

Quenchable compressed graphite synthesized from neutron-irradiated highly oriented pyrolytic graphite in high pressure treatment at 1500 °C

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Abstract

Super hard material of “compressed graphite” (CG) has been reported to be formed under compression of graphite at room temperature. However, it returns to graphite under decompression. Neutron-irradiated graphite, on the other hand, is a unique material for the synthesis of new carbon phase, as reported by the formation of amorphous diamond by shock compression. Here, we investigate the change of structure of highly oriented pyrolytic graphite (HOPG) irradiated with neutrons to a fluence of 1.4×10^{24} n/m² under static pressure. The neutron-irradiated HOPG sample was compressed to 15 GPa at room

temperature and then the temperature was increased up to 1500 °C. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) on the recovered sample clearly showed the formation of significant amount of quenchable-CG with ordinary graphite. Formation of hexagonal and cubic diamonds was also confirmed. The effect of irradiation-induced defects on the synthesis of quenchable-CG under high pressure and high temperature (HPHT) treatment was discussed.

Key Word: compressed graphite, hexagonal diamond, cubic diamond, graphite, static pressure

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1. Introduction

Carbon shows various allotropic forms such as graphite, diamond and fullerene etc. The structure of graphite and diamond are respectively formed by sp^2 -hybridized bonds and tetrahedral sp^3 -hybridized bonds. Transformation from sp^2 to sp^3 bonding can occur by giving high pressure in high temperature condition. Graphite has been found to transform to compressed graphite (CG) at room temperature (RT) within the pressure range of 10–20 GPa [1-6]. The cold-CG phase has a smaller d-spacing ($d_{002}=0.295$ nm) than ordinary graphite ($d_{002}=0.335$ nm), It is transparent and behaves like an insulator. Also, it is super hard that could crack diamond and can return to graphite upon decompression. This indicates the unquenchable nature of cold-CG phase. Studies on the formation and the structure of cold-CG have been widely done experimentally and theoretically [1-6]. However, one should note that there is another type of “compressed graphite” with a different d-spacing ($d_{002}=0.31$ nm), although the experimental studies are a few [7-9].

Neutron-irradiated graphite, on the other hand, is a novel material for the synthesis of new carbon phase, as shown by the direct transformation to amorphous diamond by shock compression [10-12], which should be the ultimate smallest grain size of nanopolycrystalline diamond [13-18]. In the present study, we investigate the phase transition of neutron-irradiated highly oriented pyrolytic graphite (HOPG) under static pressure treatment at 1500 °C and report the formation of quenchable-CG. We discuss the effect of irradiation-induced defects on the formation of CG by high pressure and high temperature (HPHT) treatment.

2. Experimental

We used highly oriented pyrolytic graphite (HOPG-ZYA) from Union Carbide, which was neutron-irradiated in JAEA JRR-2 nuclear reactor at about 60 °C to a fluence of 1.4×10^{24} n/m² ($E > 1.0$ MeV), as a starting material. The displacement per atom (dpa), which means the number of times that an atom in the crystalline lattice is displaced for the given

fluence, is estimated to be about 0.2 dpa. [19]. The graphite sample, shaped to a disk of ϕ 2.0 mm and 2.0 mm high, was enclosed in a Ta capsule to give HPHT experiments.

A cylindrical rhenium heater (0.025 mm thickness) and a pressure medium made of LaCrO_3 and Co-doped MgO were used for the high-pressure cell assembly. The high pressure cell was compressed to 15 GPa at RT and then heated at 1500 °C for 20 min, using a 3000-ton Kawai-type multi-anvil apparatus. Another experiment of static pressure was done at RT by the multi-anvil apparatus to investigate the stability of the irradiation-induced defects up to 23 GPa. The pressures were estimated from a pressure-load calibration curve that was obtained based on the phase transition of pressure standard materials (ZrTe , 12 GPa; ZnS , 15.6 GPa) at RT. Pressures at high temperatures (during heating) were expected to be lower by 1–1.5 GPa than those at RT due to plastic flow of the high pressure cell assembly. Temperature was estimated from the relationship between input electrical power and generated temperature obtained in a separate run using the identical cell assembly.

