Mat. Res. Bull., Vol. 22, pp. 1259-1266, 1987. Printed in the USA.
0025-5408/87 $3.00 + .00

SYNTHESIS OF CERIUM AND GADOLINIUM BORIDES USING BORON CAGE COMPOUNDS AS A BORON SOURCE

H. ITOH, Y. TSUZUKI, T. YOGO and S. NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 Japan

ABSTRACT

Cerium borides (CeB_4 and CeB_6) and gadolinium borides (GdB_4 and GdB_6) were synthesized using boron cage compounds $M_2(B_{10}H_{10})_3$, (M =Ce and Gd) as a boron source. A mixture of hexaboride (CeB_6 or GdB_6) and amorphous boron, was formed by thermal decomposition of the cage compound above 1000°C or 1200°C, respectively. When metal hydride was mixed with a pretreated cage compound, hexaboride tended to form preferentially with tetraboride coexisting in lower heat temterature range. However, at the atomic ratio of B/M in the mixed powder, R = B/M = 2 (M = Ce or Gd), CeB_4 or GdB_4 was prepared as an only boride phase by the heat treatment at 1100°C or 1400°C, respectively. CeB_6 or GdB_6 was formed without coexisting of tetraboride at the composition R = B/M = 6 by heat treatment at 1100°C or at 1200-1400°C, respectively. These borides contained a small amount of inclusions (oxides, borates, etc.) which can be completely removed by acid treatment in conc. HCl solution with the result of formation of single phases of these borides

MATERIALS INDEX: cerium boride, gadolinium boride

Introduction

Rare earth metal borides are known to have interesting magnetic, electron emissive or superconductive properties [1-5]. In the conventional boride formation processes by the reaction between rare earth metal (or metal oxide) and boron (or boron carbide), rare earth metals are so easily oxidized to form by-products such as metal oxide, borates, etc. [1,6] that it is required to establish a new process for preparation of pure borides of rare earth metals.

In the present work, boron cage compounds, $M_2(B_{10}H_{10})_3$ where M = rare earth metals, were chosen as a boron source for boride synthesis. These rare earth metal salts with so-called "closo" ion, $B_{10}H_{10}^{2-}$ [7,8], are solid, relatively stable at room temperature and easy to handle in laboratory. The possibility to synthesize the borides of rare earth metals (Ce and Gd) was examined with an emphasis of obtaining pure and single phase borides by thermal decomposition of the cage compounds and subsequent crystallization reaction of borides. Since a considerable amount of free boron was residual in excess in the formation process of boride (MB_4 or MB_6), rare earth metal hydride was added to balance the excess amount of amorphous boron with a purpose of controlling the composition of boride phase.

Experimental Procedure

Preparation of $M_2(B_{10}H_{10})_3xH_2O$

Decahydrodecaboric acid ($H_2B_{10}H_{10}$) was obtained by cation exchange of bis(triethylammonium)decahydrodecaborate(2-) $B_{10}H_{10}[Et_3NH]_2$, which was prepared in our laboratory by the reaction between decaborane $B_{10}H_{14}$ and triethylamine Et_3N in xylene [9]. $Ce_2(B_{10}H_{10})_3xH_2O$ and $Gd_2(B_{10}H_{10})_3xH_2O$ were prepared by the reaction [10] of cerium carbonate ($Ce_2(CO_3)_3$) and gadolinium oxide (Gd_2O_3) with the $H_2B_{10}H_{10}$ aqueous solution at pH ≥ 5.

Synthesis of Cerium and Gadolinium Borides

Figure 1 shows the procedure for synthesis of cerium or gadolinium boride. Thermally decomposed product by the treatment of $M_2(B_{10}H_{10})_3$ in vacuum (10^{-5} Torr) at 800°C for 1 hr, was mixed with cerium or gadolinium hydride ($MH_{\sim 2}$) at an appropriate ratio in a globe box (in nitrogen atmosphere). The hydride was obtained by

