JOURNAL OF MATERIALS SCIENCE **39** (2004) 4957–4960 LETTERS

Synthesis of polycrystalline diamond in the boron carbide–graphite and boron–graphite systems under high pressure and temperature

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Heavily boron-doped diamond, possessing quasi-metallic electrical conductivity [1] and high chemical resistance, is a promising electrode material [2]. The synthesis of diamond in the double boron carbide (boron)–graphite system can ensure the doping of diamond in the limiting concentrations depending solely on the P, T parameters of an experiment. The absence of additional substances in the system prevents the compensation of the acceptor admixture of boron in diamond and "drawing in" of accompanying admixtures affecting the crystalline lattice parameters.

The synthesis of diamond in the amorphous boron–graphite system is known in the literature [3]: the high-pressure high-temperature treatment of mixtures of the initial powder materials produced the diamond polycrystalline material containing, in addition to diamond, boron and boron carbide. However, it was ignored in work [3] that under pressure and at temperatures smaller than the melting temperature of B_4C, the equilibrium with participation of diamond phase in the boron–carbon system should be expected in the boron carbide–carbon subsystem.

The purpose of this work is to correlate the concepts concerning the structure of the boron–carbon phase diagram with experimental data on the diamond synthesis in this system and to investigate the specific features in the structure of synthesized diamond and some of its physical and chemical properties.

The interaction in the $B_4C(B)$–C system was studied in the "toroid"-type chamber under a pressure of 8–9 GPa. The duration of experiments at fixed P, T parameters was 3–20 s. Graphite, B_4C powder, and powder of crystalline boron with the content of impurities of about 0.5 mass% were used in the experiments.

Samples of boron and boron carbide powders were isolated from each other and placed into a graphite crucible-heater so that the samples were in contact with the crucible wall and under the same

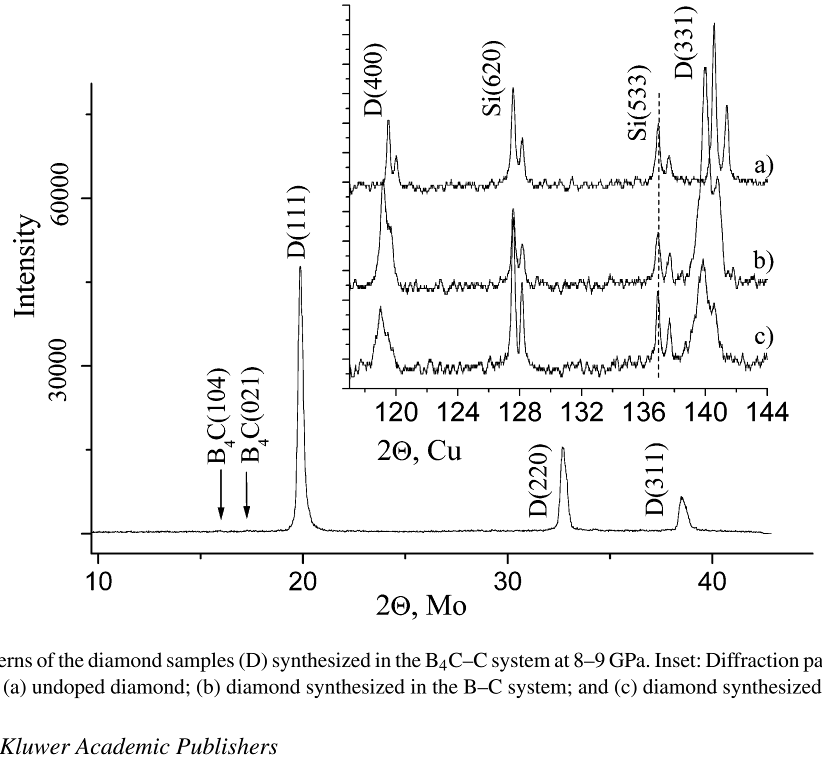

Figure 1 Diffraction patterns of the diamond samples (D) synthesized in the B_4C–C system at 8–9 GPa. Inset: Diffraction patterns of diamond samples with the silicon standard: (a) undoped diamond; (b) diamond synthesized in the B–C system; and (c) diamond synthesized in the B_4C–C system.