The recovered sample was examined by a focused X-ray diffract-meter with copper $\text{K}\alpha$ radiation ($\lambda = 1.55419 \text{ \AA}$) operated at 40 kV and 30 mA. The sample was processed by a focused ion beam (FIB) system to prepare thin foils for microstructure observation by transmission electron spectroscopy (TEM). The products were examined by X-ray absorption near edge structure (XANES) spectroscopy using the 1.5 GeV synchrotron radiation facility of NewSUBARU, [20,21] to investigate the electronic orbital structure of the recovered sample.

3. Results

Figures 1a and 1b show optical micrographs of the sample recovered from 1500 °C at 15 GPa. We can find wrinkles formed on the surface of sample by the compression (Fig. 1a) and dark and bright areas in the magnified view (Fig. 1b), indicating heterogeneous transformation.

Figure 2 shows X-ray diffraction (XRD) patterns of the recovered samples of 1500 °C/15 GPa and RT/23 GPa. The XRD patterns of un-irradiated and the neutron-irradiated HOPG samples are also shown for comparison. The G002 diffraction peak of the original HOPG downshifted and increased the width after the neutron-irradiation, reflecting the irradiation-induced expansion and disordering such as the turbulence of the basal plane [22]. The broad peak is mostly stable up to 23 GPa at RT. In the case of compression at 1500 °C /15 GPa, the G002 diffraction peak mostly returned to the original peak position of HOPG. However, one should note that the G002 diffraction peak has a sub-peak at a higher angle. The shape of the sub-peak is broader than that of G002 diffraction peak. The value of the d-spacing estimated from the top of sub-peak is about 0.32 nm.

Figure 3 shows the XANES spectrum obtained from the recovered sample from 1500 °C at 15GP, together with the reference data of a standard cubic diamond crystal. Typical diamond spectral feature of dip around at 302 eV is recognized in the XANES spectrum for the recovered sample of 1500 °C /15 GPa. This indicates that a part of the product is diamond, as seen in the XRD spectrum (Fig. 2).

Figures 4 and the inset respectively show a bright field TEM image, and the corresponding selected area electron diffraction (SAED) pattern of a part of the foil section prepared by FIB-cutting from the recovered sample. The original layered texture of the starting HOPG appears to be considerably disordered by sliding and/or buckling of the graphite planes due to the compression. The SAED pattern also indicated that the graphite layered structure was significantly distorted at local scales.

Figures 5a and 5b show high resolution transmission electron microscope (HRTEM) images, which were taken from two different areas of the recovered sample shown in Fig. 4. One should note that the lattice fringes are almost straight in Fig. 5a, while they are wavy and discontinuous in a different area in Fig. 5b. The wavy lattice image is similar to the one in the neutron-irradiated HOPG sample [22]. Moreover, the lattice spacing of the basal plane in Fig. 5a is seen to be clearly smaller than the one in Fig. 5b. The value of d-spacing estimated from the SAED pattern is about 0.31 nm.

The irradiation-induced disordering is rather stable under the RT compression as seen in Fig. 2. However, the defect introduced by the initial irradiation becomes unstable upon annealing even at temperatures below 600 °C [23,24]. In order to know the stability of the irradiation-induced disordering against the temperature, annealing experiments were done at high temperatures ranging from 800 °C to 2000 °C. The changes in Raman spectra of the neutron-irradiated HOPG on the annealing are shown in Fig. 6. Annealing effect on highly disordered graphite was insignificant at 800 °C, but the peak widths of G and D peaks became narrower at 1000 °C and 1200 °C. The Raman intensity of the G peak increased by annealing at 1400 °C while the one of the D peak decreased, thereby indicating the increase in crystallite size of graphite.

4. Discussion

In the present study, we recovered a product composed of a mixed structure of diamond, graphite and “compressed graphite” (CG), by the HPHT treatment of the neutron-irradiated HOPG at 1500 °C/15 GPa. One should note that the HRTEM images on the area of graphite clearly show a smaller d-spacing compared to ordinary graphite ($d_{002}=0.335$ nm) as shown in Fig. 5. This is a piece of direct evidence of the recovery of so-called CG. The TEM image in Fig. 4 also indicates the stable presence of CG in a highly decompressed state in a thin foil section prepared by FIB. Another piece of evidence can be seen as a broad sub-peak at a higher angle side ($d_{002}\sim 0.32$ nm) of the main peak (G002) of the ordinary (non-compressed) graphite. Note that the relative peak intensity of the sub-peak (compared to G002 of the ordinary graphite) of the sample obtained from the neutron-irradiated HOPG (Fig. 2) is stronger than that from the un-irradiated HOPG obtained after similar HPHT treatments [18]. Then, the formation of quenchable CG in the present study is likely attributed to the irradiation-induced effects, which may stabilize the interlayer bonding of the CG phase even after decompression to the ambient condition.

