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**Boron-MgO composite as an X-ray transparent pressure medium in the
multi-anvil apparatus**

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Abstract:

X-ray transparent material is very beneficial for in-situ X-ray experiments in the multi-anvil apparatus. We sintered machinable blocks of boron-MgO composite at 800-1000 °C under atmospheric pressure from a mixture of amorphous boron and brucite or $\text{Mg}(\text{OH})_2$. Machinability of composite blocks improved with increasing brucite content in starting material; brucite content higher than 15 wt.% showed reasonable machinability in forming various shapes such as octahedron, cylinder, and sleeve. We confirmed feasibility of the boron-MgO pressure medium through successfully generating lower mantle pressure (>23 GPa); its pressure generation efficiency is comparable to that of Cr_2O_3 doped MgO pressure medium. The boron-MgO composite is expected to be an excellent thermal insulator owing to extremely low thermal conductivity of amorphous boron; we confirmed its better performance of thermal insulating through a comparative heating test with zirconia sleeve in Cr_2O_3 doped MgO pressure medium. Constituting light elements, the boron-MgO composite has high X-ray transparency, which enables us to conduct various cutting edge X-ray measurements in large volume multi-anvil apparatus.

Key words: boron-MgO composite, pressure medium, thermal insulator, X-ray transparency, synchrotron X-ray, multi-anvil apparatus

I. INTRODUCTION

High-pressure and high-temperature (HPHT) experiment is an indispensable means to understand the Earth's interior¹. Diamond anvil cell (DAC) and Kawai-type multi-anvil apparatus (KMA) are two complementary apparatus to generate HPHT conditions. Comparing them, KMA can generate pressures in a much larger volume^{1,2}, and thus has been widely used in various X-ray measurements revealing physical and chemical properties of minerals under Earth mantle conditions^{1,3}.

There were remarkable breakthroughs in KMA recently: the highest pressure exceeded 100 GPa by using sintered diamond anvils^{4,5}, and the highest temperature reached as high as 4000 K by developing the boron-doped diamond (BDD) heating element⁶. Along with these developments, devising X-ray transparent cell in KMA is important as well in enhancing quality and capability of HPHT X-ray study. We demonstrated that BDD is an excellent heating material with high X-ray transparency^{6,7}. However, transparent pressure medium, thermal insulator, and gasket are demanded as well to achieve high X-ray transparency in KMA experiment.

Chromium doped MgO (~5 wt.% Cr₂O₃) have been widely used as pressure medium in KMA experiments owing to its excellent efficiency in pressure generation. The X-ray transparency of MgO pressure medium decreases with decreasing X-ray energy. The attenuation coefficient becomes too large in the low energy range (especially, <40 keV), and makes it difficult to measure high angle diffraction and X-ray spectroscopy such as X-ray absorption near-edge structure (XANES) spectroscopy. Furthermore, it has high thermal conductivity and a thermal insulator, usually X-ray opaque such as ZrO₂, is commonly placed outside of heater to reduce the heat flow.

Since amorphous boron is more X-ray transparent and better thermal insulating than MgO, boron-epoxy mixture has been frequently used as pressure medium for X-ray spectroscopy experiments^{e.g.8}. However, it has been recognized many disadvantages of using boron-epoxy mixture, such as limited pressure range (practically <10 GPa), enhancing blow-out probability, and dehydrated water from epoxy. Under this context, we developed a boron-MgO composite pressure medium, which is free from these problems. We confirmed

its better performance as a pressure medium especially for studies requiring X-ray measurements.

II. EXPERIMENTS

A. Synthesis of machinable boron-MgO composite block

FIG. 1. Procedure for making boron-MgO composite blocks.

As a starting material, commercial amorphous boron of 97% purity with a grain size of 0.8-1.4 μm and brucite of 95% purity with a grain size of $\sim 1 \mu\text{m}$, were used. Figure1 shows the procedure of making boron-MgO composite blocks. Amorphous boron and brucite powders with appropriate weight ratios, were hand-grounded with ethanol for 3 hours using a

