

Nano and micro sized EuB_6 via magnesiothermic reduction

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In this study, nano and micro sized EuB_6 was synthesized via magnesiothermic reduction in open air. Method is optimized according to temperature and reaction time. Optimum temperature and reaction time are determined to be 600°C and 4 hours. Products were analysed with x-ray diffraction (XRD), Scanning electron microscopy (SEM). XRD analysis proved formation of pure EuB_6 and SEM analysis were used to characterize structure and morphologies of samples. Nanosized and micro sized EuB_6 with heterogeneous morphology was observed.

Key words: Boron, Boride, Europium, Nanosized material.

Introduction

Since the discovery of carbon nanotubes [7], one dimensional nanostructures such as nanotubes, nanowires, and nanorods have been extensively investigated due to their interesting and novel properties and the opportunity they provide for achieving a deep understanding of physics at the nanometer scale. Recently, much attention has been paid to the preparation of rare-earth alkali metal boride nanostructures [8-10]. High melting point, high strength, and high chemical stability, as well as other special peculiarities, such as low electronic work function, stable specific resistance, low expansion coefficient in some temperature ranges and high neutron absorbability make these materials suitable for use as components of high-energy optical systems, sensors for high-resolution detectors [11].

Nuclear properties of europium hexaboride present a special interest due to very high absorption of both boron and europium atoms for thermal and fast neutrons. The EuB_6 neutron-absorbing characteristics exceed those of other materials. Another promising field is the development of thermionic coatings based on rare-earth hexaborides, which may offer the possibility of the production of inexpensive and simple high emission filaments [2].

The intricate interplay between ferromagnetism and electronic transport, which results in the effect of colossal magnetoresistance (CMR) in divalent hexaboride EuB_6 , stimulates permanent interest to this compound. It is known that rare-earth hexaborides crystallize in a CsCl-type structure in which a cube consisting of

heavy metal atoms is centered as an octahedron composed of six rigidly bound lighter atoms of boron. This group of B_6 atoms can be considered a structural unit, namely, a pseudoatom $\text{B}^* \equiv \text{B}_6$ [1]. It is worth noting that the distances between boron atoms belonging to the adjacent cells are shorter than those inside the B_6 group. The hexaboride compounds are a group of materials with a similar body-centered-cubic-like crystal structure, but disparate and intriguing electronic and magnetic properties [5]. One particular subgroup in this large class of materials includes the hexaborides, which are being used as additives for wear- and corrosion-resistant engineering components, for decorative and thermionic coatings, and for electron emission sources [5].

Due to the importance of novel materials, we several authors have reported on different methods for fabrication of hexaborides [12]. Aim of this work is to find an optimum reaction temperature and reaction time for obtaining pure EuB_6 via magnesiothermic reduction in open air.

Experimental

Europium(III) oxide Eu_2O_3 (purity > 99% particle size about 20 μm) and Boron (III) oxide B_2O_3 (purity > 99% particle size about 20 μm) was obtained by Aldrich, Magnesium Mg (purity > 98.5% particle size about 0.06-0.03 mm) was provided by Merck.

0.352 g Eu_2O_3 (1 mmol), 0,418 g (6 mmol) B_2O_3 and 0.60 g Mg (25 mmol) were mixed in a porcelain crucible. Crucible was put in a muffle furnace. Reaction temperature was adjusted to 600 °C and kept four hours in furnace in open air. After fast cooling, the precipitate was leached in concentrated hydrochloric acid (conc. HCl) for one day. Conc. HCl was decanted

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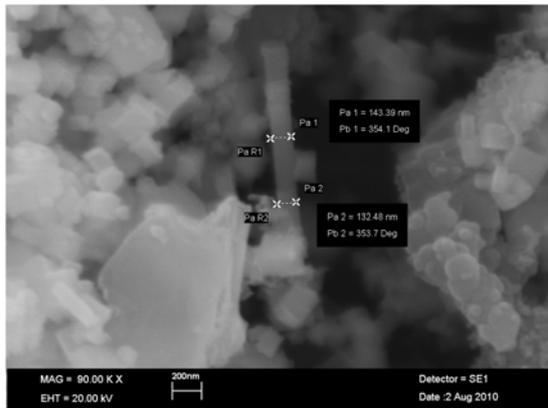


Fig. 1. SEM image of EuB_6 for $t = 4$ hours and $t = 600$ °C.

