Highly oriented pyrolytic and natural graphite under high pressure

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Abstract. The pressure dependences of highly oriented pyrolytic graphite and natural graphite were studied at long exposure under pressure. The results obtained give evidence for formation of a high-resistance phase of carbon.

1. Introduction
Carbon is one of the four most common elements by mass in the Universe (apart from H, He, and O) [1]. Graphite and diamond are its most well-known structural modifications. Applying pressure to graphite leads to a reduction in the distance between the layers, accompanied by interlayer slip and intralayer displacement of carbon atoms from their equilibrium positions [2]. At high pressure, the initial planar layered structure of graphite is destroyed leading to formation of new inter-carbon bonds in adjacent layers and to transition from sp$^2$ to sp$^3$ hybridized state. These changes give rise to new carbon allotropes such as cubic and hexagonal diamonds and cold-compressed graphite phase. However, the high pressure and temperature or shock loading [3] to the sample are required for a phase transition from graphite to diamond (for example, 5–12 GPa and 2000–3000 K with using catalysts). On the other hand, Samara and Drickamer [4] found in 1962 a new phase transformation of graphite at room temperature and the pressure of 10 GPa. Thereafter a number of research groups have carried out series of experiments at high pressures [5–21] to investigate the new phase by different techniques such as optical microscopy, x-ray diffraction, Raman spectroscopy and others. The ambiguous data were obtained, in particular, concerning with the transition pressure. It has also been found that the formation of this carbon phase depends on the type of the initial material (e.g., powder, monocrystal, pyrolitic graphite) [5]. At the same time, it became clear that a new phase has a high hardness, dielectric character and transparency. This is confirmed also by theoretical studies [2].

To predict the allotropes of carbon, the structure of the new phase was calculated by different methods and programs including CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) and USPEX (Universal Structure Prediction: Evolutionary Xtallography) [2]. The first models proposed for the structure of the cold-compressed graphite phase were (3,0)/(4,0) structure [22] and K$_4$-carbon [23–25]. However, the simulated x-ray patterns of both structures have no satisfactory agreement with the experimental data.

In 2006 Oganov et al [26] proposed the monoclinic M-carbon structure for high pressure graphite phase. Later, the more detailed calculations have performed by Li et al [27]. M-carbon structure can be considered as (2 × 1) reconstruction of the (111) surface of diamond through
the sliding and buckling of the graphite sheet. M-carbon contains 5+6+7 atom rings, which are different from the six-membered rings in graphite [2,27]. M-carbon bonds are thermodynamically more stable at high pressures than those in graphite, since they have a lower enthalpy [2]. In addition to the above-mentioned phases, the structures of Z-, W-, bct-C, S-, R-carbon and others are possible candidates for new phase of cold-compressed graphite, but they do not agree satisfactorily to the experimental data as compared to the M-carbon [2].

The phase transition of graphite under cold compression is the slow process and depends on the type of original sample [2, 5]. However, a new phase destroyed often at decompression down to atmospheric pressure, so to obtain this carbon modification to be stable is important. Inclusions of some high-pressure phase, which remains stable after decompression, were obtained in our work [28].

In this work, the attempt to get the high-pressure phase of graphite was made using a long exposure of graphite under high pressure at room temperature.

2. Experimental

Previously, we investigated high purity graphite of the brand GMZ [28]. Features have been found in the pressure dependence of resistance as well as in its relaxation times in the range of 27–35 GPa. These features were referred to a new phase nucleation. The SEM image of the sample subjected to the pressure of 45 GPa shows the inclusion of a new phase, which did not disappear after removal of the load. It has been found also that the new phase nucleation requires a long time of exposure under pressure.

In this study, two different initial graphite materials were used: highly oriented pyrolytic graphite and natural graphite powder (from Krasnoyarsk Territory). The samples were of ≈ 0.2 mm diameter and of thickness from 10 to 30 μm. The pressure was applied by means of a diamond anvil cell with electrically conductive anvils made of synthetic carbonado-type polycrystalline diamond [29]. The resistance measurements were carried out at room temperature in a course of loading–unloading cycles in the pressure range from 16 to 40 GPa. Pyrolytic graphite is highly anisotropic and pressure was applied to the sample along the c-axis. The voltage applied to the samples corresponded to the linear part of current–voltage characteristics. The measurement procedure was described in details in [30]. Time dependences of the resistance after changing the pressure were also measured.

3. Results and discussion

Shown in figure 1 is the pressure dependence of resistance of highly oriented pyrolytic graphite. Characteristic times of resistance relaxation to the stationary value were determined to be from 20 to ≈ 90 min. So, the samples were kept under stress at each pressure value (each point in figure 1) during ≈ 1.5 h at the first cycle of loading–unloading and ≈ 30 min at the next cycles. The sample resistance decreased with increasing pressure. However, it is seen from figure 1 that the resistance did not return to the initial value after the first cycle of loading (curves 1 and 2). The resulting resistance after the first decompression was essentially larger than the initial one. We connect this increase with the formation of the new phase of graphite of high resistivity. This phase is conserved at least down to 16 GPa. Indeed, the pressure dependences of the resistance coincides practically one to another during the next loading cycles (curves 3 and 4) and corresponds to this new state. Really, the new state of graphite is probably the mixture of phases. However, to identify the nature of this phase, the structure (e.g. x-ray) measurements are needed.

The pressure dependence of resistance of the natural graphite is shown in figure 2. The resistance after first loading became less than initial one (curves 1 and 2), that is opposite to the case of pyrolytic graphite. During the next loading–unloading cycles, the pressure dependences are practically identical. So, in this case we have no evidence for new phase formation.
Figure 1. The resistance of pyrolytic graphite as a function of pressure at the room temperature: curves 1–4 correspond to the first (1, 2) and second cycles (3, 4) of loading (1, 3) and unloading (2, 4). Arrows show the directions of pressure runs. The sample current is 1 mA.

Figure 2. The resistance of natural graphite as a function of pressure at the room temperature: curves 1–4 correspond to the first (1, 2) and second cycles (3, 4) of loading (1, 3) and unloading (2, 4). Arrows show the directions of pressure runs. The sample current is 1 mA.

The reason for the different behavior of oriented and natural graphite can be the different original structure of these materials [6]. If some kind of layered planar structure of pyrolytic graphite is conserved at high pressures used, the stress is applied across the graphite planes. In the case of the natural graphite, the graphite planes orientation as well as stress direction is arbitrary.
4. Conclusions

Different pressure dependences of resistances of highly oriented pyrolytic graphite and natural graphite were found. The irreversible increase of resistance of oriented pyrolytic graphite at long exposure under high pressure gives evidence for the formation of high resistivity carbon phase.

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