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LaB_6 crystals from fused salt electrolysis

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Purple crystals of LaB_6 with high melting point (2500 °C) have been elecrotrodeposited from an oxyfluoride melt consisting of La_2O_3–B_2O_3–LiF–Li_2O under an N_2 atmosphere. The growth of LaB_6 crystals has been observed under a controlled electrodeposition process. The cell set-up employed for the electrodeposition consists of a graphite crucible acting both as the cell container and anode and a centrally placed Mo rod acting as cathode. A stainless steel retort was employed to hold the graphite crucible and fix the electrodes under an N_2 atmosphere. The pre-treatment applied to the electrolyte composition before electrolysis has been described. Characterization of the crystalline product by chemical analysis, XRD studies and other physical measurements is reported.

Introduction

LaB_6 is a cubic deep purple metallic compound and finds application as an electron emitter in electron microscopes and as a promising cathode material because of its low work function (2.6 eV), high current (29A cm^2 K^{-2}) and voltage capability.[1–5] Borides of rare earth metals like Sm, Ce, Y, Yb, Dy, Ho *etc.*, exhibit a wide variety of interesting magnetic, electric and transport properties.[6]

The borides are not easy to prepare in pure form and the purification steps are also often difficult and precise stochiometry is also often hard to achieve. Usually the borides are prepared by high temperature reaction of the constituent elements in powder or pelletized form around 1800 °C initially to form LaB_4 and then to give LaB_6 under controlled conditions.

However, these methods are not only expensive but the products are also found to be contaminated with the carbides from the crucible.

Crystals of LaB_6 with high melting point (2500 °C) can be conveniently synthesized at lower temperature (850 °C) from molten salt electrolysis. In molten salt electrolysis the driving force for crystallization of LaB_6 is provided by the potential gradient as compared with the temperature gradient in the flux growth. A potential controlled experiment has been attempted and the results are reported here.

Different methods of preparation of LaB_6 are summarized in Table 1.[7–17]

Table 1 Methods of synthesizing LaB_6

Molten salt electrolysis
i $La_2O_3 + CaCl_2 + CaB_4O_7$[7,8]
ii $LaCl_3 + Li_2B_4O_7 + LiCl$[9]
iii $La_2O_3 + B_2O_3 + LiF + Li_2O$[5]
iv $La_2O_3 + Li_2B_4O_7 + Li_3AlF_6$[10]
v Mixture of oxide, borate and fluoride melts[11–13]
Solid phase reaction
La powder + amorphous B powder mixed, pelletized and fired at 1375 °C in H_2 atmosphere for 1 h then at 1800 °C in H_2–Ar in a graphite crucible[4,14]
Arc melting
Arc melting pressed B powder with three-fold excess La powder to give LaB_4 then heating LaB_4 and B *in vacuo* at 1600 °C for 15 min[15]
Flux growth
Solidification of Al flux containing La and B[16,17]
Vapour phase crystallization[18]
Floating zone
Mixture of respective oxides with B and heated in an induction oven in a tantalum crucible *in vacuo*, below 10^{-3} mmHg at 1700 °C for 1 h[2,19]

Experimental

With the aim of synthesizing cubic crystals of LaB_6 the electrolysis was carried out in a high density graphite crucible (Porosity 16%, supplied by M/s. Graphite India Ltd.) with an inner diameter of 50 mm and depth 80 mm, which served simultaneously as the anode. The cathode was a 10 mm diameter Mo rod threaded to a stainless steel rod and was centrally positioned in the melt maintained at 850 °C.

The crucible was placed at the lower end of a cylindrical stainless steel vessel, as shown in Fig. 1, having a vacuum tight top flange sealing with a water cooling arrangement. The vessel was surrounded by a wire wound furnace with temperature control. The flange contained provision for fixing electrodes, inlet, outlet for circulating N_2 gas and a thermocouple. The electrode could be raised or lowered through a special Teflon Swagelok seal arrangement at the flange.

The melt used for the electrodeposition consisted of La_2O_3 (15 mass%)–B_2O_3 (48 mass%)–LiF (18 mass%)–Li_2O (19 mass%).

The B_2O_3 may act as a fluxing agent in addition to taking part in the cell reaction while Li_2O may break down B_2O_3 aiding B electrodeposition. The viscosity of the melt was reduced by the addition of LiF.

