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Formation of Mixture of A and C Centres in Diamond Synthesized with Fe₉₀Ni₁₀-C-High-Content Additive NaN₃ by HPHT *

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Very rich nitrogen concentration with the dominant C centres and some A centres are found in diamonds grown from a Fe₉₀Ni₁₀-C-high-content NaN₃ additive system. The concentrations of C centres rapidly increase with increasing content of NaN₃ additive, while the concentrations of A centres increase slowly. The total nitrogen concentration tends to increase rapidly with increasing content of NaN₃ additive when the content of NaN₃ is below 0.7 wt%. However, the total concentration of nitrogen in the diamonds increases slowly when the content of NaN₃ is further increased up to 1.0 wt%, and the total nitrogen average concentration are calculated to be around 2230 ppm for most of the analysed synthetic diamonds. Furthermore, the nitrogen impurities in different crystal sectors of the diamonds are inhomogeneously distributed. The nitrogen impurities in the diamonds in [111] zones are incorporated more easily than that in [100].

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It is well known that diamonds are classified into types I and II according to the concentration and structure of the major impurities (nitrogen or boron) in diamonds.^[1-7] Type I is further classified into IaA, IaB, Ib and their mixed types. Type-IaA diamond contains nitrogen in a paired form (A centres), whereas type-IaB diamond contains nitrogen aggregates consisting of four nitrogen atoms (B centres), and type-Ib diamond contains singly substitutional nitrogen atoms which are called C centres.^[1-7] Most natural diamonds are of type IaA or IaB with nitrogen concentrations usually exceeding 2000 ppm, and in natural diamonds of type Ib the nitrogen content is usually below 100 ppm, and only extremely rarely up to around 300 ppm.^[7-9] However, most diamond crystals synthesized are of type Ib and the concentrations are usually 100-400 ppm.^[7,8]

It is interesting to study how the high concentrations of nitrogen are incorporated into diamond,^[7-9] not only to produce high concentrations of nitrogen diamond but also to be helpful to understand the mechanism of the growth process of natural diamond, which is an open question puzzled for many years. Recent results indicate that the forms of nitrogen in type-Ib diamond can be transformed into the forms of type Ia under appropriate temperature and pressure.^[10,11] If the diamond that contains the same concentrations of nitrogen as that of natural diamond can be synthesized by high pressure and high temperature (HPHT) in the laboratory, the type-Ia diamond with high nitrogen concentration may be synthesized in the laboratory.

In this study, large amounts of single substitutional

nitrogen atoms (C centres) accompanied by some nitrogen pairs (A-centres) were found in diamond crystals grown by HPHT synthesis from a FeNi-C system with high content NaN₃ additive. The concentration of C centres increases with the increasing content of NaN₃ additive rapidly, whereas the concentration of A centres increases slowly. The total concentration of nitrogen increases slowly with the further increase of NaN₃ up to 1 wt% and the total nitrogen average concentrations are determined to be about 2230 ppm in most of the diamonds.

The sodium azide (NaN₃, 99.99%) was used as sources of nitrogen under HPHT. The graphite powder and the Fe₉₀Ni₁₀ powder as solvent-catalyst were used in our study. The proportion of the graphite and Fe₉₀Ni₁₀ alloy powder of 75 μm in particle sizes was fixed at 1:1, and the amount of sodium azide added in graphite and alloy varies from 0 to 1wt%. The graphite powder, alloy powder and NaN₃ were mixed for 4 h firstly, and then were shaped into a disc form to fit into a cylindrical space surrounded by a ceramic material.^[12] The sample assembly was compressed in a cubic anvil of high-pressure and high-temperature apparatus (SPD-6 × 1200) with a sample chamber of 23 mm on an edge, and then heated for 15 min. Diamond crystals were grown with a system of FeNi-C-NaN₃ additive at various temperatures of 1500-1750 K under 5.0-5.8 GPa.

The samples recovered from the high pressure vessel were treated in a boiling mixture of H₂SO₄ and HNO₃ to isolate grown diamond from unconverted graphite and the metal solvent catalyst, and then observed using an optical microscope. The nitro-

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gen concentrations in diamond were measured by a Fourier transform infrared (FTIR) spectrometer on a BRUKER IFS 66 V/S spectrometer fitted with a Hyperion 3000 microscope. Spectra were taken under the absorption mode with incremental steps of $20\ \mu\text{m}$. The IR beam size was limited to $50\text{--}150\ \mu\text{m}$ square by the aperture in order to only pass through the diamond particle.

