


Article

Spectroscopic Study of the 3107 cm⁻¹ and 3143 cm⁻¹ H-Related Defects in Type Ib Diamonds

Zhonghua Song^{1,*} , Jun Su¹, Wenfang Zhu², Taijin Lu¹, Yang Wang³ and Shengmei He⁴¹ National Gemstone Testing Center, Beijing 100013, China² National Gemstone Testing Center Shenzhen Laboratory, Shenzhen 518020, China³ National Gemstone Testing Center Guangzhou Laboratory, Guangzhou 511400, China⁴ National Gemstone Testing Center Yunnan Laboratory, Kunming 650217, China

* Correspondence: songzh@ngtc.com.cn

Abstract: Hydrogen-related infrared absorption bands in natural diamonds have been extensively investigated and widely used to identify natural, treated, and synthetic diamonds grown by high pressure and high temperature (HPHT) and chemical vapor deposition (CVD) techniques. However, the evolutionary behavior of the hydrogen-related defects and the relationship between the hydrogen-related and nitrogen-related defects in natural and HPHT-treated Ib diamonds are unclear. In this article, the hydrogen-related defects, particularly the infrared absorption bands of 3107 cm⁻¹ and 3143 cm⁻¹ in natural type Ib diamonds and HPHT-treated natural diamonds, were systematically investigated using spectroscopic techniques. It was found that the 1405 cm⁻¹ absorption intensity was directly proportional to the 3107 cm⁻¹ absorption intensity; the 3143 cm⁻¹ absorption intensity increased with the increase in the 3107 cm⁻¹ absorption intensity, but there was no strict linear relationship between them. The 3143 cm⁻¹ band was not only related to the intensity of the 3107 cm⁻¹ but also related to the value of N_C/N_A in natural diamonds. When the value of N_C/N_A was less than one, the 3143 cm⁻¹ band was more pronounced. After high-temperature annealing, the absorption intensities of the 3107 cm⁻¹ and 3143 cm⁻¹ in natural type Ib diamonds became stronger. However, in HPHT synthetic diamonds, only a 3107 cm⁻¹ defect was introduced with the increase in the A centers in the diamonds. The difference and the detectability of the 3143 cm⁻¹ and 3107 cm⁻¹ bands investigated could be efficiently used to identify natural type Ib diamonds from their counterparts, including the synthetic diamonds and the HPHT-treated diamonds.

Keywords: hydrogen; nitrogen; natural Ib diamond; 3107 cm⁻¹ IR band; 3143 cm⁻¹ IR band

Citation: Song, Z.; Su, J.; Zhu, W.; Lu, T.; Wang, Y.; He, S. Spectroscopic Study of the 3107 cm⁻¹ and 3143 cm⁻¹ H-Related Defects in Type Ib Diamonds. *Crystals* **2022**, *12*, 1352. <https://doi.org/10.3390/cryst12101352>

Academic Editor: Giuseppe Prestopino

Received: 25 August 2022

Accepted: 22 September 2022

Published: 25 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Nitrogen (N), the most common impurity in diamonds, is used to classify diamonds into different types. Based on the presence or absence of nitrogen and boron impurities and their configurations in the diamond lattice, diamonds are divided into type I and type II [1]. Type I diamonds are further subdivided into type Ia and type Ib. Type Ia diamonds contain aggregated N impurities—including A centers (IaA), which consist of pairs of N atoms, and B centers (IaB), which are made up of four N atoms around a vacancy (V). Type Ib diamonds contain isolated nitrogen atoms (C center). Type II diamonds are nitrogen-free and can be further subdivided into type IIa and type IIb depending on the presence of boron. Type IIa stones lack boron and type IIb diamonds contain boron as revealed by infrared (IR) spectroscopy. Most natural type Ia diamonds contain a mixture of the A and B forms of nitrogen. These are normally described as “type IaA/B”. Moreover, many natural diamonds classified as type Ib do have some (perhaps most) of the nitrogen in the A form normally named type Ib/IaA [1].

The concentration of hydrogen in different types of natural diamonds and high-pressure–high-temperature (HPHT) grown and chemical vapor deposition (CVD) grown

diamonds has been determined using ion beam analysis techniques such as nuclear reaction analysis (NRA) and elastic recoil detection analysis (EDRA) [2]. At present, the relatively clear hydrogen defect structure is NVH (nitrogen-vacancy-hydrogen), which mainly exists in CVD synthetic diamonds [3]. Vacancy-hydrogen and divacancy-hydrogen complexes can also be detected in the electron paramagnetic resonance (EPR) spectrum [4,5]. A hydrogen defect with a vibrational mode at 3107 cm^{-1} has attracted much attention as it occurs in almost all type Ia (containing aggregated nitrogen) natural diamonds [6]. Previously, it has been considered that 3107 cm^{-1} is caused by C–H (carbon–hydrogen) stretching vibration, 1405 cm^{-1} is the result of C–H bending vibration, and the C–H structure only produces absorption in the infrared region with no absorption in the ultraviolet and visible region [7]. The follow-up studies proved that 3107 cm^{-1} is not only related to hydrogen but also related to nitrogen, and its structure is actually a VN_3H (vacancy-three nitrogen-hydrogen) structure [8]. However, the structure of hydrogen-containing defects in natural diamonds is mainly unknown, such as those hydrogen-related defects detected in the mid-infrared regions, $3143, 3153, 3189, 3236, 3310, 3342, 3393\text{ cm}^{-1}$, etc. [6].

