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A new synthesis route to light lanthanide borides: borothermic reduction of oxides enhanced by electron beam bombardment

Alessandro Latini, Francesco Di Pascasio, Daniele Gozzi*

Dipartimento di Chimica, Università di Roma 'La Sapienza', P.le Aldo Moro, 5, Box 34, 00185 Rome 62, Italy

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Abstract

Praseodymium hexaboride, uncontaminated by other boride phases, has been quantitatively synthesized in a short time, at the very high temperatures obtainable by electron beam bombardment. The synthesis is carried out in vacuum (~5×10^{-5} mbar) and, after a short annealing, the product is obtained as pure phase which does not require further purification.

Keywords: Rare earth compounds; Solid state reaction; X-ray diffraction

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1. Introduction

Light lanthanide (La→Sm) hexaborides represent a class of compounds with some technologically interesting properties. They have metallic resistivities (17×10^{-6} Ω·cm for LaB_6) and low values of the work function (~3 eV). In fact, LaB_6 is extensively used in thermoionic emitters. The hardness of these hexaborides is high (2620 ± 80 kg/mm^2 for LaB_6) comparable with the hardness of materials such as tungsten carbide WC (3000 kg/mm^2) and zirconium carbide ZrC (2600 kg/mm^2). Also their melting points are very high (>2500 °C). They are unaffected by moisture and non-oxidizing acids (unlike carbides or nitrides) and they are very resistant to oxidation even at high temperatures because of the formation on the surface of a thin protective film consisting of B_2O_3 and $Ln(BO_2)_3$ (Ln: lanthanide) [1]. They melt and evaporate congruently [2]. This makes it possible to evaporate them by thermal methods (as e-beam evaporation). Thin films of lanthanide hexaborides are used for decorative purposes because of their beautiful colors [3].

Several methods have been adopted for their synthesis: direct combination of the elements [4], borothermic reduction of lanthanide oxides, carbothermic reduction of metal oxide and boron oxide in a high temperature furnace (1500–1800 °C), solution method in molten aluminium [5], electrolysis of molten mixtures of lanthanide oxides with boron oxide [6] and high pressure-high temperature synthesis from metal oxides and boron [7].

Each of the above methods has some disadvantages. The reaction of metals or their oxides with elemental boron (or with boron oxide and carbon) is slow (to reach completion it requires more than 10 h, and in some cases, days). The carbothermic method also causes contamination of the product with carbon and carbon compounds. The solution method causes contamination by aluminium and aluminium boride. The molten salts electrolysis method leads to a mixture of borides which is difficult to separate and purify. The high pressure-high temperature synthesis is carried out by a substoichiometric amount of boron and the reaction product needs to be treated with HCl to remove unreacted lanthanide oxide and metal. The method we report in this paper allows a relatively rapid synthesis the product of which is a simple pure phase of a crystalline light lanthanide boride. The synthesis of PrB_6 is shown as an example. A further advantage of the proposed method is that it consists of a single step—only one deposition method where the final product should be a thin film.

2. Experimental

Crystalline boron pieces (Aldrich, 99.7% pure) were ground in a stainless steel mortar and then mixed with a stoichiometric amount of praseodymium oxide Pr_6O_{11}

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*Corresponding author. Tel./fax: +39-06-4991-3849.
E-mail address: daniele.gozzi@uniroma1.it (D. Gozzi).

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powder (Aldrich, 99.9% pure), according to the reaction:

$$Pr_6O_{11}(s) + 47B(s) \rightarrow 6PrB_6(s) + 11BO(g)$$

The mixture was thoroughly ground for 10 min with the addition of some milliliters of dry diethyl ether. The mixture was transferred into a boron nitride crucible which was then positioned into a water cooled electron beam gun (Ferrotec mod. EV1-8, Germany). The e-beam gun is positioned into a stainless steel vacuum chamber evacuated by a turbo pump. The vacuum system was switched on and, after a few minutes, the working pressure of 5×10^{-5} mbar was reached. Then the electron beam bombardment system was activated. The accelerating voltage used during the experiment was -3.5 kV. Initially, for 5–10 min, the powder was outgassed with a 1-mA large spot; then, the emission current was gradually increased to reach 150 mA and this treatment continued for 30 min. Subsequently, the reactants were melted with a 100–130-mA point shape spot. The time necessary to melt the reactants was a few minutes. Irradiation was then stopped, the chamber vented with N_2, and the reactants remixed. The whole procedure was repeated three times.

After the last treatment, the reaction product, which appears as beautiful brilliant electric blue fused lumps, was ground and a sample was taken for a first XRD analysis; the rest of the powder was annealed using e-beam bombardment for 1 h (large spot, 100–130 mA). After annealing, another XRD analysis was carried out. It is important to point out that it is necessary to avoid melting of the reactants from the beginning because the evolution of gaseous BO can become explosive with large losses of material.

XRD analysis was performed by a Philips X'Pert powder diffractometer using Cu $K\alpha_1$ radiation.

Peak positions and lattice parameters were calculated by the bundled software.

