

A new route for the synthesis of boron-rich rare-earth boride NdB_6 under high pressure and high temperature

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Abstract

The boron-rich rare-earth boride NdB_6 , which is a pure phase without the intergrowth of other phases, has been obtained for the first time by the reduction of rare-earth oxide with elemental boron under the extreme conditions of high pressure and high temperature. The synthesis can be carried out in air from the beginning to the end without the protection of inert gas, and the synthesis can be completed rapidly. The residual rare-earth oxide and the elemental rare-earth metal produced in the process of synthesis can be easily removed by leaching them in HCl.

Keywords: Rare-earth boride; High pressure and high temperature

1. Introduction

Borides have many curious physical and chemical properties because of the electron deficiency of boron. In particular the boron-rich rare-earth borides show different properties such as superconductivity, high efficiency thermionic emission and narrow-band semiconductivity etc. for different rare-earth elements. Therefore, boron-rich rare-earth borides have uses in many fields, and their synthesis is important.

Many synthetic methods have been developed for boron-rich rare-earth borides. For example, the sintering method, the solution method and the molten salt electrolysis method. The sintering method is synthesis of a mixture of elemental boron and rare-earth or rare-earth hydrides in a high temperature furnace [1]. The temperature for the reaction is usually above 1500 °C, and the reaction time is usually more than 10 h or even more than several days. Because of the oxidation of the elemental rare-earths in air, the reaction must be carried out in high vacuum, and also requires high-quality crucibles for the high reaction temperature. The molten salt electrolysis method is to electrodeposit the molten salts of boron oxide (or borax) and rare-earth oxide [2]. This method has three shortcomings:

inefficient use of electric power, intergrowths of several borides and difficulty of separating the product from the molten salt. The reduction method is to reduce the mixture of boron oxide, and rare-earth oxide with carbon at high temperature. Although large amounts of rare-earth boride can be produced, the stoichiometric composition can be changed because of the different volatilization of the reactant oxides and the product can be contaminated by boron, carbon or carbonates. The solution method fuses rare-earth metal and boron into molten aluminum at about 1300 °C [3], then lowers the temperature slowly to crystallize the rare-earth boride from molten aluminum. This method needs protecting by inert gas and the product contains impurities of aluminum and boron-aluminum compounds. The floating zone melting method is the best and yields single crystals [4], but it needs the precursor of powder boride, this method is very expensive because it needs complex equipment.

From the above discussions, it can be seen that each method mentioned above has advantages and disadvantages. This paper reports a new route to synthesize pure boron-rich rare-earth boride NdB_6 by the reduction of rare-earth oxide with elemental boron under the extreme conditions of high pressure and high temperature. Since the rare-earth oxide is chosen as the source of rare-earth element, the above experiments can be carried out in air from the beginning to the end without the protection of

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inert gas. And the high temperature is very easy attainable under high pressure.

2. Experimental

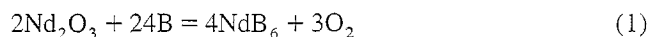
Amorphous boron (with a purity of 99.99%) was mixed with rare-earth oxide Nd_2O_3 (with a purity of 99.9%) (which was weighed in the ratio $\text{Nd}:\text{B}=1:5$) and ground uniformly, then was placed in a high pressure assembler [5,6].

High pressure synthesis was carried out using a Bridgman apparatus at a force of 4.903×10^6 N. The magnitude of the pressure generated inside the cell was calibrated by the electrical changes on the basis of the phase transformations of Bi, Tl, Ba (2.55, 2.69 and 7.7 GPa). The sample was heated electrically with a carbon heater, and the temperature was measured by inserting a Pt30%Rh–Pt6%Rh thermocouple in the cell. The high pressure synthesis procedure is to increase the pressure to the expected value, then to raise the temperature to the desired value. After maintaining the desired high pressure and high temperature conditions for 15 min, the sample was quenched to room temperature prior to the release of the applied pressure.

X-ray powder diffraction studies were performed using a Rigaku 12 kW D/max copper rotating-anode X-ray diffractometer with a graphite monochromator. Silica was used as an internal standard, and cell parameters are refined by least squares.

3. Results and discussion

Under the extreme conditions of high pressure and high temperature, the boron-rich rare-earth boride NdB_6 was prepared by the reduction of rare-earth oxide with elemental boron. The synthesis reaction is as follows:



After the reaction, there are still some excess rare-earth oxide and the rare-earth metal that can be removed by leaching them in HCl.

The optimum condition for the synthesis of boron-rich rare-earth boride NdB_6 is to maintain the pressure of 4.0 GPa and the temperature of 1600 °C for 15 min. The X-ray powder diffraction pattern of the product is shown in Fig. 1 and corresponding XRD data are listed in Table 1. NdB_6 crystallizes in the cubic system with lattice constant $a = 0.4125$ nm (average value derived from a least squares fitting of X-ray powder diffraction data). When compared with the XRD data of [7], the result shows that boron-rich rare-earth boride NdB_6 synthesized in this work is not contaminated by boron or any other impurity phase.