Al₂O₃ mortar and pestle. The mixture was then loaded in rubber balloons with diameter ~20 mm, and cold isotropic pressed using a water-based liquid medium at ambient temperature to 200 MPa. After removing rubber from molded pieces, they were heated to 1000 °C with a heating rate of 3 °C/min and baked at 1000 °C for 5-10 hours in a MgO container inside a tubular muffle furnace (outer/inner diameter: 30/26 mm) with a Ar + 1Vol.% H₂ gas flow (flow rate: 50 ml/min). Argon gas containing hydrogen was expected to reduce oxidation of boron. The decomposition temperature of brucite is between 472 and 1000 °C with a heating rate of 5.4 °C/min⁹, while the crystallization temperature of amorphous boron is higher than 1150 °C⁹. To ensure the complete decomposition of brucite and prevent the crystallization of amorphous boron, we baked the mixture at 1000 °C. Therefore, brucite is expected to sinter the mixture when it decomposes to MgO. We sintered boron-MgO composites with different weight ratio of boron and brucite (90:10, 85:15, 50:50) to examine their properties systematically. In this article, we specify boron-MgO composites using their boron weight ratios, such as B90.

The phases were identified by a micro-focused X-ray diffractometer. The sintered blocks were checked by scanning electron microscope. An octahedral shape of composite blocks was grinded using an automatic surface grinder (Okamoto, 52DX). A tube shape was machined using a lathe.

B. Testing experiments in multi-anvil apparatus

To check the properties of boron-MgO composite, such as efficiency of pressure generation, thermal conductivity, and X-ray transparency, we conducted HPHT experiments using them as pressure medium in multi-anvil apparatus (table 1).

The synchrotron X-ray experiments were conducted at Psiché (SOLEIL, France) or BL04B1(SPring-8, Japan) beamlines, while the offline experiments were conducted in Institute for Planetary Materials (IPM), Okayama University, Japan and in Bayerisches Geoinstitut, University of Bayreuth, Germany.

TABLE 1. Summary of testing experiments. The prefixes “1k”, “5k” and “H” in the run numbers correspond to the 1000-ton, 5000-ton and 6-axis presses installed at the Institute for Planetary Materials (Okayama University), respectively; that of “S” corresponds to the SUMITOMO press at Bayerisches Geoinstitut; that of “M” corresponds to the SPEED-MK.II 1500 press at the SPring-8 synchrotron facility; and that of “MA” corresponds to the Multi-anvil press at SOLEIL synchrotron facility.

Experiments for Testing Thermal Efficiency				
Run No.	Thermal Insulator	Sample	P /GPa	T / □
1k2684	B90	Amorphous C + B (3 wt.%)	15	~2000
S7478	B85	Graphite + B (3 wt.%)	15	1400
1k2707	MgO	Graphite + B (1 wt.%)	15	1900
1k2708	ZrO ₂ (0Z8C)	Graphite + B (1 wt.%)	15	1900
Experiments for Testing Pressure Generation Efficiency				
Run No.	Cell assembly	Anvil Material	Pressure Medium	Sample
MA15	10/4	TF05 WC	MgO	MgO+Au(10 wt.%)
MA11	10/4	TF05 WC	B85	MgO+Au(10 wt.%)
H443	5/1.5	TF05 WC	B85	ZnS
H444	5/1.5	TF05 WC	B85	GaP
H445	5/1.5	Sintered Diamond	B85	ZnS
H452	5/1.5	Sintered Diamond	B85	GaP
Experiments for Checking B ₂ O ₃ Problem				
Run No.	Pressure Medium	Sample	P / GPa	T / □
5K3061	B85	Forsterite	19	1600

FIG. 2. Varied shapes machined from sintered B blocks. (a) Octahedra (10 mm edge length) machined from blocks with different boron contents. (b) Edges and vertices truncated octahedra machined from B85. (c) Tube with OD/ID/L of 3.0/2.0/4.0 mm (OD: outer diameter, ID: inner diameter, L: length) machined from B85.

III. RESULTS AND DISCUSSION

A. Machinability concept and characterization

First concern on boron-MgO composite was its machinability (Fig. 2). Figure 2a shows octahedrons of boron-MgO composite as a function of boron contents. Higher boron content decreases the machinability of boron-MgO composite. Boron-MgO composite can be easily shaped into an octahedral shape by plate grinder when its boron content is lower than or equal to 85 wt.%. On the other hand, higher boron content is desirable for high X-ray transparency and thermal insulation. Thus, we assumed B85 is the best composition from viewpoints of

machinability, X-ray transparency, and thermal insulation. Therefore, our further characterization and test experiments were mainly conducted on B85.