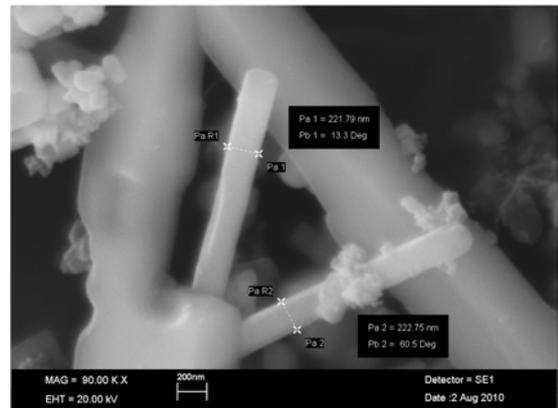


Fig. 4. SEM image of EuB_6 for $t = 8$ hours and $t = 600$ °C.

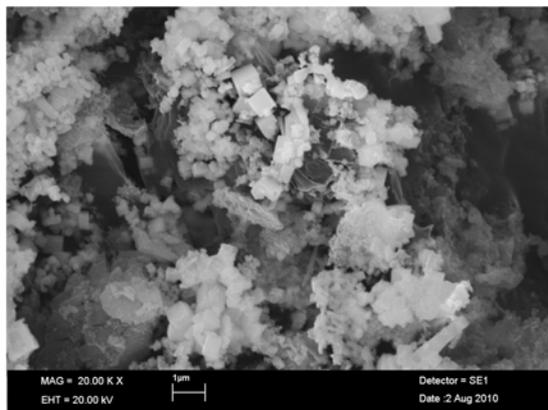


Fig. 2. SEM image of EuB_6 for $t = 4$ hours and $t = 600$ °C.

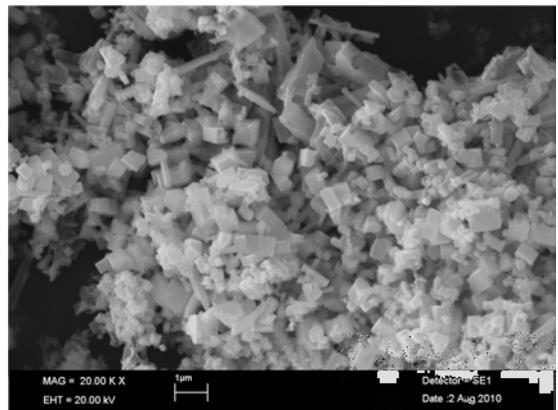


Fig. 5. SEM image of EuB_6 for $t = 12$ hours and $t = 600$ °C.

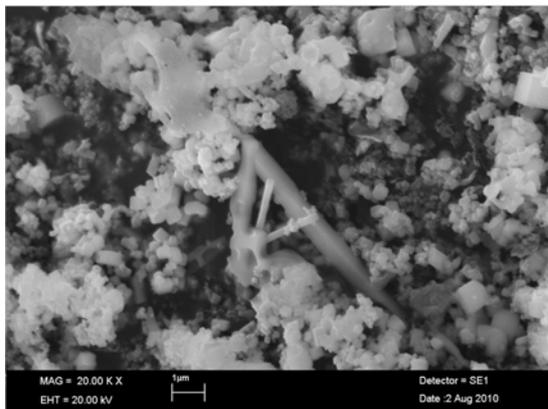


Fig. 3. SEM image of EuB_6 for $t = 8$ hours and $t = 600$ °C.

