Amorphous boron gasket in diamond anvil cell research

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(Received 21 July 2003; accepted 1 September 2003)

Recent advances in high-pressure diamond anvil cell experiments include high-energy synchrotron x-ray techniques as well as new cell designs and gasketing procedures. The success of high-pressure experiments usually depends on a well-prepared sample, in which the gasket plays an important role. Various gasket materials such as diamond, beryllium, rhenium, and stainless steel have been used. Here we introduce amorphous boron as another gasket material in high-pressure diamond anvil cell experiments. We have applied the boron gasket for laser-heating x-ray diffraction, radial x-ray diffraction, nuclear resonant inelastic x-ray scattering, and inelastic x-ray scattering. The high shear strength of the amorphous boron maximizes the thickness of the sample chamber and increases the pressure homogeneity, improving the quality of high-pressure data. Use of amorphous boron avoids unwanted x-ray diffraction peaks and reduces the absorption of incident and x rays exiting the gasket material. The high quality of the diffraction patterns makes it possible to refine the cell parameters with powder x-ray diffraction data under high pressure and high temperature. The reactivity of boron prevents its use at high temperatures, however. When heated, boron may also react with the specimen to produce unwanted phases. The relatively porous boron starting material at ambient conditions also poses some challenges for sample preparation. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1621065]

I. INTRODUCTION

Recent high-pressure studies using diamond anvil cells (DACs) provide rich insights into the physical and chemical properties of materials under extreme pressure and temperature conditions. The use of high-energy synchrotron x-ray sources, the development of new gaskets, and new designs of DACs are accelerating advances in this area of research.[1,2] A low-*Z* material, beryllium, has been successfully used as a gasket material since it allows flexible access of x rays entering and exiting the DAC axially and radially; such studies have led to discoveries of diverse phenomena under extreme conditions.[3–5] Sample quality under extreme conditions plays an important role for the success of high-pressure experiments, in which the selection of gasket material is a key factor. Rhenium is commonly used as a gasket material because of its high strength, inertness, and ease of use. As a high *Z* metal, however, rhenium strongly absorbs the incident and exiting x rays and can contribute significantly to diffracted x rays, preventing its use in many x-ray spectroscopic studies. Beryllium, a low *Z* element with low x-ray absorption, has served as a useful gasket in high-pressure x-ray spectroscopic studies in a DAC.[3–5] The capability of measuring signals from soft x-ray energies exploits the enormous potential of studying x-ray spectroscopies in a DAC.[1–5] However, since the shear strength of Be is relatively low, the thickness of the sample decreases significantly with increasing pressure, posing a practical limitation in ultrahigh-pressure x-ray spectroscopic research. Moreover, many laboratories restrict the use of Be gaskets because dust particles of Be inhaled in the drilling process can cause cancer. Diamond, the hardest material known, has also been used as a gasket material in DAC experiments to increase the thickness of the sample, thereby improving the data quality in high-pressure experiments.[6,7] Although diamond, with atomic number six, has very low x-ray absorption at hard x-ray energies, its absorption for soft x rays below 10 keV is still very high. The strong diamond powder can produce pits on the diamond culets that degrade performance.

A stiff yet light gasket material is therefore ideal for various high-pressure x-ray measurements. The gasket thickness depends only on the size of the diamond culet and the shear strength of the gasket materials, while the x-ray absorption mainly depends on the atomic number. Therefore, amorphous boron is a good candidate gasket material because of its high shear strength and low x-ray absorption. In fact, amorphous boron has been used as a sample chamber in large-volume high-pressure experiments because it is very transparent to x rays and has a low thermal conductivity.[8,9] Here we discuss and summarize the use of amorphous boron as a gasket material in high-pressure DAC experiments. The application of the gasket in x-ray diffraction,[10] *in situ* x-ray diffraction in a laser-heated DAC,[11,12] radial x-ray diffraction,[13] nuclear resonant inelastic x-ray scattering (NRIXS), and inelastic x-ray scattering (IXS) is addressed in detail, and the possibility of using boron gaskets in other high-pressure experiments is also discussed.

