

OPEN ACCESS

Synthesis of dense BC_x phases under high-pressure and high-temperature

To cite this article: L C Ming *et al* 2010 *J. Phys.: Conf. Ser.* **215** 012135

View the [article online](#) for updates and enhancements.

You may also like

- [High-pressure high-temperature behavior of polymer derived amorphous B-C-N](#)
Shrikant Bhat, Stefan Lauterbach, Dmytro Dzivenko et al.
- [Backcrossing of \$\text{BC}_3\text{F}_3\$ Accession with Local Parents of Rice Plants which Resistance to Submergence Stress](#)
M Hasmeda, F Sulaiman, H Hamidson et al.
- [Superhard monoclinic \$\text{BC}_3\text{N}\$ allotropes: First-principles investigations](#)
Nian-Rui Qu, , Hong-Chao Wang et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Synthesis of Dense BC_x Phases under High-Pressure and High-Temperature

L C Ming¹, P V Zinin¹, X R Liu², Y Nakamoto³, R Jia¹

¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI 96822, U.S.A.

²High Pressure Laboratory, Southwest Jiaotong University, Chengdu, Sichuan, China

³Center for Quantum Science and Technology under Extreme Conditions, Osaka University, Toyonaka, Osaka, 560-8531, Japan

E-mail: ming@soest.hawaii.edu

Abstract. We synthesized a new phase from the B-C system, cubic BC₄ (*c*-BC₄), by direct transformation from graphitic phases at a pressure of 44 GPa and a temperature 2020 K in a laser-heated diamond anvil cell (DAC). Both x-ray diffraction and Raman spectroscopy confirm the presence of cubic BC₄ from the sample recovered at ambient conditions. The zero-pressure lattice parameter of the *c*-BC₄ calculated from diffraction peaks was found to be 3.587 Å. The composition of the new phase is determined from electron microprobe (EMP) measurements. The value of the C/B ratio is around 4 (3.91 ± 0.26).

1. Introduction

The finding of the new diamond-like B-C phases is of fundamental importance. These phases are potential high-temperature superconductors and their development is important for understanding the nature of high-temperature superconductivity. They will shed light on the nature of the bonding of the boron atoms in a cubic unit cell containing boron and carbon. Recently, theoretical simulations of pressure- and temperature-induced phase transition in the B-C system conducted by Lowther [1] demonstrated that the incorporation of B atoms into a diamond structure should not lead to a drastic distortion of the cubic cell of a diamond. The unit cells obtained in the phases predicted theoretically (i.e., 3.745 Å for cubic BC and 3.642 Å for nearly cubic BC₃) are slightly larger than that of a diamond (3.5667 Å) [1]. Recently, new diamond-like BC_x phases (cubic BC_{1.6} and diamond-like BC₃ phases) have been synthesized from *g*-BC_x under high pressure and high temperature [2, 3]. Unfortunately, these new phases have not been fully characterized. The elemental composition of BC_x phases was determined by energy-dispersive spectroscopy (EDS), which is only sufficient for a semi-quantitative determination of B-C compounds [2-4], and the identification of the diamond-like BC₃ phase (*dl*-BC₃) was done only by Raman spectroscopy. In this report, we present experimental data on the synthesis of the cubic BC₄ (*c*-BC₄) phase and the characterization of this phase by x-ray diffraction scattering, electron microprobe (EMP) technique, and Raman scattering.

2. Experimental methods

The pressure- and temperature-induced phase transformation of *g*-BC₄ was studied at a pressure up to 44 GPa using laser-heated diamond anvil cells and angle-dispersive powder X-ray diffraction (ADXRD) at Advanced Photon Source (APS), Argonne National Laboratory. X-ray diffraction measurements

were performed using a monochromatic synchrotron radiation source ($\lambda = 0.368138 \text{ \AA}$) at the 16-ID-B beamline of the HPCAT facility at the APS.

