Synthesis of La$_X$Ce$_{1-X}$B$_6$ whiskers

M. CARLSSON, F. J. GARCÍA-GARCÍA, M. JOHNSSON
Department of Inorganic Chemistry, Stockholm University, S-106 91 Stockholm, Sweden

A. GULIAN
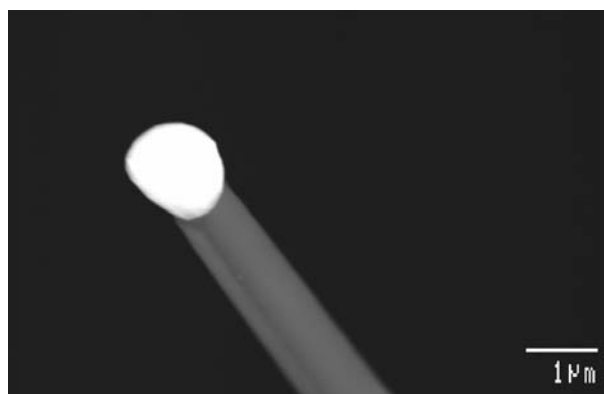*PAF/US Naval Research Laboratory, Washington, DC 20375, USA*

Lanthanum- and cerium hexaborides [1] belong to the family of Kondo-metals and have unique properties from the point of view of fundamental solid-state physics [2]. They have high values of the Seebeck coefficient and the electrical and thermal conductivities, obeying the Wiedemann-Franz law at low temperatures. Being used initially as coating materials for pink colouring of jewelleries and as low work-function materials for EM-guns, these hexaboride materials have the potential to revolutionize solid-state cryocooling [3] and single-photon detection [4]. Thin whiskers are additionally interesting for Kondo-mechanism size-effect studies [5].

The aim of this study was to investigate if La$_x$Ce$_{1-x}$B$_6$ ($0 \leq x \leq 1$) whiskers can be produced by the carbothermal vapour–liquid–solid (VLS) growth mechanism. The synthesis involves carbothermal reduction of La$_2$O$_3$, CeO$_2$ and B$_2$O$_3$ that were used as sources for La, Ce, and B, respectively. NaCl is added to the starting mixture in order to generate chlorides and oxochlorides that can transport La and Ce to the catalyst droplet. Ni was used as catalyst metal, see Table I, and is recycled during the synthesis by also forming chlorides. The whisker constituents dissolve in the catalyst droplet and La$_x$Ce$_{1-x}$B$_6$ whiskers precipitate when it becomes supersaturated. A proof of the catalytic action of Ni and the VLS mechanism is the presence of Ni droplets at whisker tips, see Fig. 1. Ni has proved earlier to be a good catalyst for both borides and carbides [6, 7]. The whisker growth terminates when the concentrations of reacting gas species near the droplets diminish below a certain level.
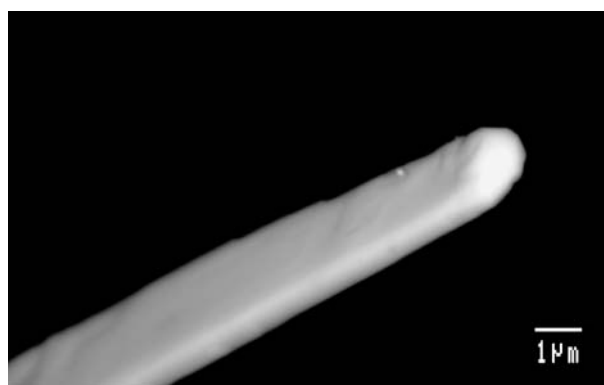
Several different whisker materials have been produced via the carbothermal vapour–liquid–solid growth
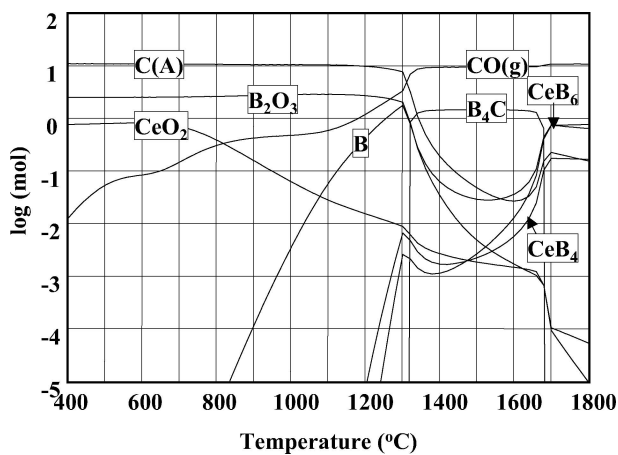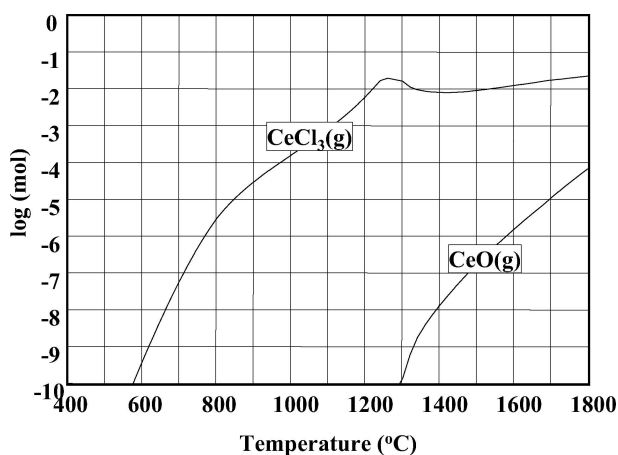