II. GASKET AND SAMPLE PREPARATION

Because amorphous boron by itself is too porous to easily use as a gasket material, amorphous boron (Alfa Aesar;

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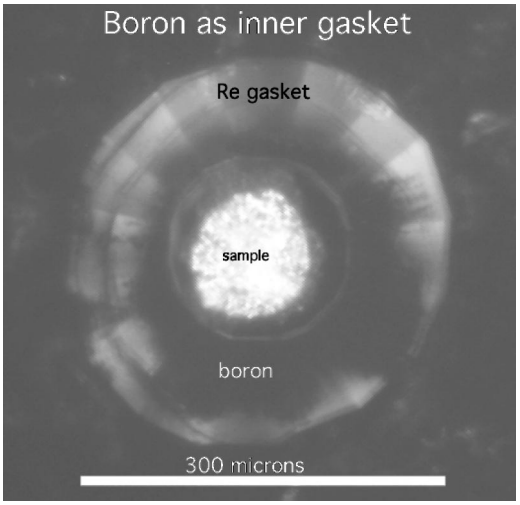

FIG. 1. Photo of Al_2O_3 and Pt samples (12:1 by weight) at 136 GPa (center bright part of the picture). Both transmitted and reflected light sources were used. Beveled diamonds with an inner culet of 150 μm and an outer culet of 300 μm were used. Amorphous boron was used as an inner, insert gasket and rhenium metal was used as an outer gasket to confine the amorphous boron. The sample chamber was originally about 100 μm in diameter, and its shape was still well preserved up to 136 GPa. Good x-ray diffraction patterns were collected without interference from diffraction peaks from the gasket material.

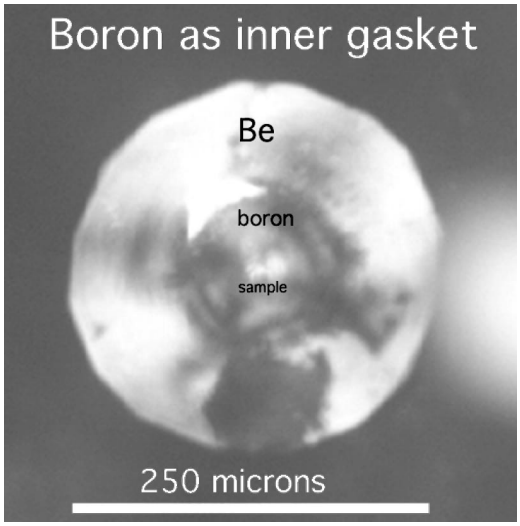

FIG. 2. Photo of a $Fe_{0.85}Si_{0.15}$ sample at approximately 55 GPa (center bright part of the picture; approximately 40 μm in diameter). Reflected illumination was used. Flat diamonds with a culet of 250 μm were used. Amorphous boron was used as a gasket insert (about 100 μm in diameter) and a beryllium gasket was used as an outer, confining gasket. A small hole of 50 μm was drilled into the inserted boron gasket and used as the sample chamber. This sample configuration has the advantage of the high shear strength of boron and the low x-ray absorption of Be. The sample was used for NRIXS experiments and radial x-ray diffraction experiments (see Fig. 6).

99% pure; part No. 11337) was mixed with epoxy (Epoxy Technology; part No. 353ND). Different mixing ratios of boron and epoxy were tested in this study, and the mixture of 4:1 (boron:epoxy) by weight was found to give the most satisfactory results.[10–12] The two materials were well mixed with acetone in a mortar and then dried. The mixture was used as a gasket insert in the drilled hole of a metal gasket such as Re, Be, or stainless steel. The metal gasket was preindented to a specific thickness, depending on the size of the culet, and then a hole slightly smaller than the culet was drilled. The hole was filled with the boron–epoxy mixture and compressed. Subsequently, another hole of 100 μm was drilled and used as the sample chamber (Figs. 1 and 2). For laser-heating experiments, a sandwich sample configuration, consisting of dried NaCl or Al_2O_3 as the thermal insulator and pressure medium on both sides of the sample, was used[11,12] (Fig. 3).