Nitrogen concentrations were calculated as follows. The concentrations of the A and C centres were calculated from the absorption coefficients at 1282 and $1130\ \text{cm}^{-1}$, respectively.^[1,4,10,13] In order to determine the absorption coefficient in the one phonon region, absorption coefficient at $2120\ \text{cm}^{-1}$ was used as a standard, which was 5.5 .^[13] However, the spectra were made of mixture of IaA and Ib nitrogen, so we must decompose the component of IaA and Ib nitrogen from the spectra measured from diamond synthesized with additive NaN_3 , before we made the calculation.^[1,4] In order to decompose the observed spectra, we assume that spectra of IaA and Ib are linearly overlapped. Then the concentrations of nitrogen from the spectra of mixture of IaA and Ib nitrogen are determined by using the method suggested by Kanda and Yamaoka^[4] and Liang *et al.*^[13] The absorption coefficients μ_{1282} and μ_{1130} are decomposed to those of the A and C centres using the equations $A_{1282} = \mu_{1282} + 0.35\mu_{1130}$ and $A_{1130} = \mu_{1130} + 0.21\mu_{1282}$.^[4] A_{1282} and A_{1130} are absorbances at 1282 and $1130\ \text{cm}^{-1}$, respectively. A and C centre concentrations are calculated by using the equations N_{1130} (ppm) = $(\mu_{1130}/\mu_{2120}) \times 5.5 \times 25$, N_{1282} (ppm) = $(\mu_{1282}/\mu_{2120}) \times 5.5 \times 16.5$,^[4,10,13,14] where N_{1282} and N_{1130} were the concentrations of the A and C centres, respectively.

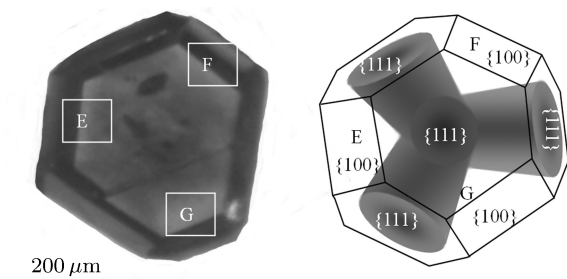


Fig. 1. Inhomogeneous distribution of colour in a diamond synthesized with $0.7\ \text{wt}\%$ of NaN_3 additive and schematic illustration of inhomogeneous distribution of colour.

The morphology of synthetic diamond changes from cubic to octahedral via cubo-octahedral with increasing growth temperature when the content of NaN_3 additive is $0\text{--}0.5\ \text{wt}\%$ in graphite and FeNi mixture powders. The crystals of $0.2\text{--}0.5\ \text{mm}$ diameter predominantly exhibit $\{111\}$ faces accompanied by $\{100\}$ faces. However, the $\{311\}$ and $\{110\}$ faces are present in addition to the $\{100\}$ and $\{111\}$ faces in di-

amond with the increasing content of NaN_3 additive ($0.7\text{--}1.0\ \text{wt}\%$), and the pole shape crystals are found.

The colours observed with an optical microscope for the most of crystals synthesized with NaN_3 additive in a FeNi-C system are green or dark green. However, the colour in some crystals is not homogeneously distributed: the $\{111\}$ sectors are dark green, whereas the $\{100\}$ areas are greenish yellow or yellow, marked as E, F and G in Fig. 1. Furthermore, bands of dark green colour extend from the centres of some crystals to the $\{111\}$ grown sectors, as shown in Fig. 1.

The typical FTIR spectrum of pure type Ib diamond is shown in Fig. 2(a). The spectrum with C centres is characterized by a highest peak at $1130\ \text{cm}^{-1}$ and a sharp peak at $1344\ \text{cm}^{-1}$.^[1,4] The typical infrared absorption spectrum of diamond crystals synthesized with $\text{Fe}_{90}\text{Ni}_{10}\text{-C-NaN}_3$ additive system is shown in Fig. 2(b). The spectrum with A centres consists of two peaks, the higher one is at $1282\ \text{cm}^{-1}$.^[1,4] The single substitutional form of nitrogen impurities (type Ib) can be detected in the one phonon region of the spectra in Fig. 2, while the absorption intensity of spectrum in one-phonon region, in Fig. 2(b), are much higher than those in Fig. 2(a). The occurrence of peaks at $1130\ \text{cm}^{-1}$ and $1282\ \text{cm}^{-1}$ in Fig. 2(b) indicate that the spectra are made of mixture of IaA and Ib nitrogen.