A symmetrical DAC was used in this study. Each cell had a pair of type I brilliant-cut diamond anvils of 0.3 carat and a culet of $300 \mu\text{m}$. A stainless steel, fully hardened, $250\text{-}\mu\text{m}$ -thick gasket was first indented to $40 \mu\text{m}$ and then a $90 \mu\text{m}$ diameter hole was drilled, which served as the sample chamber. The sample, which included a tiny ruby chip, was gradually loaded to a desired pressure and then laser-heated to high temperature. To ensure efficient laser-heating in the sample between the diamond-anvils, a thin layer of NaCl (a few microns in thickness) was placed on the upper side as well as the lower side of the sample to provide a good thermal insulation for the sample. The sample temperature was monitored using the spectra-radiometric method. The uncertainty of the temperature measurement was reported as $\pm 100 \text{ K}$. The laser moved stepwise vertically and horizontally to heat the whole sample area and the duration of the laser heating at each point was about 10 seconds. After quenching, each sample was decompressed gradually stepwise to atmospheric pressure. The sample in the gasket was then removed from the cell and rinsed with water to remove the NaCl layers on both sides of the BCx sample for x-ray diffraction and electron microscope analysis.

The Raman spectra excited by a Nd-YAG laser (532-nm, Coherent Compass, Dieburg, Germany) were taken with a confocal Raman system (WiTec alpha300). The spectrometer has an entrance slit of $100 \mu\text{m}$, a focal length of 800 mm , and is equipped with 300-lines/mm grating.

Electron microprobe analysis of the recovered BCx sample was performed using JEOL *Hyperprobe* JXA-8500F at the School of Ocean and Earth Science and Technology, University of Hawaii. In order to ensure a reliable result, a pure B_4C powder was used as the standard for calibration of boron and carbon in the sample, and the rinsed BCx sample in the gasket was first fixed with an epoxy resin and then polished until an optically flat surface from the sample was fully exposed. The result obtained from EMP measurements gives a C/B ratio of around 4 ($\text{C/B} = 3.91 \pm 0.26$).

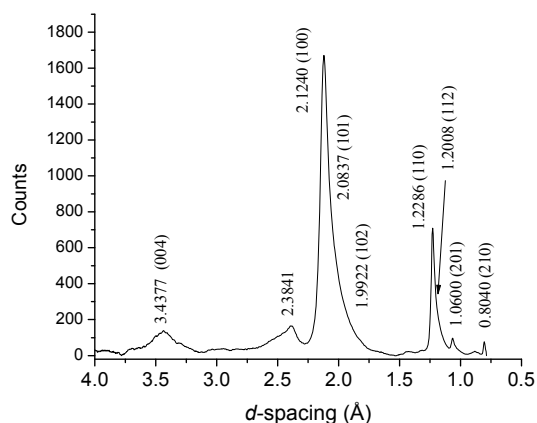


Figure 1. X-ray diffraction of the graphitic BC_4 ($g\text{-BC}_4(\text{I})$) as the starting material, where the broad peak around $2.384 \text{ \AA}$ is from the B_4C .

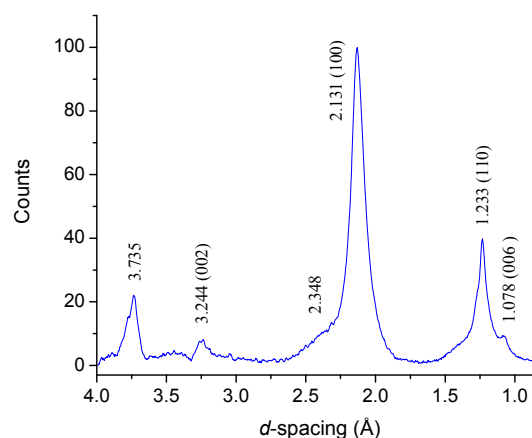


Figure 2. The ambient x-ray diffraction pattern of a post-lasered BC_4 ($g\text{-BC}_4(\text{II})$) phase recovered from 24 GPa, where two weak peaks at 3.73 and $2.347 \text{ \AA}$ are from the B_4C phase in the starting material.