FIG. 3. X-ray diffraction patterns of the sintered B85. AB: commercial Amorphous boron. The profiles of B85 and AB were measured in this study; the X-ray beams with a wavelength of 1.79026 Å were focused to 50-100 μm using an IFG polycapillary X-ray mini-lens. The profiles of MgO and Mg(OH)₂ were calculated according to d spacing (ICDD 4-829) in the international center of diffraction data (ICDD) and R040077.1 in RRUFF database.

Figure 3 compares the micro-focused X-ray diffraction pattern of commercial amorphous boron and boron-MgO composites. The commercial amorphous boron shows a series of weak sharp peaks, indicating its partially crystalline nature. Partially crystalline is a common phenomenon of commercial amorphous boron^{e.g.10}. B85 composite shows broad peaks, similar with those of amorphous boron, which suggests that amorphous boron did not crystallize significantly during baking. A small peak of MgO is identified from the X-ray pattern of B85. Figure 4 shows backscattered electron images of B85. We can recognize that patches of MgO aggregate are homogeneously distributed in the amorphous boron matrix (Fig. 4a), and particle size of boron is 2-5 μm (Fig. 4b).

FIG. 4 Backscattered electron images of sintered B85 block. (b) Magnified image of rectangle area in (a).

B. Pressure and temperature generation

FIG. 5. Cell assemblies for testing pressure generation efficiency of B85 PM. (a), Cell assembly used at SOLEIL synchrotron facility. WC cubes (TF05) with 26 mm edge length were used as second stage anvils. The edge length of anvil truncation is 4 mm. MgO or B85 octahedron with 10 mm edge length were used as PM. The edges and vertexes of octahedron were truncated. Pyrophilite with 4 mm width was used as gasket. A mixture of MgO+10 wt.% Au was used as pressure marker. (b), Cell assembly used in off line test experiment with 6-axis press at IMP. WC cubes (TF05) or sintered diamond cubes with 14 mm edge length were used as second stage anvils. The edge length of truncation is 1.5 mm. MgO or B85

octahedron with 5 mm edge length were used as PM. ZnS or GaP were used as sample. The pressure was determined through the phase transition of sample, detected through a sudden decrease of sample electrical resistance.

Figure 5 shows the cell assemblies for pressure generation tests with and without using synchrotron X-ray. As shown in Fig. 6, we confirmed that B85 has similar efficiency with MgO in pressure generation no matter with WC or sintered diamond anvils; we succeeded in generating lower mantle pressures (> 23 GPa) with B85.

FIG. 6. Load–pressure relation with B85 PM in varies cells. (a), Load–pressure relation using cell of Fig. 5a. (b), Load–pressure relation using cell of Fig. 5b; SD: sintered diamond anvils; TF05: TF05 type of WC anvils.

Figure 7a shows the cell assembly for testing thermal insulation efficiency of B90 and B85. Cells were, firstly, compressed to ~ 15 GPa at room temperature. Then, temperatures were increased. Thermocouple failed at 1600, 1400, 1900 and 1800 $^{\circ}\text{C}$, respectively, in the cells using B90, B85, zirconia, and MgO as an insulator. Figure 7b shows the power-temperature relationship with different thermal insulating materials. B90 and B85 insulators have similar thermal insulating efficiency, which are comparable to zirconia insulator, but much more efficient than MgO insulator.

FIG. 7. Cell assembly (a) and result (b) for testing boron-MgO composite as a thermal insulator. (a), A sleeve of MgO, ZrO₂, B90 or B85 with OD/ID/L of 6.5/4.0/6.0 mm was used as thermal insulator in different runs, respectively. A MgO sleeve was used between heater and thermal insulator to prevent the reaction between Re and boron. W-Re thermocouple was adopted to measure the temperature. To synthesize boron-doped diamond block in the same run, we used a graphite-boron composite (GBC) cylinder as sample. (b), Power-temperature relations of various thermal insulator.

It is known that B₂O₃ is an important flux for silicate and oxides, which helps to decrease melting temperature significantly. We experienced the effect during the development of graphite-boron composite (GBC) heater¹¹. A small amount of B₂O₃ may form during sintering boron-MgO composite even though in the atmosphere of Ar + 1% H₂. To check the B₂O₃ effect, we did a testing experiment at 1600 °C and ~19 GPa using forsterite sample (Fig. 8a). Figure 8b shows the recovered sample. Forsterite converted to Wd without abnormal melt. Unlike using GBC heater directly contacting with sample, Re heater and surrounding MgO sleeve seem to work an efficient barrier against B₂O₃ reacting with sample.