It was believed that the 3107 cm^{-1} is a defect only existing in natural diamonds, which will not appear in HPHT or CVD synthetic diamonds [9]. However, with further study of synthetic diamonds [10–12], it is found that when synthetic diamonds (including HPHT and CVD) are treated under high-pressure and high-temperature conditions, the 3107 cm^{-1} defect will be established. The defect is introduced at around $2100\text{ }^\circ\text{C}$ in the HPHT synthetic type Ib (isolated nitrogen) diamonds [10]. In CVD diamonds, hydrogen-related absorption peaks observed in the as-grown material, disappear after HPHT annealing, while the 3107 cm^{-1} defect is formed around $2200\text{ }^\circ\text{C}$ [12]. This indicates that the 3107 cm^{-1} defect is more stable than other hydrogen-containing defects in as-grown CVD diamonds.

As can be seen in the infrared absorption spectra of HPHT synthetic and the natural type Ib diamonds we tested, the 3107 cm^{-1} defects do not form at the early stage of the diamond growth while the nitrogen impurities are mainly in the form of single substitutional. However, the hydrogen-related defects with absorption (such as the 3107 cm^{-1}) in the infrared region begin to occur when the nitrogen aggregates. In this paper, the 3107 cm^{-1} and 3143 cm^{-1} defects in type Ib diamonds have been investigated through the analysis of the infrared spectra of a large number of natural type Ib diamonds, HPHT-treated natural, and synthetic Ib diamonds.

2. Materials and Methods

Within this study, we examined 48 natural faceted diamonds weighing 0.01 to 0.15 ct with C centers detectable by infrared absorption spectroscopy, and 2 faceted HPHT-grown type Ib brownish yellow diamonds. The natural diamonds were purchased from diamond merchants and the synthetic diamond were donated by Zhengzhou Sino-Crystal Diamond Co., Ltd. (Zhengzhou, China). Most of the natural faceted diamonds are too small to observe the color distribution and strain patterns. The 0.15 ct diamond displays even color distribution when checked under a $20\times$ microscope. In this study, the term “type Ib” refers to all diamonds containing only single nitrogen defects.

Three natural Ib-IaA samples and two HPHT-grown type Ib diamonds were HPHT-treated under different temperatures and pressure (Table 1). The HPHT-grown and HPHT-treated experiments were performed using a China-type cubic-anvil high-pressure apparatus.

Table 1. Detailed information on treated conditions.

Sample No.	Origin	N_A (ppm)	N_C (ppm)	First Treatment			Second Treatment		
				T ($^\circ\text{C}$)	P (GPa)	Treated Time	T ($^\circ\text{C}$)	P (GPa)	Treated Time
Diam10703	Natural	22	66	2200	7–8	15 min	–	–	–
Diam10704	Natural	56	85	1900	5–6	15 min	2200	7–8	15 min
Diam10715	Natural	108	70	2200	7–8	15 min	2400	7–8	15 min
Diap20593	HPHT Synthetic	0	123	1900	5–6	15 min	2400	7–8	15 min
Diap20653	HPHT Synthetic	0	154	2200	7–8	15 min	2400	7–8	15 min

Fourier-transform infrared (FTIR) spectroscopy was performed using a Thermo Nicolet 6700 spectrometer in the range of 6000–400 cm^{-1} (128 scans at a resolution of 2 cm^{-1}) at room temperature. A KBr beam splitter was used, and a 6 \times beam condenser focused the incident beam on the round faceted samples. For comparison purposes and for calculation of the absorption coefficients, each infrared spectrum was normalized according to 1 cm diamond thickness, where the absorption coefficient is 11.94 cm^{-1} at the intrinsic absorption at 1995 cm^{-1} [13]. The absorption coefficient at 1405 (μ 1405), 3107 (μ 3107), and 3143 (μ 3143) cm^{-1} can be so obtained through the peak height tool of the Omnic software. Nitrogen concentrations were determined from the absorption coefficient values at particular wavenumber positions for the various components and were mainly calculated using the software caxbd97n developed by Dr. David Fisher of De Beers Group according to the theory proposed in the reference [14–16].

3. Results and Discussion

3.1. Hydrogen-Related Defects in Ib Natural Diamond

Figure 1 shows the typical natural diamonds with different nitrogen concentrations represented for the main type studied in this paper. From the top line to the bottom, the absorption coefficient at 1282 cm^{-1} (A center) and 3107 cm^{-1} increases gradually, while the C center (1130 cm^{-1}) decreases. According to the relative content of C centers (isolated nitrogen) and A centers (aggregates of two nitrogen atoms), we classified them as type Ib, Ib-IaA, IaA-Ib, and so on [17]. The intensity of hydrogen-related absorption, especially at 3107 cm^{-1} and 1405 cm^{-1} , also varies with nitrogen content and type (Figure 1).

