Graphite Oxide

DOI: 10.1002/anie.200802860

Colossal Pressure-Induced Lattice Expansion of Graphite Oxide in the Presence of Water**

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Expansion of structure upon compression is a rare phenomenon that has been observed in so-called auxetic materials, and is due to incorporation of liquid media into nanopores.[1–6] Herein, we present a new class of auxetic materials with unusual compressibility anomaly. The unit-cell volume of graphite oxide (GO) pressurized in the presence of water continuously increases, reaching a maximum at 1.3–1.5 GPa. Expansion of the lattice by 28–30% significantly exceeds all previously known examples and is due to gradual pressure-induced water insertion into the interlayer space of graphite oxide structure. Solidification of water is observed at 1.3–1.5 GPa and correlates with a sharp downturn in the pressure dependence of the unit-cell volume of the graphite oxide. The effect is reversible, resulting in a unique "breathing" of the structure upon pressure variation.

Negative volumetric compressibility has previously been observed in nanoporous materials, such as zeolites and pyrochlores immersed in liquid media.[2–6] The unit-cell volume of these materials shows jump-like increase at a particular pressure owing to pressure-induced insertion of water into the pores. The volume increase for these materials is relatively small, for example, about 1.5% for gallosilicate zeolite[5] and 5–7.5% for defect pyrochlores of various compositions.[3,6] Herein we report a new observation, which is the negative volumetric compressibility of graphite oxide in water.

Graphite oxide can be synthesized by different methods.[7–9] In comparison to graphite, it has a significantly increased inter-planar distance of up to 7 Å.[10,11] Strong disorder and turbostratic packing make it difficult to establish the detailed structure of GO by diffraction methods. Graphite oxide also easily absorbs water, which results in a sharp increase of the inter-planar distance (up to 12 Å) in the hydrated state.[10–13]

Several structural models have been proposed for GO.[14–17] According to NMR, XPS, and IR spectroscopy, GO contains epoxy, carbonyl, and hydroxy groups attached to the graphene skeleton,[16,17] which results in buckling of the graphitic planes. Recent interest in GO has been due to the synthesis of graphene-related composites[18–20] along with a report on the preparation of graphite oxide paper.[21] Herein we present the first high-pressure study of graphite oxide in pristine ("dry") and in hydrated states by X-ray diffraction using synchrotron radiation.

The GO sample was prepared using Brodie's method.[7,8] The structure of the pristine GO is in good agreement with literature data.[10,11] Figure 1 shows X-ray diffraction (XRD) patterns recorded for samples of pristine ("dry") and the hydrated (in distilled water) GO in glass capillaries using synchrotron radiation at ambient conditions. The XRD pattern recorded for the "dry" sample exhibited four broad and asymmetric reflections. The peaks were fitted with

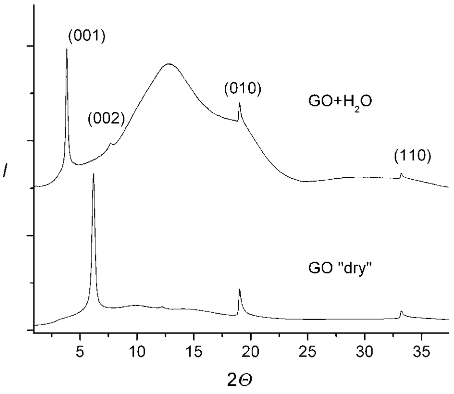

Figure 1. X-ray diffraction patterns of graphite oxide (GO) recorded at ambient conditions in air (bottom) and immersed in distilled water (top), $\lambda = 0.71170$ Å. The upper trace has been shifted for clarity.

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[**] High-pressure experiments at HASYLAB were supported by the GFZ Potsdam under the MAX80 program. This work was partially supported by the Agence Nationale de la Recherche grant NT05-3_42601. Some of the high-pressure experiments (A.T.) were performed at the Bayerisches Geoinstitut under the EU "Research Infrastructures: Transnational Access" Programme (Contract No. 505320 (RITA)—High Pressure). We thank Prof. L. Dubrovinsky for providing access to facilities at BGI and discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802860.

turbostratic graphite-like hexagonal structure using the cell parameters $a = 2.485$ Å and $c = 6.597$ Å. The broad and asymmetric shape of the (010) and (110) lines arise from turbostratic packing of layers, and are due to non-uniform interatomic distances in slightly buckled graphene planes. Compared to the "dry" GO, the XRD pattern of the sample immersed in water shows a large increase in the c parameter ($c = 10.63$ Å), whereas the a parameter remains unchanged. A broad peak between 10 and 15° (2Θ) is due to the presence of liquid water.