Here, a question arises as to how the irradiation-induced defects affect the formation of the quenchable compressed graphite. The nature of irradiation-induced

defects in graphite has been investigated for a long time [19,22-24,25-30], because it is important issues for the application of graphite as a nuclear material. Irradiation of high energy particles passing through the graphite lattice can induce the displacement of atoms by collisions. If the energy transferred to an atom in the lattice is larger than the displacement threshold energy, the atom is displaced into the lattice to form an interstitial, leaving a vacancy behind, which is called Frenkel pair. Successive irradiation can lead a transformation from graphite structure to highly disordered ones [23,24]. The irradiation-induced defects have been classified into in-plane defects of single vacancy, vacancy clusters and dislocation dipoles, single interstitial, interstitial clusters such as di-interstitials, and crosslinking defects [10,23,24]. Frenkel pairs can mutually annihilate on annealing above 300 °C [24,29]. Dislocation dipole is considered to be a reconstructed vacancy line cluster with a pair of sevenfold and fivefold rings or an eightfold ring at the ends which is formed in the later stage of irradiation [30] and induce the disordering of graphite with the buckling and rotation of basal planes. The disordered structure has been shown to be thermally stable on annealing at 600 °C [24] but a gradual recovering can occur between 800 °C and 2000 °C as shown in Fig. 6.

In the present HPHT treatment of 1500 °C/15 GPa, we detected the formation of hexagonal diamond in the recovered sample as shown in Fig. 2, although the amount is not so large. The formation of hexagonal diamond (HD) suggests the partial existence of crystalline (ordered graphitic) regions, because HD is produced from crystalline graphite by the diffusion-less, martensitic process [17]. So, well-crystalline regions are expected to have formed at local scales by the annealing of the neutron-irradiated HOPG, as seen in Fig. 6. The formation of cubic diamond (CD), on the other hand, occurs by diffusion-controlled process at the irradiation-induced defects [31] which offer preferential nucleation sites for CD [17].

The present finding of the quenchable compressed graphite in a thin TEM cross-section (Fig. 4), where pressure is supposed to be released completely (i.e. with virtually no residual stress) suggests the formation of some stable crosslinking between the neighboring basal planes to maintain the compressed state to the ambient pressure. Such a quenchable-CG with the interlayer spacing d_{002} of 0.31 nm was also synthesized from

C₆₀ fullerene powder, that was filled into a 1 mm pyrophyllite gasket and compressed between slanted sintered-diamond anvils. The pressure was increased up to 20 GPa and held for 1 hr at RT [32]. The recovered product was interpreted to be a short-interlayered carbon phase composed of buckled sp²-sp³ layers with possible interlayer bonding.

The transformation from neutron-irradiated HOPG to “amorphous diamond” under shock compression [10-12] is considered to be an extreme case of constructing the crosslinking of sp³ bonding. Such “amorphous diamond” has been obtained from neutron irradiated graphite [10-12] and C₆₀ [33], which also produce “compressed graphite” by HPHT treatment (at relatively lower temperature). This implies that the defective structures of these carbon sources play an important role in accelerating the formation of the interlayer bondings. Nonetheless, further experimental and theoretical studies are required to understand the formation mechanism and the nature of quenchable-CG, since we have no direct evidence for the formation of such interlayer bondings.

5. Conclusion

Cold-“compressed graphite” (CG) formed under compression of graphite at ambient temperature returns to graphite after decompression. Here, we found the formation of quenchable-CG from neutron-irradiated highly oriented pyrolytic graphite by HPHT treatments at 15 GPa and 1500°C. The recovered sample consists of a mixture of CG, hexagonal and cubic diamonds. HRTEM observation of a thin cross-section prepared by FIB gave the direct imaging of the quenchable-CG, which showed a smaller d-spacing than the ordinary graphite and significantly a kinked and folded layered texture formed by sliding and/or buckling of the basal planes. The formation of crosslinking bonding of carbon atoms between graphite basal planes is likely a key for quenching the CG structure to the ambient condition. Although the bonding nature and the structure of the quenchable-CG is still unclear, the present study might offer new insights to synthesize new carbon phases by utilizing defective structure in the graphite starting material.