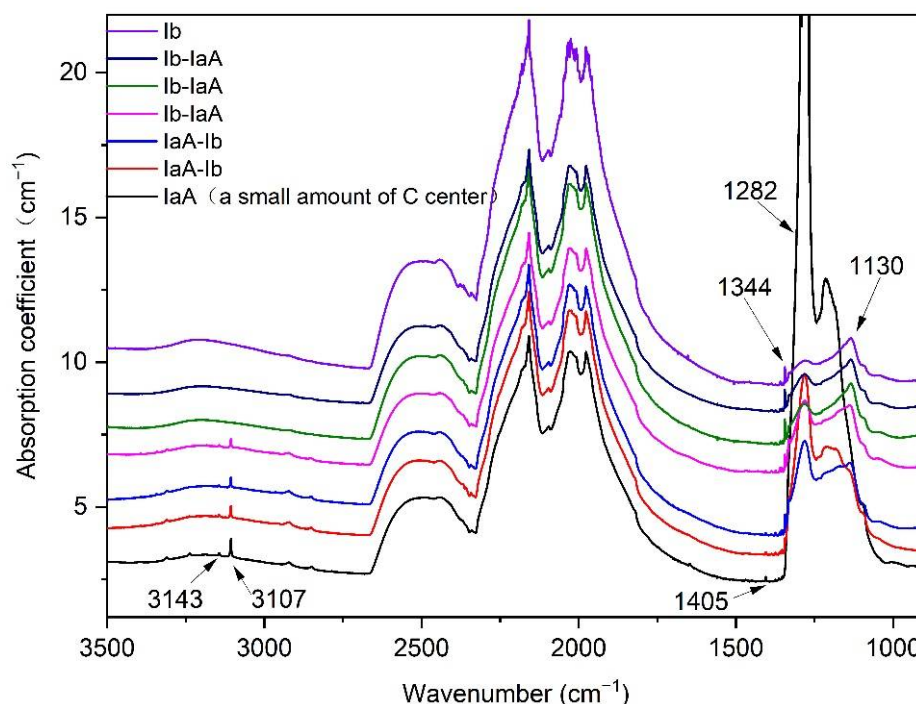


Figure 1. The absorption spectrum of type I natural diamonds with different nitrogen concentrations.

The nitrogen contents (N_C is the isolated nitrogen content, N_A is the A defect content) for the investigated diamonds were calculated using software caxbd97n, where the absorption coefficient at 3107 cm^{-1} (μ 3107) against the N_C/N_A was plotted in Figure 2. It revealed that the 3107 cm^{-1} defect is strongly influenced by the value N_C/N_A . When $N_C/N_A > 3$, in other words, the isolated nitrogen is dominant in diamonds and the diamonds have almost no hydrogen-related absorption. Generally, no absorption related to hydrogen in the infrared region can be detected in a type Ib diamond [11,18]. When A center is dominant in diamonds and C center content is relatively small, that is when $N_C/N_A < 1$, the 3107 cm^{-1}

absorption is apparent. The 3107 cm^{-1} defect is always created in the same temperature range as the N3 (three nitrogen atoms on a {111} plane, surrounding a common vacancy [1]) and B centers are formed following HPHT treatment of synthetic diamonds [8]. When the single nitrogen is dominant, the aggregate nitrogen is negligible, and no 3107 cm^{-1} defects are detected. The peak at 3107 cm^{-1} is more often found in diamonds or regions with relatively low single nitrogen content [19]. With nitrogen aggregation in diamonds, the A nitrogen content increases continuously. When the content of A nitrogen is relatively small, the 3107 cm^{-1} defect cannot be detected in diamonds. With the A nitrogen content gradually increasing, the absorption intensity of the 3107 cm^{-1} defect becomes stronger, implying that B nitrogen or N3 center may be generated in the aggregation process of C nitrogen to A nitrogen, although no B centers are detected in the IR spectra.

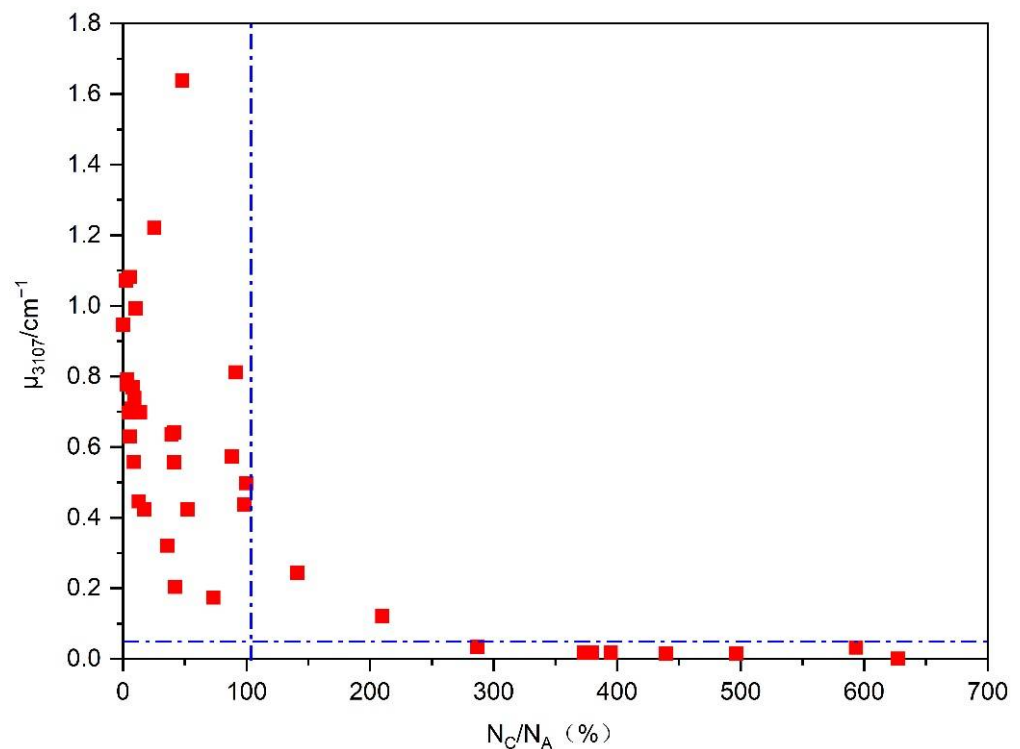


Figure 2. Relations among the concentration of single nitrogen, aggregated nitrogen and the intensity of 3107 cm^{-1} optical centers in natural type Ib diamond. When the ratio of N_C/N_A is less than 1 (the left areas of the vertical dash-dotted line), the 3107 cm^{-1} absorption is evident. When the ratio of N_C/N_A is greater than 3, the 3107 cm^{-1} absorption coefficient is less than 0.05 cm^{-1} (region below the horizontal dash-dot line).