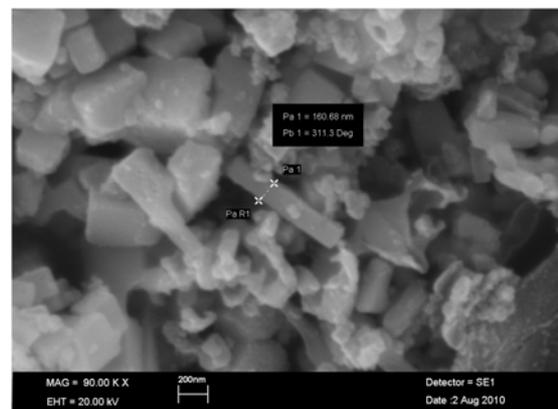


Fig. 6. SEM image of EuB_6 for $t = 12$ hours and $t = 600$ °C.

and the precipitate was again leached in concentrated HNO_3 for one day under magnetic stirring. Then black precipitate was filtered and washed with distilled water three times and dried in an oven at 100 °C.

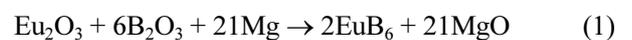
XRD patterns were recorded on a Bruker Axs D8 advance using $\text{CuK}\alpha$ (1.5406 Å) radiation.

X ray peaks were corrected for instrumental broadening and taking into account the strain effects as shown in Fig. 11. XRD results were analyzed via software program EVA. SEM images were obtained by Leo 440 and analysis of the micrographs was used to

characterize morphologies and structures of the samples as shown in Fig 1-10.

Result and Discussion

The growth of the EuB_6 was based on the following chemical reaction:



The reaction was carried out in a muffle furnace in

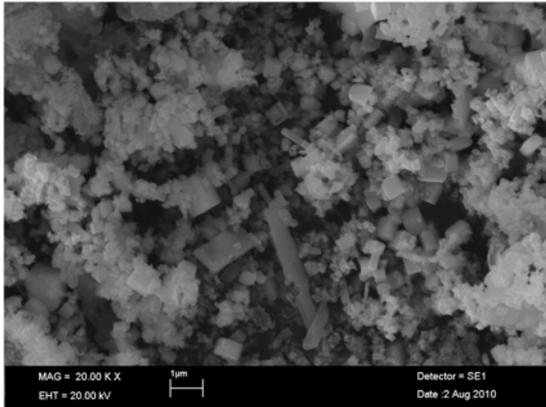


Fig. 7. SEM image of EuB_6 for $t = 16$ hours and $t = 600$ °C.

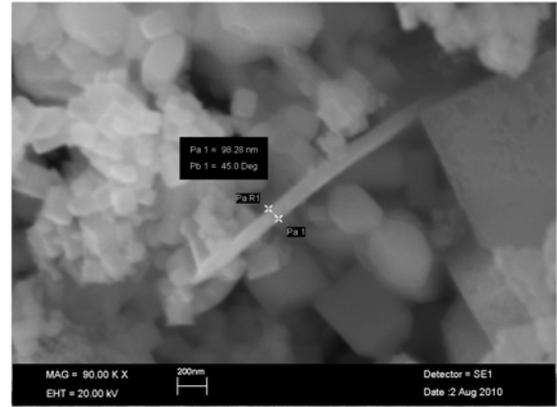


Fig. 10. SEM image of EuB_6 for $t = 20$ hours and $t = 600$ °C.

