X-ray diffraction study of B$_4$C under high pressure

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Abstract. The high pressure X-ray diffraction study of B$_4$C was carried out by using the synchrotron radiation source. The ambient crystal structure remained stable to the highest pressure 126 GPa, and the pressure induced amorphization did not occurs. The $c/a$ ratio decreased with increasing pressure that means the apex angle of the rhombohedron increases with increasing pressure. The bulk modulus was determined by the Birch-Murnaghan's equation to be 305.8 GPa.

1. Introduction
The BCS theory predicts that the low-Z material such as boron become the high Tc superconductor. The crystal structure of boron consists of the icosahedral clusters (B$_{12}$) and there are two type structures, which are $\alpha$-type and $\beta$-type. The former type is simpler than the later type, and there is one B$_{12}$ cluster in a unit cell. The boron belongs to the semiconductor, however, it has reported that the boron become to the metallic phase and translated to the superconductor under high pressure around 150 GPa $^{[1,2]}$. In order to understand the correlation between the superconductivity and the crystal structure, we had carried out the high-pressure X-ray diffraction study of $\alpha$-boron, and reported that the $c/a$ ratio increased with increasing pressure, and the ambient phase remained up to 200 GPa which is beyond the transition pressure to the superconductor $^{[3]}$.

On the other hand, the B$_4$C also interested in the superconductivity under pressure because the B$_4$C is also low-Z material and the crystal structure consists of the B$_{12}$ cluster as the boron and the space group is the same that of $\alpha$-boron and as shown in Figure 1. Calandra et al predicted theoretically that
the possibility of superconductivity of boron carbide [4], and some high pressure or stress experiments were carried out, and reported that boron carbide transform to amorphous phase by indentation [5-7], shock pressure [8], and static pressure under low- and high-temperature [9]. In this paper, we carried out the high pressure X-ray diffraction study of B₄C using the synchrotron radiation source to understand the stability of the crystal structure under pressure at room temperature and compare the pressure effect between B₄C and α-boron.

2. Experiments
It is important to identify the C composition ratio of B₁₂Cₓ, because boron carbide transforms from B₁₂C₂ to B₁₂C₃ by increasing C concentration. A conventional method in order to determine the composition ratio is the lattice parameter [10]. The lattice a and c of the sample were precisely determined by using the synchrotron radiation source to be 0.56043 and 1.20840 nm, respectively. The lattice parameters correspond that the lattice a in the rhombohedral system is 0.51666 nm, which is good agreement with the reported lattice parameter of B₁₁(CBC) [11].

The high-pressure X-ray diffraction experiments were performed at BL10XU beam line at SPring-8 and at BL18C at Photon Factory in Japanese synchrotron facilities. The typical wavelength of the X-ray was 0.0413 nm (E=30 keV). A diamond anvil cell (DAC) with top 0.15 mm φ in diameter was used as pressure generator and pressure was determined by the Ruby fluorescence method or Raman shift of diamond [12]. A 16:3:1 mixture of ethanol and methanol and water was used as a pressure-transmitting medium. The X-ray radiation source exposed for 30 min during the sample swinging mode in order to obtain the good quality diffraction data from the sample in DAC. The X-ray diffraction data was detected on an imaging plate and analyzed by the Rietveld method in order to refine the crystal parameters [13].

3. Results and discussions
Figure 2 shows the X-ray diffraction profiles of B₄C under pressure up to 126 GPa. At the 5.7 GPa, all diffraction peaks are assigned as a B₄C phase except for a diffraction peak from Rhenium gasket around 11.2 degree denoted by G, and a broad peak around 7.5 degree denoted by Gra because of the impurity of the graphite. All peaks became broader peaks with increasing pressure, however they remained up to 126 GPa. The pressure induced amorphization was not recognized as previous reports [5-9]. The intensity ratio of (003) diffraction line and (102) diffraction line around 6 degree clearly changed with increasing pressure, which suggest the change of atomic positions in the unit cell, the behavior under pressure was observed in the case of α-boron.

![Figure 2. High-pressure X-ray diffraction profiles of B₄C up to 126 GPa. The diffraction peaks of graphite as an impurity and Rhenium as a gasket denote Gra and G, respectively.](image-url)
The crystal parameters of B$_4$C under pressure were refined by Rietveld method with high accuracy. The $R$-factors for the refinements were very small, for instance, in the case of the profile at 19 GPa, the $R$-factors for $R_{wp}$, $R_p$, $R_e$ and $S$ were 1.00, 0.69, 21.01, 0.37 and 2.718, respectively. Figure 3 shows the pressure dependence of the lattice constants of $a$ and $c$ denoted by circles and triangles, respectively. The pressure dependences of the normalized $c/a$ ratio of B$_4$C and $\alpha$-boron are shown in Figure 4(a). The pressure coefficient of B$_4$C is negative, that corresponds to the apex angle of the rhombohedron denoted by $\alpha$ increases under pressure as shown in Figure 4(b). The pressure effect is opposite compared with $\alpha$-boron. It considers that the difference between B$_4$C and $\alpha$-boron might be caused by the position of the icosahedral cluster under pressure.

In the theoretical report by Lee et al.[14], the bulk moduli of $\alpha$-boron(B$_{12}$), B$_{13}$C$_2$, B$_{12}$C$_3$ were calculated to be 207.2, 216.9, and 233.9 GPa, respectively which means that bulk modulus of boron carbide become larger by increasing C concentration. Figure 5 shows the volumes of B$_4$C and $\alpha$-boron as a function of pressure to 100 GPa. The bulk modulus of B$_4$C was determined to be 305.8 GPa by the Birch-Murnaghan's equation. The value is larger than that of $\alpha$-boron [3], and the trend is agreement with the theoretical result.

Figure 3. Pressure dependences of lattice $a$, $c$ of B$_4$C.

Figure 4. (a) The comparison of the normalized $c/a$ ratio between B$_4$C and $\alpha$-boron. The pressure coefficient of B$_4$C is negative and that of $\alpha$-boron is positive. (b) The correlation between the $c/a$ ratio and the apex angle ($\alpha$) of the rhombohedron. The decreasing of the $c/a$ ratio corresponds to the increasing of the apex angle.

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4. Summary

The high pressure X-ray diffraction study of B_4C was carried out up to 126 GPa. The atmospheric phase existed stable up to 126 GPa, and the pressure induced amorphization did not occur as previous reports. The c/a ratio of B_4C decreased with increasing pressure, the result is opposite to the \(\alpha\)-boron. The bulk modulus was determined to be 305.8 GPa by the Birch-Murnaghan's equation, the value is larger than that of \(\alpha\)-boron.

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Figure 5. Pressure dependences of the normalized volume of B_4C (squares) and \(\alpha\)-boron (triangles). The bulk modulus of B_4C and \(\alpha\)-boron were determined by the Birch-Murnaghan's equation to be 305.8 GPa, and 246.8 GPa, respectively.