The 1405 cm^{-1} optical center has always been considered as the same structure as the 3107 cm^{-1} with a different vibration mode. The 3107 cm^{-1} defect has been assigned to a C–H stretch vibration, while the 1405 cm^{-1} has been assigned to a bend vibration [10]. Figure 3 shows that the absorption coefficient at 1405 cm^{-1} (μ_{1405}) is plotted as a function of the absorption coefficient at 3107 cm^{-1} . Through the automatic fitting method from the data analysis software of Origin, we found that the absorption coefficient at 3107 (μ_{3107}) and 1405 cm^{-1} (μ_{1405}) has a good linear relationship as $\mu_{1405} = 0.23 \times \mu_{3107}$. The absorption coefficient of 1405 cm^{-1} is only about a quarter of that of 3107 cm^{-1} . Therefore, when the 3107 cm^{-1} peak is very weak, the 1405 cm^{-1} is almost invisible [10]. The ratio of normalized peak areas of the 3107 cm^{-1} and 1405 cm^{-1} peaks were also calculated (see Supplementary Materials, Figure S1). The average ratio of these values is 5.26, similar to the value of 5.21 mentioned in [7]. A correlation between 1405 and 3107 cm^{-1} was previously demonstrated in the early investigation of type Ia [7,20] and fancy white color and another type IaB natural diamonds [21]. The linear relationship between 3107 and

1405 cm^{-1} likely depends on the overall amount of aggregated nitrogen and hydrogen in those diamonds [21].

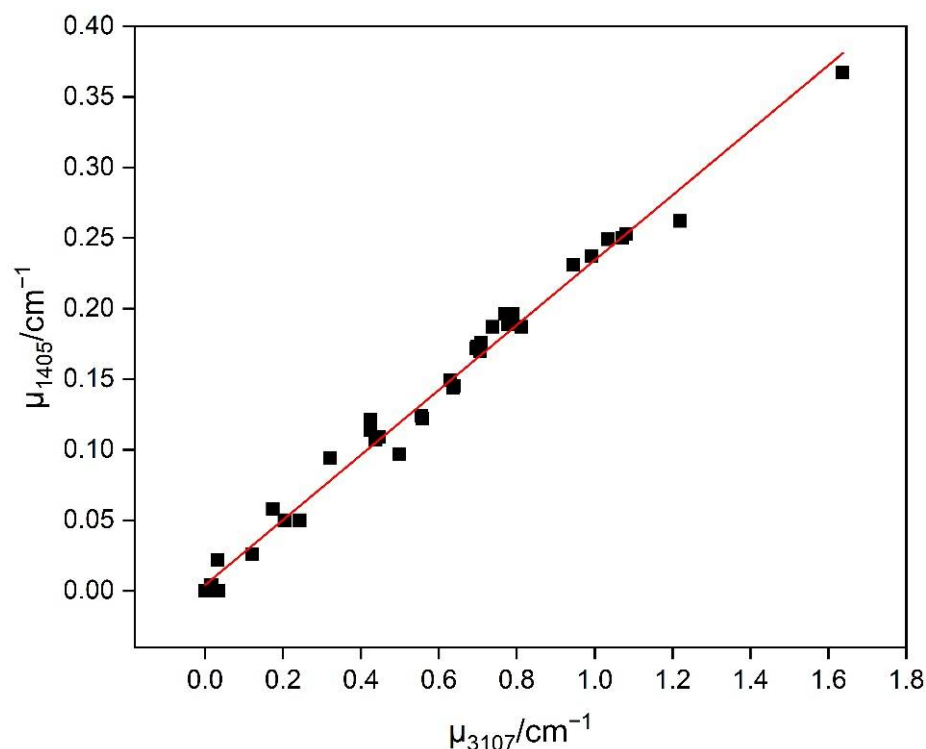


Figure 3. μ_{1405} as a function of μ_{3107} , the gradient is about 0.23, and the data displayed here are calculated from 38 natural diamond samples containing isolated nitrogen we studied, which can detect an obvious 3107 cm^{-1} absorption line.

The relationship between 3107 cm^{-1} and 3143 cm^{-1} is shown in Figures 4 and S2, from which we know there is no strict linear relationship between them. The absorption intensity of 3143 cm^{-1} is much weaker than that of 3107 cm^{-1} . Generally, the stronger the absorption of 3107 cm^{-1} , the stronger the absorption of 3143 cm^{-1} . As can be seen in Figures 4 and S2, there is no 3143 cm^{-1} defect when there is no 3107 or extremely weak 3107 cm^{-1} . If the 3143 cm^{-1} absorption is present in the diamond, there must be a 3107 cm^{-1} absorption peak. The existence of a 3107 cm^{-1} absorption peak is necessary but not a sufficient condition for the emergence of a 3143 cm^{-1} absorption peak. In type Ia Cape diamonds, there is a pronounced 3107 cm^{-1} peak, but no 3143 cm^{-1} peak [7,20], which further supports the above statement.

The 3143 cm^{-1} defect is related to single nitrogen and hydrogen and occurs only in diamonds containing isolated nitrogen [7,22]. However, the existence of isolated nitrogen is a necessary but not sufficient condition for 3143 cm^{-1} absorptions. As in Figure 5, when the value of N_C/N_A is relatively larger than 1.0, that is, the content of single nitrogen is greater than that of A nitrogen, the absorption at 3143 cm^{-1} is very weak. When the content of isolated nitrogen in the diamond is three times higher than A nitrogen, there is no absorption at 3143 cm^{-1} . When $N_C/N_A < 1$, the C nitrogen content is less than the A nitrogen content, and a noticeable peak at 3143 cm^{-1} can be detected.

