

Identification of the diamond-like B–C phase by confocal Raman spectroscopy

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Abstract

The new diamond-like B–C phase was obtained from the graphite-like BC phase in a laser-heated diamond anvil cell at high temperature 2230 ± 140 K and high pressure 45 GPa. Raman spectra of the new phase measured at ambient conditions revealed a peak at 1315 cm^{-1} , which was attributed to longitudinal-optical (LO) mode. The X–Y Raman mapping was used to investigate spatial distribution of the diamond-like phases and was shown to be a powerful tool in studying the sp^2 -to- sp^3 phase transformations occurring in the diamond cell under high temperature and high pressure.

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1. Introduction

Raman scattering from natural and synthetic diamonds has been investigated for many years. Now, there is an interest in producing diamond-like phases with elastic parameters close to those of diamond. Direct transformation from a graphitic phase to the diamond-like phase can be achieved in a diamond anvil cell (DAC) with laser-heating. The X-ray diffraction spectra of the diamond-like phases are very similar to those of diamond, making it difficult to distinguish a new phase from the bulk diamond. In this report, we will demonstrate that confocal Raman spectroscopy allows not only identifying the new phase after transformation, but also provides an opportunity to study the spatial spreading of the phase transformation using X–Y mapping of the sp^3 bond Raman peak.

2. Experiment

2.1. Synthesis of diamond-like phases

A Mao–Bell-type DAC and a symmetrical DAC each equipped with a pair of type I brilliant-cut diamond anvils with ($350 \mu\text{m}$) culet were used in the experiment. A fully hardened stainless steel gasket of $250 \mu\text{m}$ thick was first indented to $40 \mu\text{m}$, and then a hole of $130 \mu\text{m}$ in diameter was drilled. The hole was served as the sample chamber. Pressure was measured with ruby R1 and R2 fluorescence lines. Two different starting materials were used to synthesize new diamond-like phases: graphite-like BC (g-BC) phase was heated in the DAC to 2230 ± 140 K at 45 GPa, and a mixture of graphite and graphite-like hexagonal boron nitride (hBN) with a stoichiometry of CBN was heated to the temperature of ~ 1500 K at 46 GPa.

2.2. Heating systems

We used laser-heating facilities at the University of Hawaii. The laser-heating system with Nd-doped YAG laser

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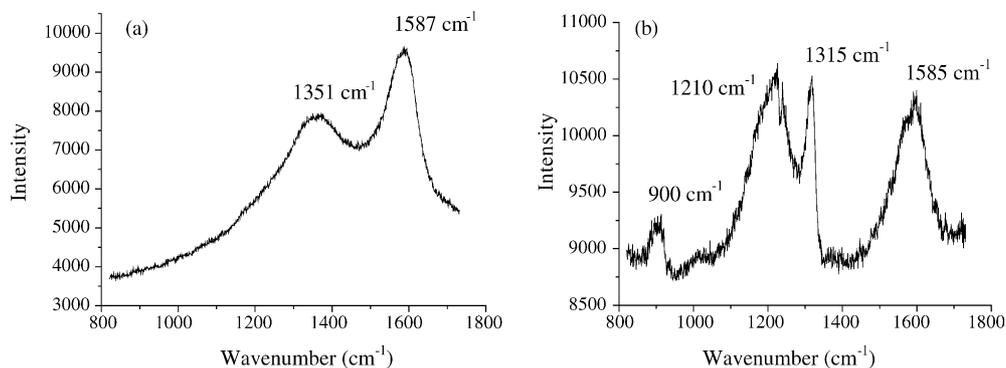


Fig. 1. Raman spectra of the BC phase measured outside (a) and inside circle (b) shown in Fig. 2.

(wavelength = 1064 nm, power = 90 W) makes it possible to heat samples up to 3000 K. A laser with a heated spot of 10–20 μm scanned the central area of both samples. To ensure efficient heating, a thin NaCl platelet was placed on the top of the BC sample facing the incident laser-beam. For the mixture of graphite and g-BN, no NaCl platelet was used. The temperatures of both samples were determined from thermal radiation [1,2]. Duration time of laser-heating at each point in the DAC was more than 10 s for all samples.

