

Synthesis and characterization of EuB₆ by borothermic reduction of Eu₂O₃

Sanjay Kumar*, Nagaiyar Krishnamurthy

Fusion Reactor Materials Section, Bhabha Atomic Research Centre Mumbai 40008, India Received 14 January 2011; received in revised form 1 April 2011; accepted 15 May 2011

Abstract

Carbon free high pure europium hexaboride is an urgent need for the fast breeder nuclear reactor program. The properties of EuB_6 are highly influenced by the presence of one or more substitutional impurities, particularly, carbon, oxygen and nitrogen. In the present investigation carbon and nitrogen free high pure europium hexaboride was synthesized by borothermic reduction of europium oxide Eu_2O_3 (using boron as a reducing agent) at relatively low temperature (< 900°C). Glassy B_2O_3 , the by-product of the synthesis process, was leached out completely in slightly acidic warm water from which boron could be recovered by usual electrolysis process. The product obtained was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and chemical analysis. Oxidation behaviour of pressureless sintered EuB_6 pellets (> 90% of theoretical density) was studied at 850°C and revealed that an adherent thin surface of Eu_2O_3 was formed which prevent further oxidation.

Keywords: borothermic reduction, hexaborides, suboxide, oxidation

I. Introduction

Europium hexaboride has attracted attention of many scientists, engineers and technicians due to its interesting properties at low temperature [1–3]. Europium hexaboride is intrinsically semiconductor which orders antiferromagnetically below 6K [4]. It is a potential candidate for the control rod in the fast breeder reactor because of high neutron absorption cross-section of both boron and europium atoms for the thermal and especially for the fast neutrons [5]. Europium hexaborides dissolve very small amount of carbon which reduces the possibility of the formation of unstable carboborides in moisture media which in turn make this compound more stable under operational conditions at high temperature. Furthermore it was shown that the EuB₆ neutron absorbing characteristics exceed the similar properties of other boron and europium-containing materials (B_4C and Eu_2O_3) [6]. EuB_6 has been considered in various hard core engineering applications because of its excellent corrosion and oxidation resistance at high temperature [7,8]. High temperature usability is enhanced due to its high melting temperature (2660°C).

Various methods for the synthesis of rare earth hexaboride have been explained but none of them described synthesis of europium hexaboride in details. Borothermic reduction of europium oxide synthesis process, reported earlier [9,10], required high temperature (1800°C) in which oxygen was removed as boron suboxide (BO). The expansive boron loss in the form of suboxide is the key issue to be resolved for the scaling-up of this process. Electrochemical and solution method of synthesis of EuB₆ were attempted and reported by various scientists and researchers [11–14]. An involvement of the chlorides at high temperature is the associated issue in the electrolysis process. Synthesis of EuB₆ by floating zone technique to prepare a single crystal europium hexaborides was also reported [10] and looks promising. However, the synthesis of the europium hexaborides in large quantity by this process is not cost effective as the substantial materials and power losses are involved throughout the synthesis process.

The present synthesis is based on the hasselfree single step brothermic reduction of europium oxide

^{*} Corresponding author: tel: +91-22-2559-0489

fax: +91-22-2550-5151, e-mail: sanjay.barc@gmail.com



Figure 1. Particle size distributions of reactants: a) Eu₂O₃ and b) boron

 (Eu_2O_3) . The reaction involved in the preparation is shown by the following equation:

$$Eu_2O_3(s) + B(s) = EuB_6(s) + B_2O_3(s)$$
 (1)

The above reaction is thermodynamically feasible at room temperature, but kinetically the reaction starts only above 760°C. To fasten the kinetics the temperature employed in the bulk synthesis was 900°C. The B_2O_3 formed in this synthesis process was in glassy phase and could not be detected in XRD analysis. The formed glassy B_2O_3 product was leached out in slightly acidic warm water from which boron could be recovered by the usual electrolysis process [15]. The synthesized europium hexaborides were free from carbon and nitrogen contamination which enhanced its usability in moisture media. The chemical analysis of the product shows substantially less amount of oxygen (< 100 ppm).