3. Results and discussion

Two samples were loaded to 24 and 44 GPa, and laser-heated to 2020 and 1984 K, respectively. After laser-heating, the sample pressure was measured again. It was found that the sample pressure remained the same for the first sample at 24 GPa, while the pressure dropped from 44 GPa to 37 GPa in the second sample. The large pressure drop in the second sample is most likely related to volume change as a result of the transition to a denser phase in the sample. The x-ray spectra of the starting material BC_4 ($g\text{-BC}_4(\text{I})$) is shown in figure 1. A weak peak at $2.384 \text{ \AA}$ is believed to be from the B_4C left in the

starting material during the process of synthesis [5]. The positions of the other eight peaks on the x-ray spectrum can be indexed using a hexagonal unit cell with $a=2.4537\pm0.0031$ Å and $c=13.45\pm0.37$ Å. Parameters of the unit cell of $g\text{-BC}_4(\text{I})$ are close to those of graphite ($a=2.463$ Å and $c=6.714$ Å) (JCPDS # 23-64) if the c -axis is doubled. However, the relative intensities of the peaks in the $g\text{-BC}_4(\text{I})$ phase are very different from those of graphite. This indicates that the $g\text{-BC}_4(\text{I})$ starting material used in this study probably has very different stacking layers of the B-C hexagons along the c -axis. Further studies are needed to fully characterize the structure details in the $g\text{-BC}_4(\text{I})$ starting material.

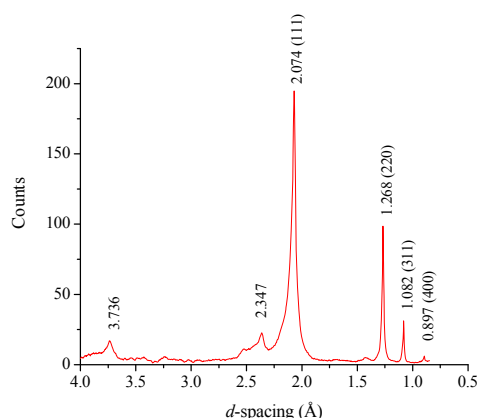


Figure 3. The ambient x-ray diffraction pattern of a post-lasered BC_4 ($c\text{-BC}_4$) phase recovered from 37 GPa. Two weak and broad peaks at 3.736 and 2.347 are from the B_4C in the starting material.

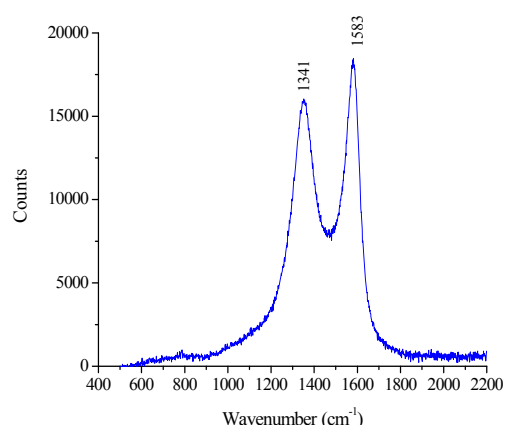


Figure 4. Raman spectrum (532 nm) of the post laser-heated $g\text{-BC}_4(\text{II})$ phase recovered from 24 GPa, with integration time of 1.5 min and laser power of 2 mW. The two modes are typical of a graphitic phase.

The diffraction pattern from the recovered sample at 24 GPa is similar to that in the starting material except the major diffraction peaks are more symmetric in shape and less in the number (i.e., a change from 8 to 5 peaks), indicating a subtle change has taken place in the BC_4 specimen at this pressure. As can be seen in figure 2, the 4 diffraction peaks thus obtained can be best indexed using a new hexagonal unit cell with lattice parameters $a=2.4654\pm0.013$ Å and $c=6.468\pm0.028$ Å, that compare well with those in the graphite. The volume change between the new hexagonal, graphite-like BC_4 ($g\text{-BC}_4(\text{II})$) phase recovered from 24 GPa and the starting $g\text{-BC}_4(\text{I})$ phase is about 0.3%.

