

X-ray Diffraction Measurements on B₄C Boron Carbide at High Pressures and High Temperatures

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Introduction

Covalently bonded solids based on boron, carbon or nitrogen form the hardest materials currently known. The unique nature of boron and boron rich compounds is the common B₁₂ structural motif. This icosahedral unit is in turn cross-linked to form a rhombohedral array in α -B, B₆O, B₆P, B₆As.¹ The electron-deficient nature of the bonding within the icosahedra leads to a shorter (and therefore presumably stronger) intericosahedral bonds. All the boron rich solids including BN and B₄C are hard, and also refractory, materials finding applications as abrasive and shielding materials for sustaining extreme conditions.

Boron carbide B₄C is the third hardest material after diamond and cubic BN. It is easily synthesized by the reaction of boron and graphite at high temperatures and is known to be stable to very high temperatures.² The structure of B₄C is shown in Fig. 1. The

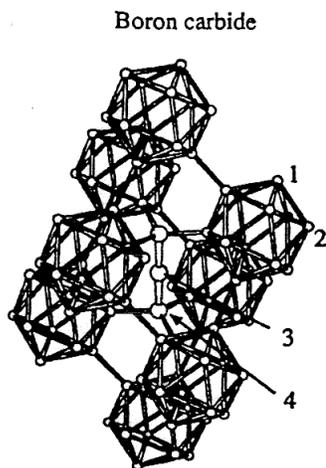


FIG. 1. Atomic structure of B₄C.

icosahedra are formed by the two B atoms at $(x, -x, z)$ and $(x', -x', z)$ sites (labeled as 1 and 2 in Fig. 1). These icosahedra are in turn covalently linked together to form a rhombohedral array. The C-B-C chain with atoms at $(0, 0, 1/2)$ and $(0, 0, \pm z)$ (labeled 3 and 4 in Fig. 1) form an additional cross-linkage between the rhombohedral arrays.³ Due to the fact that boron is trivalent and therefore cannot form covalent bonds to the six neighbors in the icosahedra, the bonding within the icosahedral units is 'electron deficient.'⁴ where the charge is localized at the center of a three-atom cluster. In contrast, the intericosahedral bonds are more covalent like and consequently stronger. This implies that the icosahedra are more compressible than the structure composed of them (inverted molecular compression). Neutron scattering studies on B₄C up to 11 GPa have shown that the bulk modulus of the structure is 23% higher than the structural units indicative of an inverted molecular compression.⁵ The bulk modulus estimated from this study is 199 GPa, which is similar to that found in α -boron. It is significantly smaller than the covalently bonded BN or diamond. Struc-

tural studies on B₄C at high pressures have been limited and do not present a consistent picture about the nature of compression in this solid. The main problem being that in the case of neutron scattering the scattering lengths of ¹¹B and ¹²C are too close, and, in the case of x-rays, the form factors of B and C are also very similar. Recent Raman spectroscopic studies up to 21 GPa and first-principle calculations however dispute this conjecture.^{3,4}

Experimental Details and Results

B₄C powder was used as starting material. In two separate runs, the sample of B₄C was loaded into diamond anvil cells with a 4:1 methanol-ethanol mixture and NaCl as the pressure media. Rhenium was used as the gasket material, and the sample in the form of pre-pressed pellets was kept at the center of a 100 μ m hole. X-ray diffraction data were collected on the 13-ID-D beamline of GSECARS. Due to the low scattering power of the sample, care had to be taken to reduce the contamination due to the Re gasket material. This was achieved by using a well-collimated 10x10 μ m x-ray beam. Pressure was measured by ruby fluorescence. At each pressure, the ruby signal was measured at several regions to estimate the pressure gradients. At the highest pressure of 49 GPa, the variation was observed to be of the order of 1.5 GPa. This assured us that the sample was not 'bridging' the gap between the diamond anvils, and the measurements are therefore not weighed by deviatoric stresses. The representative powder data from the methanol-ethanol run (shown in Fig. 2) were obtained by integrating the powder rings recorded on a 2k CCD using the 0.4246 \AA incident beam. The observed variation in cell parameters and unit cell volume are shown in Fig. 3.