No matter the peaks of 3143 or 3107 cm^{-1} , they have no linear relationship with the total content of nitrogen (Figure S3), nor with the concentration of A nitrogen or C nitrogen (Figures S4 and S5). However, in the diamonds containing high-concentration aggregated nitrogen, the 3107 cm^{-1} peak is more pronounced if it exists.

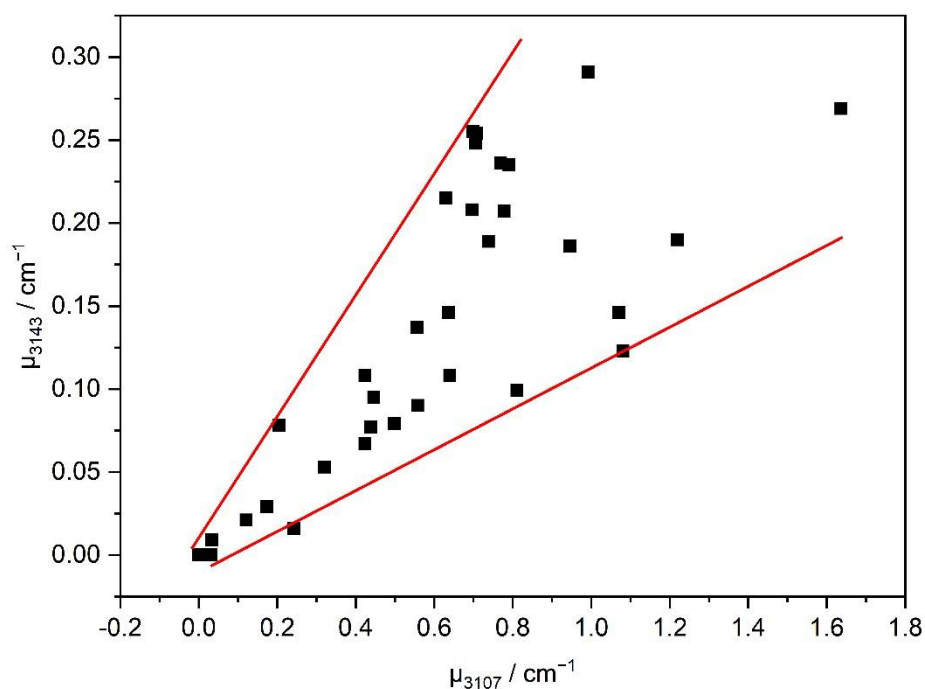


Figure 4. Variation of the absorption coefficient at 3107 cm^{-1} and 3143 cm^{-1} from 35 natural type Ib diamond samples containing isolated nitrogen we studied, which can detect an obvious 3143 cm^{-1} absorption line.

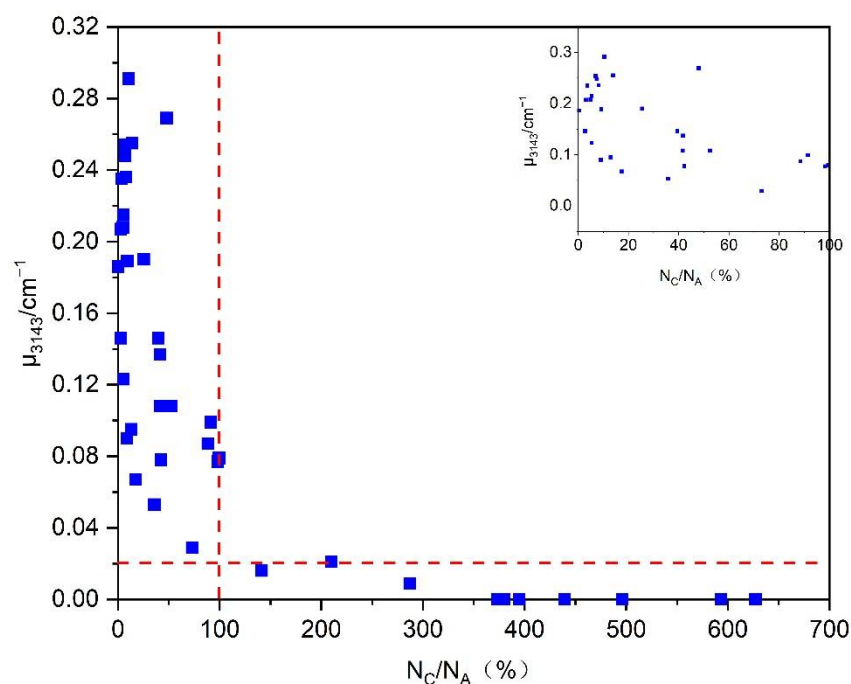


Figure 5. When the ratio of N_C/N_A is less than 1 (the left areas of the vertical dash line), the 3143 cm^{-1} absorption is more prominent. When the ratio of N_C/N_A is greater than 3, the 3143 cm^{-1} absorption coefficient is less than 0.05 cm^{-1} (below the horizontal dash line).