The x-ray spectrum of the post-lasered BC_4 ($c\text{-BC}_4$) specimen recovered from 37 GPa shows a completely different diffraction pattern (figure 3), indicating a phase transition has indeed taken place. All the graphite-like x-ray diffraction peaks were replaced by a completely new set of peaks. The fact that all the new diffraction lines are sharp and well defined implies the high-pressure phase is well crystallized. The new phase can be indexed by a cubic unit cell with lattice parameter, $a_0 = 3.5866\pm0.0003$ Å. The 4 peaks are indexed as (111), (220), (311) and (400), respectively, and together with their respective intensity, are in good agreement with those in the diamond structure with both boron and carbon atoms randomly distributed in the 8 positions in the diamond-like structure. Two weak peaks at 3.73 and 2.347 Å are probably from the B_4C phase in the starting material, indicating that B_4C remains intact, untransformed, and uncrystallized at a pressure of up to 44 GPa.

The zero-pressure lattice parameter of the cubic phase obtained in this study is larger than that of diamond (i.e., $a_0=3.5667$ Å, JCPDS No. 6-0675), which is consistent with those from theoretical prediction [1]. This value is slightly larger than that of the $c\text{-BC}_{1.6}$ phase ($a_0=3.578$ Å) [2]. The discrepancy could be caused by the difference in synthesis pressures in this study (i.e., 37 GPa), compared to 50 GPa in Zinin *et al* [2].

The Raman spectrum of the g -BC₄(II) phase recovered from 24 GPa is given in figure 4, showing two broad modes at 1342 and 1583 cm⁻¹, which are the D and G modes, respectively, typical for graphitic materials. The Raman spectrum of the cubic c -BC₄ and map of the Raman peak intensity at 1193 cm⁻¹ over the sample surface are shown in figures 5 and 6. The Raman spectrum of the c -BC₄ phase is different from those of g -BC₄(II) recovered from 24 GPa and of graphitic BC_x phases studied by Zinin *et al* [5], which supports the observation that a new phase has occurred. It displays a broad peak at 450 cm⁻¹, a second peak at 1193 cm⁻¹, another broad peak at 684 cm⁻¹, a much narrower peak around 1287 cm⁻¹. The Raman spectrum of the c -BC₄ phase is similar to that of the dl -BC₃ phase with a strong peak at 1193 cm⁻¹[4]. Figure 6 shows the distribution of the cubic phase in the quenched specimen of BC₄. The four modes observed in c -BC₄, 450, 684, 1193, 1287 cm⁻¹, are close to those observed in dl -BC₃, 490 cm⁻¹, 671 cm⁻¹, 1231 cm⁻¹, and 1305 cm⁻¹ [4]. The most intensive peak at 450 cm⁻¹ can be attributed to the Raman active stretching modes of B-B dimmers [3, 4]. The second most intensive peak at 1193 cm⁻¹ may have the same origin as the 1211 cm⁻¹ peak of the c -BC_{1.6} phase and the 1231 cm⁻¹ peak of the dl -BC₃ phase. A broad peak around 1039 cm⁻¹ can be seen in the Raman spectra of the new phase as well as in c -BC_{1.6}. It was observed in both a boron-doped diamond and a nanocrystalline diamond [6], but its origin was not discussed. We mentioned that Raman peaks of the c -BC₄ phase are broad. The cause of the broadness of Raman peaks in the c -BC₄ phase is unknown and further studies are needed.