The above reaction is carried out at a temperature which

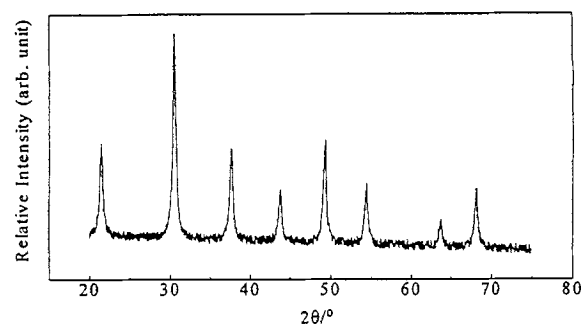


Fig. 1. XRD pattern of boron-rich rare-earth boride NdB_6 .

does not melt the oxide and boron molten, but is completed in very short time. Solid–solid reactions are very slow according to the reaction dynamics; thus there must be another reaction mechanism. In previous experiments, we had confirmed the reduction of transition metal oxides and rare-earth metal oxides under high pressure and high temperature, i.e. a pure oxide will change to elemental metal [8–10] for transition metal or lower-valence oxide for rare-earth metal [11,12] and O_2 (accompanied by the occurrence of oxygen deficiencies in oxide) [13]. In order to confirm the above reduction, Nd_2O_3 powder was subjected to high pressure and high temperature. Then the raw material and the product were examined by XRD, and the results are shown as Fig. 2. It can be seen from the XRD pattern of Fig. 2 that there exist diffraction peaks of rare-earth metal Nd in Fig. 2(b) (compared with results of Ellinger [14]) which are marked with arrows besides the raw material and h- Nd_2O_3 (compared with results of Swanson [15]) transformed from the raw material. So it can be concluded that the chemical reaction (1) is not a simple one but a complex one which can be divided into several steps. Some of the Nd_2O_3 decomposes into NdO and O_2 by reduction under high pressure and high temperature, and the valence of Nd decreases from 3+ to 2+ [13]:



then, NdO disproportionates into Nd and Nd_2O_3 because of the instability of NdO:

Table 1
XRD data of boron-rich rare-earth boride NdB_6

$2\theta(^{\circ})$	d (nm)	hkl	d^a (nm)
21.40	0.4152	1 0 0	0.4120
30.52	0.2928	1 0 1	0.2910
37.64	0.2398	1 1 1	0.2378
43.78	0.2067	2 0 0	0.2063
49.30	0.1848	2 1 0	0.1845
54.38	0.1687	2 1 1	0.1684
63.74	0.1460	2 2 0	0.1456
68.14	0.1376	2 2 1	0.1375
72.42	0.1305	3 1 0	0.1305

^aXRD data of NdB_6 in Ref. [7]

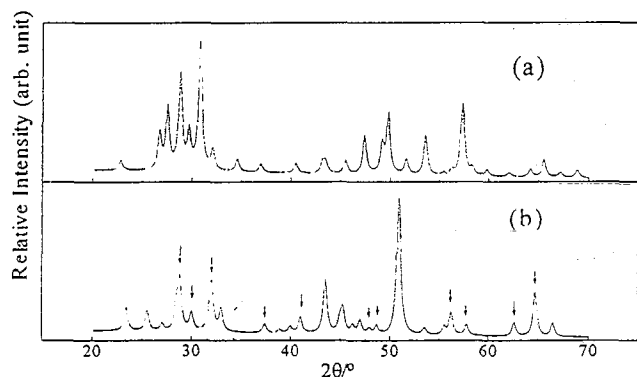


Fig. 2. XRD patterns of the (a) starting material Nd_2O_3 and (b) the product of high pressure and high temperature. Arrows indicate Nd metal phase.



The above two reactions can be considered as a total decomposition reaction:



The elemental Nd produced combines with boron into NdB_6 immediately:



The method for the synthesis of boron-rich rare-earth boride NdB_6 by the reduction of rare-earth oxide with elemental boron under high pressure and high temperature has many obvious advantages over the previous ones.

1. The synthetic reaction can be completed in a much shorter time compared with the methods mentioned above. Because the starting materials are all powders, they can be mixed homogeneously and once the reaction is carried out, the elemental rare-earth, which has higher reactivity than that of bulk rare-earth, will be produced and greatly accelerates the completion of synthetic reaction.
2. It is easy to obtain a single phase product of boron-rich rare-earth boride NdB_6 . The methods mentioned above most frequently mixed boron with a rare-earth element in a desired atomic ratio. Because of the oxidation of the rare-earth element in air, an inaccuracy in weighing would occur. So it was very difficult to obtain a pure product. Most products were mixtures of boron-rich rare-earth boride NdB_6 with either boron or rare-earth oxide. These problems can be avoided by the oxidation of elemental boron with excess rare-earth oxide Nd_2O_3 under high pressure and high temperature. It is easy to remove the residual rare-earth oxide and elemental rare-earth produced in the synthesis by leaching the product in hydrochloric acid, and then the pure phase of NdB_6 is obtained.

3. High pressure decreases the reaction activation energy, because it accelerates the diffusion between the reaction material powders.
4. High pressure can increase the coordination numbers of atoms, and it is of benefit to the synthesis of boron-rich rare-earth boride. Boron-rich rare-earth boride NdB_6 has simple cubic symmetry, with six boron octahedra at the eight vertices of a cube and Nd in eight fold coordination at the center of the cube. Thus the Nd atom has a high coordination number. For the methods mentioned above, it is very easy to produce many borides, such as NdB_2 , NdB_4 , NdB_6 etc.. If high pressure is used, the high-coordination boride NdB_6 can be synthesized directly and the impurities of NdB_2 , NdB_4 can be transformed into NdB_6 , too.
5. High pressure can provide reducing conditions which is equivalent to the use of an inert gas. Thus the high vacuum and inert gas used in the previous methods can be avoided. This will also accelerate the reduction of rare-earth oxides.

In conclusion, a new route for the synthesis of boron-rich rare-earth boride NdB_6 that yields a pure and well-crystallized product is reported here.

Acknowledgments

The authors wish to thank the National Natural Science Foundation of China for their financial support.

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