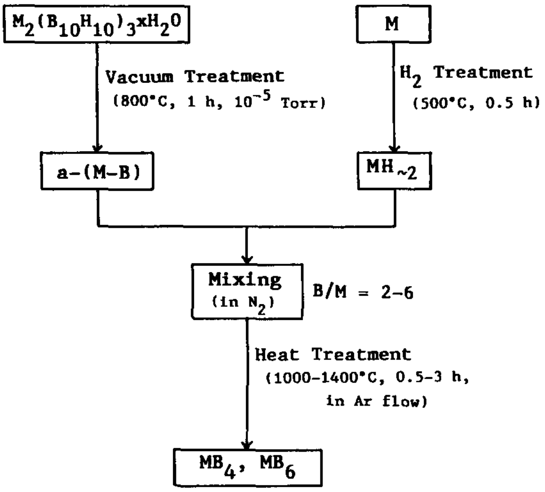

FIG. 1

Experimental procedure for synthesis of MB_4 and MB_6. a-(M-B): amorphous phase of cerium or gadolinium boride the three time treatments of cerium or gadolinium metal in a hydrogen flow at 500°C for 0.5 h followed by the treatment at 200°C for 0.5 h [11-15]. The composition of the mixed powder was defined by the atomic ratio in the specimen R = B/M = (Total moles of boron atom)/(Total moles of metal atom from cage compound and hydride), (M = Ce or Gd). Thus mixed powder (R = B/M = 2-6) was heat treated in an argon flow (flow rate: about 100 ml/min) at 1000-1400°C for 0.5-3 h.

The thermal decomposition behavior of the cage compounds was examined by using infrared spectrum analysis and thermogravimetric (TG) analysis. The formation and crystallization process of borides as well as coexisting products, was examined by X-ray diffraction analysis. The magnetic susceptibility of the products was measured at room temperature by magnetic balance.

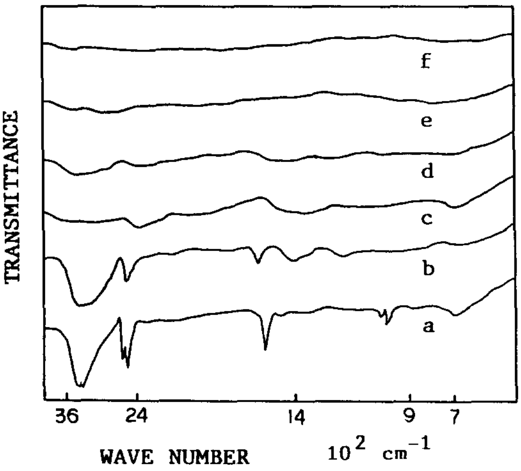

FIG. 2

Variation of infrared spectra of the specimens obtained by thermal decomposition at various treatment temperatures for 3 h at 10^{-5} Torr. (a) starting material: $Ce_2(B_{10}H_{10})_3 18H_2O$, (b) 200°C, (c) 400 °C, (d) 600°C, (e) 800°C, (f) 1000°C

Results and Discussion

Thermal Decomposition Process of Boron Cage Compounds

Figure 2 shows the variation of infrared spectra with heat treatment temperature of $Ce_2(B_{10}H_{10})_3 18H_2O$, where the amount of hydrated water was determined by TG analysis. The thermal decomposition was carried out in vacuum (10^{-5} Torr) for 3 h. The spectrum (a) of as-prepared $Ce_2(B_{10}H_{10})_3 18H_2O$ has the B-H streching band at 2500 cm^{-1} and the absorption band attributed to the "cage" of B_{10} at 1015 and 1070 cm^{-1}. A broad absortion at 3500 cm^{-1} is ascribed to the O-H streching band of hydrated water. The whole spectrum including the unascribed band at 1500 cm^{-1} was found to correspond to those of other derivatives of $B_{10}H_{10}^{2-}$ ion [10]. The absorption of B-H streching band and other bands decreases with increasing temperature and disappears at 800°C, as shown in Figure 2(e).