2.3. Raman spectroscopy

Both samples were quenched and recovered outside the DAC. Raman spectra were measured by a modular Raman system (“Nanofinder 30”) based on a confocal far-field optical microscope, XYZ-piezo stage, and spectrometer (Tokyo Instruments Inc.). The NaCl platelet was removed from the post-heated BC sample by dipping the sample into water before the measurement. The Raman signal was excited by a continuous wave (with wavelength of 488 nm) “Sapphire 488-20” DPSS CW laser from Coherent Inc. High spectral resolution (1 cm^{-1}) and high signal throughput (up to 40%) were achieved in the accessible spectral region of $100\text{--}6500\text{ cm}^{-1}$.

3. Results and discussion

Carbon polymorphs can be easily identified from their Raman spectra. The features of the Raman spectra depend on the ratios of sp^1 (polymer-like)/ sp^2 (graphite-like)/ sp^3 (diamond-like) bonds [3]. The visible Raman spectroscopy is 50–233 times more sensitive for sp^2 sites than those for sp^3 [4,5]. First, measurements of the visible Raman spectra of a diamond-like superhard phase containing B, C, and N atoms, cubic- BC_2N (c- BC_2N) showed that only the Raman band at 1326 cm^{-1} could be detected [6]. It was attributed to the longitudinal-optical (LO) mode of c- BC_2N , while the transverse-optical (TO) mode was missing in the spectra.

Raman study of the BC phase heated in DAC up to $2230 \pm 140\text{ K}$ at 45 GPa revealed two types of Raman

spectra (Fig. 1). Raman spectra (Fig. 1a) of the material outside the circle shown in Fig. 2 can be attributed to a disordered g-BC phase [3]. Graphite has a strong peak at 1581 cm^{-1} [7–9], and hBN at $1366\text{--}1370\text{ cm}^{-1}$ [9–11]. By analogy with graphite, we call the Raman peaks of the g-BC phase as D (1351 cm^{-1}) and G (1587) modes [12]. Raman spectrum (Fig. 1b) of material measured inside the circle in Fig. 2 clearly indicates that a phase transformation did occur: the D mode disappeared, while three other modes appeared at 900, 1210, and 1315 cm^{-1} , respectively. By analogy with c- BC_2N , we attribute the 1315 cm^{-1} peak to the LO mode of the diamond-like B–C phase transformed from g-BC under high pressure and high temperature. The position (1315 cm^{-1}) of the LO mode is below those positions of the Raman line for diamond (1332 cm^{-1} , see references [13–17]), c- BC_2N (1326 cm^{-1} , [6]), hexagonal diamond (1323 cm^{-1} , [3]), cubic $\text{C}_{0.3}(\text{BN})_{0.7}$ (1323 cm^{-1} , [18]), and higher than the peak of cubic-BN (c-BN) (1304 cm^{-1} , [19,20]). The Raman mode around 1200 cm^{-1} was detected in heavily B-doped polycrystalline diamond films [21,22]. Although the origin of the 1210 cm^{-1} peak is not well understood [23–25], it is most likely related to a new phase. This is because in the X–Y mapping of the Raman peaks (Fig. 3), the 1315 and 1210 cm^{-1} modes were detected from the same area. We do not rule out that the 1210 cm^{-1} peak is a TO mode of the new

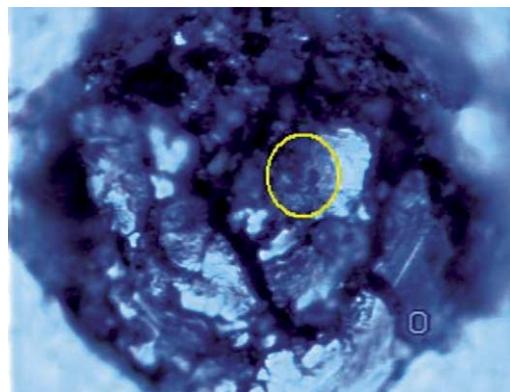


Fig. 2. Optical image of the BC sample inside gasket after laser-heating. Field of view is $100\text{ }\mu\text{m} \times 75\text{ }\mu\text{m}$.