The boron–epoxy mixture was also used to make a whole boron gasket, in which the powder mixture was compressed in a press to make a gasket at GSECARS, Advanced Photon Source.[13] The size and shape of the gasket are similar to that of a Be gasket. After curing at 400 K for 1 h in a vacuum oven, the center part of the boron gasket was preindented to the desired thickness of approximately 30 μm. A hole of 100 μm was drilled and used as the sample chamber. The amorphous boron may transform to crystalline boron if the gasket is cured at higher temperature,[14] resulting in background diffraction from the crystalline boron gasket.

III. APPLICATIONS AND DISCUSSION

The amorphous boron gasket has been applied to various high-pressure DAC experiments: *in situ* x-ray diffraction in the laser-heated DAC,[10–12] radial x-ray diffraction,[13] NRIXS, and IXS. The amorphous boron provides higher strength and creates a deeper sample chamber, giving stronger x-ray diffraction from a thicker sample and better laser-heating spots due to thicker thermal insulating layers. Moreover, use of the light and amorphous boron minimizes the x-ray absorption by the gasket material and avoids unwanted x-ray diffraction peaks from the gasket.[10–12] The amorphous boron gasket also provides better hydrostatic conditions in the sample chamber as revealed by the ruby fluorescence peaks[15] and radial x-ray diffraction measurements[4,16] (Fig. 4), because of the higher shear strength of boron. As shown in Fig. 4, the ruby R_1 and R_2 fluorescence peaks at approximately 55 GPa are well resolved from each other with the use of the boron gasket, whereas the two peaks would normally overlap each other without the use of a pressure medium at such a pressure (i.e.,

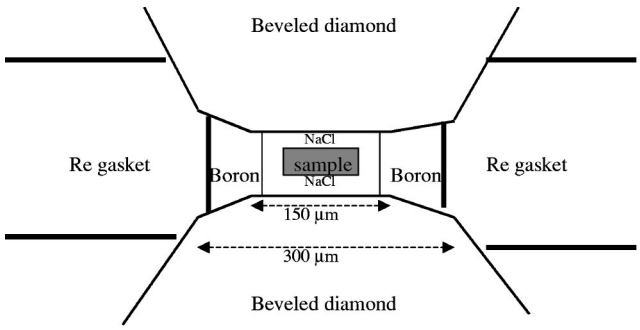

FIG. 3. Schematic of the sandwiched sample configuration with amorphous boron as a gasket insert and metal Re as a confining gasket in a diamond anvil cell. Beveled diamonds with an inner culet of 150 μm and an outer culet of 300 μm were used as an example here. The rhenium was preindented to a thickness of 30 μm and then a hole of 220 μm diameter was drilled into it. An amorphous boron and epoxy mixture (4:1 by weight) was then inserted and compressed into the hole. Another hole of 100 μm was drilled and used as a sample chamber. Dried NaCl was used as the thermal insulator and pressure medium on both sides of the sample.