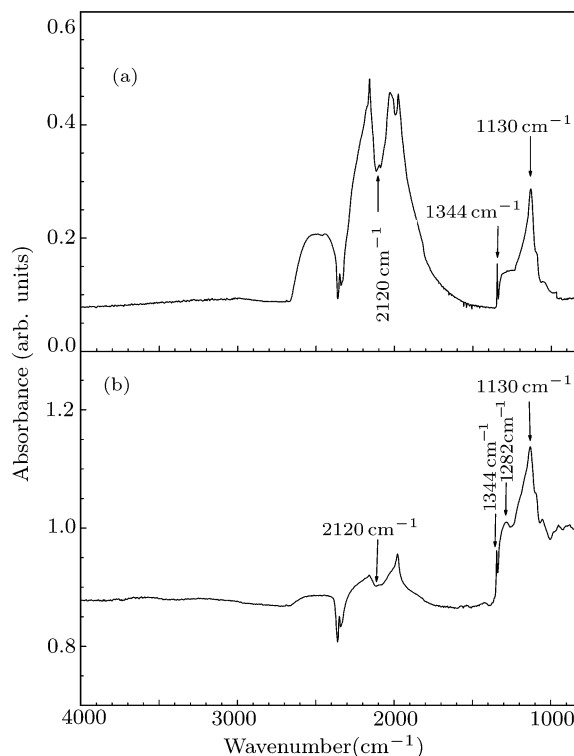


Fig. 2. Infrared absorption spectra of diamonds synthesized with different content NaN_3 : (a) $0\ \text{wt}\%$, (b) $1\ \text{wt}\%$.

Infrared spectra of the differently coloured zones of the samples (in Fig. 1) synthesized with NaN_3 additive

are shown in Fig. 3. Figure 3(a) shows the typical infrared absorption spectrum in the greenish yellow to yellow zones (marked as E, F and G in Fig. 1), which indicate the presence of mainly single substitutional nitrogen (C centres). Figure 3(b) shows the average spectrum of the whole diamond. Figure 3(c) shows the spectrum in the dark green zone. In Fig. 3, it is apparent that the absorption at 1130 cm^{-1} , which is caused by C centres, is more intense in the dark green than that in the greenish yellow to yellow zones. Additionally, the 1282 cm^{-1} (A centre absorption) is present in the spectrum of the dark green zones, whereas no A-aggregates could be detected in the greenish yellow to yellow zones (E, F and G) of the diamond.

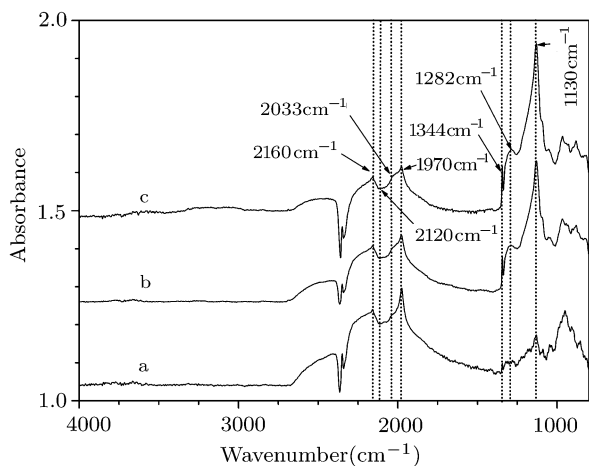


Fig. 3. Infrared absorption spectra of a diamond synthesized with NaN_3 additive in differently coloured zones: (a) E, F and G in Fig. 1, (b) the average diamond, (c) the centre with dark green.

We analyse the spectra shown in Fig. 3 and calculate the concentration of nitrogen from the IR spectrum in Fig. 3(a) for greenish yellow or yellow regions to be not more than 100 ppm. In these zones, nitrogen is shown in comparatively low concentrations. On the other hand, the concentration of nitrogen in the dark green zones is up to 1850 ppm (Fig. 3(c)), and that for the average diamond up to 1530 ppm (Fig. 3(b)). These results indicate that the nitrogen impurities enter into the diamonds more easily in [111] than in [100] zones. For most of diamonds, the inhomogeneous distribution of nitrogen impurities in different growth sectors is not considered during IR measurement, and we only measure the whole region of diamond. Figure 4 shows the infrared absorption spectra of diamonds synthesized with different-content NaN_3 additive.