(a)

(b)

Figure 1 SEM micrographs in BSE-mode showing (a) a Ni catalyst droplet terminating a LaB$_6$ whisker synthesized at 1500 °C and (b) a La$_{0.53}$Ce$_{0.47}$B$_6$ whisker synthesized at 1800 °C.

mechanism; e.g. SiC, TiC, TaC, NbC (Ti, Ta, Nb)C, N, TiB$_2$ and B$_4$C [6–13]. The synthesis of LaB$_6$ whiskers by CVD methods has been reported before [14, 15], however, CeB$_6$ in the form of whiskers has not been reported in the literature.
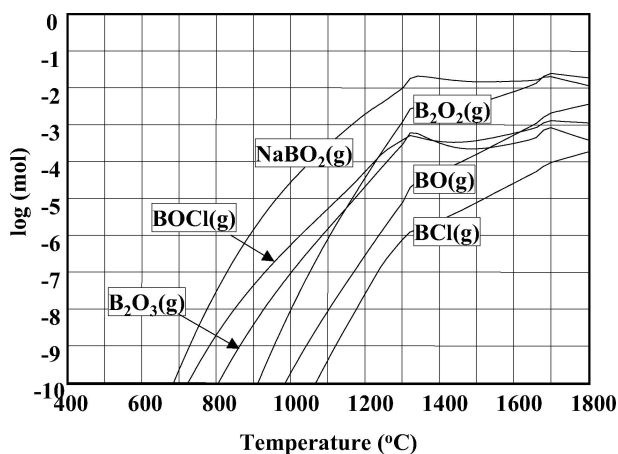
Equilibrium calculations using the computer program HSC [16], taking 140 phases into account for the system Ce-B-O-C(amorphous)-Na-Cl-Ni-Ar indicate that B$_4$C is favoured in the temperature range 1300–1650 °C and CeB$_6$ will dominate above 1650 °C. In addition boron can also form at those high temperatures, see Fig. 2a. A fast heating rate is thus needed up to the temperature range where CeB$_6$ forms in order to suppress formation of the boride compounds. Ce is mainly transported as CeCl$_3$(g) and B mainly as NaBO$_2$(g), BO(g), and BOCl(g), see Fig. 2b–c. Ni is

