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Effects of NaN_3 Added in Fe–C System on Inclusion and Impurity of Diamond Synthesized at High Pressure and High Temperature *

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Effects of NaN_3 added in Fe–C system to synthesize nitric diamond at high pressure and high temperature are investigated. Diamond crystals with high nitrogen concentration are synthesized by the system of Fe–C and NaN_3 additive at pressure 5.8 GPa and at temperatures 1750–1780 K for 15 min. The synthetic diamond crystals have a cubo-octahedral or octahedral shape with yellowish green or green colour. Some disfigurements are observed on the surfaces of most diamond crystals. The composition and content of inclusions formed by iron in diamond are changed and iron nitride is detected in diamond crystals synthesized with Fe–C– NaN_3 additive. As the amount of NaN_3 additive increases, Fe_3C decreases and iron nitride increases with $\alpha\text{-Fe}$ being nearly constant. Moreover, the nitrogen concentrations in diamond crystals synthesized with 1.5 wt% NaN_3 additive is up to 2250 ppm in substitutional form.

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Diamond crystals either found in nature or synthesized in the laboratory contain a number of impurities, some of which are incorporated in diamond in substitutional forms, others as micro-inclusions. The impurities in synthetic diamond can be controlled by its synthetic process.^[1–3] When the amounts of impurities controlled more or less are added to the catalyst or graphite, the growth rate and morphology of diamond crystals will be affected. For example, a mass of nitrogen, oxygen, or sulfur will seriously interfere with the diamond growth, and adding Al or Ti in the catalyst will restrict the growth rate of diamond crystal.^[1–6] Furthermore, some impurities can affect the physical properties of diamond. For instance, adding a few micrograms of boron in the graphite imparts an attractive blue or blue-white colour to diamond. In addition to the esthetic appeal of the blue crystals, they have valuable semiconducting properties.^[1,2,4,5] Lithium, phosphorus and nitrogen have been extensively considered for enhancing the emission capability of diamond films,^[7,8] and the optical properties of diamond directly depend on nitrogen's concentration and structures.^[8,9]

Nitrogen is a major impurity in both synthetic and natural diamond crystals. It is assumed to have different forms and concentrations in two kinds of diamonds, and thus results in some different physical properties.^[9,10] The nitrogen concentration in natural diamond usually exceeds 1000 ppm in the form of aggregates (type Ia).^[1,2] The nitrogen impurities presented in this form does not affect the colour of diamonds, and the diamond loses visible traces of yellow colour. However, diamond crystals with the nitrogen concentration of about 300 ppm could be synthesized in the conventional method under high pres-

sure and high temperature (HPHT) conditions.^[11] They are called the type-Ib diamond. The nitrogen impurities in this type of diamond are in substitutional positions^[1,2] causing the diamond to have yellow colour or deep yellow colour, high electrical resistivity, and some modified mechanical properties.^[3] Because of the differences of the nitrogen in diamond, the natural diamond usually has the better physical properties than the synthetic diamond, such as mechanical property and optical property. Thus, synthesis of high nitrogen concentrations diamond may be helpful to understand the mechanism of the growing process of natural diamond and helpful to obtain diamond with better physical properties.

We have synthesized nitrogen-rich diamond crystals in an iron–carbon system using sodium azide (NaN_3) as the source of nitrogen under HPHT conditions. The diamond crystals with single substitutional nitrogen exceeding 2000 ppm were successfully grown under temperatures 1750–1780 K and pressure 5.8 GPa for 15 min. We find that the composition and content of inclusions formed by iron in diamond have changed and we detect the presence of iron nitride.

We used graphite powder as the carbon source, pure iron powder (75 μm particle size) as the catalyst, and sodium azide (99.99%) as the nitrogen source for the diamond synthesis. They were mixed for four hours and then shaped into a disc form to fit in a cylindrical space surrounded by a ceramic material.^[12] The sample assembly was compressed in a cubic anvil high-pressure and high-temperature apparatus (SPD-6 \times 1200) with a sample chamber of 23 mm edge length, and then heated for 10 min. Pressures and temperatures were 5.8 GPa and from 1750 to 1780 K, respectively.

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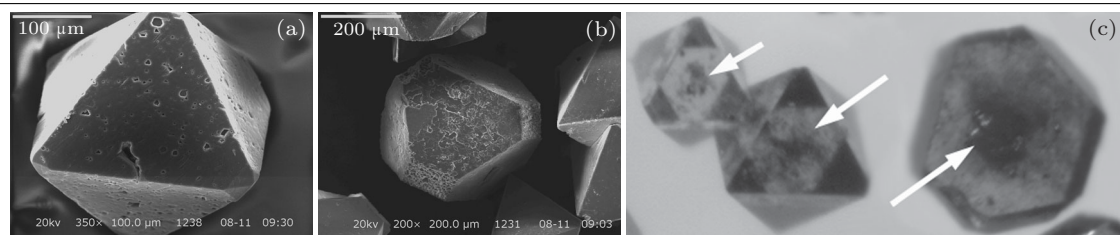


Fig. 1. SEM images of diamond crystals with (a) octahedral and (b) cubo-octahedral shape synthesized with catalyst powder and NaN_3 additive and (c) the photographs of inclusion showing the form of core in diamond.