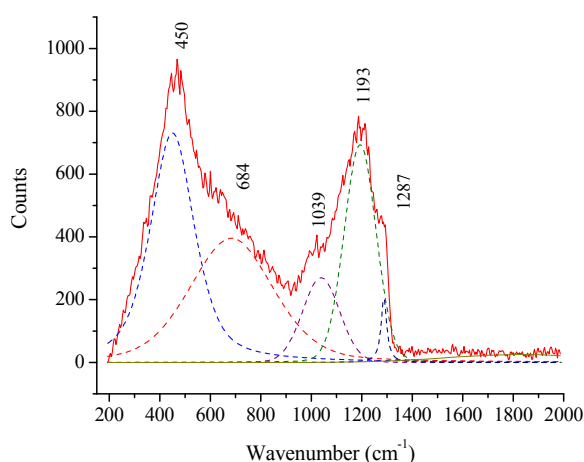


Figure 5. Raman spectrum (532 nm) of c -BC₄ phase: integration time was 4 min, laser power was 2 mW.

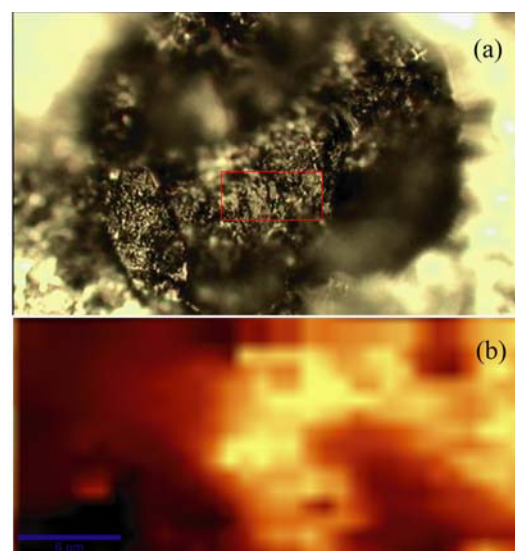


Figure 6. (a) Optical image of the c -BC₄ phase and (b) a map of the Raman peak intensity at 1193 cm⁻¹ shown in a yellow colour scale, showing the distribution of the cubic BC₄ phase in the recovered sample.

4. Conclusions

A new cubic phase, c -BC₄ was synthesized by direct transformation from a graphitic phase at pressure 44 GPa and temperature 2020 K in a laser-heated DAC. Identification of the cubic phase was obtained from x-ray diffraction and Raman spectroscopy measurements. The zero-pressure lattice parameter of the c -BC₄ calculated from diffraction peaks is 3.587 Å. The composition of the new phase was determined from EMP measurements and gave a value of C/B ratio around 4 (C/B = 3.91 ± 0.26). The x-ray diffraction measurements of the recovered sample synthesized at a pressure of 24 GPa and a temperature of 2020 K showed a very subtle transition from the hexagonal phase g -BC₄(I) phase at ambient conditions to a new hexagonal phase g -BC₄(II) phase with a volume change of 0.3%.

5. Acknowledgements

This work was supported by U.S. DOE grant NO. DE-FG02-07ER46408. The use of the HPCAT facility was supported by DOE-BES, DOE-NNSA (CDAC), NSF, DOD-TACOM, and the W.M. Keck Foundation. The use of Advanced Photon Source 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.

References

- [1] Lowther J E 2005 *J. Phys. Condes. Matter.* **17** 3221
- [2] Zinin P V, Ming L C, Kudryashov I, Konishi N, Manghnani M H, and Sharma S K 2006 *J Appl Phys* **100** 013516
- [3] Zinin P V, Ming L C, Kudryashov I, Konishi N, and Sharma S K 2007 *J. Raman Spectrosc.* **38** 1362
- [4] Zinin P V, Ming L C, Sharma S K, Hong S M, Xie Y, Irifune T, and Shinmei T 2008 *J. Phys. Conf. Ser.* **121** 062002
- [5] Zinin P V, Ming L C, Sharma S K, Liu Y, and Hong S M 2009 *Diam. Relat. Mater.* **18** 1123
- [6] Prager S, Nugent K W, Jamieson D N, Orwa J O, Bursill L A, and Peng J L 2000 *Chem. Phys. Lett.* **332** 93