TABLE I Starting materials used

Substance	Particle size	Purity (wt%)	Manufacturer	Comment
CeO$_2$			G. Frederick Smith Chemical Company, USA	Cat. No. 354
La$_2$O$_3$			Johnsson Matthey, GmbH	Cas. 1312-81-8 Lot. BA 04104
B$_2$O$_3$		99	Aldrich	
NaCl		–	Akzo	Pretzel, coarse
NaCl		–	Akzo	Microsalt
Ni	<40 μm	–	Cerac	
C	13 nm		Degussa	FW200, 21 wt% volatiles

(a)

(b)

(c)

Figure 2 Gibbs energy minimisation calculation for a starting mixture with the following molar ratios: CeO_2: B_2O_3:C(amorphous):NaCl:Ni = 1:3:11:0.25:0.1. In the calculations 140 phases were taken into account. (a) CeB_6 form above 1650 °C. B can form in the temperature range 1000–1250 °C and B_4C in between 1250 and 1650 °C. (b) Cerium is mainly transported as $CeCl_3(g)$ at the reaction temperatures. (c) Boron is mainly transported as $NaBO_2(g)$ and BO(g) at the reaction temperatures.

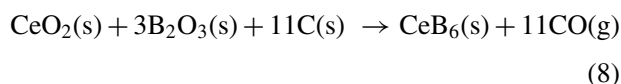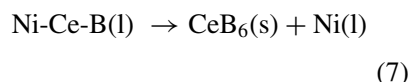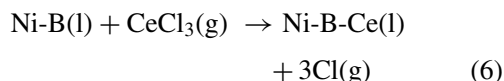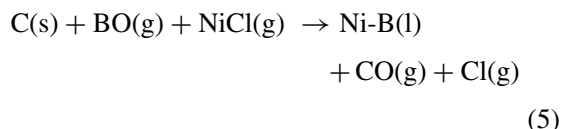mainly transported as Ni(g) and NiCl(g) at the reaction temperature. Calculations for the system La-B-O-C(amorphous)-Na-Cl-Ni-Ar indicate that the carbothermal reduction of La_2O_3 require a higher temperature than CeO_2 and also a substoichiometric amount of carbon in order to suppress the formation of B_4C and LaC_2.

Equilibrium calculations and our experience obtained in preparing different carbide- and carbonitride whiskers gives for hand that the following reactions or very similar ones represent the actual mechanism for synthesizing CeB_6 whiskers in flowing argon atmosphere using chlorine as volatilising element from a starting mixture consisting of CeO_2 + B_2O_3 + C + NaCl + Ni at 1650 °C in argon atmosphere. The reactions are not scaled in relation to each other.

$$NaCl(l) \rightarrow Na(g) + Cl(g) \qquad (1)$$
$$CeO_2(s) + 2C(s) + 3Cl(g) \rightarrow CeCl_3(g) + 2CO(g)$$
$$(2a)$$
$$B_2O_3(s) + NaCl(s) \rightarrow NaBO_2(g)$$
$$+ BO(g) + Cl(g) \quad (3)$$
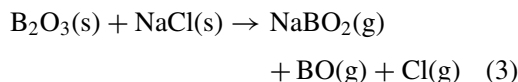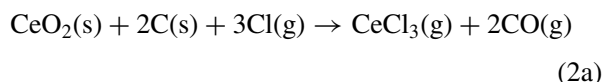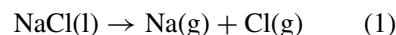
Nickel is transported and recycled by reacting with chlorine gas to form NiCl(g), which in turn reacts with $NaBO_2(g)$, BO(g) and $CeCl_3(g)$, forming an Ni-B-Ce alloy.

$$Ni(l) + Cl(g) \rightarrow NiCl(g) \qquad (4)$$
$$C(s) + BO(g) + NiCl(g) \rightarrow Ni\text{-}B(l)$$
$$+ CO(g) + Cl(g)$$
$$(5)$$
$$Ni\text{-}B(l) + CeCl_3(g) \rightarrow Ni\text{-}B\text{-}Ce(l)$$
$$+ 3Cl(g) \qquad (6)$$
$$Ni\text{-}Ce\text{-}B(l) \rightarrow CeB_6(s) + Ni(l)$$
$$(7)$$
$$CeO_2(s) + 3B_2O_3(s) + 11C(s) \rightarrow CeB_6(s) + 11CO(g)$$
$$(8)$$

