Raman spectroscopy for studying the synthesis of conducting BC$_3$ hetero-diamonds in diamond anvil cell under high temperature

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Abstract. A direct transformation of the sintered BC$_3$ phase to a novel diamond-like d-BC$_3$ phase was observed in a diamond anvil cell (DAC) at high temperature, 2500 K and high pressure, 22 GPa. For heating a specimen in a DAC a laser heating (LH) system combined with an acousto-optical filter and synchronized with a video camera was used. Combining the LH system with the acousto-optical filter allows measurement of the temperature distribution under infrared (1064 nm) LH of a specimen under high pressure in a DAC. The starting material with a composition BC$_3$ was obtained by sintering a powder of nanodiamonds with a powder of boron microparticles at 6.0 GPa during 150 s heating at 1200 °C. The quenched BC$_3$ specimen was studied by the Raman spectroscopy.

1. Introduction

Phase transformations in the boron–carbon (B–C) system have attracted considerable attention because of the prediction of high-temperature superconductivity and metallic conductivity in these materials [1]. Recently high-temperature superconductivity (55 K) [2] and nearly graphitic conductivity [3,4] were discovered in BC$_x$ materials with the high boron concentration. Unfortunately the nature of the conductivity in BC$_x$ materials is not well understood. It was proposed that the origin of the superconducting transition is associated with a formation of B–C nanosheets and bilayers in boron-doped diamonds with increasing boron concentration [5]. Therefore it is of interest to obtain a BC$_x$ compounds consisting of nano-grains of diamond sintered by boron nanosheets. In this report we conduct the synthesis of such a material under high pressure and high temperature in a diamond anvil cell (DAC). The starting material was a mixture of nanodiamonds and boron particles sintered at 6 GPa and 1200 °C. The synthesis of a new phase was conducted in the DAC heated by a powerful continuous wave (CW) ir laser. The novel BC$_3$ phase was identified by Raman scattering technique.
Figure 1. Scheme of the installation for laser heating of the samples in the DAC: O—infinity-corrected objectives; M—mirrors on kinematic mounts; L—lenses; NLM—narrow line mirror; LS—light source; pi-shaper—flat top laser beam profiler, AldOptica, model πShaper; TAOTF—tunable acousto-optic filter; BS—beam splitters; Cam—monochrome camera, Allied Vision Mako G-030B, which runs up to 309 frames per second at resolution 644 × 484 pixels; Laser 1060 nm—CW laser, IPG Photonics, YLR-100-AC-Y11, $P = 100$ W; Spectrometer—Solar Laser Systems M266 with Hamamatsu S10420-1106-01 detector; Laser 532 nm—CW laser, Oxxius LCX-532L-150-CSB-PPF, $P = 100$ µW.

2. Method

High pressure synthesis of diamond-like BC$_x$ phases in DAC was described elsewhere [6]. To measure the temperature distribution in DAC under laser heating we used a tandem acousto-optical tunable filter (TAOTF) combined with a imaging camera as described in [7, 8]. The schematic diagram of the system is shown in figure 1.

The main part of the system is TAOTF, consisting of two conjugated AO crystals, connected to a fast camera (Cam) to measure the spatial distribution of temperature on the surface of a specimen under heating by a high power laser [9]. The DAC is mounted on a 3 axis XYZ linear stage table with micrometers. A fiber ir laser is used for heating a specimen. The shape of the ir laser beam on the surface on the heated specimen could be controlled by the pi-shaper. The thermal radiation coming from the sample during laser heating (LH) is directed toward the TAOTF. The image of the heated specimen at a selected wavelength is focused by a long focal
Figure 2. (a) X-ray diffraction pattern of the BC$_3$ compact obtained at pressure of 6.0 GPa and temperature of 1200 °C. Exposure time was 150 s. D stands for diamond, and G stands for graphite peaks. (b) SEM images of the nanodiamonds.

distance lens L1, and is taken by a camera CAM. Pressure was measured using the positions of the fluorescence peaks of a small ruby chip using the diffraction spectrometer. The Solar Laser Systems M266 spectrometer was used for Raman scattering measurements.

