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Letter

A new route for the synthesis of boron suboxide B_7O

Xiaoyang Liu [a], Xudong Zhao [a], Weimin Hou [a], Wenhui Su [a,b]

[a] *Group of Solid State Physics, Jilin University, Changchun 130023, People's Republic of China*

[b] *International Center for Materials Physics, Academia Sinica, Shenyang 110015, People's Republic of China*

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Abstract

Boron suboxide B_7O is synthesized with the aid of the oxidation of boron with zinc oxide ZnO under extreme conditions of high pressure, 3.50 GPa and high temperature, 1200 °C, and characterized by means of X-ray powder diffraction. This new route for the synthesis of boron suboxide B_7O has several advantages.

Keywords: Synthesis; Boron suboxide; X-ray powder diffraction; Zinc oxide

1. Introduction

The chemistry of boron compounds is an active subject because of their abundance of chemical structures and physical properties. Higher borides differ especially from conventional compounds in their bonding and structures. These boron-rich materials exhibit a number of distinctive physical properties, and the boron suboxides are perhaps the earliest boron-rich compounds studied by chemists. In 1909, B_7O was first thought to exist by Weintraub [1] and later proven [2,3]. From then on B_2O [4,5], B_6O [6,7] and $B_{13}O_2$ [8,9] were synthesized by chemists, but firmly established formulae and structures were lacking. Since Badzian [10] pointed out that boron suboxide can be a superhard material, scientists began to pay more attention to these borides. In the former work, two methods were often used to synthesize boron suboxide: one was to reduce B_2O_3 with B, Mg or Si at high temperature, another was to oxidize B with oxidizing agents, such as MgO, CrO_3, $KClO_3$, etc., at very high temperature for a long time.

In this paper, we report for the first time a new route for the synthesis of boron suboxide B_7O by the oxidation of boron with an excess of zinc oxide ZnO under a pressure of 3.5 GPa and a temperature of 1200 °C.

2. Experimental details

High pressure–high temperature experiments were carried out using a 4.9×10^6 N belt-type high pressure apparatus. A cross-section of high pressure cell assemblage is shown in Fig. 1.

Boron was mixed with an excess of zinc oxide ZnO powder according to the following reaction,

$$7B + ZnO = B_7O + Zn$$

and ground uniformly. A cold pressed mold of the reactants of B and ZnO was placed in hexagonal boron nitride (h-BN) surrounded by a graphite cylindrical heater with walls of 1 mm thick. The mold was 6 mm in diameter and 8 mm in height. This piece was inserted into a pyrophylite cylinder and was then subjected to high pressure–high temperature conditions. h-BN was utilized to prevent migration of Si and Al from the pyrophylite to the sample.

The magnitude of pressure generated inside the cell was calibrated by the electrical changes on the basis of the phase transformations of Bi (2.55, 2.69 and 7.7 GPa). The temperature of the sample was controlled by the electric power supplied through the carbon heater,

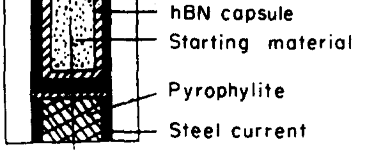

Fig. 1. Cross-section of high pressure cell assemblage.

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and calibrated by inserting a Pt30%Rh–Pt6%Rh thermocouple in the cell. After maintaining the desired high pressure and high temperature conditions for 20 mins, the sample was quenched to room temperature prior to the release of the applied pressure.

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

The products were put into 6 N hydrochloric acid (HCl) to remove the metal zinc and the excess of zinc oxide ZnO. The solid boron suboxide product remained undissolved.

3. Discussion

The X-ray powder diffraction pattern of boron suboxide B_7O synthesized in this paper is shown in Fig. 2. Corresponding XRD data of B_7O are listed in Table 1. B_7O crystallizes in the hexagonal system with lattice constants $a = 0.5435$ nm, $c = 1.2415$ nm (average values derived from a least squares fitting of X-ray powder diffraction data).

In order to establish the identity of the material synthesized in Ref. [2], a quantitative X-ray powder study was undertaken by Pasternak [2], the density of the same material, determined experimentally by flotation, was $d = 2.64$ (4) g cm^{-3}. From the unit-cell dimensions and the density, the mass of one mole of unit-cell was calculated to be 358.8. Pasternak assumed four equivalent units per unit cell, the equivalent weight for the structural unit is 89.7. This agreed satisfactorily with the theoretical formula weight of B_7O, which was 91.7, especially if one considered possible experimental errors. Compound $B_{6.5}O$ (or 1/2 $B_{13}O_2$) would have the formula weight 86.3, about 4% smaller than the observed value, therefore, the material studied was less likely to be this oxide. Thus, the existence of the boron suboxide B_7O appeared to be established.

According to the above discussions, we have confirmed that the boron-rich oxide synthesized in this work is not contaminated by boron and it is a pure phase.

The route for the synthesis of boron suboxide B_7O mentioned above has several advantages over other methods.