The X-ray diffraction pattern of the specimen treated at 800°C, showed no existence of crystalline phase, which suggests that amorphous phase of cerium boride would be formed. Figure 3 shows the X-ray diffraction patterns of specimens obtained by the thermal decomposition of $Ce_2(B_{10}H_{10})_3$ at 1000°C and 10^{-5} Torr for

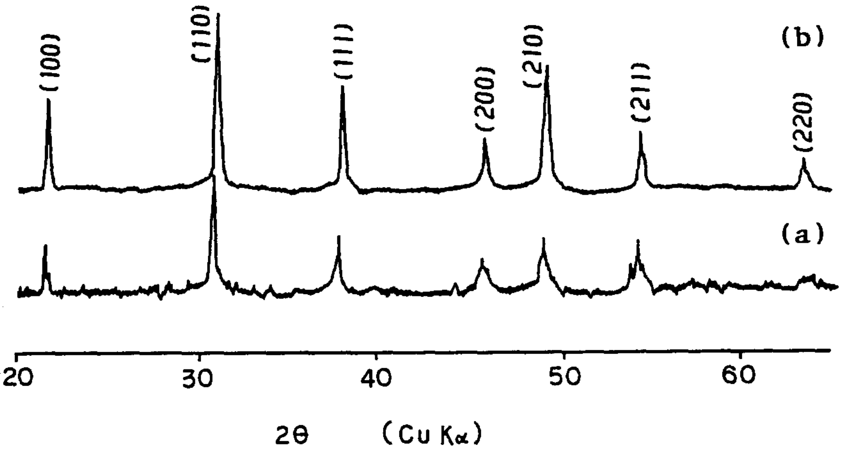

FIG. 3

X-ray diffraction patterns of CeB_6 obtained by the thermal decomposition of $Ce_2(B_{10}H_{10})_3$ at 1000°C and 10^{-5} Torr. Treatment time: (a) 1 hr, (b) 3 h

1h (a) and 3 h (b). A highly crystalline CeB_6 was formed at the treatment time of 3 h, when every lines were identified with JCPDS data of CeB_6 and the lattice constant (a = 4.141 A) was in good agreement with the reported value [16]. Broad diffraction lines of CeB_6 were observed, however, at the decreased treatment time of 1 h. The magnetic susceptibility of the specimen (b) was $\chi = 7.4 \times 10^{-6}$ emu/g, which was considerably low value compared with that of reported value ($\chi = 10.21 \times 10^{-6}$ emu/g) of CeB_6 [17]. This would be caused by the coexistence of diamagnetic amorphous free boron in the specimen, which is residual in excess in the decomposed product. The thermal decomposition behavior of $Gd_2(B_{10}H_{10})_3$ was quite similar to that of $Ce_2(B_{10}H_{10})_3$, except that the formation temperature of GdB_6 was higher than that of CeB_6, as will be described later.

Preparation of Single Phases of Tetraborides and Hexaborides

An analogous formation behavior of borides was observed in both Ce-B and Gd-B systems. In the Ce-B system, hexaboride (CeB_6) seemed to form preferentially from the cage compound at relatively low temperature of 1000°C in a wide composition range of R = 3-6 with tetraboride (CeB_4) coexisting as a by-product. The products contained a small amount of borate, oxide or unknown phase (possibly a kind of cerium borate), which would be included in the mixing procedure of cerium hydride with the pretreated cage compound. At an elevated temperature of 1100°C, hexaboride having a lattice constant of 4.140 A was formed at R = B/Ce = 6 without coexistence of tetraboride. The magnetic susceptibility of specimen with the composition of R = B/Ce = 6 was $\chi = 10.4 \times 10^{-6}$ emu/g which is mostly consistent with the reported value [17]. Tetraboride without coexistence of hexaboride was obtained at R = B/Ce = 2, where the excess cerium metal would be oxidized

TABLE 1

Products of Heat Treatment at Various Temperatures and Compositions of Starting Mixed Powder in the Gd-B System

Atomic Ratio R = B/Gd	Heat Treatment Temperature 1200°C	1300°C	1400°C
2	H, T, O, X	T, H, X	T, X
4	H, T, B	T, H, B	T, H, B
6	H, B	H, B	H, B

H: GdB_6, T: GdB_4, B: $GdBO_3$, O: Gd_2O_3, X: Unknown Phase; Treatment Time: 0.5 h

to form CeO.