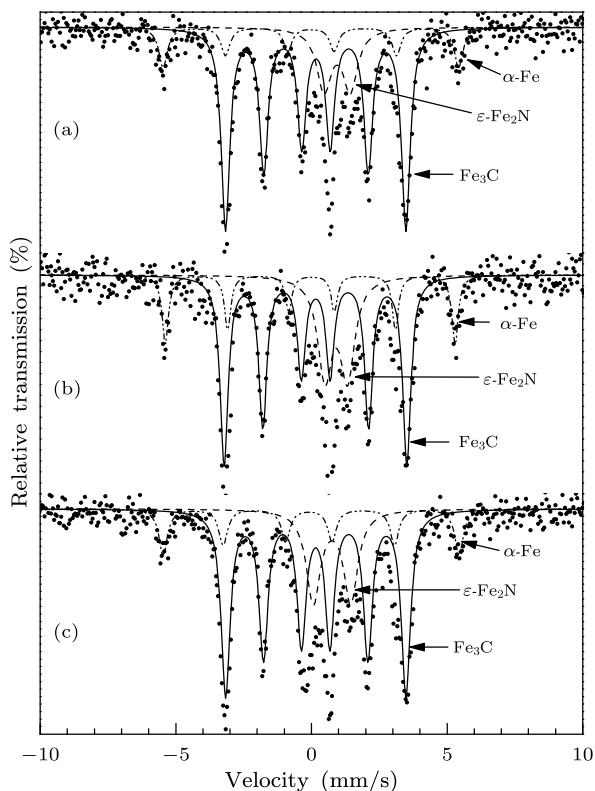


Fig. 2. Transmission Mössbauer spectra (recorded at room temperature) of diamond crystals synthesized with content NaN_3 of (a) 0.2 wt%, (b) 0.3 wt%, and (c) 0.5 wt%.

The synthesized diamond crystals were observed with optical microscope and then were examined with a scanning electron microscope (SEM). The local states of iron in the inclusions of diamond crystals were investigated by transmission Mössbauer spectroscopy on an OXFORD MS-500 at room temperature. The spectra were recorded using a $^{57}\text{Co}/\text{Pd}$ source. The concentrations of nitrogen in diamond were measured by FTIR on a Bruker Tensor37 FTIR spectrometer fitted with a Hyperion 3000 microscope.

Figure 1(a) and 1(b) show respectively the SEM images of diamond crystals synthesized with NaN_3 additive having an octahedral shape and a cubo-octahedral shape. It can be seen that the crystalline surfaces are not flat. Some triangular holes of micron size are distributed disorderly on the surfaces of the octahedral shape diamond crystals in Fig. 1(a). The orientation of the triangular hole is the same as that of the so-called ‘trigon’. Kanda *et al.*^[13] also observed similar holes on surfaces of diamond crystals synthesized with Fe catalyst. However, some lamellar

patterns with random directions are observed on the $\{111\}$ surface in Fig. 1(b). In addition to the lamellar patterns, some orderly alveolate holes of micron sizes can be observed on the $\{100\}$ surface as shown in Fig. 1(b). Fe dissolved on the diamond surfaces to produce Fe_3C during the quenching process, forming lamellar patterns and holes on the diamond surface.

Most diamond crystals synthesized with NaN_3 additive are green or yellowish green. The inclusions in crystals have a spherical core form as shown in Fig. 1(c), especially in cubo-octahedron shape crystals. The octahedral shape crystals are more translucent with a lighter green colour. In contrast, the diamond crystals synthesized from the pure Fe–C system are yellowish dark or dark in colour and without this kind of inclusion.

The surfaces of diamond synthesized from Fe–C with NaN_3 additive are obviously different from those synthesized from the $\text{Fe}_{90}\text{Ni}_{10}\text{–C}$ with NaN_3 additive.^[14,15] These differences were resulted from the different characteristics of the catalysts and the different effects of NaN_3 additives. Jia *et al.*^[16] reported that element Ni is much easier to enter the $\{111\}$ face than element Fe. When Ni was added in catalyst, the formation of Fe inclusions was restrained. Thus there were no alveolate holes and trigons on the surface of diamond synthesized from $\text{Fe}_{90}\text{Ni}_{10}\text{–C–NaN}_3$ additive system. Furthermore, NaN_3 decomposed easily, giving out active nitrogen atoms under HPHT. Active nitrogen atoms have different effects on the characteristics of catalysts Fe and Ni.