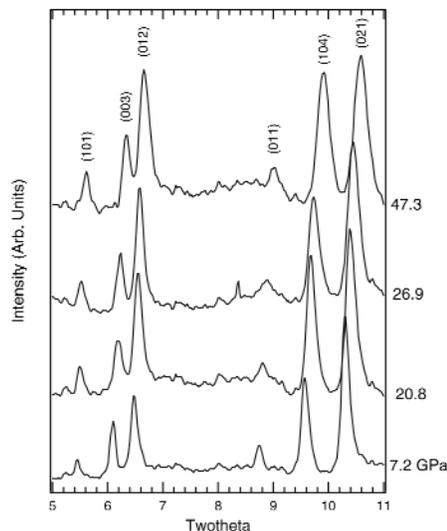


FIG. 2. Representative diffraction patterns of B₄C in 4:1 methanol-ethanol pressure medium. The background from each pattern has been subtracted.

As can be noted from an inspection of Fig. 3, the c/a ratio and the cell parameters display change in their pressure derivatives above 22 GPa. In contrast, no distinctive change is observed in the isothermal compressibility. In an effort to understand this, structure refinements at each pressure are currently being attempted. Although a full structural refinement is not possible, initial trials indicate that refinement of strain broadening is possible. We hope to use this information in conjunction with the cell parameters to understand the origin of this anomaly.

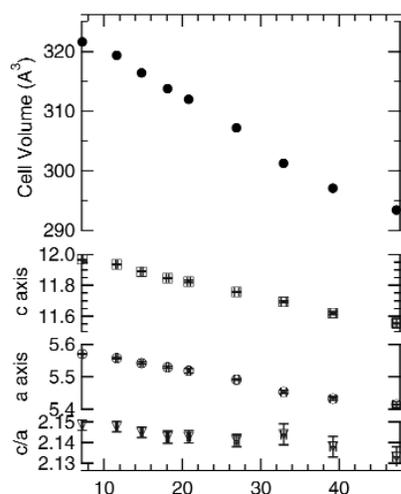


FIG. 3. The variation of cell constants, cell volume and axial ratio obtained from the analysis of the powder diffraction data. The cell parameters were obtained from a Rietveld refinement of the patterns using GSAS.⁶

In a separate run, NaCl was used as the pressure medium. This choice of medium allowed us to compare our data to that obtained from an earlier neutron scattering experiment³ and also laser heat the sample at high pressures. The motivation of this study was to (a) eliminate nonhydrostatic effects by annealing the sample, and (b) explore the possibility of decomposition at high pressure, temperature conditions. We present the representative diffraction patterns obtained at 22.5 GPa in Fig. 4.

It is evident that B_4C remains stable even at temperatures as high as 3200K at high pressures. However, the anomalous change in the pressure derivatives of cell constants shown in Fig. 2 is observed to persist in the NaCl medium also. The annealing of stresses at high temperatures allowed us to eliminate nonhydrostatic effects as an origin of this anomaly. High-temperature data obtained at 12 GPa and 22.5 GPa are being analyzed to obtain the P-V-T (pressure-volume-temperature) equation of state for this technologically important material. Radial diffraction measurements are being planned to obtain an estimate of the elastic moduli at high pressures especially above 22 GPa.

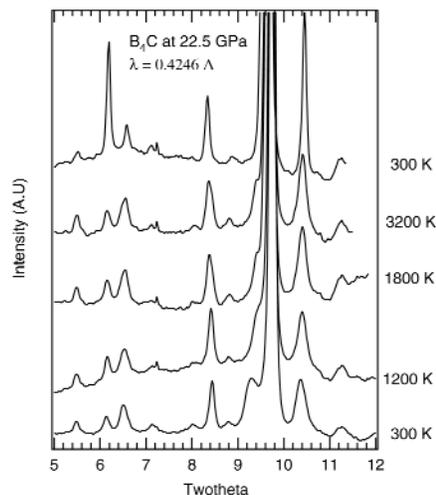


FIG. 4. Representative in situ powder patterns obtained at high temperatures. The sample was heated using a Nd: YLF laser while temperature was measured from spectroradiometry. The average temperature is listed alongside each pattern. The temperature variation is estimated to be of the order of $\pm 100K$. The (200) diffraction peak of the NaCl medium has been clipped in the figure. As can be seen, the diffraction peaks sharpen up considerably after heating, indicative of stress relaxation at high temperatures.

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