Theoretical Investigation on Synthesizing BC$_5$ Crystal

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Abstract. Recent discovery of a compound BC$_5$, whose structure is most likely diamond, invoked intensive interests in the superconductivity research. Little is known not only for its properties but for the preparation methods. For synthesizing BC$_5$, it is very important to know under what conditions this compound can be obtained. In this paper, density-functional-theoretic study has been made on the stability of BC$_5$ relative to a mixture of BC$_3$ and graphite as a function of pressure. It is shown that BC$_5$ becomes stable above 2 GPa. Therefore, high pressure synthesize is very useful.

1. Introduction
The discovery of superconductivity in heavily doped diamond has a great impact on both scientific community and industrial research [1]. Ekimov et al found $T_c = 4.2$ K for heavily doped diamond with a B concentration of $4.9 \times 10^{21}$ cm$^{-3}$ (2.8 at.%). This high concentration of B in the diamond crystals was achieved by a special technique of high-pressure and high-temperature (HPHT) method [1,2]. Soon, the superconductivity of B-doped diamond films was followed by using a more convenient method of chemical vapor deposition (CVD) [3,4]. By using this method, $T_c$ has been raised up to 11.4 K [5]. Naturally, people believe that further amount of doping could make $T_c$ higher. Efforts have been continuing to achieve further doping. However, it seems that the improvement of the B concentration is almost ceased, so that the $T_c$ is saturated about 10 K. Experimentalists are faced to a serious difficulty in B doping of further concentrations. It is argued that this difficulty is originated from the strong favor of B dimer formation in diamond; B dimers are electrically inactive [6–8]. An idea to overcome this difficulty is to return to HPHT method with further high pressures [9]. This idea stems from the observation that the formation energy of B into diamond is lowered with increasing pressure, when graphite is chosen as the starting material.

In the meantime, another route of achieving high B concentration appeared. A completely new material BC$_5$ was found [10]. In usual sense, BC$_5$ must be classified as a compound or alloy, rather than an impurity system. But, in this context, even compounds may be regarded as an extension of the impurity system, if the main features of original host crystal are retained. In fact, surprisingly, this BC$_5$ is shown to have diamond structure. The electronic structure looks very much like to that of diamond [11]. This composition amounts to 16.6 at.% of B: it is by far exceeding to the usual solubility limit of B in diamond. To our surprise, it is predicted the superconductivity with $T_c$ more than 40 K [11].
So far, only Solozhenko’s group succeeded to synthesize BC$_5$. Obviously, this situation of sample preparation severely restricts experimental study on the physical and chemical properties. It is of emergent importance to reproduce the sample of BC$_5$. In a binary B-C system, only boron carbide (symbolically written as B$_4$C) is a stable phase between pure boron and diamond [12, 13]. However, Solozhenko’s result shows that even such a metastable compound could be synthesized under special circumstances. Among the most important condition may be the starting materials; they chose a mixture of BC$_3$ and graphite as the starting material. Graphite-like BC$_3$ itself is very scarcely obtained [14,15].

In this paper, we have theoretically studied the stability of diamond-like BC$_5$ relative to BC$_3$ and graphite as a function of pressure, to identify the range at which BC$_5$ is obtained. The present paper provides a starting point for studying on the complete phase diagram.

2. Calculation Methods

In calculating the total energy of individual crystals, we intend to evaluate the activity of a chemical reaction.

$$\text{BC}_3 + 2\text{C}_{\text{graphite}} \rightarrow \text{BC}_5.$$ (1)

In this paper, we are concerned ourselves with only zero-temperature properties, and in this case the calculation is reduced to evaluation of the enthalphy difference $\Delta H$ of reaction (1). The formation enthalpy is evaluated by

$$H_f = H(\text{BC}_5) - [H(\text{BC}_3) + 2H(\text{C}_{\text{graphite}})].$$ (2)

For finite temperature, the entropy contribution must be taken into account, which will be shown in the next stage of study.

