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LETTER TO THE EDITOR

In situ diffraction measurement of the polymerization of C_{60} at high temperatures and pressures

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Abstract.   *In situ* energy dispersive x-ray measurements were performed on C_{60} fullerene at pressures of 2.6, 5.7 and 12 GPa and temperatures between 300 and 1100 K. The polymerization process was followed in detail and the dynamics of the phase changes measured. This has enabled us to map the *P*–*T* phase diagram and look at the dynamics of the phase transformations.

The ability of the C_{60} molecule to cross-link and the complexity of its dynamics produce an intricate and history dependent phase diagram in *P*–*T* space. A large amount of work has been done in recent years looking at fullerenes quenched from high pressures and temperatures and a fairly detailed reaction diagram now exists [1, 2]. At moderate pressures (3–8 GPa) and temperatures above 400 K C_{60} molecules within the cubic van der Waals crystal begin to bond through a cyclo-addition process [3–5] where the hexagon–hexagon double bonds on adjacent molecules break and form sp^3-type bridging bonds. Initially the molecules are reported to form linear chains creating orthorhombic polymeric-like structures [6, 7]. At higher temperatures cross-links form between the chains to create two-dimensional layered materials which appear to be rhombohedral above about 3 GPa and tetragonal below this. When the temperature reaches around 1000 K the molecules collapse, producing disordered materials that, although graphitic, often have hardness' 10–100 times that of normal graphite. A different regime is observed above 9 GPa. Here fcc- and bcc-like structures persist until the break down of the molecules at around 1100 K. The resultant disordered materials are reported to have hardness that can scratch the (111) face of diamond [8, 9] making them amongst the hardest known materials.

Almost all the high pressure–temperature work done so far has been performed by pressurizing and then rapidly heating a small sample, maintaining the temperature for a relatively short time (minutes), and then quenching it before releasing the pressure. It is not known if these recovered samples are the equilibrium phases and so it is important to realize that the published 'phase diagrams' are in reality just maps showing the conditions under which a certain phase can be produced under high-pressure and retained on quenching. In this work we describe *in situ* diffraction measurements at high pressures and temperatures where we have been able to follow the evolution of the phases as a function of temperature at a particular pressure. The dynamics and type of the transition was also studied by measuring the time dependent evolution of the diffraction patterns at each temperature.

The measurements were performed at the BL04B1 beam line at the Spring-8 x-ray synchrotron in Japan [10]. This beamline has a 1500-tonne multi-anvil high-pressure apparatus. The second stage consists of eight tungsten carbide anvils with a truncation edge length of 7 mm. A 50×200 μm beam of white x-rays with energies up to 150 keV was passed through a gap between the anvils to the powder C_{60} sample encapsulated in a boron–nitride tube within an MgO octahedron pressure transmitting medium. The diffracted x-rays were detected with a solid-state germanium detector positioned at a 2θ of $3.5°$. The details of a similar sample assembly are published elsewhere [11]. A graphite tube was used as a heater element and the temperature was measured using a Chromel–Almel (CA) thermocouple. The pressure was calibrated using diffraction from NaCl and gold just below the sample. The initial sample was 99.9% purity C_{60} purchased from the Materials & Electrochemical Research (MER) Corporation.

Three separate runs were performed at 2.6, 5.7 and 12.0 GPa. The temperature was raised from room temperature to 1100 K in 50 K steps, and at each step several 120-second diffraction patterns were recorded to observe the dynamics. It is not possible to extract absolute information from the intensities of an energy dispersive x-ray measurement at present. This means that traditional profile refinement methods are not applicable.
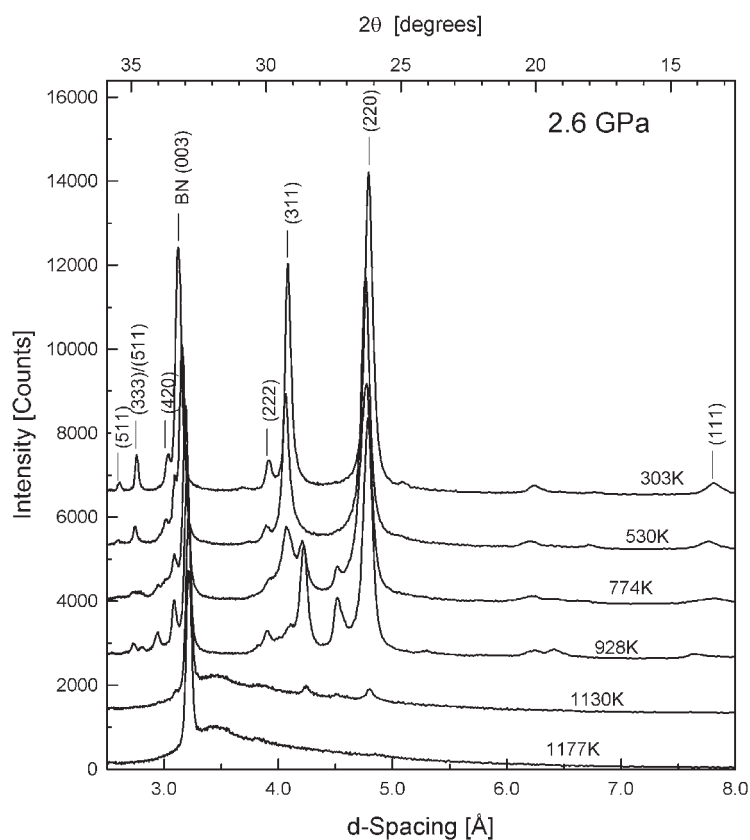

Figure 1. The temperature dependent diffraction pattern at 2.6 GPa. The index are those of the unpolymerized cubic C_{60}. The scale on the top is the 2θ angle for $K\alpha_1$ x-rays, for comparison with previous measurements.

