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Regulation mechanism of catalyst structure on diamond crystal morphology under HPHT process*

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To elucidate the regulation mechanism of catalyst geometry structure to diamond growth, we establish three catalyst modes with different structures. The simulation results show that with the decrease of the protruding height of the catalyst, the low-temperature region gradually moves toward the center of the catalyst, which causes the distribution characteristics of the temperature and convection field in the catalyst to change. The temperature difference in vertical direction of the catalyst decreases gradually and increases in the horizontal direction, while the catalyst convection velocity has the same variation regularity in the corresponding directions. The variation of temperature difference and convection velocity lead the crystal growth rate in different crystal orientations to change, which directly affects the crystal morphology of the synthetic diamond. The simulation results are consistent with the experimental results, which shows the correctness of the theoretical rational analysis. This work is expected to be able to facilitate the understanding of catalyst structure regulation mechanism on diamond morphology and the providing of an important theoretical basis for the controllable growth of special crystal shape diamond under HPHT process.

Keywords: diamond, single crystal growth, high pressure and high temperature, crystal morphology

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1. Introduction

As a kind of ultimate functional material with many excellent physical and chemical properties, diamond has been widely used in industry, science and technology, national defense and many other fields.[1–10] High temperature and high pressure (HPHT) process based on temperature gradient method (TGM) is an effective way to obtain high-quality large single-crystal diamond.[11–24] For the HPHT preparation, the temperature gradient in molten catalyst is the main driving force for the growth of diamond, while the natural convection in the catalyst caused by the temperature gradient can effectively transport carbon atoms to the seed diamond surface.[20,23] Therefore, the temperature gradient and natural convection flow in the catalyst are significant factors that determine the crystal quality, morphology, and growth rate of the synthetic diamond.

The geometric structure of metal catalyst directly affects its characteristics of internal temperature and convection distribution. In our previous research,[25] we found that the physical field distributions of convex-shape catalyst and tabular-shape catalyst are significantly different from each other, which are suitable for the synthesis of diamond with different crystal morphologies. Moreover, our study also found that increasing the protrusion diameter of the convex catalyst can significantly increase the growth rate of synthetic diamond.[26] Therefore, the geometric structure of the catalyst will have an important effect on the growth of diamond. However, the influence and regulation mechanism of catalyst geometry structure on diamond growth are not completely clear at present, which needs further studying and exploring.

In this work, we optimize the catalyst structure and establish convex catalyst modes with different protruding heights to further explore the influence mechanism of structural variances on diamond growth. The temperature distribution and the convection distribution of the catalyst in diamond synthetic cavity are simulated by the finite element method (FEM). Through the analysis of numerical results, we find that with the decrease of the convex catalyst protruding height, the horizontal temperature difference increases and the vertical temperature difference decreases significantly. At the same time, the convection velocity increases in the horizontal direction and decreases in the vertical direction. The simulation results indicate that there are significant differences in the height-to-diameter ratio among the diamonds synthesized under different modes, which means that the synthesized diamond will have different crystal morphologies. The simulation results

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are confirmed in the diamond synthesizing experiment. The results of this study not only elucidate the regulation mechanism of the protruding height of convex catalyst on the growth of diamond, but also provide an important theoretical basis for the controllable growth of different morphology diamonds under HPHT process.

2. Simulation and experimental details

The schematic diagram of the assembly structure of the high-pressure apparatus, the synthetic sample assembly and the catalyst model are shown in Fig. 1. We established three convex catalyst modes with different convex heights as shown in Fig. 1(c). The convex heights of modes A, B, and C were 4 mm, 3 mm, and 2 mm respectively, while the other dimensions were exactly the same. The numerical simulations of temperature and convection fields of three models were based on the finite element method (FEM) through the electric-thermal-fluid coupling analysis in the ANSYS multi-field coupling software package. During the calculation, the same voltage, boundary conditions, and material parameters were applied to each mode. The temperature boundary for thermal analysis was set as follows: 30 °C for the cooling water temperature, and 50 °C for the bottom temperature of the six steel rings. The velocity boundary for fluid analysis was set as follows: symmetric constraints were applied to the symmetric surface of 1/4 mode, and the velocity vectors of the other areas were set to be $V_X = V_Y = V_Z = 0$. The voltage of the top and bottom steel rings were set to be 2.8 V and 0 V respectively. The material parameters used in the simulation were cited from other literature.[27–29]