In situ high-pressure X-ray diffraction experiments on both "dry" samples and those immersed in water were performed in diamond anvil cells (DAC) using synchrotron radiation. Samples of "dry" GO showed a normal pressure dependence of the cell parameters that are qualitatively similar to those for turbostratic graphite and BN[22,23] (Figure 2). The interlayer spacing between oxidized graphene planes decreases strongly upon application of pressure, reflecting the presence of weak van der Waals bonding. The a axis modulus (one-dimensional analogue of the bulk modulus, that is, $(1/a_0)(\partial a/\partial p)_{p=0}$) of 445 GPa has been obtained using one-dimensional analogue of Murnaghan's equation, and is typical for graphite-like structures. Volumetric compressibility data were fitted to yield a bulk modulus $B_0 = 5.17$ GPa and the corresponding pressure derivative $B'_0 = 15.5$ ($V_0 = 35.97$ Å^3). "Dry" GO thus shows the normal compressibility behavior expected for turbostratic graphite-like materials.[22,23]

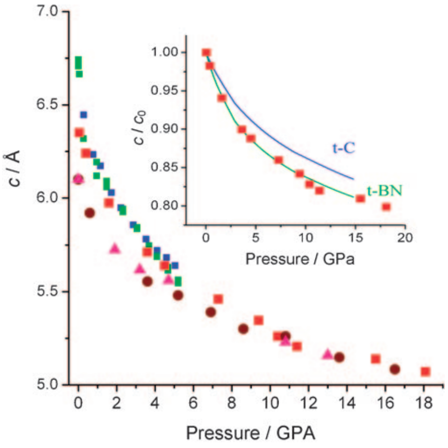

Figure 2. Pressure dependence of the c parameter in dry GO. Compression runs for two different samples: (■) and (■). Pressure cycling experiment: (■) 1st compression, (●) decompression, (▲) 2nd compression. Inset: the compressibility of graphite oxide in the c direction compared to those of turbostratic carbon (t-C)[23] and turbostratic boron nitride (t-BN).[22]

In contrast to "dry" samples, the GO immersed in water exhibits anomalous pressure dependence with negative volumetric compressibility in the low-pressure region and an exceptionally large increase in the interlayer spacing (up to 28–30%), reaching a maximum at a pressure of about 1.3–1.5 GPa (Figure 3a). Above 1.4–1.5 GPa, the pressure dependence of unit-cell volume shows the usual characteristics, and compressibility becomes positive. The maximum on the curve (the pressure dependence of (001) d spacing) was also reproduced on decompression and in the second pressurizing cycle as well.

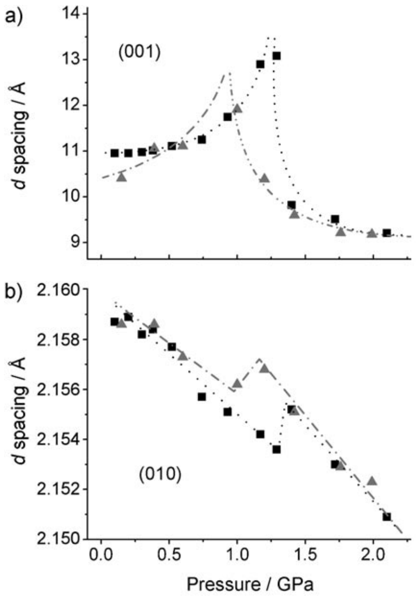

Figure 3. Pressure dependence of peak positions for a) (001) and b) (010) reflections recorded from a graphite oxide sample immersed in excess water: ■ compression, ▲ decompression.

The maximum value of the d spacing depends on the relative amounts of graphite oxide and water loaded into the cell. The remarkable increase of the interlayer d spacing (ca. 30%, Figure 3) was found under pressure, only when powder samples were loaded into the gasket hole with an excess of water. In some experiments, more powder was pre-pressed into the gasket hole, thus leaving minimal space for addition of water. The c parameter of the loaded samples was found to increase much less, only by 3–5% at circa 1.5 GPa. The obvious explanation is that in these experiments GO powder sucked in all free water available in the sample, and the interlayer spacing could not increase any further owing to the deficiency of water. The difference in magnitudes of maxima in the value of the d spacing for samples with water deficit and water excess unambiguously proves that the anomaly is connected to the insertion of water into the structure of graphite oxide.

