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Fast and Low-Cost Synthesis of LaB_4 and LaB_6 Mixture and GdB_6

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Abstract: In this study, we synthesized LaB_4 and LaB_6 mixture and GdB_6 with direct magnesiothermic reduction reaction at 700°C in open air in good yield. Reactions of magnesium, boron(III) oxide and lanthanum(III) oxide and gadolinium (III) oxide was carried out in a muffle furnace at 700°C. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis were used to characterize morphologies and structures of the samples. XRD analysis proved that LaB_4 and LaB_6 mixture and GdB_6 were synthesized. The formation of two types of wires for LaB_4 and LaB_6 mixture and one type of nanosized wire for GdB_6 and was by SEM.

Key words: lanthanum · Gadolinium · Metal boride · Nanosized material

INTRODUCTION

Since the discovery of carbon nanotubes [1], 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 [2,4]. 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,[5,7] sensors for high-resolution detectors [8].

Rare earth metal borides are of special interest, due to their physical, magnetic and electrical properties. The lanthanide elements, unlike the transition metals, tend to form boron-rich materials rather than the metal-rich phases. These rare earth hexaboride structures consist of frameworks of boron octahedra arranged as units in a body centered cubic lattice [11]. The covalent bonding within the boron polyhedra is believed to impart great stability, hardness and high melting points to these borides. The thermoionic emissive properties of the rare earth hexaborides have been studied in detail and these materials have been found to possess very low work functions which are, in fact, lower than for any other known materials (i.e. work functions of 2.74 and 2.22 eV for LaB_6 and YB_6, respectively). Of all the rare earth borides, lanthanum hexaboride is of particular interest due to its use as an electron emissive (thermoionic) material [11]. Lanthanum hexaboride has the highest electronic emissivity of any known material and its performance is unaffected by the presence of either nitrogen or oxygen. Lanthanum hexaboride thin film cathodes have recently been successfully used to replace nickel cathodes in display panels. These rare earth boride cathodes have been shown to work very efficiently at significantly lower voltages than the corresponding nickel cathodes. The sputtering rates of the LaB_6 thin films in these cathodes were also found to be only about one third the rate of sputtering of the traditional nickel cathodes [11].

Magnesiothermic reduction is a well known technique for production of metal borides however, use of inert atmosphere and high temperature is required according to literature [14]. Formation of MgO and $Mg_3B_2O_6$ during the synthesis is unavoidable. MgO and $Mg_3B_2O_6$ are acid soluble and LaB_6 and LaB_4 are resistant to mineral acids. It is easy to remove impurities by applying concentrated mineral acids, however, there is not any work in the literature using concentrated acids for removal of impurities. In this work, we synthesized GdB_6 and LaB_6 and LaB_4 mixture free of MgO and $Mg_3B_2O_6$ impurities.

MATERIALS AND METHOD

Preparation of LaB_4 and LaB_6 Mixture: Lanthanum(III) oxide La_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.