- It is easy to obtain the single phase product of B_7O. In the past, the most frequently used synthesis of boron suboxide B_7O was to mix boron with boron oxide B_2O_3 according to the atomic ratio which led to the formation of B_7O, and the reaction was carried out. Because of the reduction of oxide under high pressure and high temperature [11], i.e. a pure oxide will change to elemental metal and O_2 under high pressure and high temperature, it was very difficult to obtain a pure product. Most products were mixtures of boron suboxide B_7O with either boron or boron oxide B_2O_3. However, an inaccuracy in weighing would also lead to the same result. These problems can be avoided by the zinc oxide ZnO oxidation which accelerates the complete oxidation of boron, and the final product of B_7O can be formed repeatedly. It is very easy to remove the residual zinc oxide ZnO and elemental zinc produced in the process of synthesis by leaching the product with hydrochloric acid (HCl).
- The zinc produced in the course of synthesis is of benefit to the solid state reaction. Once the reaction of boron with ZnO occurs, liquid zinc is formed (melting

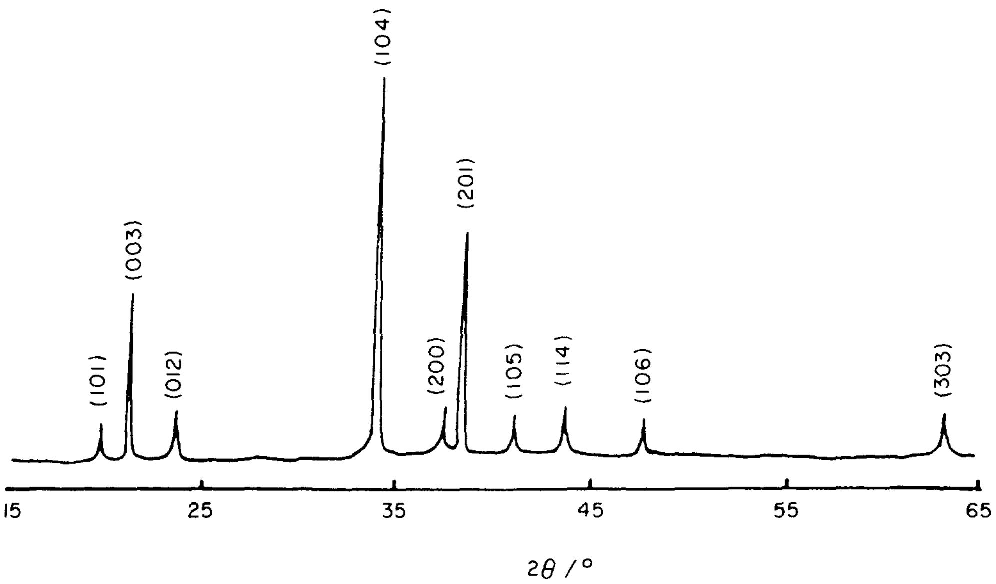

Fig. 2. X-ray powder diffraction pattern of synthesized boron suboxide B_7O.

Table 1
XRD data of boron suboxide B_7O

2θ	*hkl*	d_c (0.1 nm)	d_c (0.1 nm)	d^a (0.1 nm)
20.14	101	4.408	4.401	4.343
21.40	003	4.136	4.137	4.114
23.68	012	3.757	3.750	3.715
34.71	104	2.584	2.590	2.571
38.24	200	2.353	2.353	2.284
38.89	201	2.315	2.312	2.251
41.11	105	2.195	2.196	2.178
44.40	114	2.040	2.044	2.049
47.94	106	1.897	1.894	1.855
63.40	303	1.467	1.467	1.464

[a] Obtained by R.A. Pasternak [2].

point of zinc is 419 °C), and this liquid is beneficial in bringing about the complete solid state reaction.

- There are specific reasons for choosing ZnO as the oxidizing agent. Although there are many oxidizing agents used in high pressure and high temperature experiments, such as CrO_3, $KClO_3$, MgO, Ga_2O_3 etc., each of them has its advantages and disadvantages when it is put into practice. For example, CrO_3 and $KClO_3$ can be used as oxidizing agents under high pressure and high temperature based on their decomposition reactions:

$$4CrO_3 = 2Cr_2O_3 + 3O_2\uparrow$$

$$2KClO_3 = 2KCl + 3O_2\uparrow$$

However, a problem arises with their use, namely containing the gas under high pressure and high temperature. This is a very difficult problem for high pressure experiments. If sufficient care is not taken, high pressure "shooting" will occur. Although a Pt capsule is very effective for this containment, it is expensive to use. MgO, Ga_2O_3 and other metal oxides have, however, another problem, that is the metal produced in the process will react with boron and form metal borides. If zinc oxide ZnO is chosen as the oxidizing agent, the above two problems would be avoided. Unlike the decomposition reactions of CrO_3 and $KClO_3$ under high pressure and high temperature, there is no gas produced in the process of oxidation of boron with zinc oxide ZnO, and furthermore Zn does not form stable borides under the reaction conditions.

In conclusion, a new route for the synthesis of boron suboxide B_7O that yields a pure and well-crystallized product is reported here.

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