Variation of unit-cell volume of GO is dominated by change of interlayer distance (c parameter), and the contribution from the change of a parameter is rather small. However, the d spacing of the (010) reflection also shows a smaller but a step-like increase upon compression and similar decrease upon decompression (Figure 3b). The step-like increase in the a parameter occurs at 1.4 GPa simultaneously with the steep decrease in the c parameter. Strong compression of GO in (001)-direction likely results in flattening, stretching, and slight lateral expansion of the buckled oxidized-graphene planes. A similar effect is known for other auxetic materials (for example, polymer chains), where compression in the direction perpendicular to chain elongation results in stretching and lateral expansion.[24]

The compressibility of the GO/water sample shows normal dependence above the pressure point of the maximum (Figure 3). The change in sign of the compressibility of GO at 1.4–1.5 GPa correlates with the freezing of liquid water into the ice VI structure (Figure 4). Above 2.2 GPa, ice VI undergoes a phase transition into ice VII in agreement with well established phase diagram of water.[25] The solidification point of water coincides with the sharp decrease in the interlayer distance of graphite oxide and small increase in the *a* parameter. The patterns recorded at pressures at or above 1.4 GPa exhibited strong reflections from hexagonal ice VI.

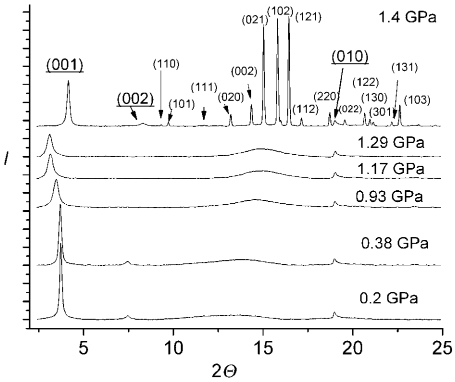

Figure 4. X-ray diffraction patterns recorded upon pressure increase for a graphite oxide sample immersed in excess water (see also Figure 3, $\lambda = 0.71170$ Å). GO reflections are shown by underlined symbols, all other reflections are indexed by ice VI structure (tetragonal $P4_2/nmc$, $a = 6.1867$ Å, $c = 5.6932$ Å).

It can be concluded that the increase in the interlayer spacing of GO in the low-pressure region is caused by liquid-like water insertion. Reflections from ice VI detected in the pressure range just above the maximum (1.4–2.2 GPa) originate from bulk water, which fills inter-grain voids. However, water confined between GO layers should also undergo a transition from the liquid-like to the solid state that results in an increase in density, the formation of a rigid structure, and a return to the normal pressure dependence of compressibility above 2 GPa. The difference in interlayer *d* spacing between wet and dry samples was about 2.5 Å at 3.5 GPa, and remained almost unchanged up to a pressure of 8.8 GPa.

The effect observed in our experiments with GO is somewhat similar to the high-pressure behavior of zeolite/water systems, but with some general differences. Zeolites are materials with nanopores, which are rigid due to the covalent bonds of the alumosilicate skeleton. This results in a relatively small change of their volume upon water insertion. The pore space in zeolites opens for insertion of water at some pressure point, which results in a step-like increase of the pore volume and unit-cell parameters.[2–6] In contrast to alumosilicates, GO has a layered structure with weak van der Waals bonding between oxidized graphene sheets. The interlayer space of GO can be described as slit nanopores that are open for exchange with the liquid media. This results in a "breathing" effect upon pressure variations. Slit pore volume expands gradually upon application of pressure owing to incorporation of additional water and contracts when pressure is released.

The total density of the system, according to the Le Chatellier principle, should increase upon application of pressure. Therefore, despite the GO structure expansion, the total density of hydrated graphite oxide should increase. It is known that density of water confined in nanosized pores is higher than the density of bulk water.[26] The interaction of water with the oxidized graphene layers possibly results in different pressure dependence of densities for confined and bulk water, which is responsible for observed "breathing" effect of GO structure. A large number of experimental and theoretical studies have been published on the phase transitions of confined water[27–30] which are considerably different from those of bulk water. Hydrated graphite oxide can be considered as a model material for studies of confinement effects.

In conclusion, graphite oxide was studied by XRD using synchrotron radiation at ambient conditions and at high pressure. A negative compressibility is observed for graphite oxide immersed in water, with an extraordinary increase in the unit-cell volume. A maximum increase of about 30 % is reached at 1.3–1.5 GPa. The increase of the unit-cell volume is explained by pressure-induced incorporation of water into the interlayer space of the graphite oxide. The change from negative to positive compressibility at 1.4–1.5 GPa correlates with the freezing of water into ice VI. It should be noted that similar effect could be expected in GO immersed into other liquid media, such as methanol, ethanol, and acetone.

Received: June 16, 2008
Published online: September 22, 2008

Keywords: auxetic materials · compressibility · graphite oxide · high-pressure · X-ray diffraction

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