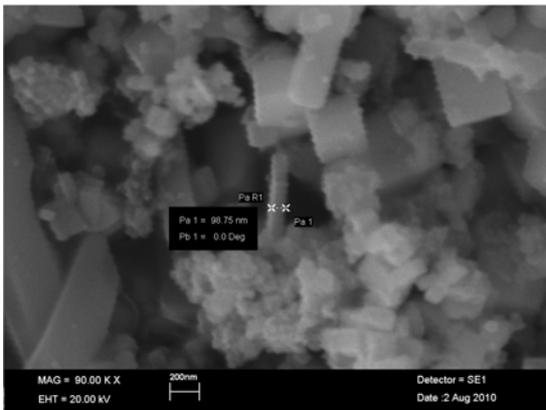


Fig. 8. SEM image of EuB_6 for $t = 16$ hours and $t = 600$ °C.

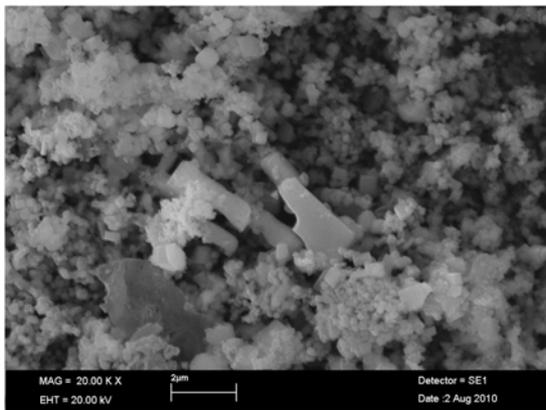


Fig. 9. SEM image of EuB_6 for $t = 20$ hours and $t = 600$ °C.

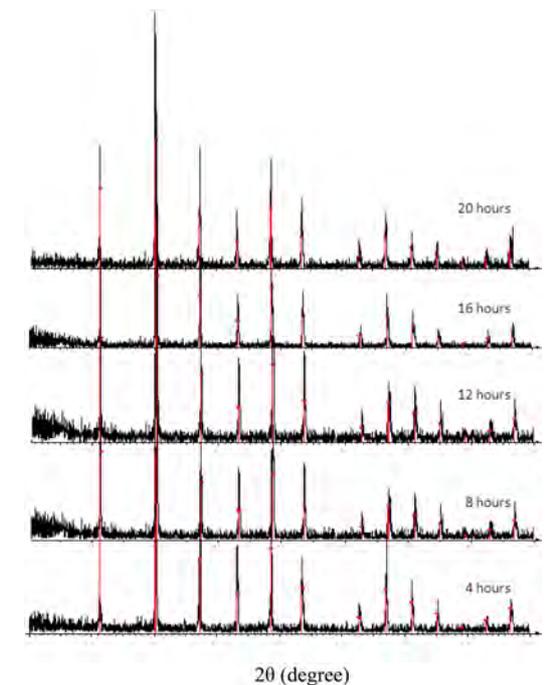


Fig. 11. XRD spectra of EuB_6 samples at different reaction times.

open air. Excess of Magnesium used to increase yield of reaction, excess of magnesium vaporises slightly, reaction gets faster and yield increases. To investigate optimum condition of reaction, first reaction temperature parameter was changed from 500 °C to 900 °C. Yield of reactions were calculated for each parameter. As it is seen in figure 1, optimum reaction temperature is 600 °C. Because melting point of magnesium is 649 °C, optimum temperature would not be a surprize, magnesium stays much time in the reaction media than for higher temperatures. For this reason, effectiveness of magnesium

as reducing agent is increased.

Second, we changed the reaction time parameter to find out optimum reaction time from 1 to 20 hours. Yield of reactions were also calculated for each time parameter. As it is seen in figure 2, optimum reaction time is determined as four hours.