FIG. 8. (a) Cell assembly for checking B_2O_3 problem and (b) microscope image of recovered sample. Fo: forsterite, Wd: Wadsleyite, TC: thermocouple.

C. X-ray transparency

FIG. 9. Calculated X-ray transmission of B85 and MgO with a sample length of 20 mm. Element symbols and corresponding black lines mark energy of their characteristic X-ray. The packing fraction is 0.6. The calculation was done using public web unity by Robert et al. 2013¹², based on python software package *Absorb*.

High X-ray transparency of PM, especially in low energy range, is very beneficial in various X-ray imaging, scattering and absorption measurements (e.g. structural analysis of non-crystal materials using X-ray diffraction method and *XANES*). Figure 9 compares the X-ray transparency between B85 and MgO blocks. Owing to smaller atomic number of boron than Mg and O, B85 has higher X-ray transparency than MgO, especially at low energy range from 15 to 70 keV. Therefore, PM made of B85 has great advantage for various X-ray imaging, scattering and absorption measurements, especially in low energy range.

FIG. 10. Assembly and result of X-ray diffraction test. (a) Schematic sketch of X-ray passage for testing X-ray diffraction test. (b) and (c) signal of X-ray diffraction at varies 2theta and X-ray energy for cell assemblies with L=2.5 mm and 10 mm, respectively. The cell assemblies were placed on the top of WC anvils. An X-ray beam with size of 0.1mm in horizontal and 0.2 mm in vertical direction, was used for obtaining the energy dispersed

X-ray (EDX) patterns of silica glass at SPring-8. The EDX patterns were obtained with 600s exposure time at 4, 12 and 22 degrees by a Ge solid state detector. deg. is short for degree.

To confirm the better performance of B85 block, we did X-ray diffraction testing experiments using silica glass as sample (Fig. 10). Figure 10a shows the schematic sketch of X-ray passage. A silica glass rod with 3 mm diameter was place in the center of B85 or MgO block. Since the X-ray absorption coefficient of elements is almost independent with pressure, the test was conducted at ambient pressure. To simulate the conditions of different cell sizes, we checked the X-ray diffraction data using assemblies with 8 and 23 mm total lengths. Figure 10 b and c shows the results. The signal of sample using B85 block is obviously higher than that using MgO block, especially at low energy range. The signal is almost undetectable using MgO block for energy lower than 30 keV. The signal with 8 mm MgO assembly (3 mm sample +5 mm MgO) is comparable with that of 23 mm B85 assembly (3 mm sample +20 mm B85), that is, the X-ray absorption coefficient of B85 is ~ 4 times lower than that of MgO. The signal of diffraction decreases quickly with increasing 2theta angle. Thus, B85 has an advantage over MgO for high angle diffractions.

FIG. 11. (a) Cell assembly for testing X-ray transparency and (b) 2D image of X-ray diffraction intensity at varies 2theta and X-ray energy. A focused X-ray beam was used for obtain the EDX patterns of melt at Psiché, SOLEIL. The EDX patterns were obtain by a Ge solid state detector with a step angle of 0.2 degree. Diffraction time of 5, 10 and 20 seconds per pattern were used for angle ranges from 2.5 to 12, from 12 to 20 and from 20 to 25 degree, respectively.

Figure 11a shows an assembly for testing the performance of B85-PM for structural analysis of melt using X-ray diffraction method. Figure 11b is the results of X-ray scattering data of Fe-S melt at ~5 GPa; energy dispersed X-ray diffraction patterns were obtained from 2.5 to 25 degree with a step of 0.2 degree. Owing to highly transparency of B85-PM and B85-window in gasket, it was confirmed that 20 second measurement time is enough to acquire a fine pattern even at high angles (from 20 to 25 degree); the average diffraction time was ~15 seconds yielding the total diffraction time shorter than 25 minutes. Therefore, the better performance of B85-PM was demonstrated in X-ray scattering measurement in melt structure study.

IV. CONCLUSIONS AND PERSPECTIVES

We succeeded in synthesizing boron-MgO composite blocks, exhibiting their machinability, and demonstrating their performance in HPHT X-ray study; among boron-MgO composites, we recommended B85 as most suitable for PM and gasket window. Consequently, we believe that B85 contributes to future X-ray study up to lower mantle conditions.

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