A principal requirement for carbothermal VLS growth is that the direct carbothermal reduction process (reaction 8) is thermodynamically possible but kinetically retarded. If LaB_6 is synthesised instead of CeB_6 then reaction (2a) should be replaced with reaction (2b) and La should then of course be present instead of Ce in reactions (6)–(8).

$$La_2O_3(s) + 3C(s) + 6Cl(g) \rightarrow 2LaCl_3(g) + 3CO(g)$$
$$(2b)$$
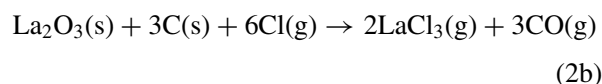
A few different $La_xCe_{1-x}B_6$ compositions were prepared; the molar ratios in the starting mixtures are given in Table II. The starting powders were mixed in a high-speed blender and put into a simple graphite reactor designed for 5–10 g of starting mixture, which was covered by a perforated graphite lid allowing gas exchange between the interior of the crucible and the furnace chamber. The reactor was heated in flowing argon (0.7 dm^3/min) in a graphite furnace (Thermal Technology, Inc., Santa Rosa, CA). Various reaction temperatures in the range 1200–1800 °C were tested, all with a temperature ramp of 60 min up to the plateau and a holding time of 1.5–3 hrs.

TABLE II Starting mixtures used for preparing $La_xCe_{1-x}B_6$ whiskers

	LaB_6	$La_{0.99}Ce_{0.01}B_6$	$La_{0.53}Ce_{0.47}B_6$	CeB_6
La_2O_3	1	1	1	–
CeO_2	–	0.02	1.8	1
B_2O_3	7.6	7.6	11.4	3
C	23.2	23.2	44.6	11
NaCl	0.5	0.5	0.95	0.25
Ni	0.2	0.2	0.38	0.1

The number of moles are normalised to La_2O_3 and CeO_2 respectively.

TABLE III Unit cell parameter for $La_xCe_{1-x}B_6$ from XRD

Aimed composition	Synthesis temperature (°C)	a-axis (Å) of the $La_xCe_{1-x}B_6$ from XRD
LaB_6	1500	a
LaB_6	1650	4.1573(5)
$La_{0.99}Ce_{0.01}B_6$	1500	a
$La_{0.99}Ce_{0.01}B_6$	1650	4.1564(3)
$La_{0.53}Ce_{0.47}B_6$	1500	a
$La_{0.53}Ce_{0.47}B_6$	1650	4.1485(2)
$La_{0.53}Ce_{0.47}B_6$	1800	4.1492(2)
CeB_6	1500	a
CeB_6	1650	4.1386(4)
CeB_6	1800	4.1348(3)

[a]To few diffraction lines from $La_xCe_{1-x}B_6$ observed in order to refine the unit cell. $La_xCe_{1-x}B_6$ was not observed at lower temperatures than 1500 °C.

Prior to the analysis of the resulting specimens, the product was separated from excess carbon by adding water/surfactant, treating the mixture with ultrasound and allowing the boride phase to settle. The synthesis bulk products were characterised by powder X-ray diffraction (XRD), by using a Guinier-Hägg focused camera in subtraction geometry. Cu $K_{\alpha 1}$ radiation ($\lambda = 1.540598$ Å) was used, and finely powdered silicon ($a = 5.430880(35)$ Å) was added as an internal standard. The recorded films were evaluated in an automatic film scanner [17]. The unit cell of $La_xCe_{1-x}B_6$ was refined with the program PIRUM [18]. Subsequent analysis of the X-ray powder diffraction patterns allowed us to conclude that $La_xCe_{1-x}B_6$ forms in the temperature range 1500–1800 °C and above 1650 °C it was the dominating phase. At 1800 °C $La_xCe_{1-x}B_6$ was the only phase present according to XRD, (see Table III).