3.2. Hydrogen-Related Defects in HPHT-Treated Type Ib Natural Diamonds

When three natural type Ib/IaA diamonds were treated from brownish yellow to orangey yellow at high-pressure and high-temperature conditions (Figure S6), the intensity of the hydrogen-related absorption at 3107 and 3143 cm^{-1} in the infrared region increased significantly. After annealing at $2200\text{ }^\circ\text{C}$, the strength of the 3107 cm^{-1} absorptions increased

significantly (Figures 6 and 7), while the 3143 cm^{-1} had a relatively minor enhancement. For the sample of Diam10703 with high-isolated nitrogen content ($N_C/N_A \approx 3$), there are no absorption at 3143 cm^{-1} and very weak absorption at 3107 cm^{-1} (absorption coefficient is 0.016 cm^{-1}) before treatment. When annealed at the temperature of $2200\text{ }^\circ\text{C}$, with the aggregation of more isolated nitrogen into the A defect (that is, the increasing in the content of A nitrogen), the strength of the 3107 cm^{-1} absorption is obviously enhanced [13], and a weak but obvious absorption at 3143 cm^{-1} appeared in the sample of Diam10703 (Figure 7). We can draw the same conclusion from the other two samples of Diam10704 and 10715 (Figure 7), and further prove that there is a certain relationship between the 3143 and the 3107 cm^{-1} absorptions and the nitrogen form concluded from 3.1.

After high-temperature annealing, most noteworthy is the creation of a quite distinct peak at 3157 (3156.8) cm^{-1} in all three samples (Figure 7). The 3157 cm^{-1} absorption has never been reported in natural diamonds before, and we just detected it in several natural type IaA diamonds containing very little nitrogen. Hainschwang et al. [23] reported that the 3156 cm^{-1} peak is related to hydrogen and produced under HPHT annealing conditions in the FTIR spectra of CO_2 and “Pseudo- CO_2 ” diamonds. Compared with the 3157 cm^{-1} in this article, they may indicate the same defect.

3.3. Hydrogen-Related Defects in HPHT-Treated Type Ib Synthetic Diamonds

The HPHT as-grown synthetic diamonds are always type Ib and contain negligible aggregated nitrogen [24]. No optical feature associated with the hydrogen in the HPHT as-grown crystals has been identified to date [10,18]. However, when as-grown synthetic Ib diamonds were annealed at a temperature above $2100\text{ }^\circ\text{C}$, a weak absorption line at 3107 cm^{-1} formed [10]. Figure 8 compares the infrared absorption spectra of the HPHT synthetic diamond samples after the two HPHT treatments. Before treatment, the sample contained isolated nitrogen; no aggregated nitrogen or 3107 cm^{-1} absorptions were detected. After annealing at a temperature of $1900\text{ }^\circ\text{C}$, a small amount of single nitrogen aggregated to A nitrogen ($N_A \approx 22\text{ ppm}$), but no absorption was produced at 3107 cm^{-1} . Annealing at a temperature of $2200\text{ }^\circ\text{C}$ finally formed a very weak absorption line at 3107 cm^{-1} , with an absorption coefficient of 0.01 cm^{-1} . Although hydrogen, which may be initially trapped in an optically inactive state during crystal growth, is necessary for forming the 3107 cm^{-1} centers, the high-temperature annealing excess of $2100\text{ }^\circ\text{C}$ may be the main deciding factor [10]. At such a high temperature, more aggregated nitrogen such as A, B, and N3 centers are formed simultaneously [25].

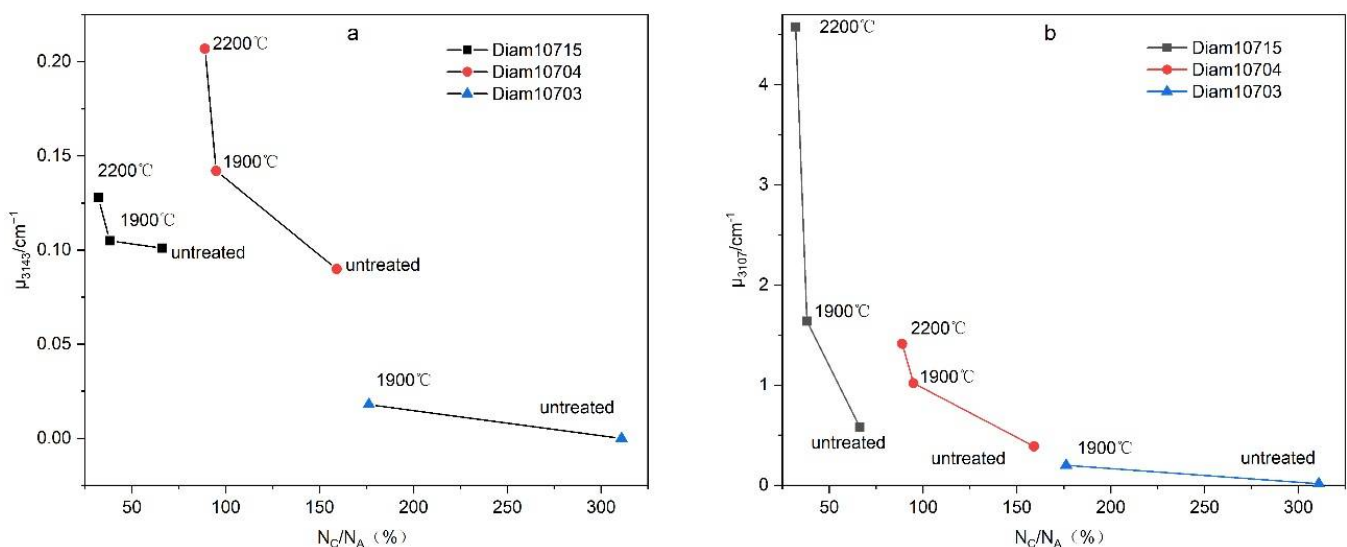


Figure 6. The intensity changes of 3107 and 3143 cm^{-1} absorption of three natural type Ib diamonds before and after 15 min HPHT-treated process. The 3107 (a) and 3143 (b) cm^{-1} absorption peak height increased with the increasing of the annealing temperature.