Formation behavior of boride in the Gd-B system was investigated in higher temperature range of 1200-1400°C. Table 1 shows the products obtained at various temperatures and compositions of starting mixed powder (R = B/Gd = 2,4,6) in the Gd-B system. The products are shown in the order of yield. At the treatment temperature of 1200°C, the major product was hexaboride GdB_6 in the range of R = B/Gd = 2-6, in which tetraboride was obtained as a by-product at lower value of R = B/Gd = 2-4. A small amount of borate ($GdBO_3$), oxide (Gd_2O_3) or

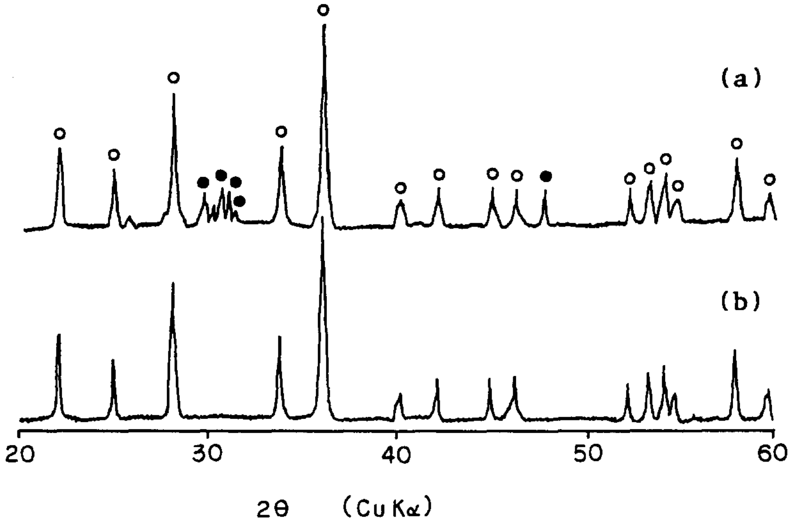

FIG. 4

X-ray diffraction patterns of the specimens (R = B/Gd = 2) treated at 1400°C for 0.5 h in an argon flow (a) and subsequently acid treated in conc. HCl solution (b). ○ GdB_4, ● unknown phase unknown phase were also included in the products similarly to the Ce-B system. Hexaboride without coexistence of tetraboride was obtained above 1200°C in case of the stoichiometric composition of R = B/Gd = 6. At an elevated temperature of 1300°C, tetraboride GdB_4 was formed as a major product in the composition range R = B/Gd = 4, when GdB_6 and a small amount of borate or unknown phase coexisted. Only at the heat treatment temperature of 1400°C, GdB_4 was obtained without coexistence of hexaboride at the composition R = B/Gd =2, although an unknown phase possibly including excess amount of gadolinium was detected.

It is suggested from the results on the boride formation behavior in the Ce-B and Gd-B systems, that hexaboride can be prepared preferentially from the thermally decomposed product of cage compounds in lower temperature range. This behavior would be depressed at higher temperatures, however, owing to the decomposition of boron cage, so that either tetraboride or hexaboride tends to form in accordance with the compositon of the mixed powder.

Figures 4 and 5 show the X-ray diffraction patterns of the specimens with the starting mixed powder composition R = B/Gd = 2 and 6, which were treated at 1400°C for 0.5 h in an argon flow (a), and subsequently acid treated in conc. HCl solution (b). Sharp diffraction lines of GdB_4 or GdB_6 [16] can be observed together with weak lines of the unknown phase or $GdBO_3$ in as-prepared specimen (Figures 4(a) and 5(a)), respectively.

