

Electrosynthesis of cerium hexaboride by the molten salt technique

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ABSTRACT

Molten salts are well thought-out as the incredibly promising medium for chemical and electrochemical synthesis of compounds. Hence a stab has been made on the electrochemical synthesis of CeB₆ using molten salt technique. The electrolyte consisted of lithium fluoride (LiF), boron trioxide (B₂O₃) and cerium chloride (CeCl₃). Electrochemical experiments were carried out in an inconal reactor in an argon atmosphere. Electrolysis was executed in a high-density graphite crucible, which doles out as the electrolyte clutching vessel as well as the anode. The cathode was made up of a molybdenum rod. The electrolysis was carried out at 900 °C at different current densities intended for the synthesis of CeB₆ crystals. After the electrolysis, the cathode product was removed and cleaned using dilute HCl solution. The crystals were scrutinized by X-ray diffraction (XRD) to make out the phase and the purity. It has been observed that CeB₆ crystals are synthesized at all current densities and the product has traces of impurities.

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1. Introduction

Rare earth hexaborides (RB₆) have attracted much attention because of their appealing physical properties such as superconductivity, valence fluctuation and magnetic ordering [1]. Specific attention has been focused in the past few years on rare earth metal borides in broadspectrum and to hexaboride in particular owing to their high melting temperature, strength and chemical stability in heaps of antagonistic environments [2,3].

Hexaborides are of great technological significance as thermo ionic cathodes in electronic devices and decorative coatings [4,5]. Hexaborides (MB₆) can be monovalent metals or semiconductors depending on whether the metal ion M is trivalent or divalent, respectively [6]. Although elemental boron is a semiconductor and pure boron nitride is an insulator, the metal borides are found to be an excellent metallic conductor with conductivities higher than those observed for the pure metals [7]. Even some of the hexaborides reveal super conducting property at low temperatures [7–9]. Metal borides exhibit an inimitable structural type depending on the boron ratios [8–12].

The main structural facet of the rare earth hexaboride is the firm framework of the boron atoms and the cavities that are

occupied with the rare earth ions. These structures consist of a framework of boron octahedrals arranged as units in a body centered cubic lattice [13]. The covalent bonding within the boron polyhedral is alleged to impart great stability, hardness and high melting point to these bonds [14].

CeB₆ is one of the rare earth borides having excellent field emitter properties with low work function ≈ 2.5 eV and low volatility, lower operating temperature and longer operating time and longer service life when they are used as thermionic electron emitter materials [15,16]. It has found relevance in nuclear technology [17] because of its high thermal neutron cross-section of ¹⁰B [18]. Cerium hexaboride has been prepared by electron beam evaporation, pulsed laser deposition and magnetron sputtering and its characterization has been studied [19]. Recently, cerium hexaboride single-crystal nanowires have been synthesized using platinum as the catalyst [20]. To our knowledge, molten salt synthesis of CeB₆ has not been attempted. Hence, an effort has been made to synthesize this interesting compound by the molten salt technique.

2. Experimental work

The molten electrolyte consisted of cerium chloride (CeCl₃), boron trioxide (B₂O₃) and lithium fluoride (LiF). Stoichiometric

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quantities of reactants were assorted and calcined in a vacuum oven at 250 °C. The powders were made into small pellets of size 2 × 1 cm using a hydraulic press. Then the pellets were again calcined at 300 °C for 24 h.