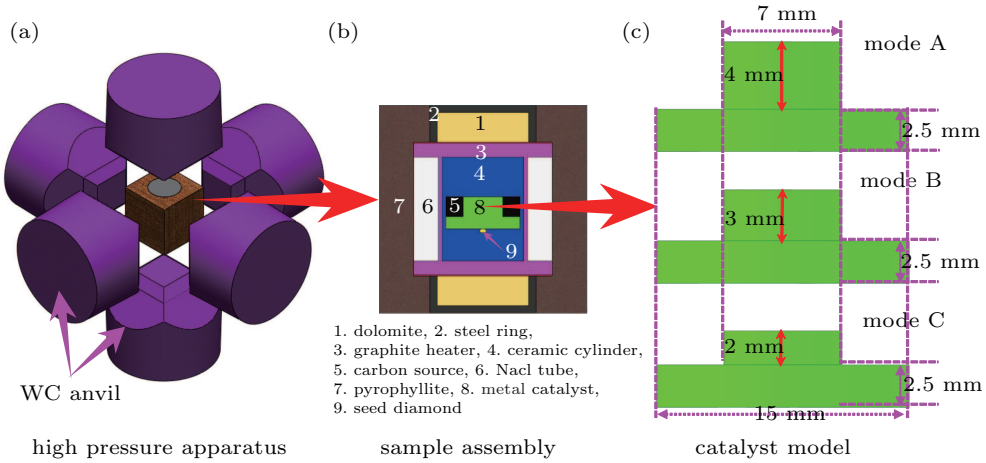


Fig. 1. (a) High-pressure apparatus for diamond synthesis, (b) diamond synthesizing assembly cavity, and (c) catalyst structure modes A, B, and C with different protruding heights.

The diamond synthesizing experiments were performed in the China-type cubic high-pressure apparatus (CHPA) with a sample assembly of 42 mm×42 mm×42 mm and using Fe–Ni alloy catalyst at 1300 °C and 5.7 GPa. It must be noted that before the HPHT treatment, the raw graphite powder was compressed into a carbon ring, and the convex catalyst structure was made of the solid $Fe_{64}Ni_{36}$ alloy catalyst wafers with different diameters. High purity graphite powder (99.9% purity) and the diamond with a {100} crystal surface of size 0.6 mm×0.6 mm were used as the carbon source and seed diamond, respectively. The synthetic pressure was estimated by oil press load, which had been calibrated based on the corresponding relations between the pressure-induced phase transitions of Bi, Tl, and Ba. The temperature near the seed diamond in synthesis process was measured by using a Pt-30%Rh/Pt-6%Rh thermocouple. After the synthesis experiments, a mixture solution of HNO_3 and H_2SO_4 was used to remove the impurities remaining on the surfaces of the collected diamonds. Optical microscope was employed to observe the morphology of synthetic diamond.

3. Results and discussion

In order to study the influence mechanism of catalyst structure on diamond crystal morphology, we establish three convex catalyst modes with different protruding heights. Their temperature and convection fields are simulated and analyzed by FEM. Figures 2(a)–2(c) and 2(d)–2(f) show the temperature and convection characteristic distribution results of modes A, B, and C. From the temperature results, we can first observe that the temperature field is symmetrically distributed, with the high temperature region contacting the carbon source and the low temperature region being located around the seed location. Then we can see that with the reduction of the convex catalyst protruding height, the temperature distribution characteristics of the catalyst protruding part change significantly. The distribution proportion of the yellow region in the middle begins to decrease, while the light green area begins to increase. According to the corresponding relationship between temperature and color bar, we can figure out that the temperature difference in the vertical direction of the catalyst decreases. As shown in Figs. 2(a)–2(c), the vertical temperature difference ΔT_Y^{A} is

63 °C in mode A, ΔT_Y^B is 61 °C in mode B, and ΔT_Y^C is 55 °C in mode C. In addition, the ΔT_X^A, ΔT_X^B, and ΔT_X^C in modes A, B, C are 53 °C, 54 °C, and 55 °C respectively, which indicate that the temperature difference in the horizontal direction slight increases with catalyst protruding height decreasing.