The whisker yield and morphology were investigated using a light microscope and a scanning electron microscope (Jeol SEM 880), respectively. It was found that whiskers were formed in the temperature range 1350–1800 °C with a maximum yield at 1500 °C. The obtained whiskers had a wide size distribution and often a plate like appearance. The whiskers were 10–2000 μm in length and 0.2–10 μm in diameter (see Figs 1 and 3). In addition to (La, Ce)B_6, also B_4C, La_2CO_5, $LaBO_3$ and La_2C_3 were formed in the temperature range 1500–1650 °C as identified by XRD in the synthesis products. This result has not been possible to compare with equilibrium calculations since thermodynamic data were not available for La_2CO_5, $LaBO_3$ or La_2C_3. For whiskers with a targeted composition of $La_{0.53}Ce_{0.47}B_6$ EDS measurements showed that the average content of the heavy elements was 54 at.% La and 46 at.% Ce at a synthesis temperature of 1650 °C. The refined unit cell parameters followed Vegard's rule with a perfect La/Ce solid solution (the reported unit
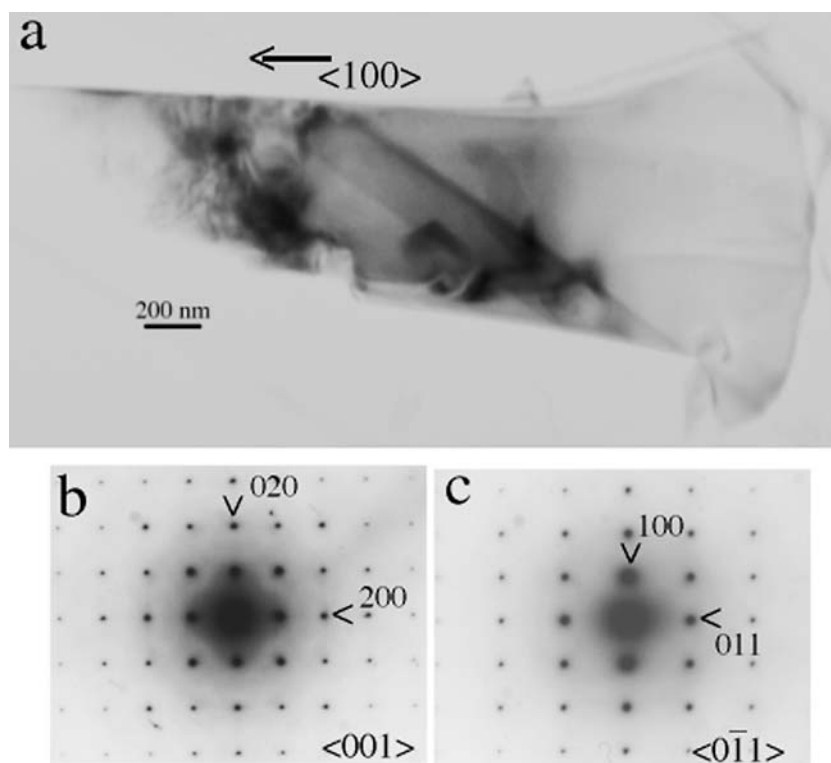

Figure 3 (a) A low magnification image of a typical $La_{0.53}Ce_{0.47}B_6$ whisker. The growth direction $\langle 100 \rangle$ is indicated. The electron diffraction patterns along the zone axis (b) $\langle 100 \rangle$ and (c) $\langle 0{-}11 \rangle$ of the crystal are shown.

cell parameters for LaB_6 and CeB_6 are $a = 4.15690(5)$ Å, JCPDS 34-0427, and $a = 4.1412(11)$ Å, JCPDS 38-1455, respectively), see Table III.

The $(La,Ce)B_6$ phase was additionally studied by transmission electron microscopy. A Jeol TEM 2000FX, operated at 200 kV and equipped with a LINK AN10000 energy dispersive X-ray, EDS, spectrometer was used. Well-defined whisker like crystals was found, as shown in Fig. 3a. The obtained La/Ce ratios by EDS were always in agreement with the result found above and no distortion away from the reported cubic structure could be detected in diffraction mode. In Fig. 3b–c two zone axis electron diffraction patterns down the $\langle 100 \rangle$ and $\langle 0$–$11 \rangle$ directions of the cubic structure are presented. Additionally the growth direction was determined to be the $\langle 100 \rangle$.