Acknowledgments

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Figure captions

Fig. 1. (a) Optical micrographs of recovered sample synthesized at 15 GPa and 1500 °C and (b) a magnified view.

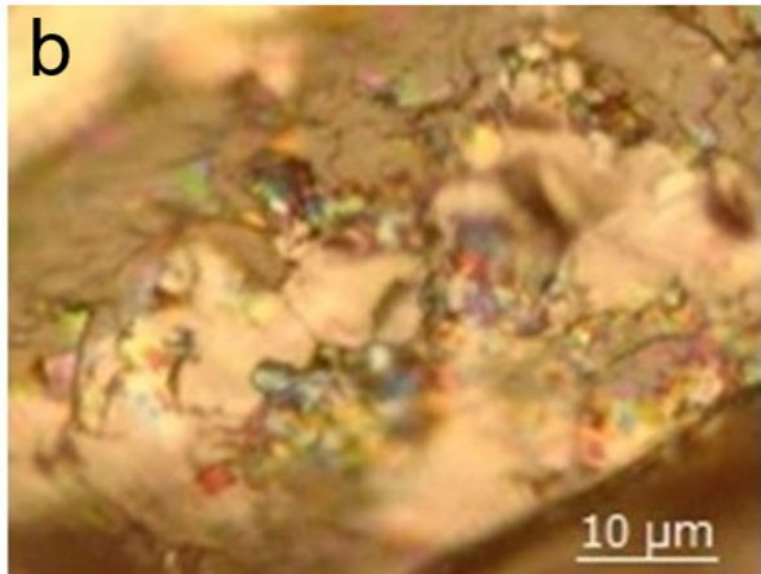
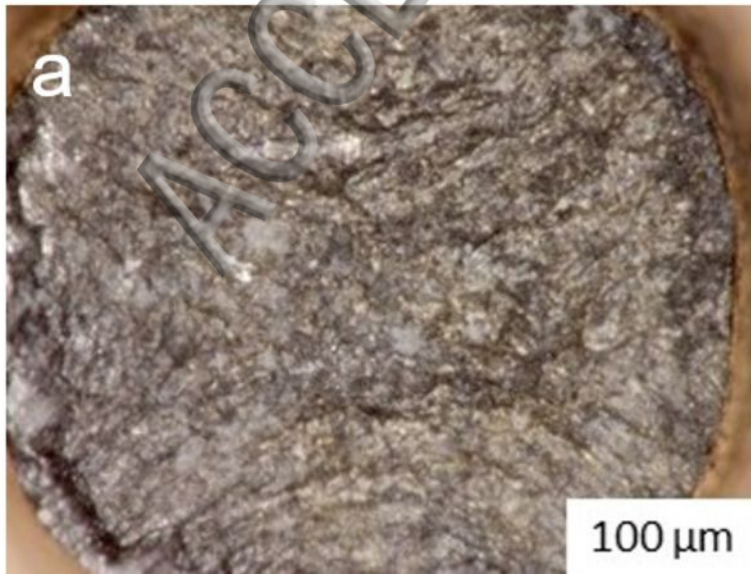
Fig. 2. X-ray diffraction spectra observed in the experiment of (1) original HOPG, (2) neutron-irradiated HOPG, (3) the recovered sample from RT/23 GPa, and (4) the recovered sample from 1500 °C /15 GPa.