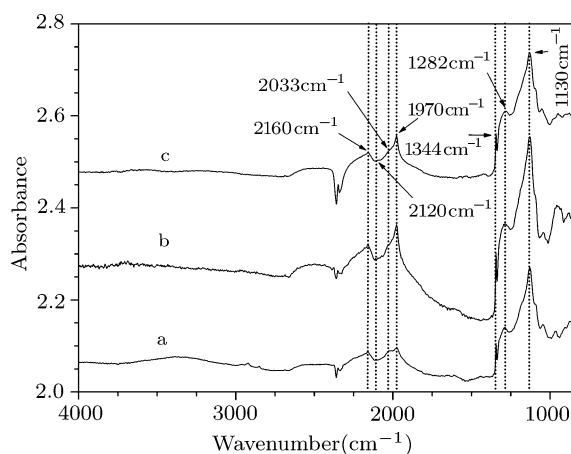


Fig. 4. Infrared absorption spectra of diamonds synthesized with different content NaN_3 additive: (a) 0.5 wt%, (b) 0.7 wt%, (c) 1 wt%.

Table 1. Concentration of nitrogen in diamonds synthesized with different content NaN_3 .

Nos.	NaN_3 (wt%)	Type of diamond	Concentration of nitrogen in diamond (ppm)		
			IaA type nitrogen (A centre)	Ib type nitrogen (C centre)	Total nitrogen
1	0.3	Ib	None	1130 ± 113	1130 ± 113
2	0.5	Ib+IaA	None / 95 ± 63	1780 ± 180	1800 ± 176
3	0.7	Ib+IaA	165 ± 91	1870 ± 67	2008 ± 126
4	1.0	Ib+IaA	201 ± 70	2054 ± 252	2228 ± 221

Spectra taken from 86 crystals are analysed and the regions of nitrogen concentrations are listed in Table 1 with varying contents of NaN_3 additive. The nitrogen quantities in Table 1 are presented in average and standard deviation form. The average concentrations of C centres rapidly increase with increasing amount of NaN_3 additive used for the synthesis, but the concentration of A centres increase only slowly and fluctuated. When the content of the NaN_3 additive is 0.5 wt%, the A centres are only observed in some of the spectra of some crystals. In these spectra the A centre average concentration is found to be 95 ppm, whereas the average concentration of C

centres increase sharply to be 1780 ppm. The A centres are always observed in the spectra of diamonds synthesized with 0.7 and 1.0 wt% of NaN_3 additive. The A and C centre concentration average respectively about 165 ppm and 1870 ppm for most of the diamonds synthesized with 0.7 wt% of NaN_3 additive, whereas the A and C centre average concentrations are about 200 ppm and 2054 ppm, respectively, for most diamonds grown with 1.0 wt% of NaN_3 additive. The largest A centre concentration is determined to be about 360 ppm in a diamond synthesized with 1.0 wt% of NaN_3 additive.

The total nitrogen concentration tend to increase

rapidly with increasing NaN_3 content as long as the NaN_3 content is below 0.7 wt%. The total concentration of nitrogen in the diamonds increase only slowly as soon as the NaN_3 is further increased up to 1.0 wt%. Although a total concentration of nitrogen exceeding 2600 ppm is determined for two diamond crystals synthesized with 1.0 wt% NaN_3 additive, the total nitrogen concentration is calculated to be around 2230 ppm for most of the analysed synthetic diamonds.

As shown in Table 1, crystals growing with the same amount of NaN_3 additive do not always show the same nitrogen concentration. These variable results may be due to the fluctuation of the growth temperature and NaN_3 content even during the same run in the same cell. This could be explained by the presence of a temperature gradient and/or inhomogeneous distribution of NaN_3 in the cell.

In summary, the dominant C centres and some A centres are found in diamonds grown from a FeNi–C system with high content of NaN_3 additive. The total nitrogen concentrations increase strongly with the increasing content of NaN_3 additive as long as the content of NaN_3 is below 0.7 wt%. With the further increase of NaN_3 up to 1.0 wt% the total concentration of nitrogen continues to increase, but much slower than that at lower contents. The total nitrogen concentration is determined to be about 2230 ppm for most of the diamonds. The largest A centre concentration is about 360 ppm in diamonds synthesized

with 1.0 wt% of NaN_3 additive. The nitrogen impurities in different crystal sectors of these diamonds are distributed inhomogeneously. The nitrogen impurities can enter into the diamonds more easily in [111] than that in [100] growth sectors.

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