3. Results and discussion

Remixing of the reactants is necessary because the bottom and the walls of the crucible, which are in contact with the body of the gun, are cold. No interaction was observed between the crucible and the reaction product. Electron beam bombardment permits extremely high temperatures to be reached and thus it is possible to overcome problems due to solid state diffusion barriers which can be the rate limiting step in this type of reaction. This method allows the synthesis in a relatively short time (4–5 h total work, including the time necessary for evacuating and venting the chamber) of refractory materials such as carbides and borides which are suitable for preparation in vacuum unlike nitrides or oxides. The possibility of attaining high temperatures, together with control of the position and shape of the beam, allows the completeness of the reaction and elimination of the phases thermodynamically less stable by their decomposition. XRD patterns support these arguments. The pattern in Fig. 1A corresponds to the sample taken before annealing. It shows that the PrB_6 phase has well been formed and is crystalline, even if there are still some weak peaks which do not belong to this compound (see insert in Fig. 1A). However, in the pattern shown in Fig. 1B, corresponding to the annealed sample, these peaks have disappeared (insert Fig.

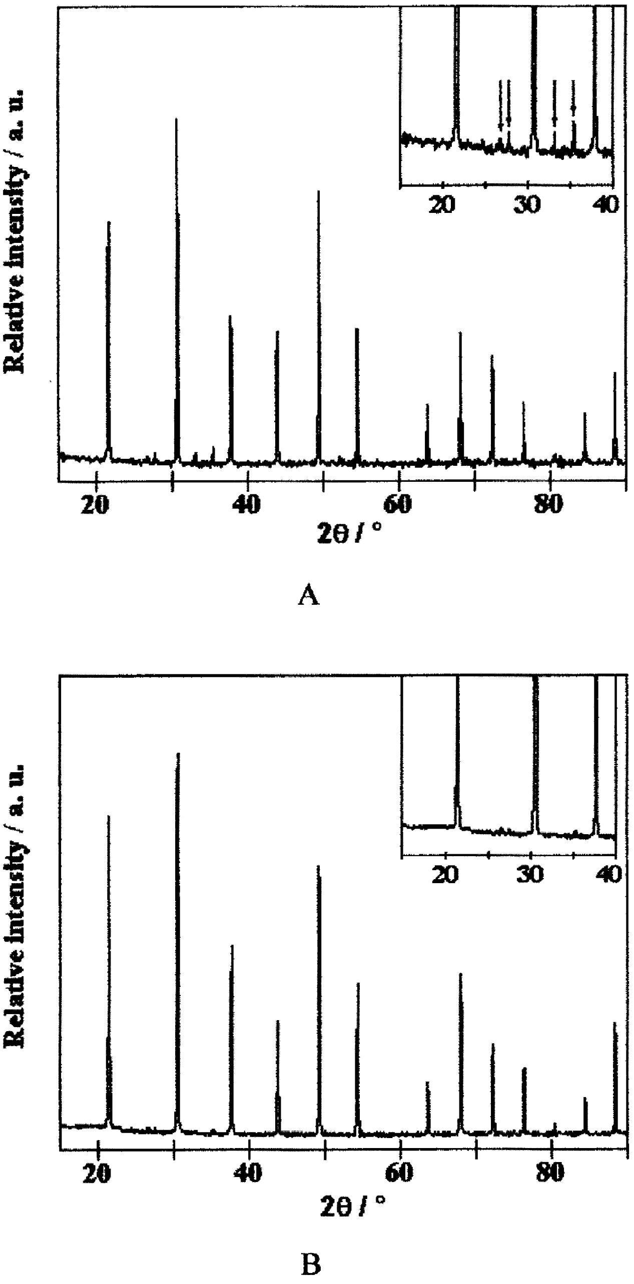

Fig. 1. (A) X-ray diffraction pattern of PrB_6 before annealing. Magnification is given in the insert. The black arrows indicate weak peaks that are not assignable to PrB_6. (B) X-ray diffraction pattern of PrB_6 after annealing. Magnification is given in the insert. The weak peaks not assignable to PrB_6 have disappeared.

Table 1
X-ray diffraction data of PrB_6

hkl	$2\theta/°$ exp.	$d/Å$ exp.	$d/Å$ (Ref. [8])
100	21.48339	4.13281	4.1318
110	30.56563	2.92234	2.9226
111	37.66754	2.38607	2.3850
200	43.77072	2.06647	2.0656
210	49.26490	1.84810	1.8477
211	54.32290	1.68736	1.6867
220	63.63274	1.46108	1.4605
300	67.98899	1.37768	1.3770
310	72.21398	1.30712	1.3063
311	76.35423	1.24622	1.2456
222	80.41346	1.19322	1.1926
320	84.43352	1.14636	1.1458
321	88.40757	1.10480	1.1042

1B). The experimental XRD data of the annealed sample and the reference data [8] are both reported in Table 1. The agreement appears to be excellent.

In conclusion, this procedure seems to be very efficient and several advantages can be outlined in comparison with other synthesis procedures, such as:

- The synthesis can be carried out in a simple way and quantitatively in a relatively short time.
- The product is crystalline and easily purified.
- The cold walls of the crucible and the apparent absence of interaction between the crucible and the reaction product avoid external contamination.
- The electron beam source permits both the synthesis and thin film deposition of the reaction product.
- The methodology can be extended to many other refractory compounds such as transition metals and lanthanide metals borides and carbides.

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