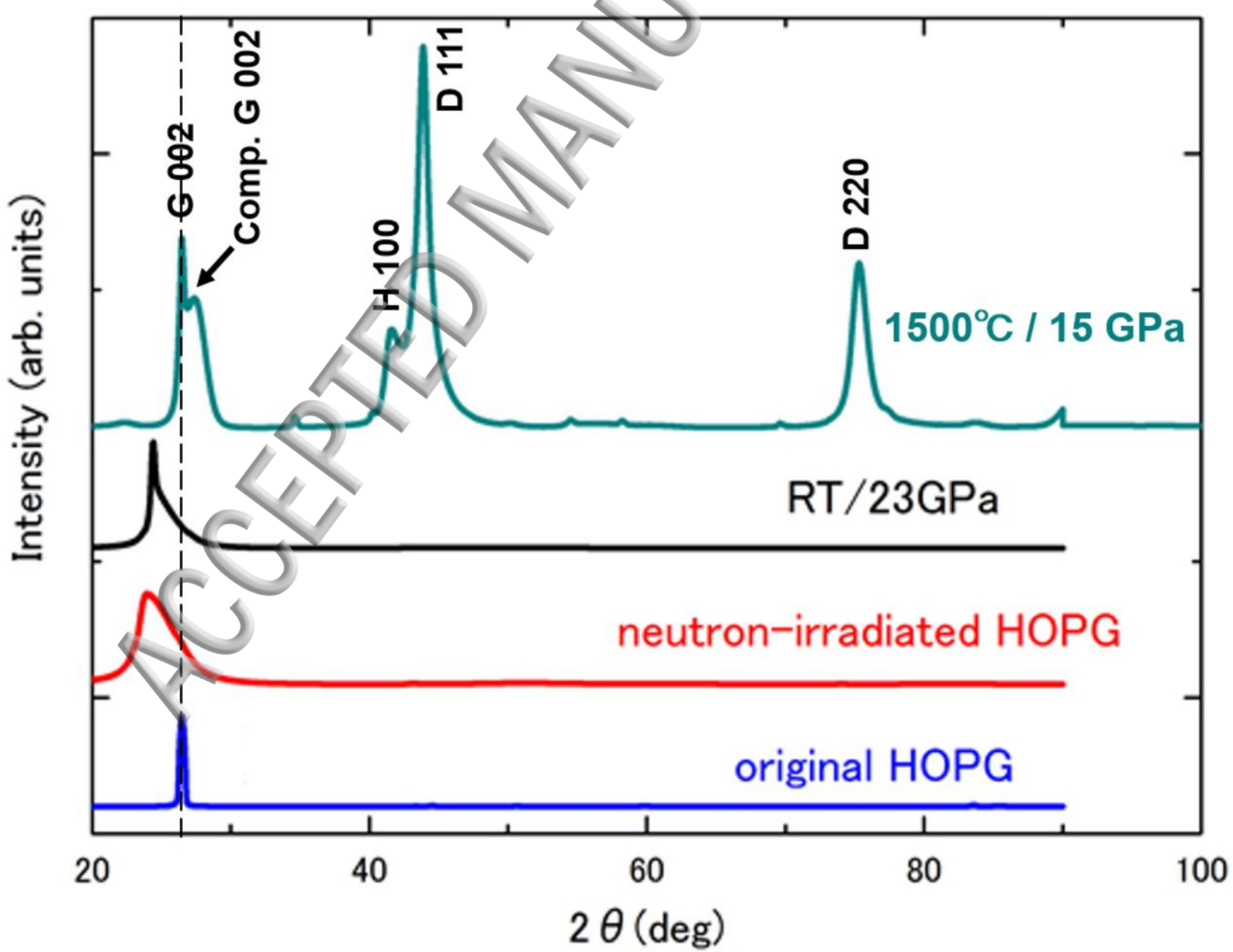
Fig. 3. XANES spectra of (1) RT/23 GPa, (2) 1500 °C /15 GPa, and (3) standard diamond.

Fig. 4. TEM image and SAED pattern of recovered samples treated at 15 GPa and 1500 °C.

Fig. 5. Lattice images and a diffraction pattern for neutron-irradiated HOPG which was treated at 15 GPa and 1500 °C. The lattice spacing of the basal plane in photo a is seen to be clearly smaller than the one in photo b. The SAED pattern taken in the area of photo a is shown as an inset.

Fig. 6. Change in Raman spectrum on annealing for HOPG irradiated with neutrons to a fluence of 1.4×10^{24} n/m².