Starting mixtures according to Table II but without NaCl and/or Ni were tested. All these mixtures yielded whiskers at 1650 °C. In the absence of NaCl the transport of Ce, La and B seemed to take place via oxide gas species according to reactions (9) and (10). This is supported also by Fig. 2b–c indicating that such gas species can form also in the presence of NaCl.

$$B_2O_3(s) + C(s) \rightarrow 2BO(g) + CO(g) \qquad (9)$$

$$CeO_2(s) + C(s) \rightarrow CeO(g) + CO(g) \qquad (10)$$

Also nickel can be transported without the presence of NaCl at the same high temperature by forming Ni(g). However, the fact that whiskers could form both without NaCl and Ni makes this system very different from others investigated and all active growth mechanisms are not clarified yet. It can be concluded that $(La, Ce)B_6$ whiskers can be formed by a carbothermal VLS mechanism in the temperature region 1650–1800 °C and that other growth mechanisms also seem to be operating, perhaps the VS mechanism.

References

1. K. WINZER, *Solid State Commun.* **16** (1975) 521.
2. A. C. HEWSON, in "The Kondo Problem to Heavy Fermions" (Cambridge University Press, 1993).
3. S. R. HARUTYUNYAN, V. H. VARDANYAN, A. S. KUZANYAN, *et al.*, *Appl. Phys. Lett.* **83** (2003) 2142.
4. A. GULIAN, K. WOOD, D. VAN VECHTEN, *et al.*, *Nucl. Instrum. Meth. Phys. Res. Sect. A: Acceler., Spectr., Detect. Assoc. Equipm.* **520** (2004) 36.
5. V. CHANDRASEKHAR, A. ZAWADOWSKI, C. VAN HAESEDONCK (eds.), in Proccedings of the NATO Advanced Research Workshop on Size Dependent Magnetic Scattering (Hungary), May 29–June 1, 2000 [In: NATO Sci. Ser., II, 2001; 50] (Kluwer Academic Publishers, Dordrecht, Netherlands, 2001) p. 265.
6. M. CARLSSON, M. JOHNSSON and M. NYGREN, *J. Amer. Ceram. Soc.* **82** (1999) 1969.
7. M. CARLSSON, P. ALBERIUS-HENNING and M. JOHNSSON, *J. Mater. Sci.* **37** (2002) 2917.
8. C. DAI, X. ZHANG, J. ZHANG, Y. YANG, L. CAO and F. XIA, *J. Amer. Ceram. Soc* **80** (1997) 1274.
9. N. AHLÉN, M. JOHNSSON and M. NYGREN, *ibid.* **79** (1996) 2803.
10. M. JOHNSSON and M. NYGREN, *J. Mater. Res.* **12** (1997) 2419.
11. J.-B. LI, G.-Y XU, E. Y. SUN, Y. HUANG and P. F. BECHER, *J. Amer. Ceram. Soc.* **81** (1998) 1689.
12. M. JOHNSSON, *J. Mater. Sci. Lett.* **19** (2000) 1571.
13. M. CARLSSON, J. G. GARCIA and M. JOHNSSON, *J. Cryst. Growth* **236** (2002) 466.
14. S. MOJITAMA, Y. TAKAHASHI and K. SUGIYAMA, *ibid.* **44** (1978) 106.
15. E. I. GIVARGIZOV and L. N. OBELENSKAYA, *ibid.* **51** (1981) 190.
16. "HSC Chemistry, Ver 5.0" Outokumpo Research oy, Pori, Finland (2002).
17. K. E. JOHANSSON, T. PALM and P. E. WERNER, *J. Phys. Sci. Instrum.* **13** (1980) 1289.
18. P. E. WERNER, *Arkiv för Kemi* **31** (1969) 513.