SEM images for each reaction time parameter are given in figures (Fig. 1-10). EuB_6 samples are in heterogeneous morphology. Mixture of cubic, prismatic and wire shapes are seen in the figures. Nano and microsized cubes are dominant for $t = 4$ hours (Fig. 1, 2). Microsized wire formation and heterogeneous figures are seen for $t = 8$ hours (Fig. 3-, 4). Microsized prismatic figures are dominant for $t = 12$ hours.(Fig. 5, 6). Nanosized wire with 98 nm thickness is obvious and microsized cubes are seen for $t = 16$ hours. (Fig. 8). Nanowire formation with 98 nm thickness is seen for $t = 20$ hours also, there are some

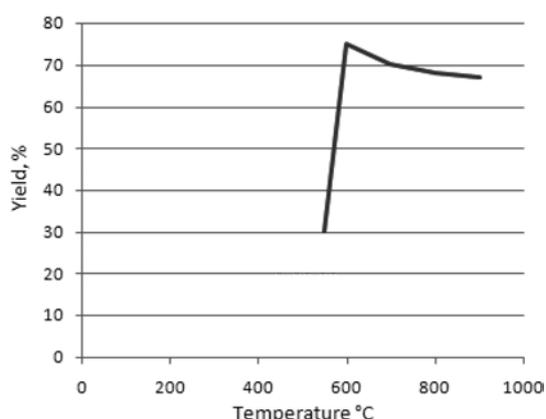


Fig. 12. Variation of yield with temperature.

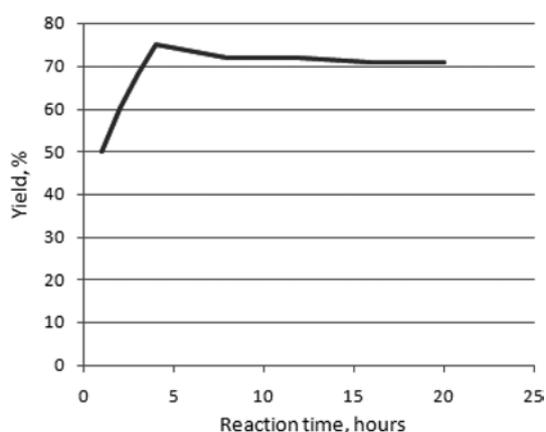


Fig. 13. Variation of yield with reaction time at 600 °C.

heterogeneous morphology (Fig. 9, 10). In our previous work, LaB_6 samples preferred to form wires more than EuB_6 samples [1]. In another work hexaboride samples favored cubic shapes [4]. Samples of EuB_6 are more in nano and micro sizes as seen in figures. Cubic growth of EuB_6 crystals are also seen in literature work [12]. The reaction temperature plays a crucial role in determining the shape of the final product [13]. Also, nucleating seeds, kinetic control, selective activation energy modulations of surfaces through the use of capping molecules are found to be crucial for anisotropic growth. By delicately balancing and controlling these parameters, it is possible to control the shapes of nanocrystals [13]. Careful controlling of temperature and reaction time parameters for fabrication of novel nanostructures are open for further exploration.

X-ray spectra of samples proved formation of pure EuB_6 . Leaching of reaction product with concentrated HCl is for removal of impurities. However, leaching with nitric acid was also required in order to remove some borate impurities present in the samples. Nitric acid with high oxidation potential is capable of removing all impurities. Pure EuB_6 samples, insoluble in mineral acids synthesized successfully.

Recently Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD) and mechanochemical processes (MCP) and some others are described for production of borides of lanthanides. However, requirement of low pressure, vacuum, high temperature and special devices, these methods are expensive routes to produce lanthanides of borides [12]. Because of their potential use in industry, there is an increasing need to fabricate them with cheaper price [1]. Results of our investigation showed that magnesiothermic reduction method is suitable for production of pure EuB_6 successively. We used moderately low temperature, open air and only oxides as starting materials.

Conclusion

Pure nano and micro sized EuB_6 was synthesized successfully. Reaction conditions are 600 °C and four hours in open air. Cleaning with hydrochloric acid is unsuccessful in removing unwanted borate phases. Subsequent cleaning with nitric acid results in the removal of all impurities. Careful controlling of temperature and reaction time parameters for fabrication of novel nanostructures for EuB_6 are open for further exploration.

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