Absorption intensity (arb. units)



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(3) Standard diamond

(2) 1500°C/15GPa

(1) RT/23GPa

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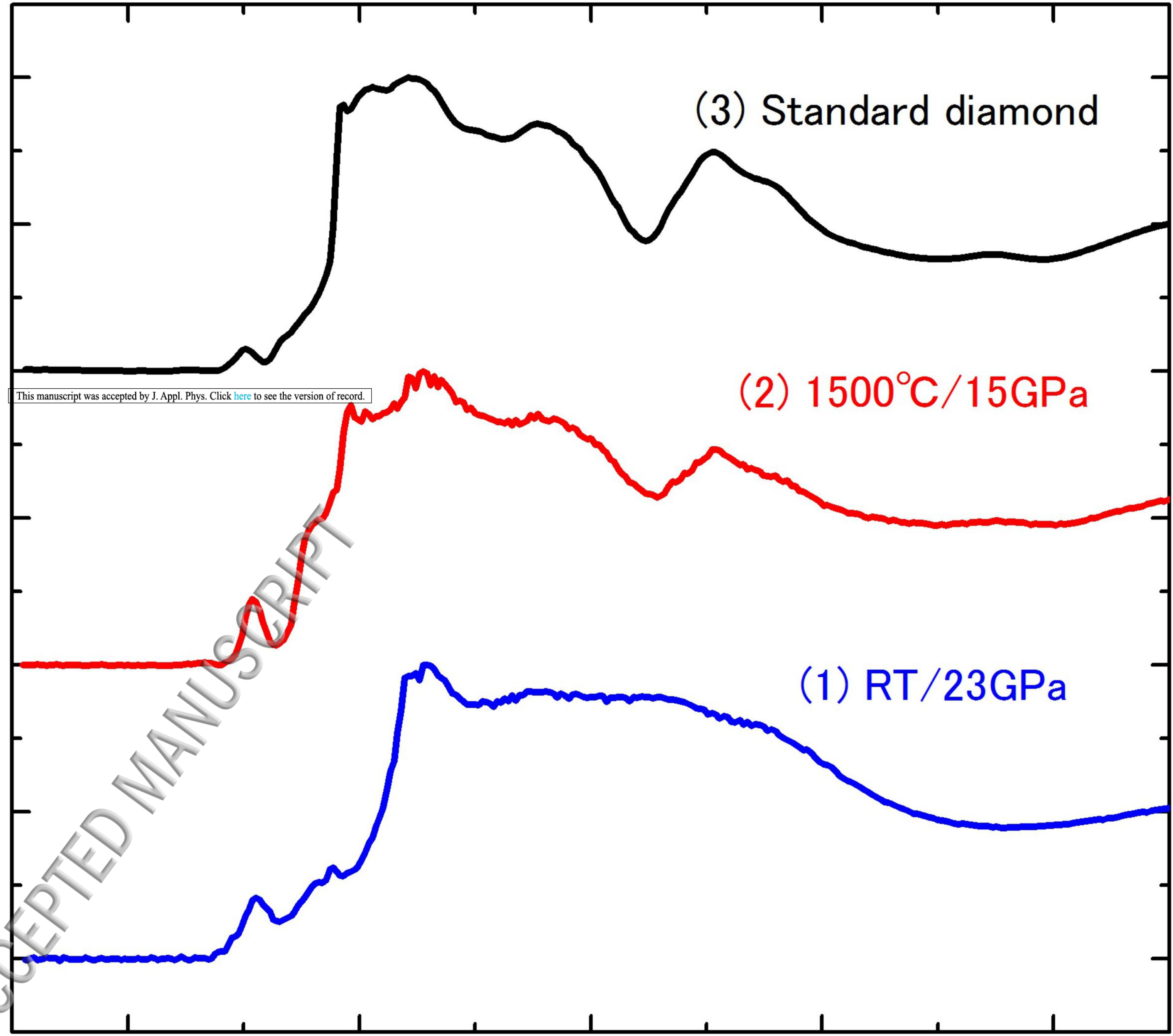
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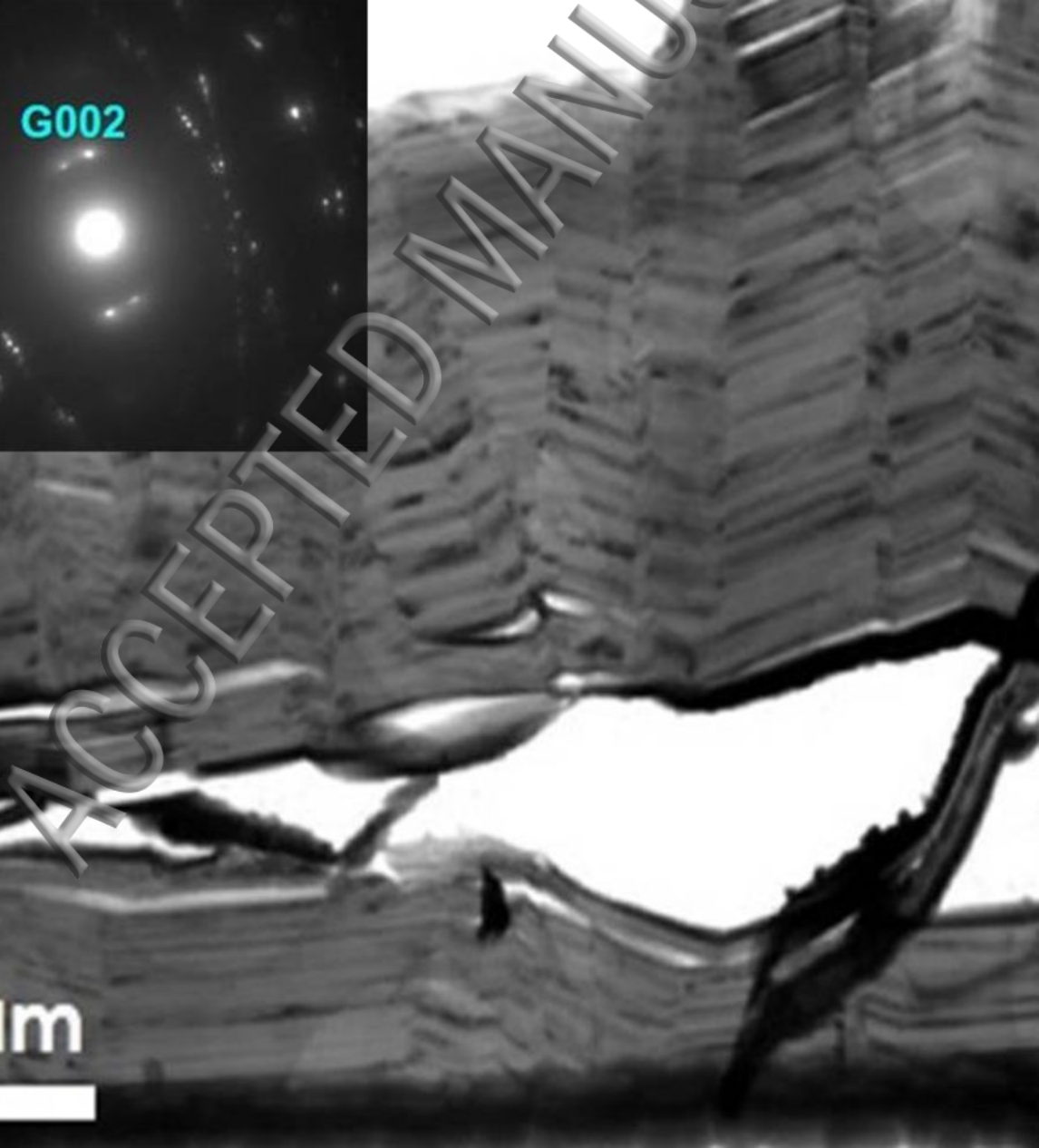
310