The experimental arrangement for the synthesis of hexaboride is schematically shown in Fig. 1. The electrolytic cell consisted of a high-density graphite crucible (supplied by M/S Graphite India Ltd., Bangalore) served as the container for the electrolyte and also as the anode. The cathode was made from a molybdenum rod of 1 cm dia fixed to a stainless steel rod. The anode–cathode assembly was centrally sited in an inconel reactor vessel. The graphite crucible was filled with the required amount of palletized electrolyte salts and the intact assembly was placed in an electrically heated furnace. The furnace was kept around 900 °C. The reactor was initially evacuated and purged with inert atmosphere. The anode–cathode assembly can be raised or lowered through a unique Teflon swage lock arrangement for the adjustment of electrodes. The electrolysis was performed at different current densities, namely 0.5, 1, 1.5 and 2 A/cm² at 900 °C. After a preset period of electrolysis, the cathode was removed and the deposited crystals were detached. The crystals were washed with acid solution and finally rinsed with triple distilled water. The crystalline phase identification of the synthesized crystals was examined using XRD (Philips XL30W/TMP X-ray diffractometer). The morphology of the crystals was characterized using a scanning electron microscope (SEM) (JEOL-JSM-3.5 CF-Japan). Electron paramagnetic resonance (EPR) studies were performed with microwaves frequency 9.857403 GHz with fields corresponding to about 6500.000 G sweep width using a Bruker Bio Spin GmbH EPR spectrometer. Electrical properties of cerium hexaboride (CeB₆) compounds were determined using the four-probe method with an OMEGA TYPE ES-246. This instrument

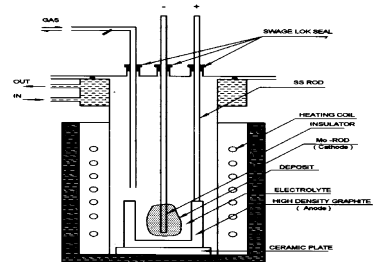


Fig. 1. Experimental set-up for the synthesis of CeB₆.

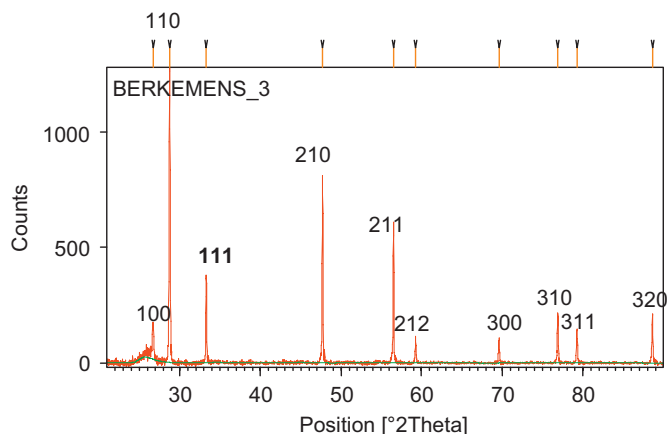


Fig. 2. X-ray diffraction patterns of CeB₆ obtained at a current density of 0.5 A/cm².

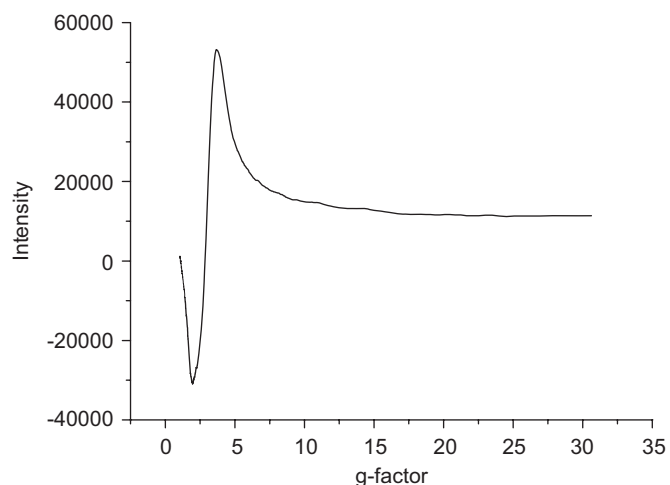


Fig. 3. EPR spectra for CeB₆.