The Huber G670 imaging-plate Guinier camera (Cu K$_{\alpha 1}$ radiation with $\lambda = 1.5405981$ Å, Huber Technology, Tutzing, Germany) was used for x-ray diffraction measurements. The Huber Technology G670 imaging-plate Guinier camera (Cu K$_{\alpha 1}$ radiation with $\lambda = 1.5405981$ Å, Huber Technology, Tutzing, Germany) was used for x-ray diffraction measurements. Study of the microstructure and elemental composition analysis were conducted by a scanning electron microscope (SEM)—FEI Helios NanoLab 660 equipped with AMETEK EDAX (electron dispersive x-ray spectroscopy) microanalysis system. Raman spectra were collected at room temperature using TriVista 555 triple grating spectrometer with a liquid-nitrogen-cooled CCD detector. A 488 nm line of the Ar+ ion laser was used for excitation. To avoid overheating or burning out of the samples, the laser power was kept at a minimum (approximately 0.5 µW) and the Olympus BX51 microscope with 50 × objective was used for laser focusing and scattered light collection.

The starting BC$_3$ phase was obtained by sintering a mixture of nanodiamonds and boron powder (25%) with a size of 0.1–0.3 µm. The powders were sintered at a pressure of 6 GPa and a temperature of 1200 °C for 2 min.

The x-ray pattern of the staring BC$_3$ phase is shown in figure 2(a). The pattern consists of peaks associated with diamond and graphite indicating that during sintering, the diamond is partially graphitized. The SEM image of the staring BC$_3$ phase is shown in figure 2(b).

Sintered BC$_3$ specimen [figure 3(a)] was placed in a steel gasket and NaCl was used as an insulating medium. Then the sample in the DAC was compressed to pressure of 22 GPa. The optical image of the area of the laser heating 1 taken by an optical system with 50 ×, Plan Apo, infinity corrected (Edmund Optics) objective is shown in figure 3(b).

3. Results and discussion

The Raman spectrum (not shown) of the sintered BC$_3$ phase consists of peaks associated with vibrations of graphite and diamond. The main Raman peak of the mixture at room conditions
Figure 3. Optical images of powder of sintered BC$_3$ phase (a) before loading into gasket and (b) at 22 GPa: 1—laser heating area.

Figure 4. (a) Image of two-dimensional temperature distribution $T(x, y)$: $x$–$y$ scan. (b) Raman spectrum of diamond-like BC$_x$ nano-phase after laser heating in DAC.

with a center at 1620 cm$^{-1}$ is characteristic for amorphous carbon and denoted G-bands. A peak centered at 1346 cm$^{-1}$ is seen in Raman spectra of disordered graphite (D-band). The sintered BC$_3$ specimen was heated by ir laser for 5 minutes, and the power of the laser was 23 W. Diameter of heated area was around 15 $\mu$m and the maximal temperature achieved was 2500 K [figure 4(a)]. After the laser heating at 22 GPa the shape of the Raman spectrum changes [figure 4(b)]. For Raman spectrum excitation the stabilized diode CW laser with 532 nm wavelength and 150 $\mu$W output power was used. The exposition time of Raman detector was 60 s.

The Raman scattering spectrum in figure 4(b) indicates that the quenched samples are a mixture of two phases: graphite and diamond-like BC$_3$. The appearance of peaks around 1200 and 1300 cm$^{-1}$ indicates that a phase transition did happen. Obtained compound consist of
a heavily boron-doped diamond. Previously, in [10] was shown that a superconductivity effect may exist in similar boron-doped diamonds compounds. The broad peak at 417 cm\(^{-1}\) can be attributed to the Raman active stretching modes of B–B dimers. The most distinguishing peak is a sharp peak centered at 1324 cm\(^{-1}\). This peak can be attributed to vibrations of a diamond lattice with a high boron concentration [11]. Peak centered at 970 cm\(^{-1}\) is often detected in boron-rich hetero-diamond. A broad band centered at 1612 cm\(^{-1}\) indicates the presence of a graphitic phase. The Raman scattering of graphite is 50 time as high as that of diamond therefore the concentration of the graphitic phase is small. The peak centered at 1215 cm\(^{-1}\) can be also associated with Raman scattering of a boron-rich hetero-diamond [6].

4. Conclusion
A direct transformation of the \(g\)-BC\(_3\) phase to a new diamond-like \(d\)-BC\(_3\) phase was observed in a DAC at high temperature 2500 K and high pressure 22 GPa. Analysis of the peak positions of the novel BC\(_3\) phases leads to the conclusion that positions of the peaks of the \(d\)-BC\(_3\) is more similar to the peak pattern of the boron-rich hetero-diamonds. It is planned to study the conductivity of the specimen using a conductive atomic force microscope.

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