Synthesis of large diamond crystals containing high-nitrogen concentration at high pressure and high temperature using Ni-based solvent by temperature gradient method*

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This paper reprots that with Ni-based catalyst/solvent and with a dopant of NaN_3, large green single crystal diamonds with perfect shape are successfully synthesized by temperature gradient method under high pressure and high temperature in a China-type cubic anvil high-pressure apparatus (SPD-6×1200), and the highest nitrogen concentration reaches approximately 1214–1257 ppm calculated by infrared absorption spectra. The synthesis conditions are about 5.5 GPa and 1240–1300 °C. The growth behaviour of diamond with high-nitrogen concentration is investigated in detail. The results show that, with increasing the content of NaN_3 added in synthesis system, the width of synthesis temperature region for growth high-quality diamonds becomes narrower, and the morphology of diamond crystal is changed from cube-octahedral to octahedral at same temperature and pressure, the crystal growth rate is slowed down, nevertheless, the nitrogen concentration doped in synthetic diamond increases.

Keywords: high temperature and high pressure, nitrogen-doped diamond crystal, temperature gradient method, additive NaN_3

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1. Introduction

It is well known that nitrogen is one of the most common atomic impurities in both natural and synthetic diamonds, and the physical properties of diamond are significantly influenced by the form and concentration of nitrogen atom. Up to today, nitrogen impurity has been investigated for more than 60 years. Now, diamonds are mainly classified into type Ia, Ib, IIa and IIb on the base of their form and concentration of nitrogen and boron. Nitrogen in type Ia and Ib is in aggregated and isolated form, respectively. Type IIa is the purist diamond containing undetectable impurity, whereas type IIb contains boron impurities.[1,2]

The nitrogen concentration (NC) in natural diamond varies from less than 1 ppm (1 ppm = 1×10^{-6}) to 1000 ppm, and most natural diamonds belong to type Ia usually containing nitrogen more than 1000 ppm.[3] Although diamonds with nitrogen less than 300 ppm in aggregated form are prepared in the laboratory by annealing or growth at high temperature,[4,5] the NC is far lower than natural diamond of type Ia. If the nitrogen state in high nitrogen-doped diamond can be transformed from dispersed form to aggregated form, real type- Ia diamonds can be manufactured by annealing high nitrogen-doped diamond. Therefore, it is extremely important to grow diamond with high NC. It was reported that Kanda *et al.*[6] and Borzdov *et al.*[7] successfully synthesized diamonds with high NC more than 1000 ppm at a quite high pressure (higher than 7.0 GPa), but the crystal shapes grown at a quite high pressure were incomplete. In recent years, our research group using NaN_3 or $Ba(N_3)_2$ as dopant succeeded in synthesizing diamond crystals with NC around 1600–2400 ppm.[8,9] As diamond growth rate is so fast that difficult to be controlled in industrial diamond growth pattern, crystal defects and the inclusions are much excessive in diamond lattice.[10] The factors above have effects on the

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calculation of NC by infrared (IR) absorption spectra. Furthermore, the size of diamond restricts the potential applications, and many properties of crystals are difficult to measure. Accordingly, we use the temperature gradient method (TGM), at high-pressure and high-temperature (HPHT) conditions, by adding NaN_3 as dopant into the synthesis system of Ni-based solvent and carbon source, to grow diamond crystals containing high nitrogen content. In addition, the growth behaviour and NC in diamond crystals are also investigated in detail.

2. Experimental details

The experiments are carried out in a china-type cubic anvil HPHT apparatus (SPD-6×1200). The growth chamber of TGM is shown in Fig. 1. Synthesis chamber size is about 10 mm, synthesis temperature varies from 1240 °C to 1300 °C. The temperature difference between the carbon source and seed crystal is about 30–50 °C and {111} seed surface is selected as growth facet. The temperature is calculated from a relation between the temperature and input power, which had been calibrated using a Pt6%Rh–Pt30% Rh thermocouple.[11] The pressure is around 5.5 GPa, which is estimated by the curve that is established based on the pressure-induced phase transitions of bismuth, thallium, and barium.

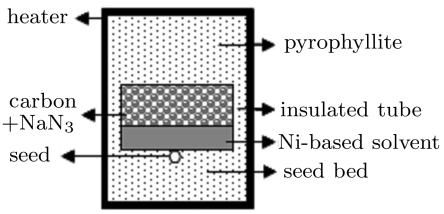


Fig. 1. Assembly for synthesis of large diamond crystal.

High-purity graphite is employed as carbon source. Catalyst/solvent is Ni-based ($Ni_{70}Mn_{25}Co_5$) alloy, and sodium azide (NaN_3, 99.99%) is directly added to the graphite powder as nitrogen source.