The constituents of the melt in the form of powder were mixed as per the predetermined mass ratio and pressed in the form of pellets of 30 mm diameter, and 20 mm thickness in a steel die at a load of 5 ton cm^{-2}. The loss of electrolyte by volatilization during the melting process was found to be appreciably reduced by this technique.

The graphite crucible containing the electrolyte pellets was placed in a stainless steel vessel and subjected to predrying at 500 °C for 5 h under partial vacuum by means of an oil vacuum pump. The electrolyte was then melted slowly under a continuous flow of N_2 (after passing through hot copper turnings followed by molecular sieves) which flushed the system. The melt was equilibrated at 850 °C for *ca.* 1 h preceding electrolysis.

After the Mo cathode was centrally positioned and immersed into the melt, experiments were carried out at different potentials, with a cathode current density of *ca.* 500–600 mA cm^{-2} to compare the nature and composition of the deposits at varying potentials and results are given in Table 2. Electrochemical studies[5] of a similar bath composition under

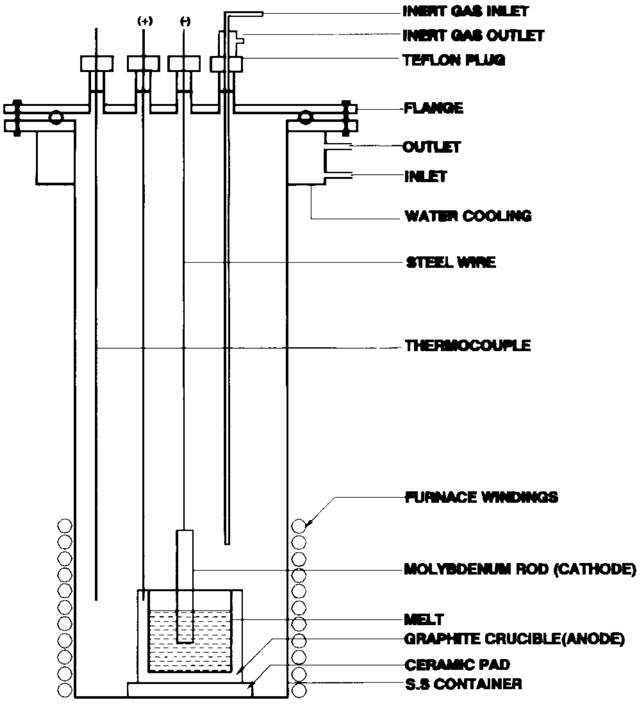

Fig. 1 Electrolytic cell for growth of LaB_6 crystals.

Table 2 Potential range, nature and composition of the deposit

Experiment code	Potential range in volts	Composition[a] (%)		Nature
		La	B	
GAP 23	1.90–1.93	64.84 (68.17)	25.63 (31.83)	clusters of deep and light purple crystals
GAP 30	2.10–2.40	62.28 (68.17)	26.67 (31.83)	clusters of deep purple cubic crystals

[a]Required values in parentheses.

a ramped applied voltage indicated a decomposition potential of 1.85 V. Experiments carried out at potentials of 1.90–1.93 V were found to yield products with higher La content as compared with the product from electrolysis at higher potentials, which may be attributed to recombination.

Results and discussion

La and B are simultaneously reduced at the cathode to form LaB_6 while oxides of carbon are evolved at the anode.

After electrolysis the Mo cathode covered with the deposit was raised above the melt level and allowed to cool in an N_2 atmosphere before being taken out of the cell. The as grown deposit was scraped off onto a glass plate and electrolyte adhering to the boride was leached with a warm 5% HCl solution followed by a 2% NaOH solution and then washed with distilled water. The current efficiency of the process was found to be in the range 85–90%.

Nature of the deposit

The deposits were found to consist of clusters of cubic deep purple crystals which ranged from 25 to 250 μm as shown by SEM (Fig. 2).

Chemical analysis

A known quantity of powdered sample of LaB_6 was dissolved in dilute HCl after fusing with an AR Na_2CO_3–$NaNO_3$ mixture at 950 °C in a Pt crucible. The boron content was determined by titrating the sample solution, to which mannitol was added, with a standard NaOH solution. Lanthanum was estimated by precipitating it as oxalate with saturated oxalic acid solution followed by dissolution of the precipitate in warm dilute H_2SO_4 and titrating the solution with standard $KMnO_4$. The La and B contents in the synthesized samples are given in Table 2.