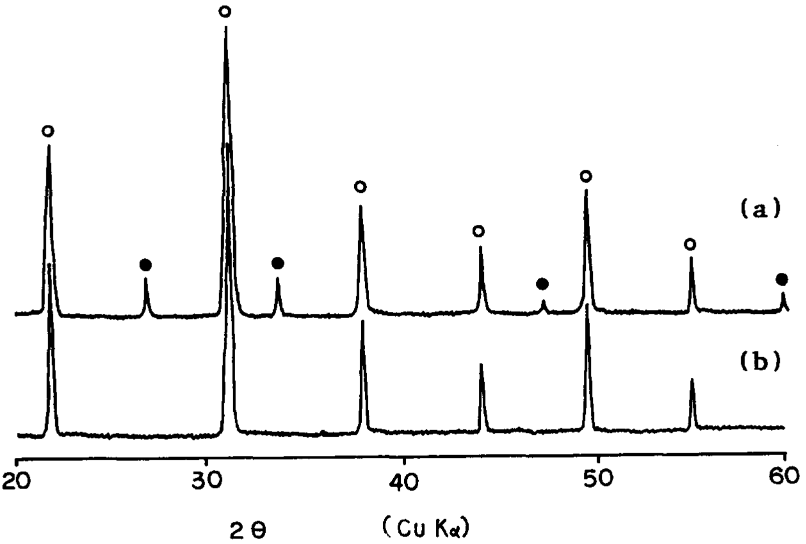

FIG. 5

X-ray diffraction patterns of the specimens (R = B/Gd = 6) treated at 1400°C for 0.5 h in an argon flow (a) and subsequently acid treated in conc. HCl solution (b). ○ GdB_6, ● $GdBO_3$

These unknown phase or $GdBO_3$ were completely eliminated, however, by treating the specimen in conc. HCl solution for 15 min at room temperature, as shown in Figures 4(b) and 5(b). A single phase of crystalline GdB_4 or GdB_6 is considered to be formed by acid treatment of the specimen.

An analogous variation of lattice constant and magnetic susceptibility as described in the Ce-B system was confirmed in the Gd-B system. At the composition of R = B/Gd = 15, in which $Gd_2(B_{10}H_{10})_3$ was treated at 1200°C for 0.5 h without any addition of gadolinium hydride, the lattice constant (a = 4.113 A) was a little larger than the reported value (a = 4.109 A) [17] and the magnetic susceptibility has a comparatively low value of 67.3 x 10^{-6} emu/g, which would be compensated by the presence of diamagnetic boron. The specimen which was obtained at 1300°C for 0.5 h at the composition R = B/Gd = 6, gave a decreased lattice constant of 4.111 A, and increased magnetic susceptibility of 114.2 x 10^{-6} emu/g that is conversely high value than the reported value (χ = 99.8 x 10^{-6} emu/g) [17]. This would be attributed presumably to the coexistence of paramagnetic $GdBO_3$, as detected in Figure 5(a). After the acid treatment in conc. HCl solution, the magnetic susceptibility (χ = 104.9 x 10^{-6} emu/g) was fairly consistent with the reported value [17].

Conclusions

Cerium borides and gadolinium borides were synthesized in the temperature range of 1000 to 1400°C using the boron cage conpounds $M_2(B_{10}H_{10})_3$, (M = Ce and Gd) as boron source. The following conclusions were obtained on the formation of tetraborides and hexaborides by the thermal decompositon of the cage compounds and the subsequent heat treatment of the mixture of decomposed amorphous phase and metal hydrides.

1) There was little difference in the formation behavior of borides between the cerium and gadolinium systems except that the formation temperature of gadolinium boride was somwhat higher than that of cerium boride.

2) Tetraboride (CeB_4 or GdB_4) was formed as an only boride phase in an argon atmosphere by the heat treatment of the starting mixed powder having the composition R = B/M = 2 at higher temperature range. Hexaborides tended to form preferentially from the cage compounds in a wide range of compositions of the mixed powder especially in lower heat treatment temperatures. Hexaboride (CeB_6 or GdB_6) was prepared without coexistence of tetraboride by the treatment of the specimen having the composition R = B/M = 6 in an argon atmosphere.

3) These borides was found to contain a small amount of inclusions (oxides, borates, etc.), which can be completly removed by acid treatment in conc. HCl solution for 15 min at room temperature with a result of formation of single phases of the borides. The present synthetic procedure of rare earth metal borides using boron cage compounds as a boron source could be applied to the systems of other binary or ternary rare earth

metal borides.

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