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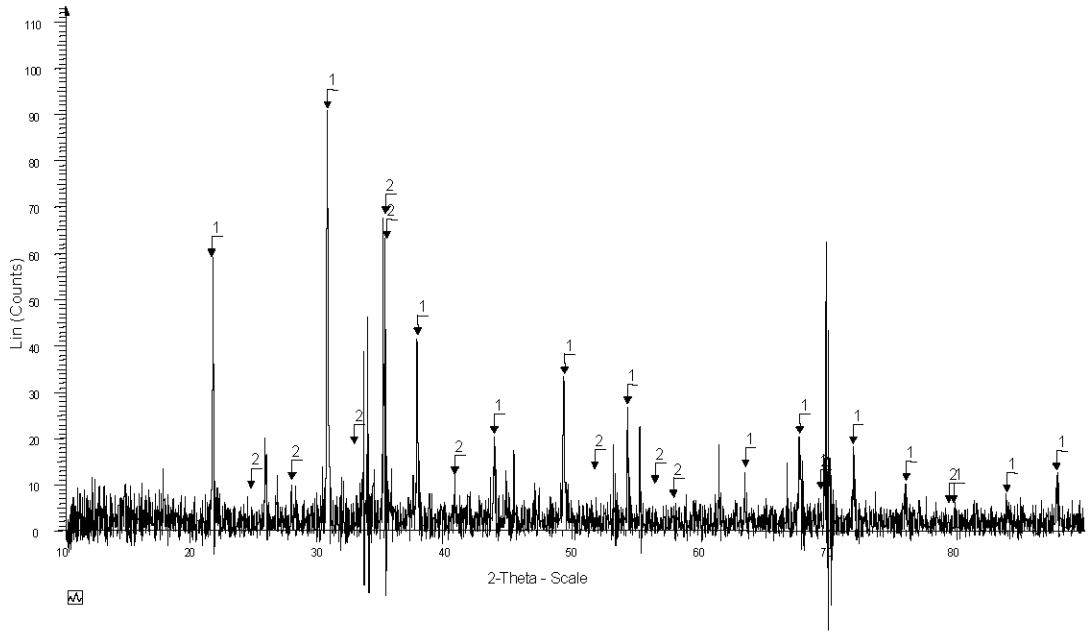

Fig. 1: XRD spectra of LaB_6 (1) and LaB_4 (2) mixture.

0.326 g La_2O_3 (1 mmol), 0,420 g (6 mmol) B_2O_3 and 0.600 g Mg (25 mmol) were mixed in a porcelain crucible. Crucible was put in a muffle furnace. Reaction temperature was adjusted to 700°C and kept two 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 and the precipitate was again leached in 1 M HCl for one day under magnetic stirring. Then purple precipitate was filtered and washed with distilled water three times and dried in an oven at 100°C.

Preparation of GdB_6: Gadolinium (III) oxide La_2O_3 (purity >99.9 % particle size about 20 μm) obtained by Fluka 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.

0.363 g Gd_2O_3 (1 mmol), 0,420 g (6 mmol) B_2O_3 and 0.600 g Mg (25 mmol) were mixed in a porcelain crucible. Crucible was put in a muffle furnace. Reaction temperature was adjusted to 700°C and kept two 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 and the precipitate was again leached in 1 M HCl for one day under magnetic stirring. Then purple precipitate was filtered and washed with distilled water three times and dried in an oven at 100°C.

XRD patterns for both sample were recorded on a Bruker Axs D8 advance using CuKα (1.5406 Å) radiation. X ray peaks were corrected for instrumental broadening and taking into account the strain effects as shown in Fig. 1. 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 2.

RESULTS AND DISCUSSION

The growth of the LaB_6 and LaB_4 nanowires was based on the following chemical reaction:

$$La_2O_3 + 6B_2O_3 + 21Mg \rightarrow 2LaB_6 + 21MgO \quad (1)$$

$$La_2O_3 + 4B_2O_3 + 15Mg \rightarrow 2LaB_4 + 15MgO \quad (2)$$

The reaction was carried out in a muffle furnace at 700°C. We applied magnesiotermic reduction in open air which is fast and easy, rather than CVD technique. Procedure used in this study can significantly reduce the cost of synthesis by avoiding use of low pressure, $LaCl_3$, BCl_3 inert gases and special furnaces. In order to increase reactivity of magnesium as being liquid, reaction temperature was kept above its melting point (649 °C). At this temperature, excess of magnesium vaporizes slightly and reaction rate gets faster.

