

Identifying C-N Heterodiamonds with SEM, TEM and Raman Scattering

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The prediction by Liu and Cohen [1] of the existence of a β - C_3N_4 phase with a bulk modulus and hardness similar to diamond has led to an enormous effort to synthesize this material. However, search for new superhard materials in the last decade indicates that the synthesis of phases with hardness exceeding that of diamond is unlikely. Now, it seems worthwhile to refocus the search for new superhard phases on synthesis of materials more useful than diamond, rather than those harder than diamond. Such phases are predicted to be inside the B-C-N system. Superhard diamond-like phases from the B-C-N triangle are highly desirable, as they might combine the best properties of the elemental or binary compounds of the system, such as a diamond and a cubic boron nitride (cBN), and are expected to be thermally and chemically more stable than diamond, and harder than cBN. The new phases can be obtained under high (>20 GPa) pressures and temperatures (>2000 K). In this report we show that electron microscopy plays an important role in the identifying the new phase.

A Mao-Bell type diamond anvil cell (DAC) together with the laser-heating system was used to synthesis diamond-like phase from the graphitic phase. The laser-heating system with a Nd-doped YAG laser (wavelength = 1064 nm and a max. power of 9W at TEM₀₀ mode) is able to heat samples up to 3000 K. A laser with a heated spot of 10-20 μ m scanned the central area of both samples (Fig. 1a). After heating, sample was quenched to room temperature and gradually decompressed to 1 atmospheric pressure (Fig. 1b). The recovered samples were examined using synchrotron-based X-ray diffraction, Raman spectroscopy for phase identification, and ED-SEM and EELS for composition determination. Results thus obtained will be presented and the probably high pressure phase will be discussed

Graphite-like C_3N_4 (g- C_3N_4) phase was used to synthesize new phases. Two samples were heated in the DAC to 1530 K at 48 GPa and to 2000 K at 33 GPa, respectively. After quenched and decompressed to the atmospheric pressure from high-pressure, the recovered sample has been studied by scanning electron microscope. Figures 2a is the SEM image of the C_3N_4 sample. The resolution of energy-dispersive detector of the JEOL JSM-5900 SEM was sufficient for quantitative chemical analysis of C_3N_4 compounds. EDS measurements of the sample heated to 1500 K at 48 GPa conducted at five point shown in Fig. 2a provide the following value of the C/N ratio as 0.92 ± 0.16 . Similar ratio was obtained for a diamond-like sample obtained under 2000 K and 33 GPa. The C/N composition was found to be homogeneous over the surface of the sample. Fig. 2b is the TEM image of the graphitic C_3N_4 . It is interesting to note that that C/N ration in g- C_3N_4 phase was 0.65 ± 0.07 . EELS measurements (Fig. 3) are in a good agreement with into ED-SEM measurements. The possible reason of the change of the N/C ratio during phase transformation is discussed in the report.

References

- [1] A. Y. Liu and M. L. Cohen, *Science*, vol. 245, pp. 841-842, 1989.
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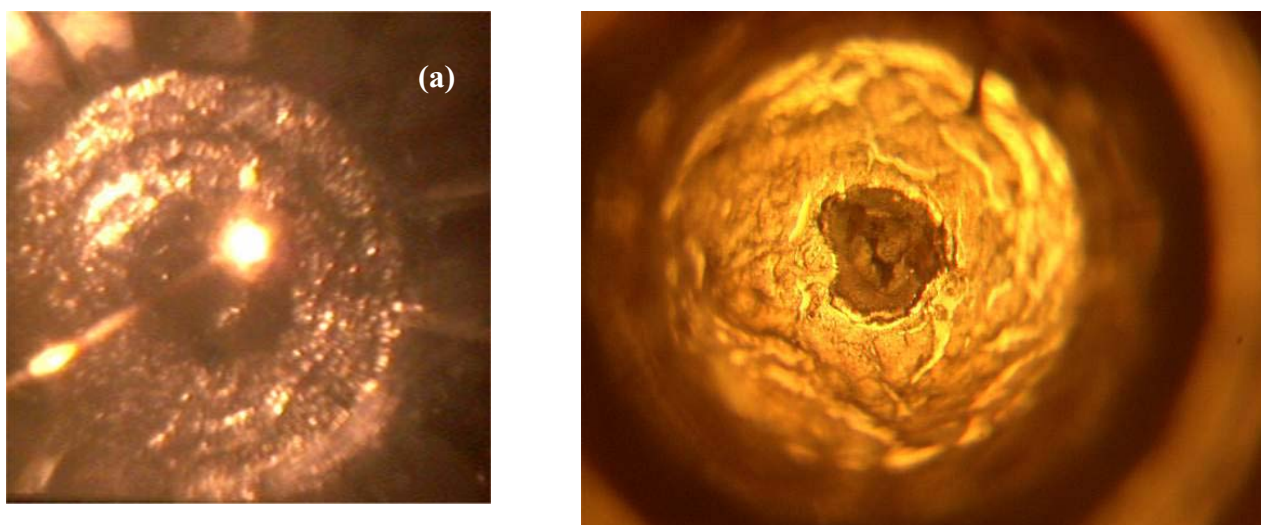