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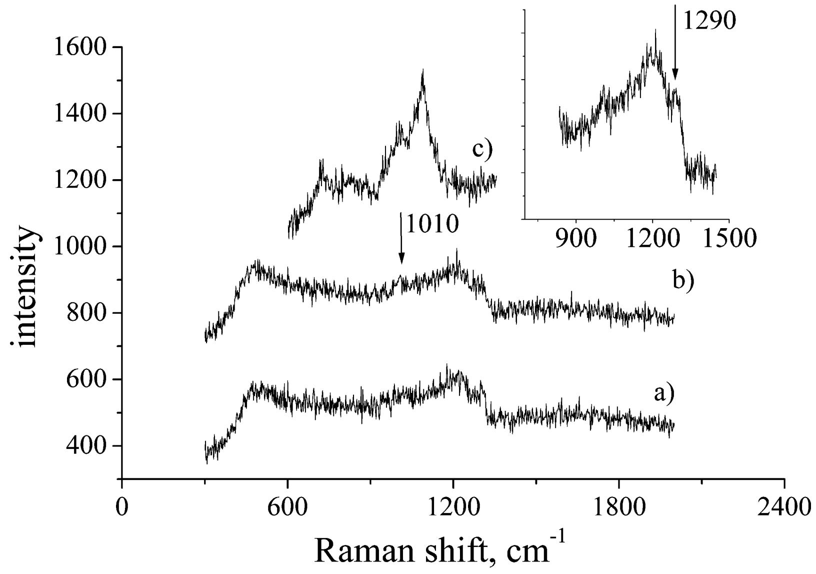

Figure 2 Raman spectra of samples: (a) diamond synthesized in the B–C system; (b) diamond synthesized in the B_4C–C system; and (c) B_4C. Insert: Raman spectrum of the diamond synthesized in the B_4C–C system.

temperature conditions. It was established that with the temperature rise above 2500 K, polycrystalline diamond forms under pressure in the boron–graphite and boron carbide–graphite systems (the crucible being the source of graphite). The synthesis of diamond at the contact of graphite with boron carbide was found to occur at lower temperature than at the boron-graphite contact. Based on the existing ideas about the transformation of graphite to diamond in the presence of traditional metal–catalysts, it is possible to suggest that the synthesis of diamond in the systems studied here starts at the temperature exceeding the eutectic B_4C–graphite-liquid temperature.

A change in the boron concentration in diamond is known to be accompanied by changes in the cubic cell parameter and in the frequency of the characteristic diamond Raman mode [4, 5]. We calculated the cubic cell parameter for the synthesized diamond samples based on the X-ray diffraction line of diamond (331) with the use of line (533) of the silicon standard. The diamond cell parameters for the samples obtained in the B_4C–C and B–C systems and for the commercial samples of diamond powder (undoped with boron) are equal to 3.575 ± 0.001, 3.573 ± 0.001 and 3.5672 ± 0.0003 Å, respectively. The X-ray diffraction patterns of the samples obtained by the authors of this work and of the diamond powder synthesized in accordance with the industrial technology are presented in Fig. 1.

The concentrations of dissolved boron in the diamond lattice determined according to the Vegard low amounted to about 1.7 and 1.4 at% for diamond samples with the cell parameters equal to 3.575 and 3.573 Å, respectively. The Raman spectra of the synthesized diamond samples were obtained (Fig. 2), and the shift of the characteristic diamond line (1332 cm^{-1} for undoped diamond) by approximately 40 cm^{-1} toward low frequencies was detected. The Raman spectra resemble the spectra obtained for diamond films heavily doped with boron [5]. It should be noted that some specific features in the Raman spectra of B_4C and doped diamond can be of a unified origin. Additional information about the state of the crystalline lattice of doped diamond can be retrieved from the consideration of the diamond characteristic Raman mode frequency versus the diamond cell volume dependences. The plot of the characteristic Raman mode frequency of undoped diamond versus the cell volume [6] extrapolated into the region of spatial extension is shown in Fig. 3. The experimental data reported in [6] were obtained for the pressures ranging from atmospheric to 42 GPa. The relevant results (obtained at normal pressure) of our work and the data for diamond undoped [7] and doped [8] with boron are depicted on the coordinate plane. It follows from the analysis of the data presented that the substantial decrease in the Raman mode frequency of doped diamond can imply a decrease in the rigidity of interatomic bonds in the crystalline lattice (the