LaB_6 has cubic crystal system with unit cell parameters a = 4.15690, b = 4.15690, c = 4.15690 and $\alpha = \beta = \gamma = 90.00°$. LaB_4 has tetragonal crystal

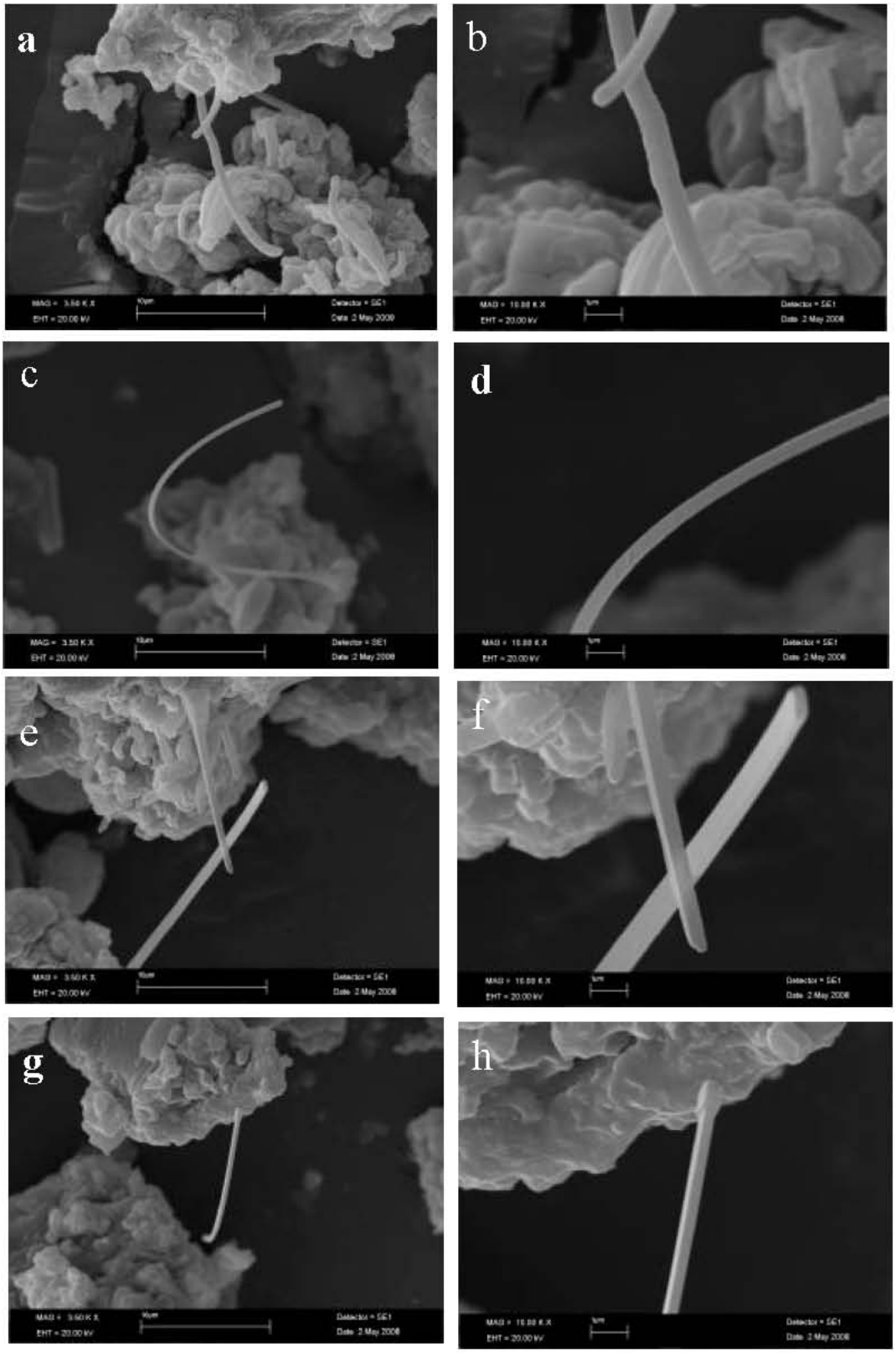

Fig. 2: SEM images of LaB_4 and LaB_6 mixture

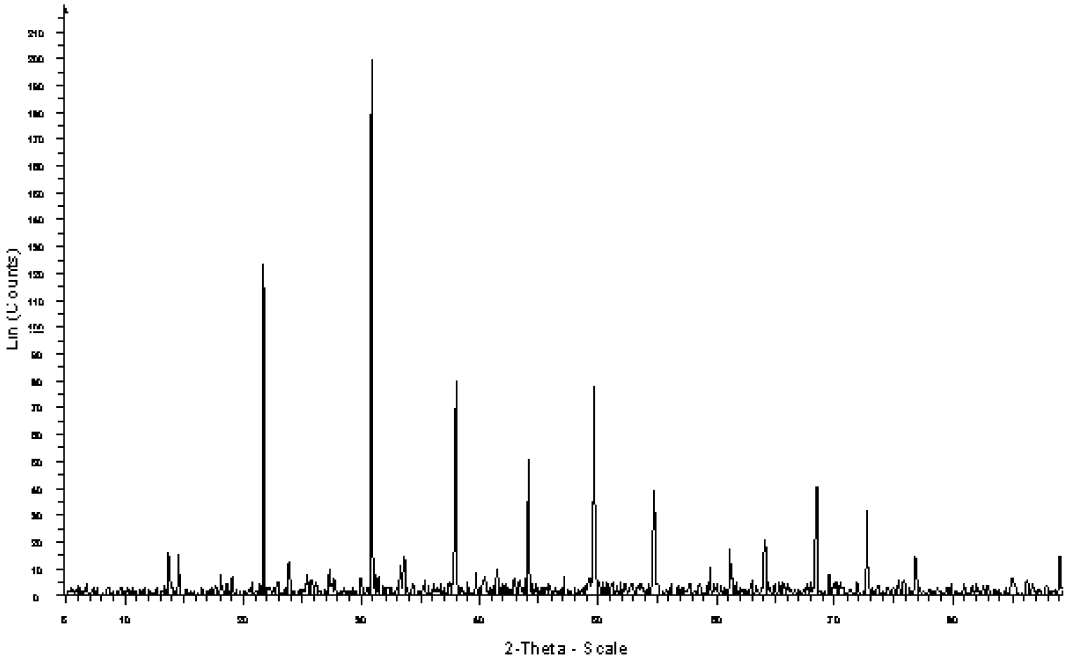

Fig. 3: XRD spectra of GdB_6.

system with unit cell parameters a = 7.32300, b = 7.32300, c = 4.18100 and $\alpha = \beta = \gamma = 90.00°$. XRD results show that LaB_4 and LaB_6 mixture is free of impurities that should present. That is because, leaching with conc. HCl for one day.

It was seen from the SEM analysis that grown crystals were composed of regular shaped agglomerates. SEM images show that synthesized nanowires were 0.5-1μm thick and 10-15 μm long. There are two types of crystal growth as seen in Fig. 2, one is growing cylindrically (a, b, c, d of Fig. 2) the other is growing rectangular (e, f, g, h of Fig. 2). Reason for formation of nanostructures may be attributed to rapid quenching after completion of the reaction in the furnace at high temperature. Rapid quenching will result with crystals of small size. Results of our investigation shows that direct magnesiothermic reduction reaction is suitable for production of borides of Lanthanum in high yield (79%). This method is cheap and easy as compared with other techniques.

Method of synthesis above mentioned literatures were only for formation of thin film rather than fabrication. However, it is a requirement to produce nanowires of LaB_6 and LaB_4 in much more cheaper route due to its increase of use in the industry.

GdB_6 has cubic crystal system with unit cell parameters a = 4.10711, b = 4.10711, c = 4.10711 and $\alpha = \beta = \gamma = 90.00°$.

XRD results show that GbB_6 is formed however, there are little impruties with low intensity peaks, which are B_2O_3 and Gd_2BO_3. Purity of sample is very good because of leaching with conc. HCl for one day. Formation of GdB_6 formation is based on the following reaction

$$Gd_2O_3 + 6B_2O_3 + 21Mg \rightarrow 2GdB_6 + 21MgO \quad (3)$$

As in the case of LaB_4 and LaB_6 production, excess of Mg was used for increasing yield of reaction. excess of magnesium vaporizes slightly and reaction rate gets faster and yield increases.

