Synchrotron X-ray Study of Nanostructured Superhard BC_2N Material

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Introduction, Methods, and Materials

The high-pressure synthesized BC_2N samples were examined by synchrotron x-ray diffraction with a short monochromatic wavelength of $\lambda = 0.4246$ Å. The x-ray beam was collimated to a very fine size of 5×7 μm^2 so that different positions within the BC_2N chunk could be illuminated separately. Thus, we were able to reveal crystal structural variations in the BC_2N chunks at different locations assumed to have experienced subtle variations in pressure and temperature (P-T) synthesis conditions. The diffracted x-rays were collected by using an image plate in angle-dispersive mode to cover a 2θ range up to 32°, corresponding to a minimum d spacing of 0.77 Å. One obvious feature of the x-ray pattern is that the diffraction peaks are significantly broadened (middle pattern, Fig. 1) by a factor of 5 to 6 compared to the micrometer-sized powder diffraction standard CeO_2 (bottom pattern, Fig. 1). We rocked the sample with an amplitude of 5 μm for some runs in order to increase the counting statistics, whereupon it was found that the width of the diffraction peaks was further broadened (top pattern, Fig 1) to as much as about 8 to 10 times typical CeO_2 line widths. By using Scherrer's equation, we obtained a crystallite size for the synthetic BC_2N sample in a range of about 4 to 8 nm. This indicates that our unique sample preparation procedure does indeed result in nanostructured superhard material bulks with significant technological advantages.

Results and Discussion

The major diffraction peaks of the crystalline BC_2N are consistent with an fcc zinc-blende (ZnS) structure with a unit cell parameter of $a = 3.595(7)$ Å. This unit cell dimension lies between diamond ($a = 3.567$ Å) and cBN ($a = 3.616$ Å), as predicted for the high-pressure phase of BC_2N. Our observation contradicts the results of Solozhenko et al. [1], who found a unit cell ($a = 3.642$ Å) larger than that of cBN. Our result agrees with the Knittle et al. [2] report of $a = 3.602$ Å and the Komatsu et al. [3] report of $a = 3.605$ Å. A recent synthesis experiment conducted by Utsumi et al. [4] at 25 GPa and 2300K yielded the same unit-cell parameter as that of the present study.

Notice that unlike our work, the above-mentioned experiments did not produce large bulks of well-sintered samples. These authors were therefore unable to conduct hardness measurements on their BC_2N superhard flakes. We find it difficult to index two minor diffraction peaks at $d = 3.88$ and 2.84 Å ($2\theta = 6.27°$ and 8.57° in Fig. 1), which were not reported by any previous studies. These peaks may be the results of either a coexisting minor phase or a superlattice cell resulting from long-range ordering.

We also collected synchrotron x-ray diffraction patterns in the energy-dispersive mode on different BC_2N samples synthesized under different P-T conditions. Shown in Fig. 2 is a small diffraction window focused in the region between the $<111>_{pc}$ and $<220>_{pc}$ peaks of the fcc lattice. The BC_2N samples synthesized at lower pressures show clear additional peaks and apparent peak splitting (most obviously for the $<200>_{pc}$ peak), suggesting the existence of a superlattice, lower symmetry, or an additional phase.

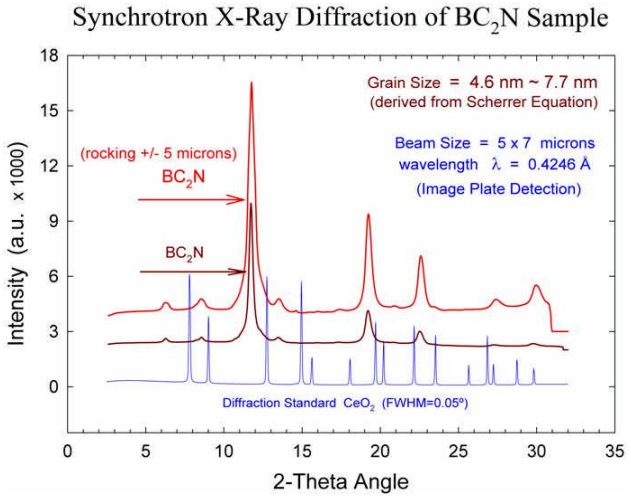

FIG. 1. Monochromatic synchrotron x-ray diffraction patterns taken in angle-dispersive mode at the APS. The top diffraction pattern was taken with the nanostructured superhard BC_2N sample rocking with an amplitude of 5 μm. The middle pattern was taken with a stationary sample. The bottom pattern is a standard diffraction pattern (CeO_2) and shows instrumental resolution. The grain size of the BC_2N sample deduced from the Scherrer equation ranges from 4 to 8 nm.

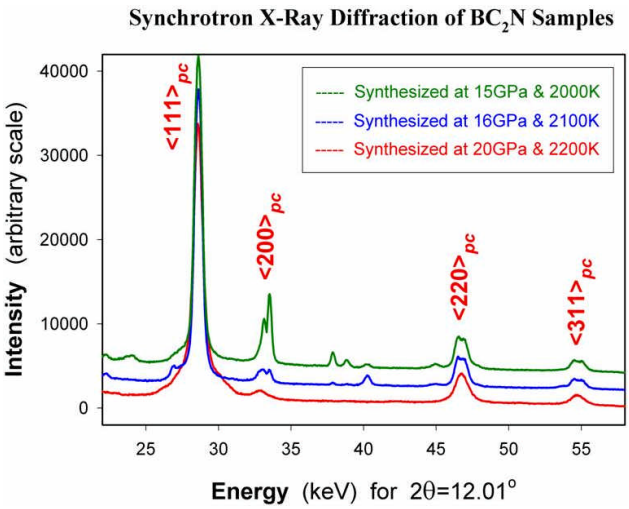

FIG. 2. Synchrotron x-ray diffraction patterns taken in energy-dispersive mode at the APS. The top pattern corresponds to a sample synthesized at 15 GPa and 2000K. The middle pattern is for a sample with an identical composition but synthesized at 16 GPa and 2100K. The synthesis conditions for the nanostructured BC_2N superhard material in the bottom pattern are 20 GPa and 2200K. The presence of peak splitting and superlattice diffraction peaks at lower pressure and temperature are indicative of a material with lower symmetry. The patterns clearly indicate a trend toward higher symmetry (cubic, zincblende structure) with increasing pressure and temperature.

The sample synthesized at higher pressures appears to have higher symmetry. Interestingly, the $<200>_{pc}$ peak reported in our study was not shown in the data of Komatsu et al. [3], Solozhenko et al. [1], and Utsumi et al. [4]. Significantly, their starting material was graphitic BC_2N. We also notice that Knittle et al. [2] reported the appearance and disappearance of the $<200>_{pc}$ peak in their synthesis products on the basis of using various proportions of "graphitic" and "mixed" starting materials. We suspect that the appearance of the $<200>_{pc}$ peak is an indication of the segregation of the BN- and C- layers within the crystal structure, and we are currently working toward modeling the crystallographic structure.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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