The crystal structure of BC$_5$ has not been well characterized. Experimentally, the X-ray powder pattern matches with that of diamond structure [10]. Although there is a risk to determine the crystal structure from a powder pattern only, we adapt diamond structure to BC$_5$ simply because there is no choice presently. Starting from the perfect diamond, we can construct BC$_5$: the primitive unit cell of diamond structure is a rhombohedron with two basis atoms, and three rhombohedra constitute a hexagonal system which possesses six atoms; then one of the six C atoms is replaced with a B atom; and BC$_5$ is obtained as shown in Fig. 1. Of course, replacing atoms in this way must break the original crystal symmetry. The envisaged space group is P3 (C$^3_1$)$_3$). To what extent the symmetry break affects the diffraction pattern is investigated by calculating the powder diffraction pattern.

Even the crystal structure of BC$_3$ is not obvious. Within a layer, the structure shown in the right hand side of Fig. 1 is the most probable one [16]. The shown structure is $AA$ stacking. However, it is known that $AB$ stacking is more probable [17,18]. On the other hand, compatibility of $AB$ stacking with hexagonal symmetry is difficult. Hence, in this study, we leave the stacking problem alone, simply assuming $AA$ stacking. The assumed space group is P6 (C$^6_3$)$_3$).

Density-functional-theory (DFT) calculations within local density approximation (LDA) were performed to calculate the total energy. Plane-wave pseudopotential method was used. The used code is ’Osaka 2002nano’ [19]. We generated Troullier-Martins pseudopotential [20]. The kinetic cutoff energy for the plane-wave expansion is 100 Ry for graphite, BC$_3$ and diamond, while is 166 Ry for BC$_5$. For $k$ sampling, six points by Chadi Cohen mesh [21] is used for graphite, while 6x6x6 k-points mesh by Monkhorst-Pack mesh [22] is used for BC$_3$, and 2x2x2 k-points mesh for BC$_5$.

3. Results and Discussion

Pressure dependence of the volume of diamond, graphite, BC$_3$, and BC$_5$ is shown in Fig. 2. From the initial slope, bulk modulus $B$ is obtained. Static properties of these crystals are compared
Figure 1. Crystal structure of BC$_5$ and BC$_3$ assumed in this study.

between experiment and calculation in Table 1. Agreement with the experiments is good. In this form, we can see the parallelism in the relationship between diamond (BC$_5$) and graphite (BC$_3$). Apparently, BC$_5$ is a dense phase like diamond, and BC$_3$ is a dilute phase like graphite. Compared with graphite, the crystal BC$_3$ is slightly expanded. Insertion of B atom in the C network makes the honeycomb bond slightly weak, which is confirmed by the charge density [23].

Figure 2. Normalized volume of the unit cells for diamond, BC$_5$, graphite and BC$_3$ as a function of pressure.

The crystal structure of BC$_5$ is a controversial issue. Solozhenko et al showed the evidence for the diamond structure by X-ray diffraction pattern [10]. Furthermore, the lattice parameter of cubic BC$_5$ is just on the line of an extrapolation of Vegard’s rule on heavily B-doped diamond.

In our calculation, the crystal symmetry is lowered to $P6$, and hence the ratio $c/a$ is slightly deviated from that of perfect cubic, $\sqrt{6}$. In spite of this, the X-ray diffraction pattern seems almost the same as that of diamond, as shown in Fig. 3. The hexagonal peaks such as (001) are so weak that these peaks would be missed in power diffraction pattern, unless very careful experiment is performed. The similarity between the calculated and diamond pattern is reasonable, because the local environment of C and B atoms is very similar to that of the original diamond. The direction (001) in hexagonal corresponds to (111) direction in cubic.
Table 1. Static properties of diamond, graphite, BC$_3$, and BC$_5$ at ambient pressure. The volume of cell $V_0$ is evaluated by the hexagonal unit cell for easy in comparison. Bulk modulus $B_0$ is also listed.