From the convection results as shown in Figs. 2(d)–2(f), we can observe that the distribution of convection field is also symmetrical. The higher convection velocity and strength regions are mainly concentrated above the seed, while regions near the carbon source at the edge of the catalyst are weak. According to the corresponding relationship between convection velocity and color bar, we can see that the convection velocity decreases from 11.8×10^{-6} m/s to 9.8×10^{-6} m/s as shown in Figs. 2(d)–2(f). In addition, we can also observe that with the decrease of the catalyst height, the catalyst convection intensity at the convex position increases obviously, which indicates that more carbon sources will be consumed as indicated in Fig. 2(f). Because regions with strong convection intensity represent the areas where carbon sources will be consumed preferentially.

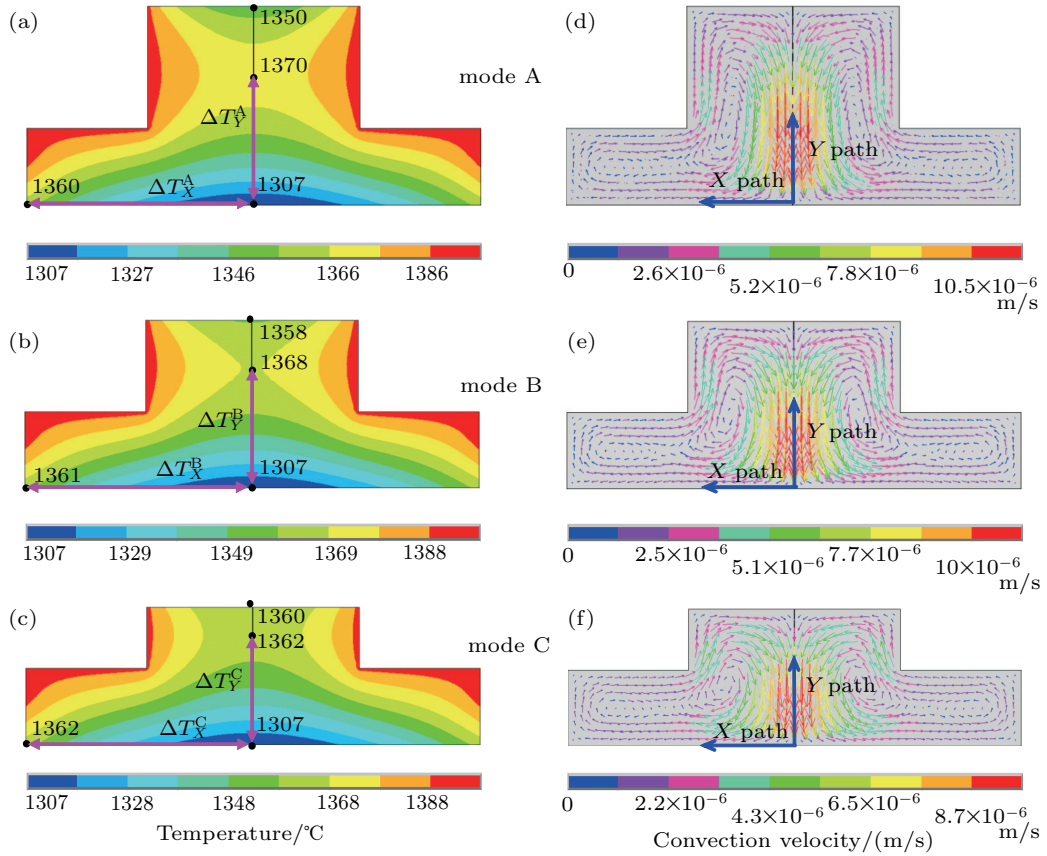


Fig. 2. Numerical simulation results of (a)–(c) temperature and (d)–(f) convection of convex catalyst of modes A, B, and C.

Through the above observation, we can figure out that the change of the catalyst convex height can influence the distribution characteristic of the temperature field and the convection field inside the catalyst, which will have an important influence on the growth of the synthetic diamond. The change of temperature difference and convection velocity in the vertical and horizontal direction in the catalyst will directly determine the diamond morphology. To compare the changes of temperature difference and convection velocity more intuitively, we choose X (horizontal direction) and Y (vertical direction) paths as shown in Fig. 3.