II. Experimental

The materials used in the synthesis process were: i) europium oxide (Eu₂O₃) powder with purity of 99.99% (E-Merck make) and 3 μ m median particle diameter and ii) boron powder with purity of 99.9% (with less than 0.01% C, 0.02 % Fe and 0.02% Si) and 40 μ m median particle diameter. All these raw materials were oven dried at 100°C under rotary vacuum to remove moisture before use. Particles size distribution and XRD pattern of the raw materials are presented in Figs. 1 and 2, respectively.

Reactants in stoichiometric quantity, according to the reaction (1), were prepared by weighing accurate quantity of individual components and mixed homogeneously. The SEM image of the reactants mixture is illustrated in the Fig. 3 and confirmed the homogeneity of the boron and europium oxide mixture. The obtained reactant mixture was pelletized by uniaxial pressing at pressure of 88 MPa using 12 mm die plunger. The pellet was used for thermal analysis study (TG-DSC Setaram tag 24 Thermoanalyser).



Figure 2. X-ray Diffraction of (a) produced EuB₆ (b) Eu₂O₃ (c) oxidized EuB₆ and (d) boron



Figure 3. SEM micrograph of reactant mixture (Eu₂O₃ and boron)



Figure 4. Gibbs energy versus temperature curve for the various product combination of Eu₂O₃ and boron mixture



Figure 5. DSC and TG of Eu₂O₃ boron mixture to find the exact process temperature, The DSC axis is arbitrary unit



Figure 6. SEM micrograph of prepared EuB₆

For the regular synthesis of EuB_6 , weighed quantity of Eu₂O₃ and B were mixed homogeneously in a tungsten carbide mortar pestle and then powder mixture was pelletized as described earlier. The pellets were kept in an alumina tray which was further placed inside the controlled atmosphere reaction chamber of silicon carbide furnace. The reaction chamber was purged with argon gas for an hour and then temperature was raised to 900°C at rate of 20°C/min. The argon gas flow rate was kept at 2 l/hours and flow was continued throughout the synthesis process. The temperature of the furnace was measured using chromal-alumel type thermocouple. The furnace was kept at 900°C for about 4 hours to complete the reaction. After the completion of the process, the furnace was cooled down to room temperature. Pellets from the reaction chamber were gently removed and then crushed into the powders using tungsten carbide mortal pestle followed by ball milling. The powder obtained was leached in slightly acidic warm water and the residue was oven dried under rotary vacuum at 100°C.

Phases of the oven dried powder samples were studied by X-ray diffraction (Enel PW 1830 Diffractometer). Particle size distribution of the calcined powder product was studied using the laser light scattering technique (CILAS PSA 10642L Particle size analyser) while the morphological features were probed by scanning electron microscopy (SEM Philips FE1 XL 30).

For the sintering process, EuB_6 powders were compacted in pellets of 12 mm diameter and thickness of ~2 mm, by uniaxial pressing at the pressure of 170 MPa. The sintering of the pellets was done at temperature 1800°C for 4 hours. The sintered density was measured by Archimedes method, while the microstructural features of the sintered specimens were studied using SEM.

Oxidation study of pressureless sintered pellet (>90% of theoretical density) with total surface area of 1.6 cm²/g in the form of half circle was conducted in a resistance-heated furnace. All surfaces of the semicircle samples were polished with emery paper and finally with diamond paste up to 3Δ finish. In order to avoid oxidation during heating, the sample was directly inserted into the furnace after the furnace temperature reached 850°C. The sample was oxidized for different time intervals (0.5, 1, 2, 4, 8, 16, 32, and 64 h) at 850°C. The oxidation products were identified by XRD. The morphology and nature of oxide layer formed were analyzed by SEM.