After HPHT synthesis, the collected samples were first put into the dilute nitric acid at 100 °C for 1 hour to isolate the diamond crystal from metal. And then the diamond crystals are treated in the mixed concentrated acid of H_2SO_4 and HNO_3 (3/1) to remove impurity remained on crystal surface. At last, the grown diamond crystals are observed by the optical microscope, and NC in diamond are measured by using Fourier transform infrared (FTIR) spectrometer. For the IR absorption measurements, a Bomem M110 FTIR spectrometer fitted with a Spectra Tech IR-PLANTM microscope was used. The IR beam size was rescaled to a 150 μm square aperture so as to pass only the diamond crystals.

3. Result and discussion

3.1. Growth condition of diamond crystals with high NC

As additive NaN_3 added in growth chamber of HPHT, the diamond-growing environment was filled with nitrogen by decomposing NaN_3. The rich nitrogen led to the narrower growth region of high-quality diamond crystals, as indicated in Fig. 2. When the amount of NaN_3 additive exceeds 0.8 wt%, high-quality diamond crystals can hardly be gained, for the regrown graphite and polycrystal would be easily grown. It reveals that the V-shape section for the diamond's growth, which is the region between the solvent/carbon eutectic melting line and diamond/graphite equilibrium line under pressure and temperature, is moved upwards in P–T (pressure–temperature) phase diagram, since the additive NaN_3 is added in the synthesis chamber. Therefore, growth of diamond crystal requires higher temperature and pressure as well as high precision control. It indicates that growth of large diamond single crystals with high N_C is much more difficult than that of tipical type-Ib diamonds.

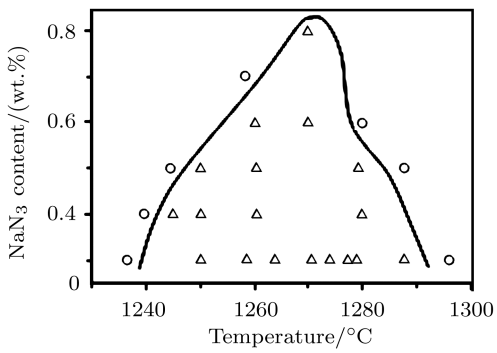


Fig. 2. Temperature growth region for adding different content of NaN_3 in chamber. ○ crystal with incomplete shape; △ crystal with complete shape.

3.2. The morphology of high nitrogen-doped diamond crystals

Generally, the crystal shape is cube-octahedral grown at low temperature (about 1250 °C), mean-

while, the crystal morphology shows the change from cube-octahedral to octahedral at same temperature and pressure, when the amount of additive NaN_3 varies from 0.05 wt.% to 0.3 wt.%. At doping of 0.3 wt.%, the shape of grown crystal is almost octahedral which is mainly dominated by {111} facet, whereas {100} facet is disappeared, as displayed in Fig. 3. The phenomenon can be explained by the specific surface energy. It is known that the drop of specific surface energy is observed at growth of crystals from solutions, melts or a gas phase adsorption.[12] It is also known that, there is one uncompensated bond for each surface atom for {111} surface, while two for {100} surface.[13] When nitrogen substitutes carbon atom in surface, there is no uncompensated bond coming from nitrogen atom for {111} surface; however, there is still one uncompensated bond to be left for {100} surface. Therefore, nitrogen doped in diamond crystal lattice gives rise to dramatic decrease of specific surface energy in {111} surface, and the facets with low specific surface energy will be dominant during crystal growth. It apparently explains the fact that, with an increase of NC in the growth environment, the growth habit of a diamond crystal varies from cubo-octahedral to octahedral.

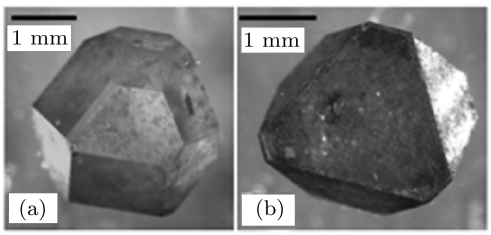


Fig. 3. The optical microscopy photos of diamond crystals grown at same temperature (1250 °C): (a) with NaN_3 0.05 wt.%; (b) with NaN_3 0.3 wt.%

3.3. The growth rate of nitrogen-doped diamond crystals

By using TGM, the area of crystal surface increases with the growth time, whereas the deposition rate of carbon source per unit area remains constant, so the growth rate increases with the increase of growth time.[14] Furthermore, the size of crystal-growing facet and the temperature gradient between carbon source and crystal seed, can influence the crystal growth rate. Accordingly, researching into the effects of nitrogen content in growth environment on diamond-growing rate, we find that these influence factors are controlled to be fixed for each synthesis cycle. The average growth rates of different nitrogen-doped samples are shown in Fig. 4. It can be seen from the diagram that with increasing the nitrogen content in diamond-growing environment, crystal growth rate apparently decreases. The phenomenon can be explained by the variations of carbon solubility. The solubility of carbon dissolved in metal/catalyst is reduced, for the solvent/carbon eutectic melting line and diamond/graphite equilibrium line are all moved upwards in P–T phase diagram, when the content of additive NaN_3 is increased. Therefore, the reduction of solubility slows the velocity of carbon atom separating out from solvent/catalyst. For this reason, the growth rate of diamond crystals is slowed down.