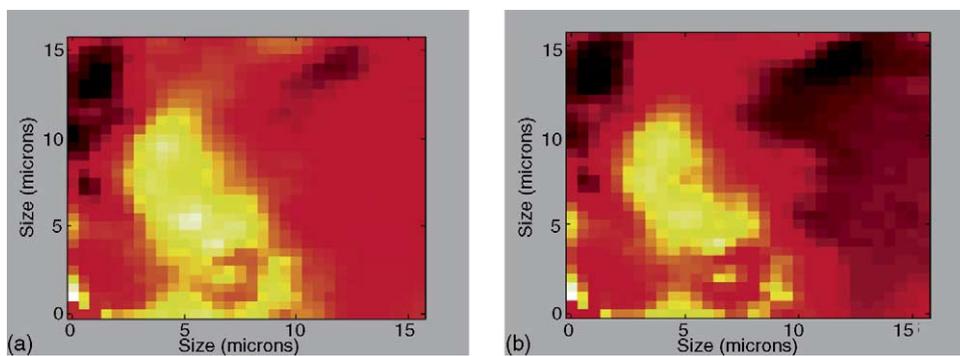


Fig. 3. Intensity X - Y mapping of peak 1315 and 1210 cm^{-1} after background subtraction.

B–C phase that was missing in the c-BC₂N Raman spectra. The c-BN has both LO and TO modes in its first-order Raman spectrum at 1304 and 1056 cm^{-1} , respectively [19,20]. The origin of the 900 cm^{-1} mode is not yet clear.

Emergence of the G peak on the spectrum in Fig. 1b has the following explanation. The laser does not heat sample homogeneously. Certainly, there is a strong temperature gradient both laterally (along sample surface) and vertically (with depth) in the laser-heated sample. Therefore, we expect that the transformation of g-BC phase to a diamond-like phase has taken place only near the surface of the sample, where the temperature is at the highest. Since Raman scattering is more sensitive for sp^2 bonds than those for sp^3 bonds [4,5], even a small amount of the graphite-like phase or sp^2 bonds present in the heated sample gives a strong G peak. This scenario is supported by our observation that the greater the aperture angle of the lens (i.e., the smaller the focal depth of the confocal Raman system), the more pronounced is the 1315 cm^{-1} peak. With a small aperture lens $40\times$ ($NA=0.55$) the peak at 1315 cm^{-1} was detected only inside a small area in the central part of the sample (Fig. 3). When a $100\times$ ($NA=0.9$) objective lens was used, the 1315 cm^{-1} peak was detected everywhere inside circle in Fig. 2.

In the second experiment, a mixture of graphite and hBN was heated at 46 GPa to about 1500 K (Fig. 4). Raman spectra obtained with the nanofinder showed clearly that the diamond (1332 cm^{-1} peak) had been synthesized under laser-heating

in DAC (Fig. 5a). The LO peak of c-BN is not seen in Fig. 5a because its Raman scattering cross-section is smaller than that of diamond. The Raman spectrum collected outside the heated area (Fig. 4) shows Raman peaks typical for graphite (Fig. 5b). Fig. 6 shows the X - Y image of the peak intensity of the 1332 cm^{-1} peak. The bright area corresponds to the area, where graphite was converted into diamond under laser-heating; the dark area shows unconverted sample. The X - Y image of the diamond peak confirms that direct transformation of graphite into diamond has taken place locally (Fig. 6).