Figures 3(a) and 3(b) show the temperatures along the X path and the Y path in modes A, B, and C. There is a slight change in temperature along the X path, while a very significant change in temperature along the Y path. It can be seen that the temperature difference along Y path in mode C is significantly smaller than that in mode A. Through the comparison between temperatures along X and Y paths, it can also be found that the vertical temperature difference in mode C is the smallest, while the horizontal temperature difference is the largest. Figures 3(c) and 3(d) show the convection velocity along X and Y paths in modes A, B, and C. we can see that mode C has the maximum convection velocity along X path, but the minimum convection velocity along Y path. In contrast, mode A has a minimum convection velocity along X path and a maximum convection velocity along Y path. This indicates that the horizontal and vertical convection velocities in the catalyst have reciprocal variation with the decrease of the protruding height of the catalyst.

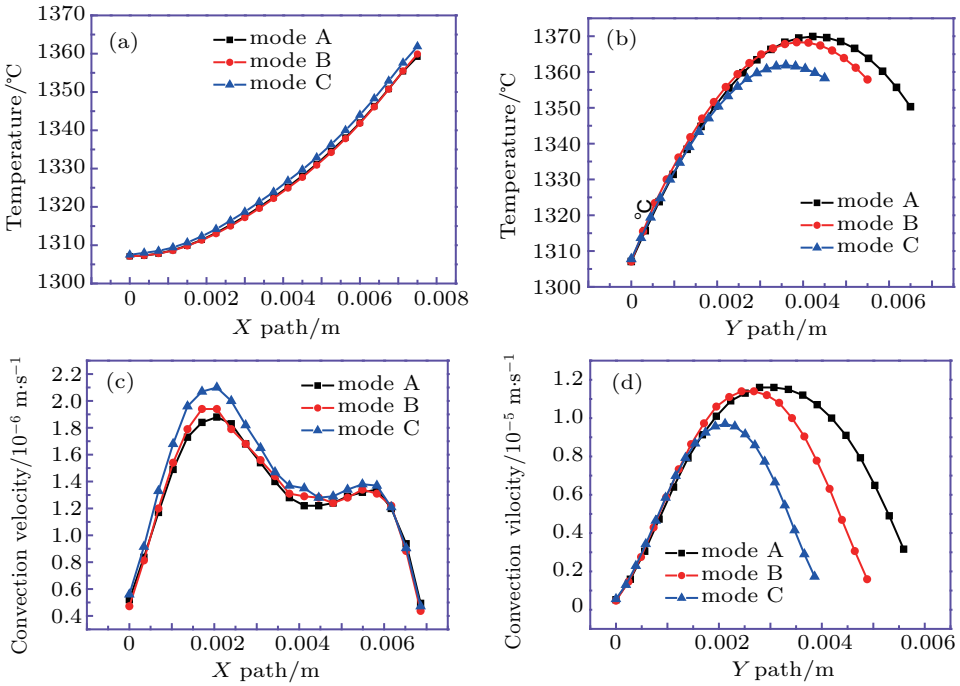


Fig. 3. (a) Temperatures along (a) *X* path and (b) *Y* path in modes A, B, and C. Convection velocity along (c) *X* path and (d) *Y* path in modes A, B, and C.

According to the melt-solvent theory, the temperature difference between the carbon source and diamond seed is the main driving force for diamond growth. Carbon atoms can be transported from carbon source to seed by temperature difference. Moreover, the solubility of carbon in the catalyst solvent depends on temperature. The higher the temperature, the greater the carbon solubility is. The dissolved carbon in the molten metal catalyst is transported to the seed surface by catalyst convection flow, and the magnitude of the convection velocity represents the quantity of carbon transported to the seed, and the more the transported carbon, the faster the growth of diamond is. Therefore, when the temperature gradient and convection velocity are different in the direction of each crystal face of diamond, the growth velocity in the corresponding direction will be inconsistent, which will affect the crystal morphology of synthetic diamond. From the temperature and convection results above, we can judge that the diamonds synthsized by using three modes will have different growth rates in the vertical and horizontal direction: the diamond in mode A has a maximum growth rate in the vertical direction and a minimum growth rate in the horizontal direction, while the growth rate of diamond in mode C is just the opposite to the scenario in mode A. The results indicate that the diamond synthesized by using modes A, B, and C may have different height-to-diameter ratios.