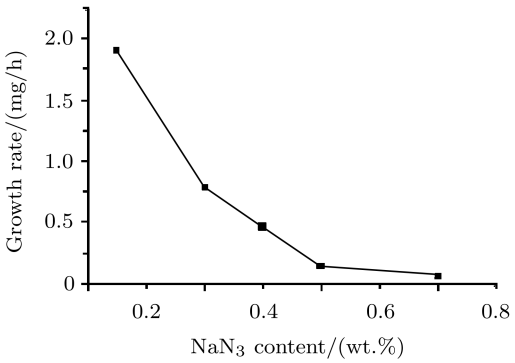


Fig. 4. Curves of growth rate versus the added amount of NaN_3.

3.4. The NC in diamond crystals

The NC in diamond crystals can be calculated according to IR spectra,[15,16] and the calculated method depends on the nitrogen state. The samples synthesized with different content of additive NaN_3 are measured by IR spectrometer. As it is known that the nitrogen atoms existed in type-Ib diamonds are mainly in a single substitutional form (C heart), which corresponds to the IR absorption peak of 1130 cm^{-1} and 1344 cm^{-1}. It can be seen from the IR absorption spectra shown in Fig. 5 that the nitrogen-doped diamonds are type-Ib diamond crystals, even though heavy degree of NaN_3 is doped (0.6 wt.% and 0.8 wt.%).

The formulas accepted by researchers to calculate N_C for type-Ib diamonds are listed as follows:[8,9]

$$\mu(1130\ \mathrm{cm}^{-1}) = [A(1290\ \mathrm{cm}^{-1}) - A(1370\ \mathrm{cm}^{-1})]/0.31, \quad (1)$$

$$\mu(2120\ \mathrm{cm}^{-1}) = [40 \times A(2030\ \mathrm{cm}^{-1}) + 87 \times A(2160\ \mathrm{cm}^{-1})]/127 - A(2120\ \mathrm{cm}^{-1}), \quad (2)$$

Nitrogen concentration N_C:

$$N_C(\mathrm{ppm}) = \mu(1130\mathrm{cm}^{-1})/\mu(2120\mathrm{cm}^{-1}) \times 5.5 \times 25, \quad (3)$$

where μ and A are absorption intensity and recorded values of absorbance, respectively. Using the method above, we can easily calculate the N_C in diamond according to IR spectra, and the calculated results are shown in Table 1. It can be seen that with increasing the content of NaN_3, N_C doped in diamond increases, and the highest N_C can reach about 1214–1257 ppm. However, the N_C doped in diamond can reach about 1520 ppm, which is synthesized with Fe-based ($Fe_{59}Ni_{25}Co_{16}$) catalyst/solvent by using NaN_3 as dopant reported by Zhang *et al.*[17] The maximum N_C doped in diamond synthesized with Ni-based catalyst/solvent is lower than that diamond synthesized with Fe-based catalyst/solvent. This fact indicates that the property of metal solvent obviously affects the bonding of C–N bonds, and the formation of C–N bonds is easier in Fe-based catalyst/solvent than that in Ni-based solvent at high NC environment.

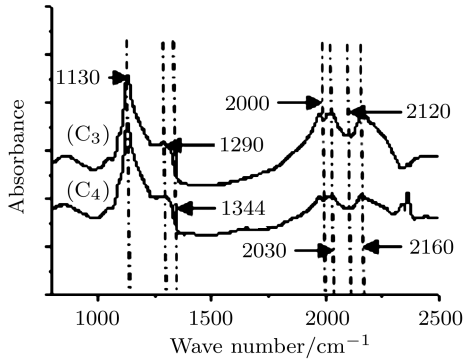


Fig. 5. The FTIR spectra of diamond synthesized by TGM heavily doped by NaN_3 (C_3) 0.6 wt.%; (C_4) 0.8 wt.%.

Table 1. Nitrogen concentration in diamond doped with different amount of additive NaN3.

sample	NaN_3 amount/wt.%	N_C/ppm
C_0	0	200–300
C_1	0.3	373–412
C_2	0.5	669–762
C_3	0.6	865–964
C_4	0.8	1214–1257

4. Conclusions

Diamond crystals containing different N_C are successfully synthesized, and the highest N_C can reach approximately 1214–1257 ppm, calculated by IR spectra. The maximum N_C doped in diamond is lower than that diamond synthesized with Fe-based as catalyst/solvent. This fact indicates that the property of metal solvent affects the bonding of C–N bonds, and the formation of C–N bonds is easier in Fe-based catalyst/solvent than that in Ni-based catalyst/solvent at high NC growth environment. It also finds that with increasing the content of additive NaN_3 doped in diamond-growing environment, the width of temperature growth region for high-quality diamond becomes narrower, and the morphology of diamond crystal is changed from cube-octahedral to octahedral at same temperature and pressure, and the growth rate is slowed down, nevertheless the N_C doped in diamond crystal increases.

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