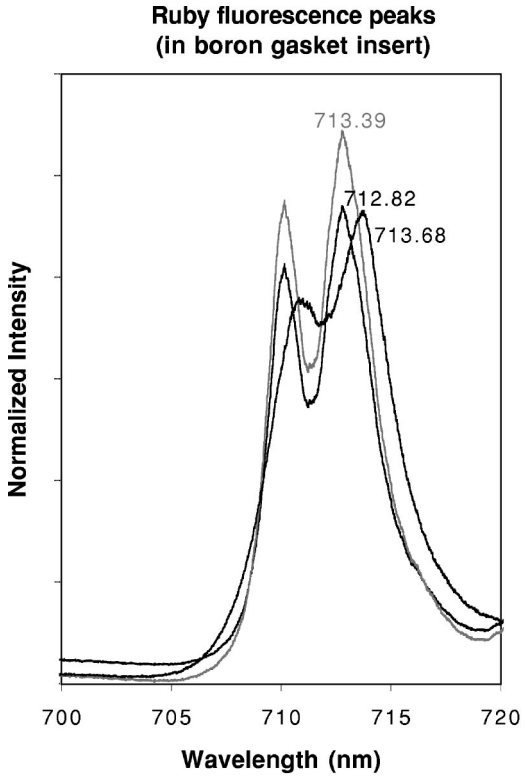

FIG. 4. Ruby fluorescence peaks at approximately 55 GPa using amorphous boron as an insert gasket. Three ruby fluorescence spectra (numbered according to the wavelength of the R_1 peak) are taken from three ruby chips within a region 50 μm in diameter. The ruby R_1 and R_2 peaks are well resolved from each other. The standard deviation of the measured pressure of three small ruby chips is 1.3 GPa (1σ). The ruby R_1 and R_2 peaks tend to overlap under nonhydrostatic conditions (without any pressure medium) at around 55 GPa; the use of a stiffer boron gasket reduces the nonhydrostatic conditions in the sample chamber.

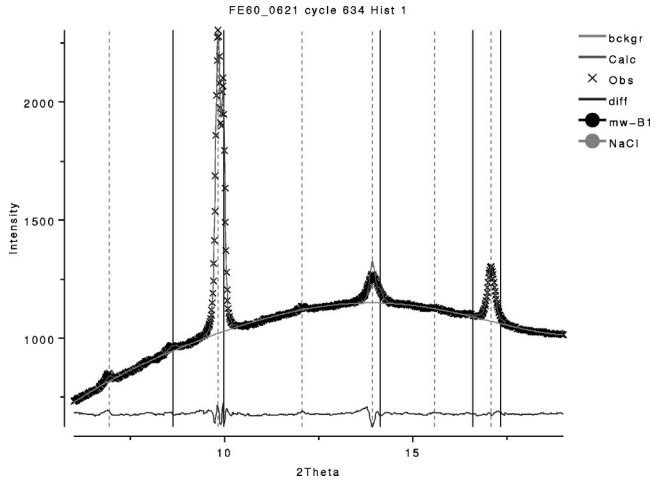

FIG. 5. LeBail crystal structure refinement, performed using the GSAS program, of the x-ray diffraction pattern of $(Mg_{0.39}Fe_{0.61})O$ collected in an *in situ* laser-heated DAC experiment at about 102 GPa and 1500 ($\pm$150) K (Ref. 12). The space groups of $(Mg_{0.39}Fe_{0.61})O$ and NaCl are $Fm\bar{3}m$ and $Pm\bar{3}m$, respectively. $\times$: Original x-ray diffraction pattern; vertical solid lines and dashed lines: diffraction peaks of $(Mg_{0.39}Fe_{0.61})O$ and NaCl, respectively; gray curve: background; horizontal solid curve (diff): difference in calculated diffraction pattern and original x-ray diffraction pattern after background subtraction.

a sample in a Re, Be, or stainless steel gasket only). Since the nonhydrostatic effect on the peak broadening has been minimized, x-ray diffraction peaks can be better resolved. The shape of the sample chamber with an boron gasket inserted is still well preserved even at 136 GPa after many laser-heating cycles (Fig. 1); this lengthens the lifetime of the sample. Good x-ray diffraction patterns of magnesiowüstites and Al_2O_3 are obtained up to 102 GPa and 2550 K and 136 GPa and 2800 K, respectively, without any interference from diffraction peaks due to the gasket material and background noise (Fig. 5).[12] The high quality of the diffraction patterns makes it possible to refine the cell parameters with powder x-ray diffraction data under high pressure and high temperature (Fig. 5).[12] Amorphous boron with boron nitride (BN) seats has been used to study the structure of amorphous iron to 67 GPa.[10] The use of an x-ray transparent BN seat with an amorphous boron gasket insert makes it possible to correct the x-ray absorption and to subtract the background in structural investigation of amorphous materials in a DAC.[10] Although boron also has a high melting point and relatively high shear strength at high temperature, care must be taken in using the boron gasket in externally heated DAC experiments because of its high reactivity and possible crystallization at high temperature.[14]