Figure 1 shows some of the data from the 2.6 GPa series. The indexing is based on the initial cubic unit cell for simplicity. At low temperatures the pattern can be indexed on the cubic lattice of the pristine C_{60}, but as it is heated one set of peaks disappear and a new set, which can be indexed on a tetragonal lattice, appears. The two coexist over a large range of temperatures, but by 1100 K the material is almost completely tetragonal. The lack of any large increase in peak width and the coexistence of the two phases indicate that the phase change is heterogeneous, i.e. there are distinct crystallites of the tetragonal phases that have seeded and are growing within the cubic matrix. At 1130 K it is clear that a disordered phase is also present, indicating that the C_{60} cages have started to collapse. The time constant for this transformation is slow at 1130 K and took several minutes to complete.
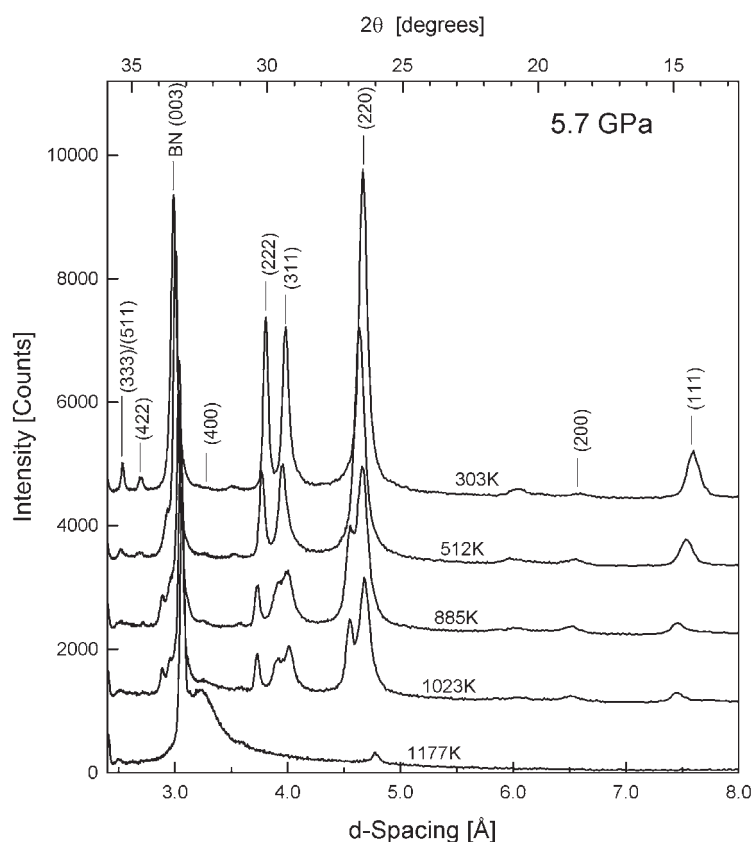

Figure 2. The 5.6 GPa series. The small peak seen in the 1177 K data at 4.75 Å is a fluorescence peak.

At 5.7 GPa (figure 2), the ambient temperature diffraction pattern can also be indexed on a cubic structure. The molecular form factor for C_{60} depends on the ratio of the molecular dimension to the lattice parameter; and so, as the pressure increases, the peak intensities change. The molecular structure factor also means that the (200) and (400) peaks have no intensity at ambient pressure. But as the lattice parameter changes, with pressure and polymerization, this accidental absence disappears. A new phase, that can be indexed on a rhombohedral structure, appears above 650 K where the (311) and (220) cubic reflections begin to broaden and then split. In contrast with the 2.6 GPa series the phase change appears