Table 1. Composition and content of inclusion formed by iron in diamond crystals.

Catalyst	Composition and content of inclusion formed by iron (wt%)		
	$\alpha\text{-Fe}$	Fe_3C	Fe_xN
Fe	17.4	82.6	-
Fe+0.2 wt% NaN_3	14.3	69.9	15.8
Fe+0.3 wt% NaN_3	16.9	59.2	23.9
Fe+0.5 wt% NaN_3	17.0	55.3	27.7

The transmission Mössbauer spectrum of the local states of iron in the inclusions of crystals synthesized from the pure Fe–C system indicated that two kinds of iron forms, Fe and Fe_3C were present in the inclusions of these crystals. However, as shown in Fig. 2 for crystals synthesized from the Fe–C system with NaN_3 additive, iron nitride was found in the inclusions in addition to $\alpha\text{-Fe}$ and Fe_3C . These results are in agreement with the results in Ref. [17]. The parameters given by Kopcewicz *et al.* vary somewhat depend-

ing on the experimental conditions and the method of sample preparation. However, the hyperfine parameters in the transmission Mössbauer spectra are consistent with most of the results reported in the literature. Table 1 shows the composition and content of inclusions, estimated from the transmission Mössbauer spectra. As the amount of NaN_3 additive increases, Fe_3C decreases and iron nitride increases with $\alpha\text{-Fe}$ being nearly constant. These results were indicated that NaN_3 additive was suitable for decreasing the content of Fe_3C phase in diamond's inclusion.

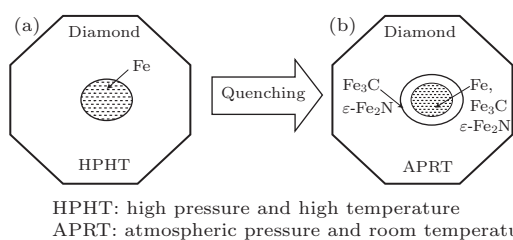


Fig. 3. Schematic images of tentative explanation for presence of inclusion formed by iron in crystals.

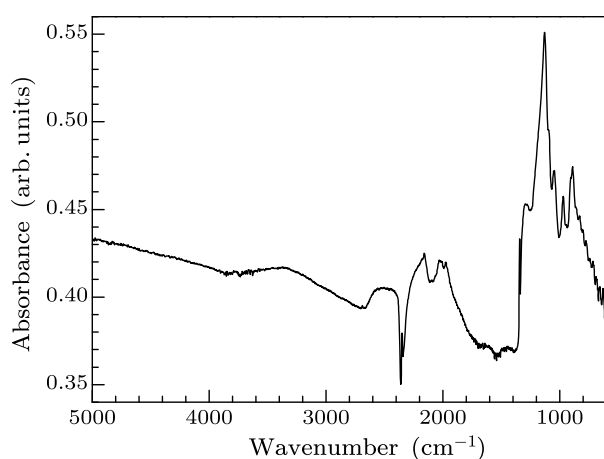


Fig. 4. Infrared absorption spectra of diamond crystals synthesized with amount NaN_3 of 1.5 wt%.

The variation of inclusion content in diamond can be explained further by the schematic images shown in Fig. 3. There was a strong affinity between iron and carbon atoms under HPHT, leading to residual iron in diamond during the synthesis process. Part of these iron atoms reacted with carbon or nitrogen atoms in diamond and formed Fe_3C or iron nitride in the quenching process. In pure Fe-C system, only Fe_3C was formed. When NaN_3 was added in Fe-C system, large numbers of nitrogen atoms were available, and the iron nitride phase was also formed.

The infrared absorption spectra for diamond syn-

thesized with content NaN_3 of 1.5 wt% are shown in Fig. 4. The substitutional form of nitrogen impurities, i.e. type Ib, can be detected in the one phonon region of the spectra. The nitrogen concentrations in diamond were determined using the IR spectra and the method suggested by Kanda *et al.*^[11] Spectra taken from 15 crystals were analysed. The concentration of nitrogen for diamond synthesized from the Fe-C system added 1.5 wt% NaN_3 was about 2250 ppm, much higher than the highest value 800 ppm, obtained in diamond synthesized with conventional metal solvent-catalysts by HPHT.^[10]

In summary, the diamond crystals with high nitrogen concentration have been successfully synthesized from the Fe-C system with NaN_3 additive. The synthetic diamond crystals have a cubo-octahedral shape or an octahedral shape with yellowish green or green colour. Moreover, the composition and content of inclusion formed by iron in diamond have changed and iron nitride was detected in crystals synthesized with Fe-C- NaN_3 additive. The nitrogen concentrations in diamond crystals synthesized with 1.5 wt% NaN_3 additive is up to 2250 ppm in substitutional form.

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