Radial x-ray diffraction experiments with a Be or boron gasket in a DAC have been used to study the elasticity and plasticity of materials.[4,16] Nonhydrostatic stress is essential and is deliberately produced in the sample without the use of any pressure medium.[4,16] The differential stress (t) is

$$t=\sigma_3-\sigma_1, \tag{1}$$

where σ_3 and σ_1 are axial and radial stress, respectively. A polychromatic x-ray beam is commonly passed through the Be gasket radially, and energy-dispersive x-ray diffraction patterns are collected at various steps of ψ (the angle between the diamond cell stress axis and the diffracting plane normal). The d spacing varies linearly with $\cos^2\psi$,

$$d(hkl)=d_P(hkl)[1+(1-3\cos^2\psi)Q(hkl)], \tag{2}$$

where the intercept $d_p(hkl)$ represents the d spacing under hydrostatic pressure and the slope $Q(hkl)$ is the lattice strain under the uniaxial stress condition.[4,16] Shifts in d spacing as a function of ψ can be explained in terms of elastic deformation under stress, whereas the variations in intensities are due to the crystal alignment deduced during plastic deformation.[16] The radial x-ray diffraction patterns of hexagonal-close-packed (hcp) $Fe_{0.85}Si_{0.15}$ were collected at approximately 59 GPa in a Be gasket and at 55 GPa in a boron gasket insert with a Be confining gasket (Fig. 6). The x-ray diffraction spectra of hcp $Fe_{0.85}Si_{0.15}$ in the Be gasket are similar to those of hcp Fe [Fig. 6(a)].[4] At low ψ, high intensities are observed for hcp (002) and low intensities for hcp (100); at high ψ the opposite is true. The hcp-$Fe_{0.85}Si_{0.15}$ sample in a boron gasket displays a different intensity distribution [Fig. 6(b)]; the highest intensity is observed for hcp (002) at $\psi=10°$ and for hcp (100) at $\psi=60°$. Shifts in d spacings as a function of ψ [the slope $Q(hkl)$ in Eq. (2)] in the two samples are also different, indicating the difference in differential stress (t) conditions and plastic deformation

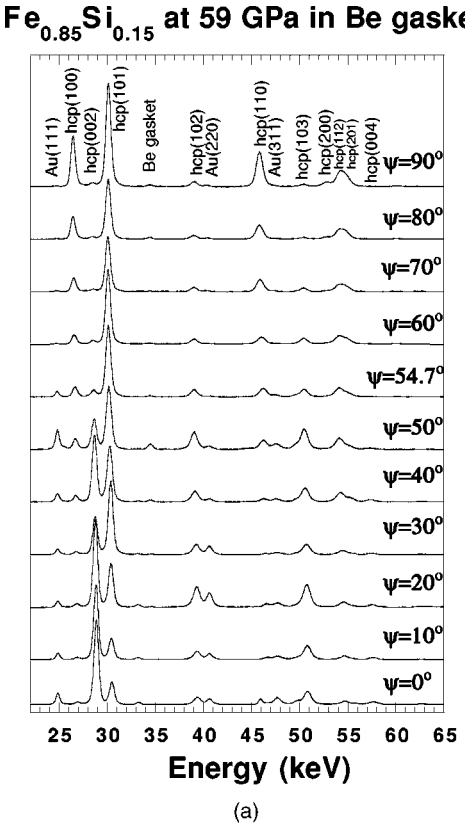

FIG. 6. Radial x-ray diffraction patterns of hcp $Fe_{0.85}Si_{0.15}$ as a function of ψ (the angle between the diamond cell stress axis and the diffracting plane normal). (a) hcp $Fe_{0.85}Si_{0.15}$ in a Be gasket. (b) hcp $Fe_{0.85}Si_{0.15}$ in an amorphous boron gasket insert and a Be outer confining gasket (see Fig. 2).

caused by the gasket materials.[16] Therefore, use of amorphous boron complicates interpretation of the preferred orientation and rheology of the sample.