Fig.1. Optical images of the C_3N_4 at high pressure in the cell: (a) during the laser-heating, where the bright spot is the heating spot, (b) the the recovered post-lasered sample of C_3N_4 from high pressure.

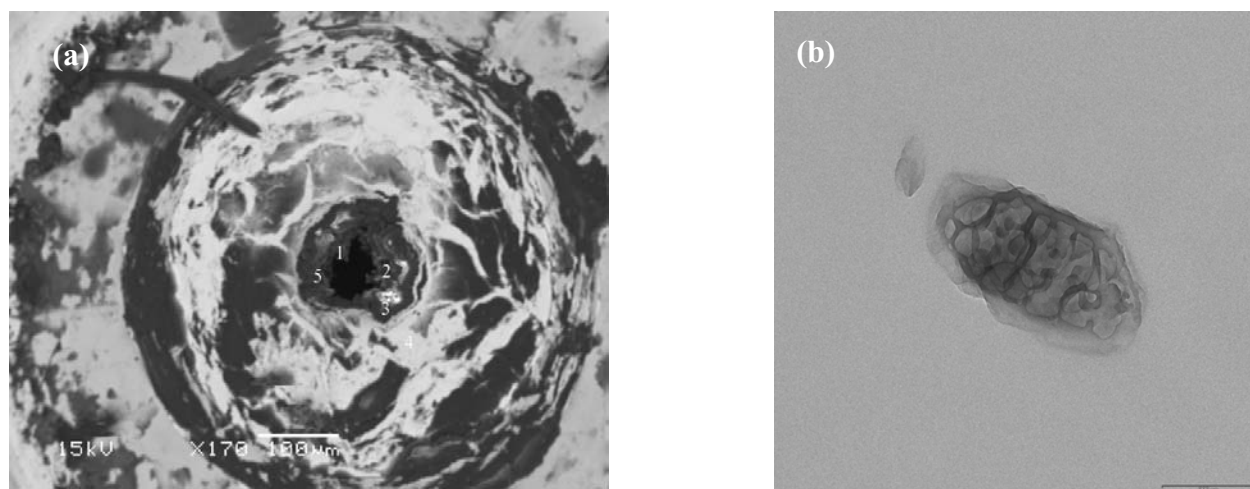


Fig.2. (a) SEM image of the recovered C_3N_4 sample. Marker is 50 μm . (b) TEM image of the starting graphitic- C_3N_4 phase. Marker is 20 nm

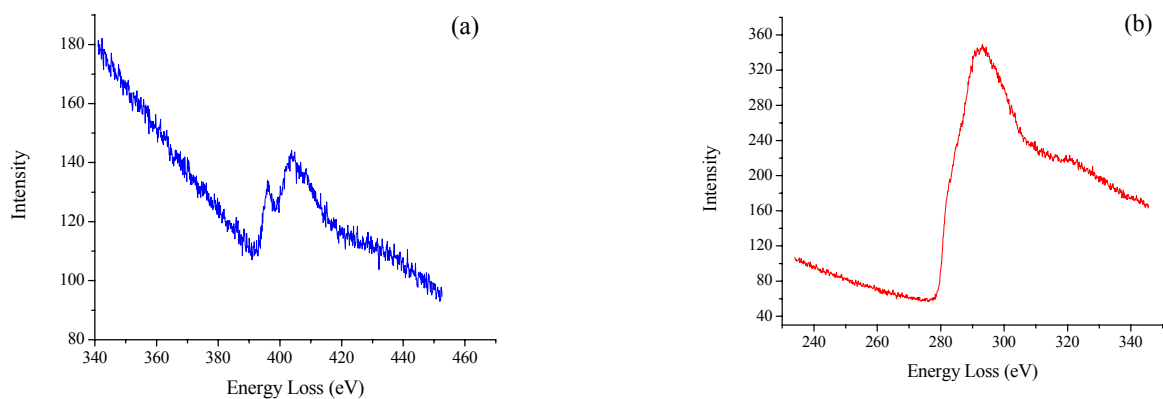


Fig. 4. EELS spectra of nitrogen (a) and carbon (b) in the graphitic C_3N_4 .