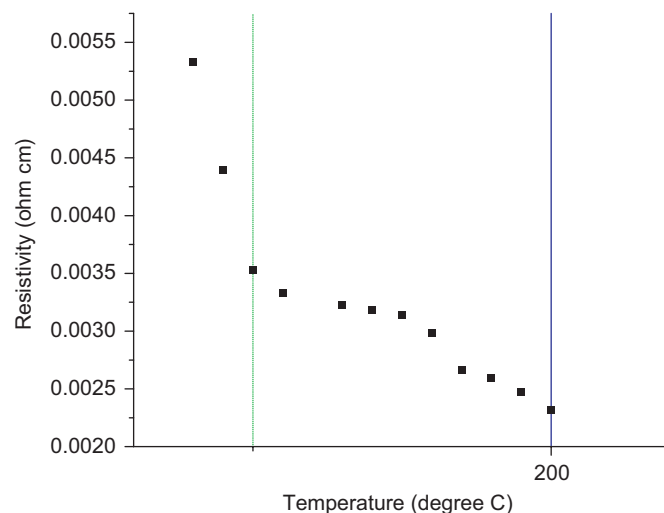


Fig. 4. Resistivity versus temperature curve.

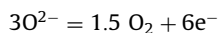
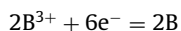
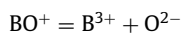
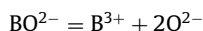
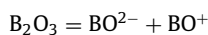
was used to study the electrical behavior of our compound up to a temperature of 200 °C (Figs. 2–4).

3. Results and discussions

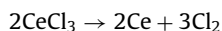
In all the experiments, it is observed that a good adherent deposit is seen at the Mo cathode. At all the current densities, the color of the final product is found to be bluish-black. The quantity of deposit is found to amplify with the increase in current densities. It is observed that the nature of the deposit fluctuates with the molar ratios of Ce:B. It is also noticed that at lower cathode current density, the deposition of the crystals is found to be less in quantity. The amount of deposit is found to linearly increase with the increase in current density (Table 1).

The lattice constant value of the crystals is determined from the XRD data, which is found to be 4.13989 Å. The value is in good accord with the reported value. A single impurity occurs at the 212 phase, which corresponds to CeB₄. The crystallite size has been found to be 59 nm at 0.5 A/cm². Various mechanisms have been anticipated for the deposition of rare earth borides. At the outset, the dissociation of B₂O₃ takes place and gives rise to boron ions at the first instance. The reaction routes can be

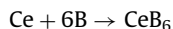
written as follows:



The commonly accepted mechanism of boron deposition in molten salts is a single-step three-electron electrochemical reaction [16–18,21–28]. At the same time the dissociation of CeCl_3 occurs, giving the Ce^{3+} ions followed by the deposition at the cathode. The reaction can be written as follows:



The electrolytically dissociated Ce and B ions deposit at the Mo cathode forming the compound CeB_6 . The electrochemical parameters are similar to current density; cell voltage also influences the stoichiometry of the compound. It can be further explained that the combined deposition of two electro-active species at the potential more positive than their own deposition potentials at the inert cathode is possible due to the high exchange current density of the cations in the molten salt [29,30]. Thus the deposition of CeB_6 is viable by the following reaction:



Since both the ions are more reactive, there is every likelihood of the formation of intermediate composition such as CeB_4 along with other impurities like Ce_2O_3 and B_2O_3 . But in our studies, we have observed the existence of CeB_4 (212) as an impurity phase along with our product, which has been determined from XRD data.

Lithium fluoride increases the fluidity and the electrical conductivity of the molten melt. It is also possible to be more firm at high temperatures. Moreover, the decomposition potential of LiF is more cathodic than the other fluoride salts [31,32], which is an advantage for the formation of CeB_6 .

Table 1

Comparison of experimental and reference values of determining parameters

Determining parameters	Experimental value	Reference value
Lattice constant	4.13989 Å	4.14 Å [19]
Crystallite size	59 nm	20–100 nm [19]
g-factor	1.96465	Close to 2 [35]
Frequency	52.690 GHz	About 60 GHz [35]