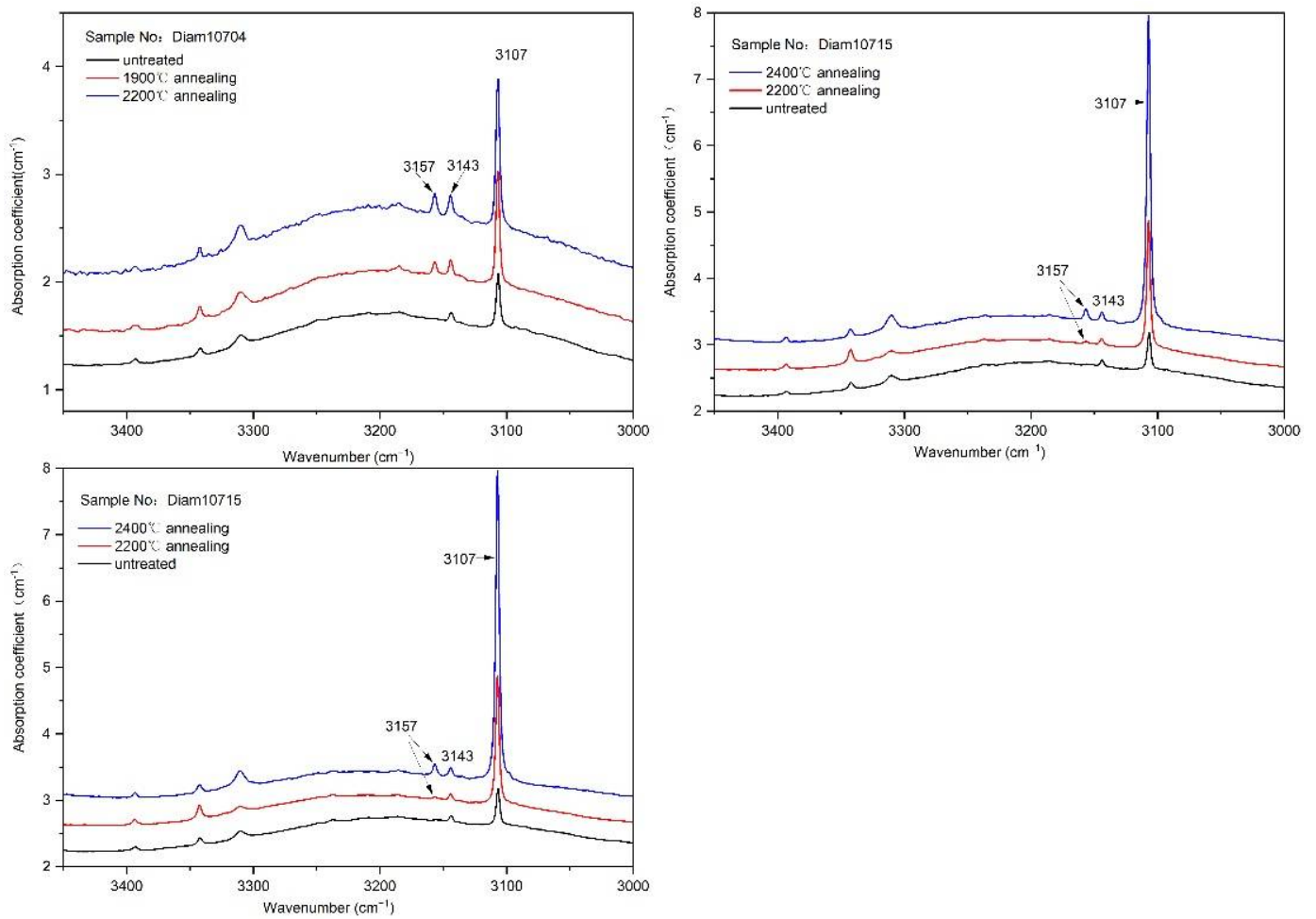


Figure 7. The absorption difference in the infrared region before and after HPHT-treated natural diamonds.

