phases differ in colour and thermodyna-

mic properties. Iso-structural non-stoichiometric Th_{1-x}B₆ has, however, been studied in detail using neutron diffraction techniques and density measurements.⁵ For this compound it was demonstrated that thorium vacancies occur up to *x*~0.22 and that the unit cell volume increases with increasing number of thorium vacancies.

In the present work, the hexaborides were prepared by reaction in vacuum between rare earth sesqui-oxide (RE₂O₃) and boron (so-called boro-thermal reduction) at 1700–1800 °C for approximately 4 h according to

The compositions Sm_{0.97}B₆ and Sm_{0.94}B₆ were obtained from SmB₆ and Sm_{0.9}B₆ in the required proportions using ZrB₂ crucibles at 1800 °C for 4h. The unit cell dimensions were determined using a Guinier-Hägg powder X-ray camera with strictly monochromatic CuKα₁ radiation (*λ*=1.540598 Å) and zone-refined silicon as an internal calibration substance (*a*=5.431065 Å). The unit cell dimensions were least-squares refined using a local program.⁶ Most of the samples were analysed chemically. The boron and RE content of the borides was determined using conventional mannitol and EDTA titration respectively.

The results of the cell dimension determinations (including standard deviations) and chemi-

* On leave from Institute of Materials Problems, Ukrainian Academy of Sciences, Krzyzhanovskii Street 3, 252142 Kiev, USSR.

Table 1. Chemical analyses and cell dimensions for SmB₆ samples.

Composition	Chemical analyses		Cell dimensions <i>a</i> (Å)	<i>V</i> (Å ³)
	% Sm	% B		
SmB ₆	69.76	30.19	4.1334(2)	70.62(1)
Sm _{0.97} B ₆ ^a	n.a.	n.a.	4.1317(2)	70.53(1)
Sm _{0.94} B ₆ ^a	n.a.	n.a.	4.1301(2)	70.45(1)
Sm _{0.90} B ₆	67.1	32.2	4.1280(2)	70.35(1)
Sm _{0.89} B ₆	67.35	32.49	4.1272(1)	70.30(1)
Sm _{0.81} B ₆	65.0	34.4	4.1281(1)	70.35(1)
Sm _{0.79} B ₆	64.36	35.34	4.1272(2)	70.30(1)
Sm _{0.71} B ₆	62.17	37.63	4.1277(1)	70.33(1)

^a Prepared from SmB₆ and Sm_{0.90}B₆ (master alloys).

Fig. 1. The unit cell parameter a of $\text{Sm}_{1-x}\text{B}_6$ as a function of x .

cal analyses are in Tables 1–3. The X-ray photographs were taken at a temperature of $(21 \pm 1)^\circ\text{C}$. The uncertainty in the temperature determination introduces a relative error of $5/10^6$, that can be neglected in comparison with

one standard deviation.

The cell dimensions and chemical analyses for SmB_6 are given in Fig. 1 and Table 1. The cell parameter of SmB_6 decreases linearly from 4.1337 Å at the stoichiometric composition to 4.1276 Å at the composition $\text{Sm}_{0.89}\text{B}_6$ (Fig. 1). In samples with higher boron content the cell parameter of SmB_6 is constant indicating the occurrence of a two-phase regime. A considerable excess of boron was required for the SmB_{66} diffraction lines to occur in the powder pattern of a boron-rich sample due to the low scattering power of SmB_{66} . In boron-rich samples, prepared by arc-melting mixtures of $\text{Sm}_{0.90}\text{B}_6$ and crystalline boron and subsequently by heat treating the alloy at 1800°C for 8 h, SmB_{66} and SmB_6 occurred simultaneously, the latter with $a=4.1274(3)$ Å (see Table 3). The unit cell dimension of stoichiometric SmB_6 in the present study is in close agreement with the values reported in other recent investigations.⁷⁻⁹

The present results differ significantly from those reported by Niihara² for samples prepared at 1650°C using the same method of synthesis as

Table 2. Chemical analyses and cell dimensions for some LaB_6 and EuB_6 samples.