Cerium hexaboride (CeB_6) is a prominent compound, where quadrupole magnetic interactions play an indispensable role [33–38]. The magnetic dipole and electric quadrupole moments are alleged to be allied with the Ce^{3+} ions forming a simple cubic lattice [32,33]. It has been reported that in a zero magnetic field the quadrupole (i.e. orbital ordering) with the formation of an antiferro quadrupole phase occurs at $T_Q = 3.2$ K and precedes the formation of an antiferro magnetic phase (dipole ordering) at $T_d = 2.3$ K. In this region $T > T_Q$, cerium hexaboride is a paramagnetic metal P-phase and demonstrates the dense Kondo system. The Kondo temperature for CeB_6 is $T_Q \sim 1$ K [33–38] and the expected line width will be about

$$W \sim \frac{K_B T_K}{\mu_B} 1.5T$$

where W is the line width, K_B is the Boltzmann constant ($1.3807 \times 10^{-23} \text{ J K}^{-1}$), T_K is the Kondo Temperature (K) and μ_B is the Bohr magneton ($9.2740 \times 10^{-24} \text{ J T}^{-1}$).

Therefore, EPR-like modes with a g -factor value close to 2 may be observed in CeB_6 at frequencies of about 60 GHz, analogous to a resonant field of about 2 T and in the temperature range $T > T_Q \sim 1$ K including the AFQ phase (39). We have observed the g -factor value at 1.96465 and frequencies about 52.690 GHz. This observation is in good agreement with the above literature value [39].

It has been reported that one of the most important traits that gives rise to the anomalies of transport and thermodynamic characteristics in this analogue of monovalent metal with strong electron correlations is the coincidence between the number of itinerant electrons (n_e) and of the cerium 4f-sites (n_{4f})- $n_{4f} \approx n_e$ [40]. Fermi structure of CeB_6 consists of nearly spherical ellipsoids centered at the X points of the Brillouin zone with the necks in the [110] directions or with small electron pockets [41,42]. This type asymptotic behavior usually corresponds to the regime of weak localization in the charge carriers transport and it is established for CeB_6 in the entire temperature interval [43].

Fig. 5 shows the electrical behavior of CeB_6 prepared by the molten salt technique. From the figure, it is revealed that the electrical resistivity is found to decrease with increase in temperature. The significant decrease in resistivity occurs at 180 °C. Beyond this temperature a sizeable decrease in resistivity is observed. As it is obviously deduced from the double logarithmic plot, the $\rho(T)$ reliance in CeB_6 is well described by the power law

$$\rho(T) \sim T^{-1/\eta}$$

where $\rho(T)$ is the resistivity ($\Omega \text{ cm}$) and T is the temperature (K).

It is worth mentioning that the observed value agrees with the logarithmic Kondo-like dependence $\rho \sim -\ln T$.

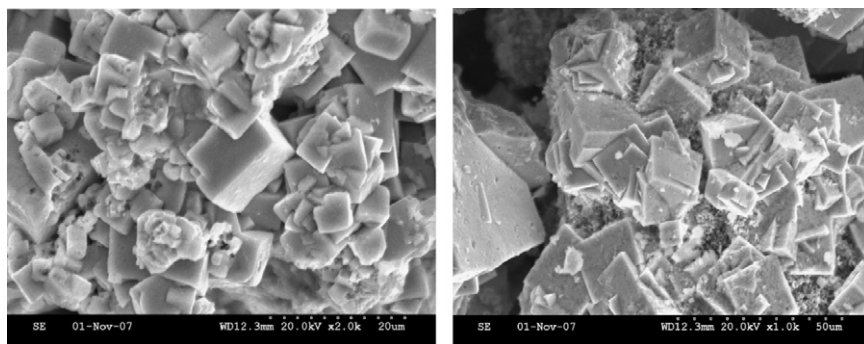


Fig. 5. SEM pictures of CeB_6 .

The SEM micrographs illustrate the grain size of the crystals with homogeneous distribution of a plate-like structure. At higher current densities the grains are found to be larger in size.

4. Conclusion

From the above studies, it has been concluded that the pure compounds of CeB₆ can be synthesized using molten salt electrolysis. Current density promotes the rate of deposition and influences the morphology of the ultimate product. The synthesized product is found to be pure with a degree of impurity phase.

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