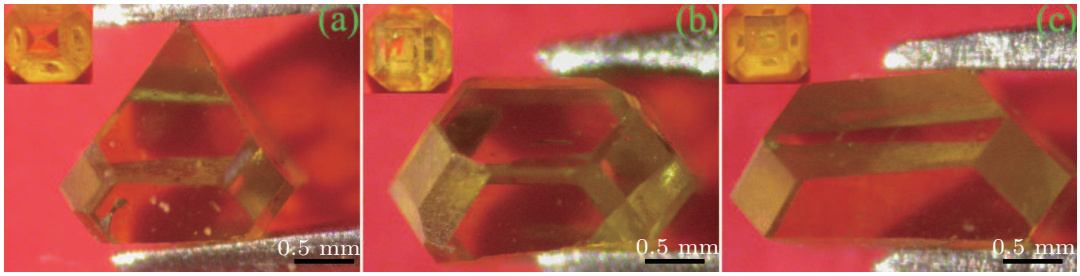


Fig. 4. Diamonds synthesized on CHPA with Fe–Ni catalyst under 5.7 GPa and 1310 °C for (a) mode A, (b) mode B, and (c) mode C.

To verify the judgement based on numerical results, we establish diamond synthetic experiments on CHPA with $Fe_{64}Ni_{36}$ alloy catalyst under a temperature of 1300 °C and pressure of 5.7 GPa. Three modes are used to synthesize diamond under the same conditions, and the synthesis time is 24 h. Figure 4 shows the diamonds synthesized by using modes A, B, and C. We can clearly observe from the Fig. 4 that the diamonds synthesized under modes A, B, and C have obvious different height-to-diameter ratios. The crystal synthesized in mode A has the smallest diameter but the largest height, while the crystal synthesized in mode C has the largest diameter but the smallest height. Synthetic experimental results are completely consistent with our predictions based on the numerical results. In addition, there are no obvious inclu-

sions nor burrs in the synthesized diamond, indicating that the synthesized diamond has good crystal quality. The numerical and experimental results show that the crystal morphology of diamond can be regulated effectively by optimizing the geometric structure of the catalyst.

4. Conclusions and perspectives

In this work, we design three different catalyst structure modes to illuminate the regulating mechanism of catalyst structure on diamond crystal morphology. The temperature and convection field in the catalyst are simulated by FEM, and the diamond synthesis experiment is carried out at 1300 °C and 5.7 GPa with $Fe_{64}Ni_{36}$ alloy catalyst. According to the simulation and experimental results, we can draw tsome conclusions below.

(i) The distribution characteristics of the temperature and convection field in the catalyst change obviously with geometric configuration, the compression of the catalyst convex height leads the low temperature to transfer inward, while the convection strength increases but the convection velocity decreases.

(ii) With the decrease of the convex height of the catalyst, the temperature difference in the vertical direction of the catalyst decreases, while the temperature difference in the horizontal direction increases. Meanwhile, the convection velocity has the same variation regularity.

(iii) The change of temperature difference and convection velocity in the vertical and horizontal directions of the catalyst lead to the growth rate in the corresponding direction to change, which further affects the crystal morphology of the synthetic diamond.

According to the research results in this paper and our previous studies, we can summarize the influence mechanism of geometric configuration of convex shape catalyst on the growth of diamond single crystal as follows.

Firstly, with the catalyst protrusion height unchanged, the change of the protrusion diameter of the catalyst has an important effect on the growth rate of diamond. The increase of protrusion diameter of the convex shape catalyst can significantly increase the growth rate of diamond.

Secondly, with catalyst protrusion diameter unchanged, the change of the protrusion height of the catalyst has an important effect on diamond morphology. The decrease of the catalyst protrusion height will significantly affect the height-to-diameter ratio of synthetic diamond.

References

[1] Barletta M, Rubino G, Valle R and Polini R 2012 *ACS Appl. Mater. Interfaces* **4** 694

[2] Masuya S, Hanada K, Oshima T, Sumiya H and Kasu M 2017 *Diamond Relat. Mater* **75** 155

[3] Pezzagna S, Rogalla D, Wildanger D, Meijer J and Zaitsev A 2011 *New J. Phys.* **13** 035024

[4] Liu X B, Jia X P, Zhang Z F, Li Y, Hu M H, Zhou Z X and Ma H A 2011 *Cryst. Growth.* **11** 3844

[5] Kanda H, Akaishi M and Yamaoka S 1999 *Diamond Relat. Mater.* **8** 1441

[6] Fuchs G D, Burkard G, Klimov P V and Awschalom D D 2011 *Nat. Phys.* **7** 789

[7] Achatz P, Williams O A, Bruno P, Gruen D M, Garrido J A and Stutzmann M 2006 *Phys. Rev. B* **74** 155429