In practice, it is not desirable to use a Be gasket for radial x-ray diffraction with a monochromatic x-ray beam, because diffraction of the crystalline Be contributes significantly to the signal at the detector. The amorphous boron gasket, on the other hand, allows incoming and diffracted x rays to pass through, that is, the whole diffraction ring can be collected using an area detector.[13,17] We have successfully compressed $Fe_{0.9}Ni_{0.1}$ and $Fe_{0.85}Si_{0.15}$ alloys to approximately 60 GPa in a boron gasket. The technique has also been used to study the elasticity and rheology of MgO to 47 GPa.[13] However, caution should be taken in interpretation of the data, because the essential condition, differential stress, in such experiments is different than that using a Be gasket.

The Be gasket is commonly used in NRIXS in a DAC because of its relatively low x-ray absorption above 6 keV.[1,18] The thickness of the sample decreases significantly with increasing pressure due to the relatively low shear strength of the Be gasket. The relatively low shear strength of the Be gasket causes a reduction in sample thickness. NRIXS signals origin only from particular isotopes such as ^{57}Fe with 14.413 keV x rays, and the materials surrounding the sample do not contribute to the detected signals.[18] We used the amorphous boron as a gasket insert in a Be gasket in a high-pressure NRIXS study of a $Fe_{0.85}Si_{0.15}$ alloy to 55 GPa (Fig. 2). Such sample configuration is found to be very useful because it takes advantage of the high shear strength of boron and the low x-ray absorption of Be. Hence, the thickness of the sample is increased with minimum x-ray absorption, and the nonhydrostatic conditions in the sample chamber are reduced (Fig. 4). This enables NRIXS experiments to reach higher pressures with shorter counting times and higher signal intensity, which were difficult to achieve previously with thin samples in Be gaskets.

We have also used the boron gasket insert for high-resolution IXS on hcp Fe at 75 GPa at BL35XU, SPring-8. Although using a boron gasket insert increases the sample thickness, the amorphous boron, unfortunately, contributes substantial background, and hinders observation of the longitudinal and transverse acoustic phonons of Fe.[19] Such problems may be prevented with use of a crystalline boron gasket such as β-boron,[20] which should have distinct phonon peaks at high pressures. Boron gaskets should also be useful in IXS for measuring electronic excitations in the study of electronic structures.[1]

High-resolution x-ray emission spectroscopy has been used to study the magnetic moment of transition metal monoxides such as FeO and (MgFe)O in a DAC.[5,21] The emission spectrum of high-spin Fe is characterized by a main peak $K\beta_{1,3}$ with an energy of 7058 eV and a satellite peak $K\beta'$ with an energy of 7045 eV. To reduce the loss of x rays due to absorption by diamond anvils, the incident and emitted x rays were passed through the Be gasket.[5] Moreover, perforated anvils were used to reduce the large x-ray attenuation of the diamond anvils in the study of x-ray absorption fine structure (XAFS).[22,23] The increase of sample thickness allowed by using an insert boron gasket with a Be confining gasket would result in better signal intensity and shorter collection times in these experiments.

In summary, the advantages of using amorphous boron gaskets are (1) a deeper sample chamber due to the high

strength of the gasket, thus giving stronger x-ray diffraction from a thicker sample; (2) better laser-heating properties due to thicker thermal insulating layers; (3) a reduction in x-ray diffraction peaks from the gasket material; (4) better hydrostatic conditions in the sample chamber; (5) minimum x-ray absorption from the gasket material. The reactivity of boron prevents its use at high temperatures, however. When heated, boron may also react with the specimen and produce unwanted phases. The relatively porous boron starting material at ambient conditions also poses some challenges for sample preparation.

ACKNOWLEDGMENTS

The authors thank beamlines X17C, NSLS, GSECARS, XOR, HPCAT of APS and BL35XU of SPring-8 for the use of the synchrotron beam time and the ruby fluorescence system. APS is supported by U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-ENG-38, and the State of Illinois under HECA. They are grateful to J. Liu, V. Struzhkin, J. Hu, N. Sata, J. Devine, W. Sturhahn, J. Zhao, A. Baron, and S. Hardy for their assistance in this study. This research was supported by DOE and NSF.

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