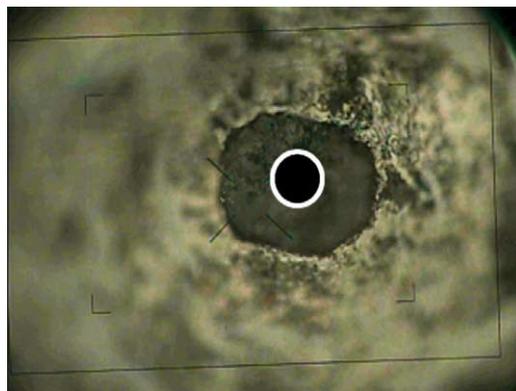


Fig. 4. Optical image of the gasket and sample (mixture of two graphitic phases) heated by laser inside the circled area, field of view was $600\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$.

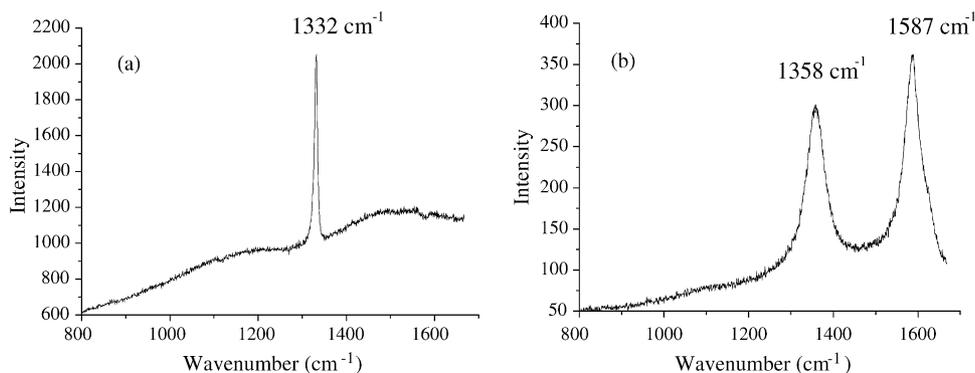


Fig. 5. Raman spectra of the mixture of two graphitic phases after heating under high pressure measured inside (a) and outside the circle (b) in Fig. 4.

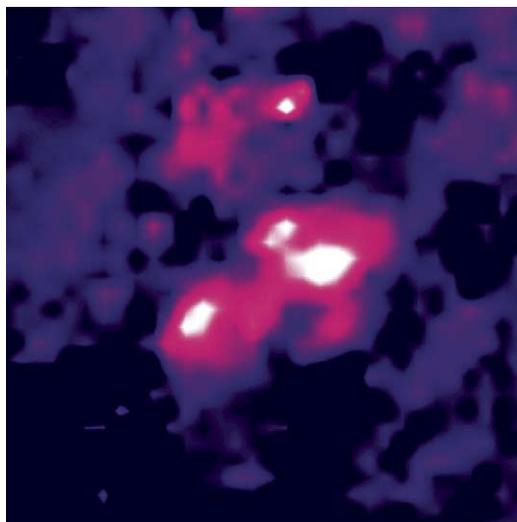


Fig. 6. Image of the mixture of two graphitic phases after heating under high pressure. Raman intensity X – Y mapping of peak 1332 cm^{-1} , field of view was $16\text{ }\mu\text{m} \times 16\text{ }\mu\text{m}$.

The transformation area ($<5\text{ }\mu\text{m}$) is much smaller than the diameter of the laser-beam ($30\text{ }\mu\text{m}$). It is expected that the transformation area will be increased when an NaCl platelet is used on the sample top.

In summary, the measured visible laser-excited Raman spectra of a new diamond-like B–C phase reveal a peak at 1315 cm^{-1} , which is attributed to the LO mode. A direct transformation from the g-BC phase to a new diamond-like B–C phase was obtained in a diamond anvil cell at high temperature $2230 \pm 140\text{ K}$ and high pressure 45 GPa . It is also demonstrated that X – Y Raman mapping of the diamond-like phase promised to be a powerful tool in studying the phase transformation that occurred under high temperature and high pressure.

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