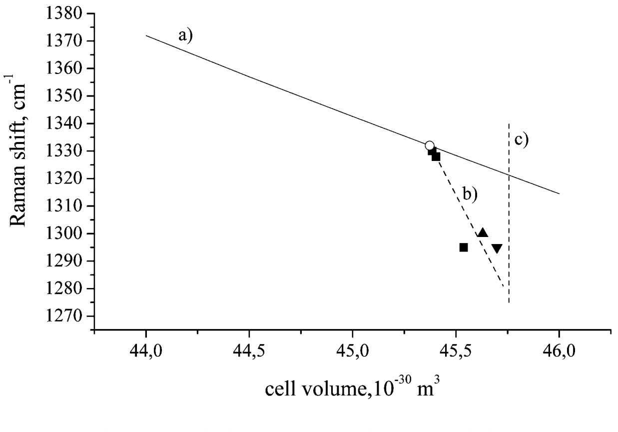

Figure 3 The characteristic Raman mode frequency of diamond versus the elementary cell volume: (a) data of work [6] for undoped diamond extrapolated into the region of spatial extension of lattice; (b) tentative straight line based on the results of this work and the published data for diamond undoped [7] and doped [8] with boron; and (c) the maximum known value of the elementary cell volume for diamond doped with boron [9]. Published data: ○—undoped diamond: ■—boron-doped diamond films [8]; our data: ▲—diamond synthesized in the B–C system, ▼—diamond synthesized in the B_4C–C system.