Similar reaction conditions were applied for both boride samples. SEM images of GdB_6 samples showed heterogeneous morphology. Formation of nanosized wires were observed with approximately 100 nm diameter and 2 to 4 μm length.

Since it is used as electron emitter device, it would be important to fabricate them with a cheaper technique. Recently, use of Chemical Vapor Deposition (CVD) and mechanochemical processing (MCP) for fabrication of LaB_6 is often, but due to requirement of low pressure, high temperature and special devices, these are expensive routes to produce borides of lanthanides. Because, the uses of LaB_6 as thermoionic electron emitter is increasing, cost of synthesis is important for industrial scale productions. The aim of preparation route illustrated here was to reduce the cost of synthesis by avoiding use of low pressure, $LaCl_3$, BCl_3, inert gases, special furnaces and ball mills.

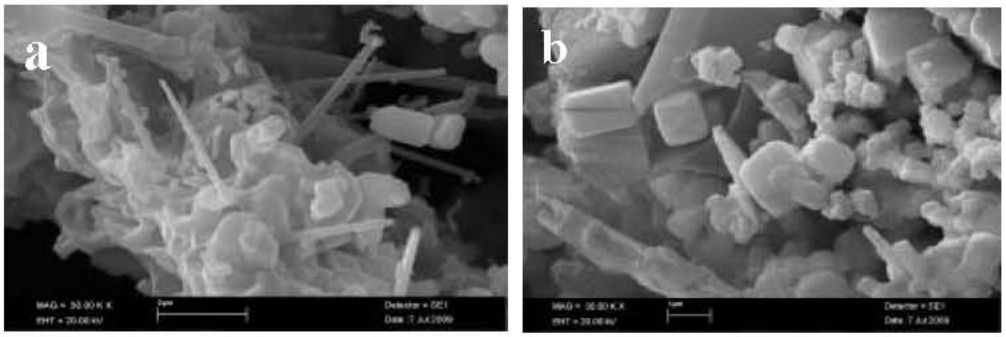

Fig. 4: SEM images of GdB_6.

Boustani *et al*. initiated an experimental and theoretical study on the formation and stability of charged lanthanum hexaboride clusters LaB_6 at field evaporation. Multi-charged LaB_n clusters were produced by field evaporation of LaB_6 single crystals [12]. The measured appearance probability of various clusters in a flux was compared with the calculated energetic stability of the corresponding free clusters. The appearance probability of cluster ions in the atom probe spectra was estimated by calculating its rating in many selected spectra. The calculations were based on *ab initio* quantum chemical methods. The main conclusion is that highly stable free lanthanum boride clusters are related to a low probability of field evaporation for these species from the LaB_6 tip, while the unstable clusters leave the surface with higher probability and were preferably observed in the ion flux. The most stable clusters (large atomic number n and small charge m in LaB_{nm}) has some resources for redistributing the inter-atomic bonds and thus to remain attached to the surface, while unstable clusters do not have any resources and must leave the surface in any case. The lanthanum atom in the geometries of the most stable lanthanum boride clusters is mostly localized on the tip of the boron clusters or bonded to the boron atoms equidistant [12]. Although, probability of forming many type of lanthanum borides are existent, one can produce LaB_4 and LaB_6 with changing some reaction parameters such as, temperature of reactants and molar ratio of reactants. Most stable model seems to be LaB_6 and molecular modeling of LaB_6.

CONCLUSION

We have succeeded to grow high-quality LaB_4 and LaB_6 mixture and GdB_6 crystals reproducibly by magnesiothermic reduction method using open air muffle furnace. As a result, synthesis of borides of lanthanides (La and Gd) was achieved at very low temperature and open air. This shows that low cost synthesis and production of route is proposed.

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