Composition	Chemical analyses		Cell dimensions a (Å)
	% La	% B	
LaB_6	68.2	31.7	4.1563(1)
$\text{La}_{0.94}\text{B}_6$	66.9	33.0	4.1565(1)
$\text{La}_{0.9}\text{B}_6$	65.4	34.4	4.1561(2)
$\text{La}_{0.81}\text{B}_6$	63.1	36.4	4.1562(2)
$\text{La}_{0.75}\text{B}_6$	61.2	38.4	4.1567(2)
EuB_6	n.a. ^a	n.a.	4.1844(5) ^b
$\text{Eu}_{0.79}\text{B}_6^c$	64.77	35.10	4.1849(2)

^a Stoichiometric. ^b As measured with the Debye-Scherrer technique. ^c After arc-melting of the EuB_6 sample.

Table 3. Cell dimensions of phases in two-phase regimes. The samples were heat-treated at 1800°C for 8 h.

Phases in equilibrium	Phase	Cell dimensions (Å)
$\text{SmB}_{66} + \text{Sm}_{1-x}\text{B}_6$	SmB_{66}	$a=23.4683(5)$
	$\text{Sm}_{1-x}\text{B}_6$	$a=4.1274(3)$
$\beta\text{-rh. B} + \text{La}_{1-x}\text{B}_6$	$\beta\text{-rh. B}$	$a=10.929(1)$
		$c=23.821(3)$
	$\text{La}_{1-x}\text{B}_6$	$a=4.1565(1)$
$\beta\text{-rh. B} + \text{Eu}_{1-x}\text{B}_6$	$\beta\text{-rh. B}$	$a=10.928(2)$
		$c=23.823(4)$
	$\text{Eu}_{1-x}\text{B}_6$	$a=4.1849(2)$

in this work. Niihara reported a cubic unit cell dimension of 4.1305 Å for stoichiometric SmB_6 and a non-linear decrease to 4.1278 Å for the composition $\text{Sm}_{0.68}\text{B}_6$. It is not easy to understand the large difference between Niihara's results and ours, in particular not the width of the homogeneity range. The temperatures used are nearly the same. The smaller unit cell of stoichiometric SmB_6 , reported by Niihara, might be due to impurities of other rare earth elements and/or the grinding of crystalline boron in a sardonyx mortar prior to heat treatment. According to our experience, such a procedure contaminates the sample with abraded particles from the mill. These particles may then react with the sample at the high temperatures of the heat treatment.

Stoichiometric SmB_6 displays valence fluctuations between Sm^{3+} and Sm^{2+} with a nearly temperature independent concentration ratio.¹⁵ Paderno *et al.*⁹ have observed that the main part of the valence change in $\text{Sm}_{1-x}\text{B}_6$ occurs in the composition region $x=0.0$ to $x=0.1$, which closely coincides with the region of variable cell dimensions as determined in the present investigation.

Table 2 shows that the average of the cubic unit cell parameter for LaB_6 is 4.1564(2) Å and that no significant variations occur within the homogeneity range. This result is in agreement with several recent reports.^{4,10,11} The chemical analyses, however, indicate a variable composition (B/La ratio, see Table 2) for LaB_6 . The structural mechanism behind the compositional changes has not been established. Since the cell dimensions do not change significantly with composition, it does not seem probable that the composition is changed by the occurrence of a variable number of vacancies at the metal position. An experimental study of this question is currently in progress.

The cell dimensions of phases participating in two-phase equilibria are given in Table 3. The unit cell dimensions of β -rhombohedral boron saturated with lanthanum and europium respectively do not differ significantly from those of the pure β -rh. boron used ($a=10.9276(5)$ Å; $c=23.8141(15)$ Å).¹² The solid solubility of lanthanum and europium respectively in β -rh. boron is consequently very small (probably less than 0.1 atomic per cent) while that of several of the transition elements has been found to lie between one and four atomic per cent.¹²

The cubic unit cell dimension $a=23.4683(5)$ Å for the samarium-rich compound SmB_{66} (see Table 3) is smaller than the value 23.474(2) Å for single-phase SmB_{66} reported by Soloviev and

Spear¹³ and also smaller than the value 23.487(3) Å for boron-rich SmB_{66} reported by Schwetz *et al.*¹⁴ It is notable that the unit cell parameter of SmB_{66} increases with decreasing samarium.

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