320

Photon energy (eV)

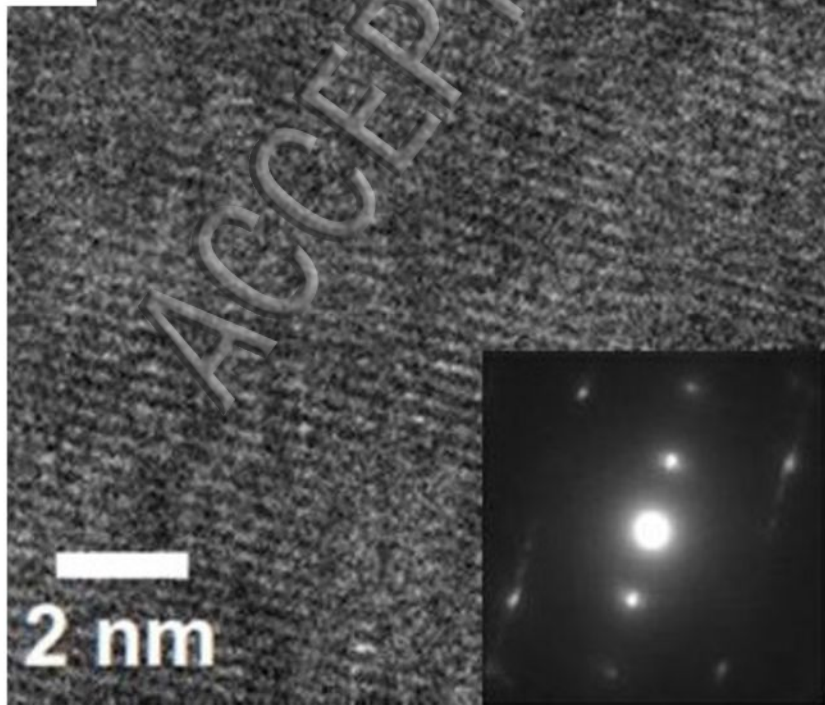


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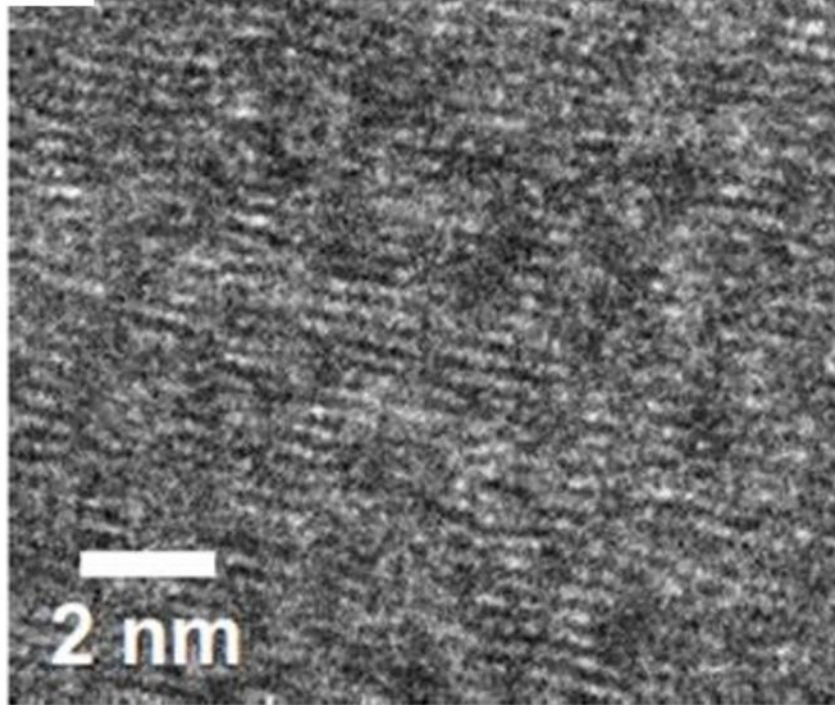


2 μm

a



b



Intensity (arb. Unit)

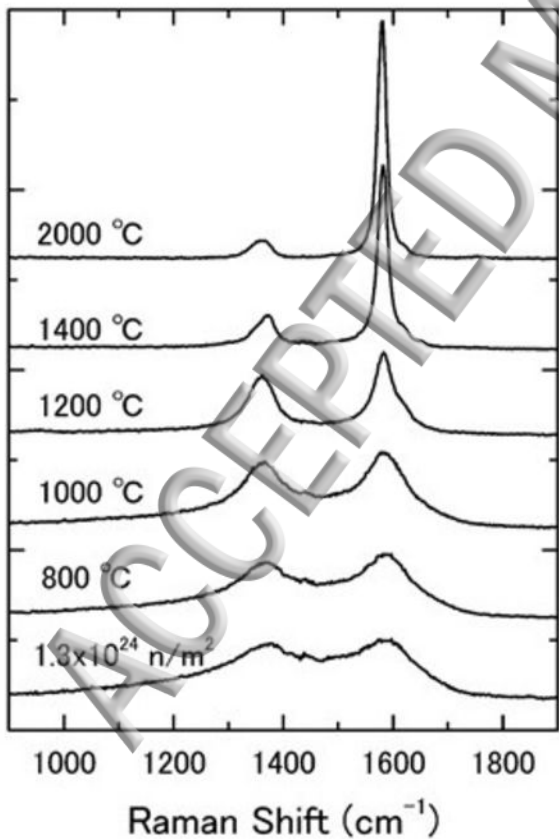


Fig. 6