[8] Chen Y L, Guo H, Li W W, Wu D J, Zhu Q, Zhao B B, Wang L, Zhang Y, Zhao Y, Liu W Y, Du F F, Tang J and Liu J 2018 *Appl. Phys. Express* **11** 123001

[9] Qin Y K, Xiao H Y, Liu L N, Sun R R, Hu Q B, Bao Z G, Zhang Y S, Li S S and Jia X P 2019 *Acta Phys. Sin.* **68** 020701 (in Chinese)

[10] Maze J R, Cappellaro P, Childress L, Dutt M V G, Hodges J S, Hong S, Jiang L, Stanwix P L, Taylor J M, Togan E, Zibrov A S, Hemmer P, Yacoby A, Walsworth R L and Lukin M D 2009 *Adv. Opt. Concepts Quantum Comput. Memory Commun. II* **7225** 722509

[11] Palyanov Y N, Kupriyanov I N, Borzdov Y M, Khokhryakov A F and Surovtsev N V 2016 *Cryst. Growth.* **16** 3510

[12] Fang C, Jia X P, Chen N, Li Y D, Guo L S, Chen L C, Ma H A and Liu X B 2016 *J. Cryst. Growth* **436** 36

[13] Han F, Li S S, Jia X F, Chen W Q, Su T C, Hu M H, Yu K P, Wang J K, Wu Y M, Ma H A and Jia X P 2019 *Chin. Phys. B* **28** 028103

[14] Chen L C, Miao X Y, He X M, Guo L S, Fang S, Wang Y, Wang Z K, Fang C, Ma H A and Jia X P 2018 *J. Cryst. Growth* **498** 67

[15] Wang J K, Li S S, Jiang Q W, Song Y L, Yu K P, Han F, Su T C, Hu M H, Hu Q, Ma H A, Jia X P and Xiao H Y 2018 *Chin. Phys. B* **27** 088102

[16] Sumiya H and Tamasaku K 2012 *Jpn. J. Appl. Phys.* **51** 090102

[17] Xiao H Y, Qin Y K, Liu L N, Bao Z G, Tang C J, Sun R R, Zhang Y S, Li S S and Jia X P 2018 *Acta Phys. Sin.* **67** 140702 (in Chinese)

[18] Kovalenko T V, Lysakovskyi V V, Kvasnytsya V M, Ivakhnenko S O, Suprun O M and Burchenia A V 2019 *J. Cryst. Growth* **507** 327

[19] Wang J Z, Li S S, Su T C, Hu M H, Hu Q, Wu Y M, Wang J K, Han F, Yu K P, Gao G J, Guo M M, Jia X P, Ma H A and Xiao H Y 2018 *Acta Phys. Sin.* **67** 168101 (in Chinese)

[20] Tatsumi N, Tamasaku K, Ito T and Sumiya H 2017 *J. Cryst. Growth* **458** 27

[21] Burns R C, Hansen J O, Spits R A, Sibanda M, Welbourn C M and Welch D L 1999 *Diamond Relat. Mater.* **8** 1433

[22] Fan X H, Xu B, Niu Z, Zhai T G and Tian B 2012 *Chin. Phys. Lett.* **29** 048102

[23] Li Y, Li Y D, Wang Y, Zhang J, Song M S, She Y C and Chen X Z 2018 *CrystEngComm* **20** 4127

[24] Shiryaev A A, Zolotov D A, Suprun O M, Ivakhnenko S A, Averin A A, Buzmakov A V, Lysakovskyi V V, Dyachkova I G and Asadchikov V E 2018 *CrystEngComm* **20** 7700

[25] Li Y D, Jia X P, Chen N, Chen L C, Guo L S, Wang C X, Li G and Ma H A 2017 *CrystEngComm* **19** 137

[26] Li Y D, Wang C X, Chen L C, Guo L S, Zhang Z F, Fang C and Ma H A 2019 *RSC Adv.* **9** 32205

[27] Li R, Ding M M and Shi T F 2018 *J. Cryst. Growth* **491** 111

[28] Han Q G, Li M Z, Jia X P, Ma H A and Li Y F 2011 *Diamond Relat. Mater.* **20** 969

[29] Li R, Wang Y F, Liu J, Jia X P and Ma H A 2020 *Diamond Relat. Mater.* **101** 107593