| Crystal | $a_0$ (Å) | $c_0$ (Å) | $V_0$ (Å$^3$) | $B_0$ (GPa) |
|---------|-----------|-----------|--------------|-------------|
| diamond | 3.53      | -         | 32.9         | 460         |
| exp. [24]| 3.567     | -         | -            | 443         |
| BC$_5$  | 2.539     | 6.303     | 35.2         | 410         |
| calc. [11]| 2.55      | 6.38      |              |             |
| exp. [10]| 3.635     | -         |              |             |
| graphite| 2.44      | 6.70      | 34.6         | 45.1        |
| exp. [9,25]| 2.46     | 6.375     | 35.0         | 35.8$^9$    |
| BC$_3$  | 5.12      | 3.76      | 42.6         | 25.6        |
| calc. [18]| 5.12      | 3.36      | 38.1         |             |
| exp. [17]| 4.92      | 3.35      | 35.2         |             |

In this sense, it may say that BC$_5$ keeps the diamond structure. The deviation from diamond may be a problem of only resolution in the used measurement. Another way of interpretation is that the cubic symmetry holds on the average of randomly distributed B atoms; in this case just our supercell model is not enough.

The relationship between the lattice parameter and the composition is an important criterion for the correctness of the structure. In Fig. 4, different data are plotted among B-doped diamond and BC$_5$. The relationship between the lattice parameter and the composition is referred to as Vegard’s rule, the value for B-doped diamond varies from author to author, as shown in this figure. The present $a_0$ is obtained by the volume $V_0$ of the hexagonal system, by assuming the cubic ratio $c/a = \sqrt{6}$. It is well known that the LDA underestimate the lattice parameter about 1 %. When this general trend is taken into account, our result is in good agreement with experiment, 3.635 Å. This value is within the linear extrapolation of Vegard’s rule found in B-doped diamonds.

In this way, the lattice parameter favors to diamond structure for BC$_5$. However, J. S. Tse suggested us another crystal form for BC$_5$ [26]. The structure of BC$_5$ may be still an open question.

Let us examine the formation enthalpy $H_f$ of Eq. (1). The formation enthalpy $H_f$ is plotted as a function of pressure in Fig. 5. At ambient pressure, the sign of $H_f$ is positive, which suggests that BC$_5$ is unstable. As increasing pressure, we see that $H_f$ of BC$_5$ is decreased, and the sign is change at $P = 2$ GPa. This transition pressure is approximately equal to that of diamond-graphite transition [30]. It is reasonable to obtain similar transition pressure between BC$_3$-BC$_5$ and graphite-diamond transition, because of the parallelism mentioned above.

Solozhenko et al. obtained BC$_5$ at high pressure. They reported that the quenching of BC$_5$ started from $P = 24$ GPa and 2200 K. This pressure is very high compared with the present transition pressure 2 GPa. It is not surprise to see such a discrepancy in the transition pressure. In our calculation, we compare only the bottoms of the energy between the local minimum configurations. In actual processes of crystal growth, the energy barrier is more important, which is not seen in our calculation. A similar pressure around 20 GPa is required to graphite-diamond transition [31–33]. In any case, it is reasonable to use HTHP technique to obtain BC$_5$ from a mixture of graphite-like starting materials.
**Figure 3.** The left shows Calculated X-ray diffraction pattern for BC$_5$ at high pressures. The wavelength of $0.3738$ Å is assumed for the incident X-ray. The right shows Solozhenko’s experiment [10].

**Figure 4.** Lattice parameter of B-doped diamond and BC$_5$ as a function of B concentration $c_B$. The data are taken from Ekimov et al [27], Bustarret et al [28], and Dubrovinskaia et al [29] for B-doped diamond, whereas Solozhenko et al [10] for BC$_5$. Note that the B concentration $c_B$ of Solozhenko et al is of the source gas, so that it is not necessarily the concentration in the solid films.
Figure 5. Formation enthalpy BC$_5$ from BC$_3$ and graphite as a function of pressure

4. Summary
The formation enthalpy of BC$_5$ from a mixture of BC$_3$ and graphite has been evaluated as a function of pressure. At ambient pressure, BC$_5$ is not stable. But, $P > 2$ GPa, BC$_5$ becomes stable, so that high-pressure synthesize is reasonable. From X-ray diffraction pattern, BC$_5$ seems to have diamond structure. However, there still have chance to find different structures, because the full three-dimensional structure is somehow smeared in powder diffraction patterns.

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