to be homogeneous with cross-links between the molecules appearing randomly within the fcc matrix. Above 1000 K the C_{60} cages again begin to collapse, forming a graphitic phase.
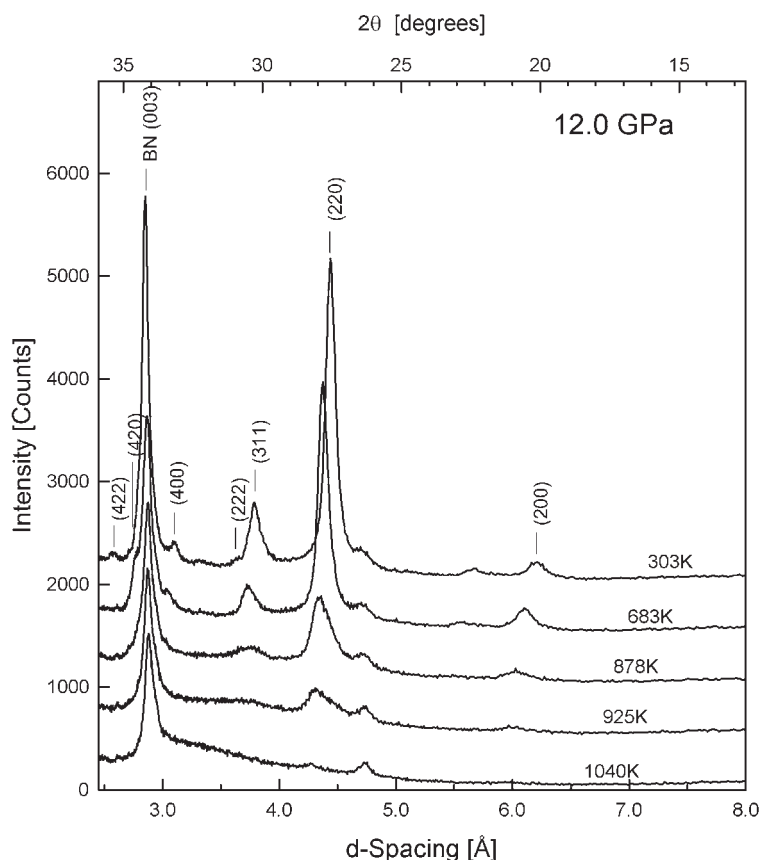

Figure 3. The 12.0 GPa series. The fluorescence peak at 4.75 Å can be seen in the 1040 K data.

The 12.0 GPa series (figure 3) is considerably different. The peaks are broad, almost triangular in shape, indicating significant strain. As the material is heated it remains cubic but the peaks continue to broaden until between 900 K and 1000 K where the C_{60} cages collapse.

The differences in these phase-changes are almost certainly linked to the dynamics of the C_{60} molecule. At low pressures it is still able to rotate semi-freely and sp^3-bridging bonds will form between molecules when the hexagon–hexagon double bonds align. An individual dimer in the cubic matrix is likely to be energetically unfavourable at these pressures, but a cluster may well be stable. In this case it is possible to think of the phase change as a crystallization of the tetragonal phase within the cubic structure.

At higher pressures the dynamics are slower. One possible mechanism for the transformation at these pressures is via shear motion of the (111) face, which promotes bond alignment and sp^3 bonding. There is clear evidence from the electron microscopy of the formation of rhombohedral lamellae parallel to (111) in the parent cubic lattice [12]. The diffraction pattern of the resultant rhombohedral phase has peaks that are not significantly broader than the initial cubic phase. This means that the rhombohedral domains are of a

reasonable size and are not overly strain broadened.

At 12 GPa the process is different again. The lattice parameter has reduced to below 12.5 Å, enabling bonds to form at random between the molecules, in all directions. This preserves the cubic lattice but produces a highly strained structure. This polymerization is three dimensional, inhibiting all shear and deformation and producing the characteristic high harnesses. It is significant that whereas the BN lattice parameter increases with temperature at all pressures due to normal thermal expansion, the cubic lattice parameter for the C_{60} decreases, dominated by the three dimensional polymerization. The shift in lattice spacing and the asymmetry of the diffraction peaks, especially of the (220) cubic reflection, indicate variability in the density of the sp^3-bonding. Although there is clear evidence for a retention of the cubic symmetry in the three-dimensional polymerized state, there is no evidence for a significant increase in the intensity of the (200) and (400) reflections that are normally forbidden due to the molecular form factor, that has been reported in the quenched specimens.

Our *in situ* data is consistent with the published 'reaction diagrams'. The only major discrepancy is that we find no strong evidence for the existence of an orthorhombic phase. It may be possible to understand this if there is significant strain broadening caused by the quenching process. In this case the (211) and (311) peaks would merge and the subsequent profile will look orthorhombic.

The collapse of the C_{60} cages into the disordered phase is slow, with a time constant of several minutes and occurs at roughly the same temperature at the three different pressures. Although the mechanism may be similar the resultant material does look very different. At 5.7 GPa the (002) graphitic peak is relatively well defined although the material is much harder than conventional graphite due to the folding and cross-linking of the graphitic planes [13]. But at 2.6 GPa and 12.0 GPa, although the highest point of the peak is still at the (002) graphitic d-spacing, it is so broad it is not obvious that we can describe it as graphitic. At 12 GPa the material is also reported to be very hard, so presumably the material has a large sp^3-bonded component and has three-dimensional bonding.

In conclusion, we have conducted the first *in situ* polymerization of C_{60} at high pressures and temperatures using x-ray diffraction. In pressure there are three main regions: below 3 GPa the tetragonal phase forms within the cubic matrix, above 3 GPa shearing on (111) planes promotes the formation of the rhombohedral phase, above 9 GPa the hydrostatic pressure is enough to allow bonding in all directions. Apart from the lack of an orthorhombic phase, this phase diagram is very similar to the pressure–temperature diagrams created by looking at sample recovered from high-pressure.

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