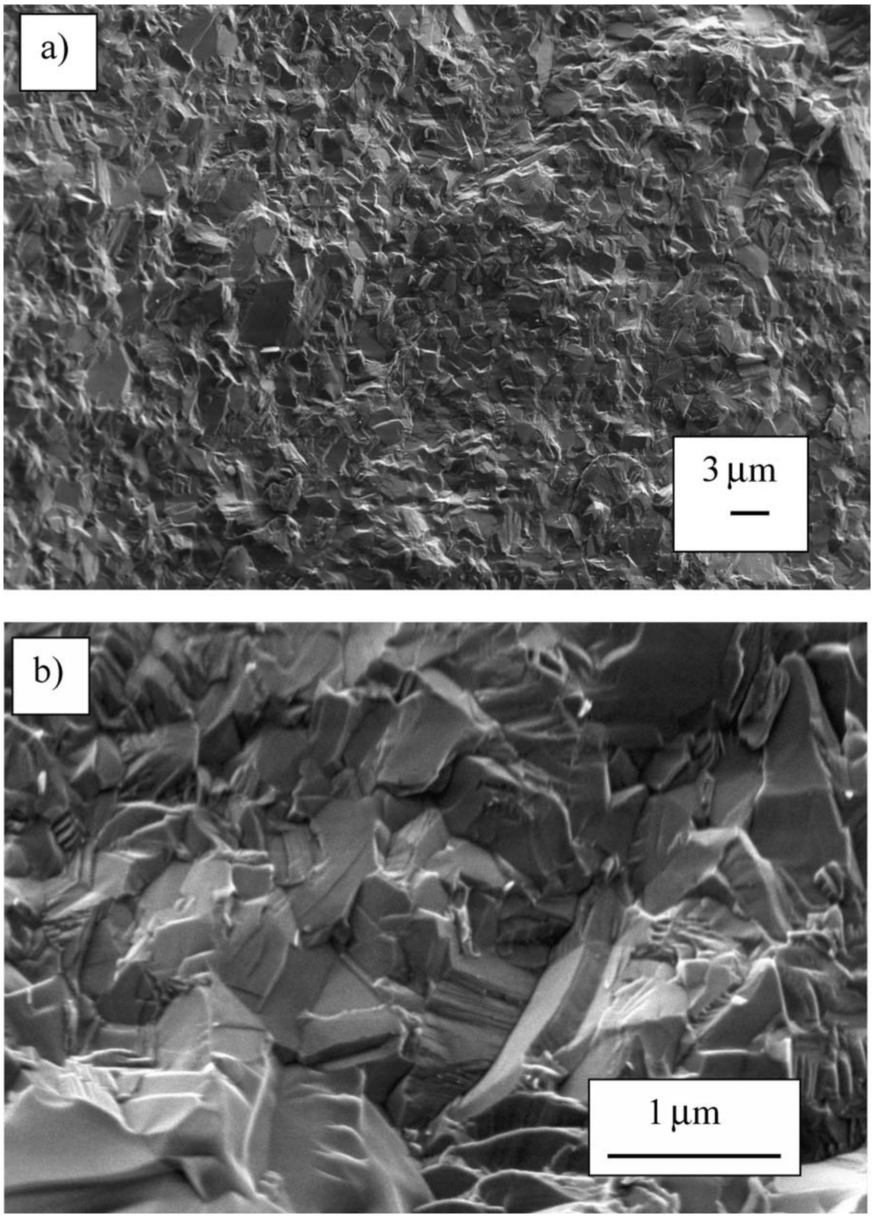

Figure 4 Microstructure of the fracture of the polycrystalline diamond sample obtained in the B_4C–C system at a pressure of 8–9 GPa and a temperature of 2600–2800 K.

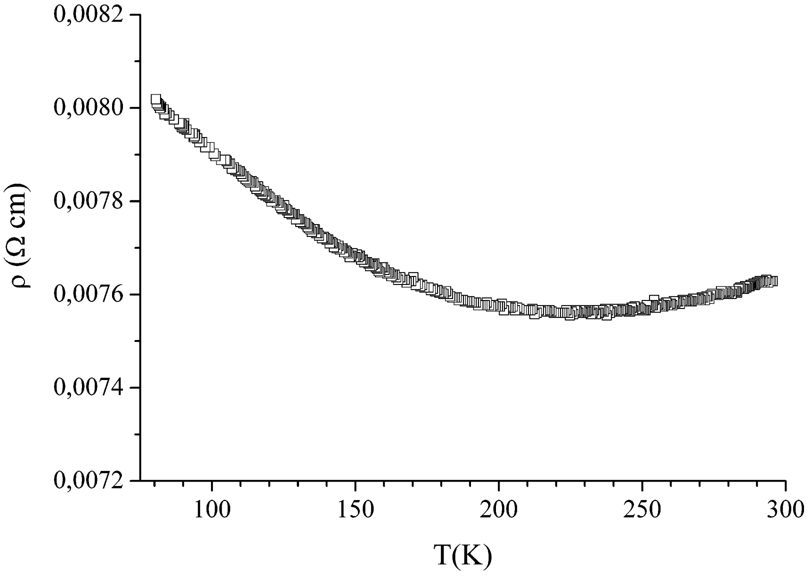

Figure 5 The temperature dependence of electrical resistance (ρ) for the diamond sample containing less than 5% of B_4C and synthesized in the B_4C–C system.

Raman mode frequency of diamond is proportional to the square root of the force constant) and the appearance of anharmonicity in atom oscillations. The maximum value of the lattice parameter of diamond synthesized in the B_4C–C system (3.575 ± 0.001 Å) is smaller than that obtained in work [9] for diamond synthesized in the boron–carbon–hydrogen system (3.5767 Å).

We succeeded in obtaining superhard polycrystalline samples of diamond (Fig. 4) 1–3 mm in size, containing less than 5% of B_4C in the B_4C–graphite system. In this case, starting materials, graphite plate, and B_4C powder, were placed one above the other in the heater. The grain size in the diamond aggregates estimated from the data of transmission microscopy was less than 10–20 μm. We investigated the behavior of the specific electrical resistance in the temperature interval 80–296 K for this type of samples (Fig. 5). It was established that the character of electrical conductivity of the samples varies from semiconducting to metallic with the temperature rise above 220–230 K. Throughout the studied temperature interval, the specific electrical resistance of samples was less than 10^{-2} Ω cm. The chemical resistance of diamond aggregates was determined through the subjection of samples to the action of a solution of nitric and sulfuric acids during 4 hr at the boiling temperature of the solution. The mass loss of the samples was less than 1%, which is the evidence of their high chemical resistance.

In conclusion, bulk samples of polycrystalline diamond containing less than 5% of B_4C are obtained in the double B_4C–C system. The maximum value of the lattice parameter of diamond synthesized in the presence of boron carbide was 3575 ± 0.001 Å. The samples have electrical resistance less than 10^{-2} Ω cm and can be used as engineering materials wherever a combination of electrical conductivity and unique physicochemical properties of diamond is required.

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Received 14 January
and accepted 9 March 2004