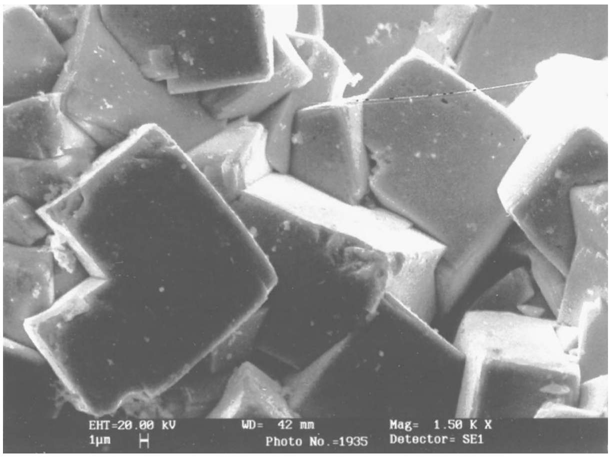

Fig. 2 SEM micrograph of LaB_6 crystals.

XRD analysis

A powdered sample of LaB_6 was subjected to XRD analysis (using Cu-Kα radiation) and the XRD pattern is shown in Fig. 3. The lattice constant of LaB_6 was determined from the XRD data (Table 3) and the value $a = 4.156$ Å was found to match the reported value.[20] The absence of any additional

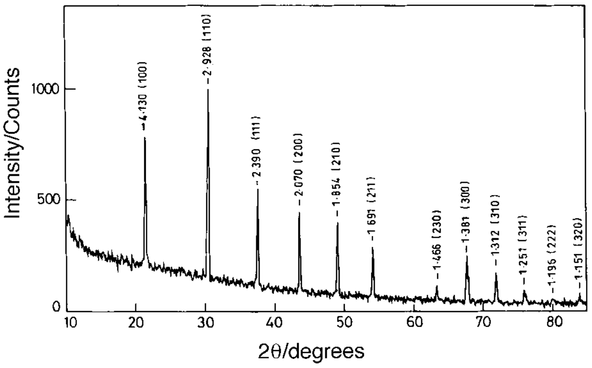

Fig. 3 XRD pattern of LaB_6.

Table 3 XRD data corresponding to cubic LaB_6 (Cu–Kα radiation)

$2\theta/°$	d_{obs}/Å	d_{std}/Å	I/I_0	hkl
21.486	4.130	4.149	82	100
30.457	2.928	2.941	100	110
37.565	2.390	2.398	53	111
43.684	2.070	2.079	40	200
49.061	1.854	1.862	41	210
54.160	1.691	1.966	29	211
63.381	1.466	1.471	15	230
67.791	1.381	1.385	27	300
71.882	1.312	1.314	20	310
75.970	1.251	1.253	13	311
80.059	1.196	1.199	08	222
84.037	1.151	1.153	09	320

Crystal data for LaB_6: $M = 180.20$, cubic, $a = 4.145$ Å (4.153 Å[20]), density = 4.75 g cm^{-3}.

peaks in the XRD pattern and the formation of the product in the form of cubic crystals indicated its high purity.

Density

The density of the crystals was determined pycnometrically[21] using xylene as the liquid medium and the measured value of 4.75 g cm^{-3} is in good agreement with the reported value.[2]

Mechanism of boride deposition

Various mechanisms have been proposed for boride deposition. According to Meerson and Smirnov[22] this occurs by simultaneous discharge of refractory metal and boron, *e.g.* Ti^{4+} and B^{3+} form from a borate–fluoride bath in a primary process. Antony and Welch[23] suggested electrodeposition of boron followed by reaction with a refractory compound *e.g.* ZrB_2, whereas Andrieux[24] suggested reduction to metal of the refractory metal oxide and B_2O_3 is accomplished by alkali or alkaline earth metals which first deposit over the cathode from the respective metal halide flux. For example, Ca formed from calcium salts chemically react with B_2O_3 to give CaB_6.

For the formation mechanism of LaB_6, it is possible to postulate that electrolytically reduced La reacts either with electrolytically reduced B or with B_2O_3, although it is not clear, as yet, which mechanism operates.

Conclusion

Purple coloured cubic crystals of LaB_6 could be favourably synthesized by electrodeposition employing an oxyfluoride melt consisting of La_2O_3–B_2O_3–LiF–Li_2O maintained at 850 °C under an N_2 atmosphere in a graphite container which simultaneously acts as an anode with a centrally positioned Mo rod as cathode operating at 1.90–1.93 V with a cathode current density of 500 mA cm^{-2}.

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