III. Results and discussion

Formation of highly pure EuB_6

Gibbs free energy versus temperature curve for the reactant mixture of Eu_2O_3 (s) and B (s) with various product combinations were calculated and presented in

the Fig. 4. It can be seen that the reaction (d) with B_2O_3 and EuB₆ as products, is thermodynamically feasible at room temperature, however higher temperature was required for the other reactions. To ascertain the kinetically feasible temperature of the reaction (d), DSC and TG of small portion of the sample were done in the argon atmosphere up to the temperature of 900°C at the heating rate of 8°C/Min. The DSC along with TG curve is illustrated in the Fig. 5. The weight loss of about 0.8% has taken place at the range of 60 to 400°C, which could be attributed to the removal of absorbed water in the capillaries and bonded water. Above 400°C, the sample has achieved mass stability, indicating the completion of the evaporation processes. An interesting observation was the appearance of an exothermic peak at 760°C accompanied with no mass change. The XRD analysis of the product heated at 760°C confirmed presence of EuB₆. However a few peaks of Eu₂O₂ phase were also present. No other crystalline phase was detected in XRD pattern illustrated in Fig. 2. This clearly confirmed the kinetically feasible temperature of the equation (1) with glassy phase B_2O_3 as one of the by-products.

Another experiment was done at 900°C to enhance the kinetics to complete the reaction and confirm the formation of B_2O_3 . The product obtained at 900°C was dissolved in slightly acidified (5% HCl) warm water. The solution was properly stirred, filtered and residue was oven dried under rotary vacuum. Weight loss of about 15% was observed throughout the process which corresponds to stoichiometric B_2O_3 formed during the reaction. B_2O_3 being the glassy phase could not be detected in XRD analysis. Leached product contained less than 100 ppm of oxygen. However, carbon and nitrogen impurities remained below the detectable limit.

The SEM of the leached product EuB_6 is shown in the Fig. 6. It can be seen that the particles of EuB_6 are uniformly distributed which was verified by the distribution of particle size curve shown in Fig. 7. The particle size is seen to be around 4–10 µm indicating the absence of grain growth which is obvious because of low processing temperature. Fine pores of around 2 µm are visible at grain junctions. The small particle size is found to be promising for sintering process.

Oxidation of EuB₆ sintered pellets

The oxidation reaction of europium hexaboride can be presented by the following equation:

$$EuB_{6(s)} + O_{2(g)} = B_2O_3(l) + Eu_2O_3(s)$$
(2)

Free energy curve for the oxidation reaction was calculated and presented in Fig. 8. The free energy curve confirms the thermodynamical feasibility of the oxidation reaction at low temperature.

The percentage weight gain data obtained during the oxidation of dense (> 90 % of theoretical density) EuB_6 pellets at various time intervals are presented in Fig. 9.



Figure 7. Particle size distributions of prepared EuB₆



Figure 8. Gibbs free energy curve for oxidation of EuB₆

It can be seen that the rate of oxidation decreased with time and became zero. After long duration of oxidation (> 16 hours) about 1.2 % weight loss was observed (Fig. 9) that could be due to the evaporation of B_2O_3 formed during the oxidation. XRD analysis of the oxidized surface shown in Fig. 2 clearly indicates the formation of Eu_2O_3 which might form an adherent layer to prevent



Figure 9. Weight gain during oxidation of dense pellets at 850°C



Figure 10. SEM Image of oxidized surface of EuB₆ after 64 hours

further oxidation. SEM image of oxidized surface of the EuB₆ sample is illustrated in Fig. 10. The SEM image shows the adherent surface in which grains are not clearly visible. Prima facie results indicate the formation of adherent surface of Eu_2O_3 which prevents the oxidation. B_2O_3 formed during oxidation, being glassy phase, was not detected in XRD analysis.

The oxidation behaviour of the sintered (> 90 % of theoretical density) pellet was also studied using thermogravimetry technique. Thremogram of the sintered pellet at 850°C is shown in Fig. 11. It is clear from the figure that the oxidation rate decreases with time and becomes almost zero after 8 hours. This was due to the formation of adherent surface of Eu_2O_3 during oxidation process. The thermogravimetric results further support the formation of adherence surface.

IV. Conclusions

Highly pure carbon free EuB_6 has been prepared at relatively low temperature. Boron from the obtained by-product B_2O_3 could be easily recovered by commercially available process. Low temperature synthesis prevents the agglomerates formation and keeps



Figure 11. Thermogravimetric analysis of oxidation reaction of EuB₆ pellet with ~90 % of theoretical density

particle size very small which is essential for the sintering process. The small particle size favours pressureless sintering. Oxidation study shows the usability of these materials at high temperature because of adherent oxide layer of Eu_2O_3 formation which prevents further oxidation.

Acknowledgement: The Authors would like to sincerely acknowledge their colleague Dr. Alok Awasthi for several scientific discussions.

References

- J.L. Gavilano, B. Ambrosini, P. Vonlathen, H.R. Ott, D.P. Young, Z. Fisk, "Low temperature nuclear magnetic resonance studies of EuB₆", *Physica B: Phys. Condensed Matter*, 259 (1999) 168–169.
- J. Kunes, W.E. Pickett, "Kondo and anti kondo coupling to local moments in EuB₆", *Phys. Rev. B* 69 (2004) 1–9.
- H.R. Ott, J.L. Gavilano, B. Ambrosini, P. Vonlanthen, E. Felder, L. Degiorgi, D.P. Young, Z. Fisk, R. Zysler, "Unusual magnetism of hexaborides", *Physica B*, 281-282 (2000) 423–427.
- 4. J. Etourneau, "Critical survey of rare-earth borides: occurrence, crystal chemistry and physical properties", J. Less Common Metals, **110** (1985) 267–281.
- 5. Ph. Dunner, H.J Heuvel, M. Horle, "Absorber materials for control rod system of fast breeder reactors", *J. Nuclear Mater.*, **124** (1984) 185–194.
- Yu. Paderno, V. Paderno, N. Shitsevalova, V. Filippov, "The peculiarities of the structure formation in directionally crystallized eutectics EuB₆-MeB₂", *J. Alloy. Compd.*, **317-318** (2001) 367–371.
- M. Futamoto, M. Nakazawa, U. Kawabe, "High temperature surface composition of hexaborides thermionic electron emitters", *Vacuum*, 33 (1983) 727–732.
- J.F. Edward, I. Binder, B. Post, "Europium hexaborides and lanthanum teraboride", *J. Am. Chem. Soc.*, 80 [30] (1958) 3479–3481.
- S. Kumar, R.D. Bedse, A. Awasthi, "Studies on the preparation of rare earth borides", pp. 507 in *ATM Technical program and Abstract International Symposium on Energy Related materials NMD-ATM 2007*. Eds. G.K Dey, Mumbai, India, 2007.
- T. Tanaka, E. Bannai, S. Kawai, "Preparation of EuB₆ single crystal", *J. Crystal Growth*, 40 (1977) 125–128.
- G. Bukatov, S. Kuznetsov, M. Gaune-Escard, "Electrochemical synthesis of rare-earth metal (Eu, Nd) borides in molten salts" *Russian J. Electrochem.*, 43 [8] (2007) 929–935.
- G.A. Bukatova, S.A. Kuznetsov, M.G. Escard, "The electrochemical synthesis of europium borides", *J. Min. Metall.*, **39** [1-2] (2003) 251–259.
- V.N. Gurin, M.M. Korsukova, S.P. Nikanorov, I.A. Smirnov, N.N. Stepanov, S.G. Shulman, "The preparation of single crystals of the rare earth borides by the solution method and a study of their properties", *J. Less-Common Metals*, 67 (1979) 115–123.

- 14. X. Junqi, C. Xiaolong, Z. Yanming, Z. Chunyun, D. Qiwei, J. Jikang, "Self-catalyst growth of EuB₆ nanowires and nanotubes" *J. Crystal Growth*, **303** (2007) 466–471.
- Nelson P. Nies, "Preparation of boron by fused salt electrolysis", J. Electrochem. Soc., 107 (1960) 817– 820.