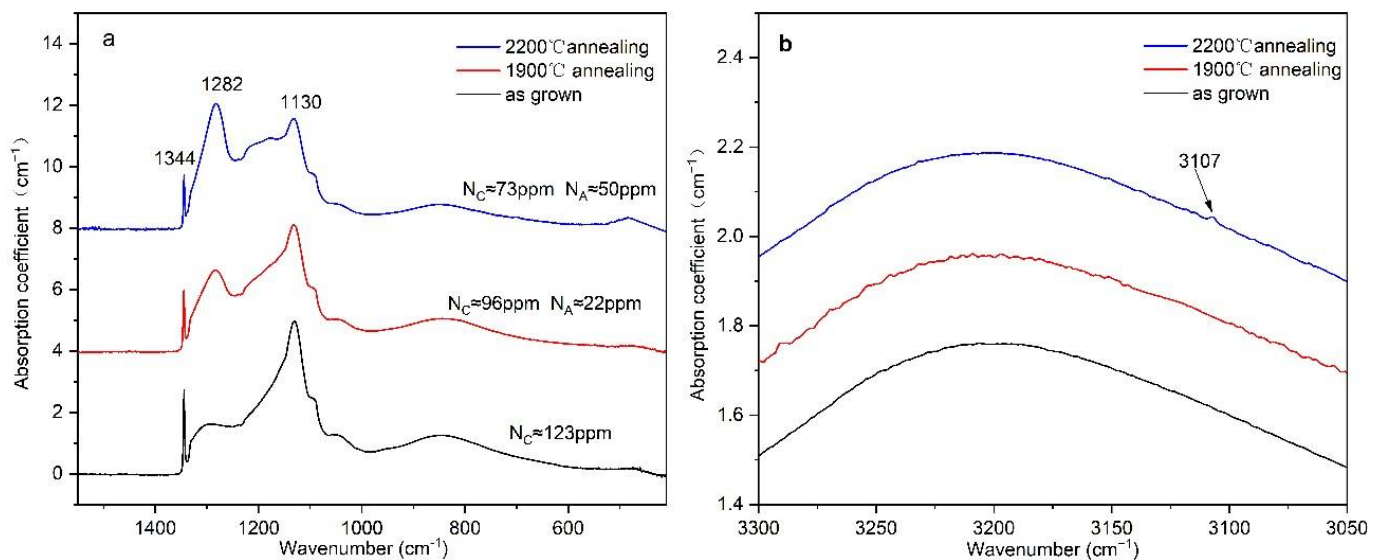


Figure 8. The absorption difference in the infrared region between the as-grown and HPHT-treated synthetic diamonds. In the region of 400–1500 cm^{-1} (a), the peak at 1130 cm^{-1} decrease gradually and 1282 cm^{-1} increase; when the nitrogen concentration of A centers is more than C centers, there is a weak absorption peak at 3107 cm^{-1} (b).

Figure 9 displays the other synthetic sample that experienced annealing at a temperature of 2200 and 2400 °C. When type Ib diamonds are heated at around 1500 °C, nitrogen impurities in synthetic diamonds diffuse to form close-by pairs called A centers [26]. The relative concentrations of A and C centers are different; the higher the annealing temperature, the more the concentration of the A nitrogen, and the less of the C nitrogen. With the A center content increase, the 3107 cm⁻¹ absorption coefficient increases from 0.02 cm⁻¹ to 0.04 cm⁻¹ (Figure 9), and no other hydrogen-related absorption such as 3143 cm⁻¹ is produced. Whether the 3143 cm⁻¹ absorptions can occur in HPHT-treated synthetic diamonds requires further experimental investigation.

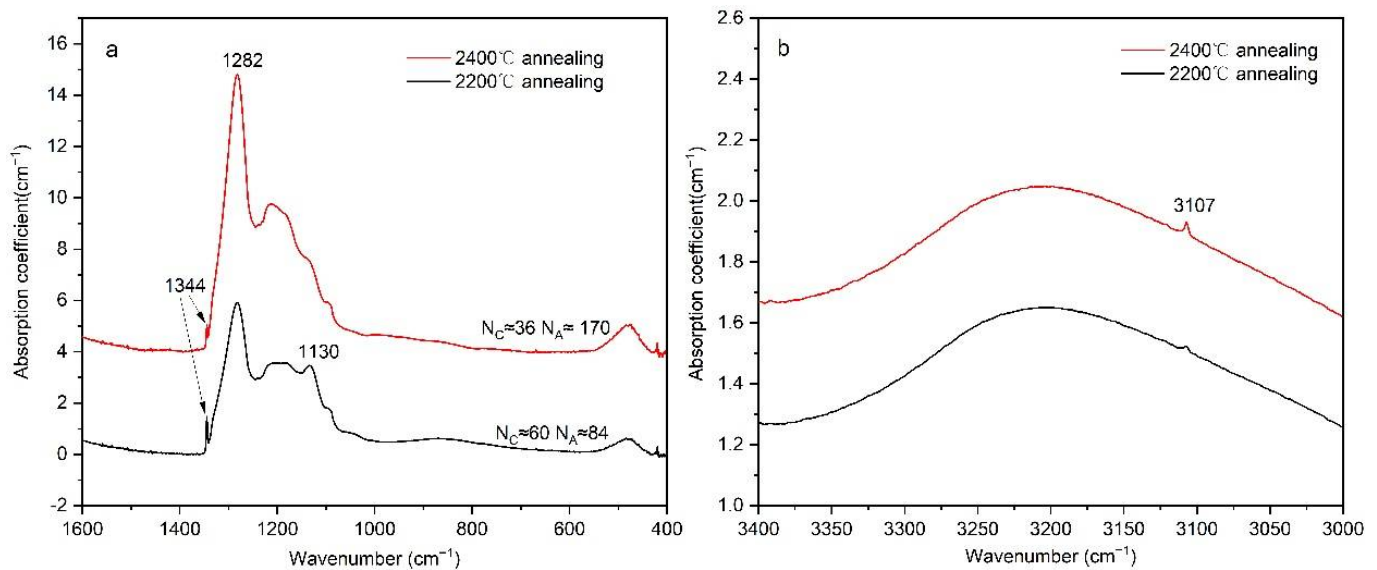


Figure 9. The 3107 cm⁻¹ peak becomes stronger and stronger with the annealing temperature. With the A center content increase from 84 to 170 ppm (a), the 3107 cm⁻¹ absorption coefficient increases from 0.02 cm⁻¹ to 0.04 cm⁻¹ (b).

It can be seen from the above analysis that there is no 3107 cm⁻¹ absorption [17] in type Ib diamonds (only containing C nitrogen), while there is a distinct 3107 cm⁻¹ absorption line in type Ia Cape diamonds without any single nitrogen [27]. Therefore, it can be explained that the 3107 cm⁻¹ absorptions are only related to aggregated nitrogen [8] and have nothing to do with isolated nitrogen. The 3143 cm⁻¹ defect will not appear in diamonds dominated by C nitrogen and can be detected only when both single nitrogen and aggregated nitrogen exist in natural diamonds, especially when the diamonds contain much aggregated nitrogen. In addition, the 3143 cm⁻¹ has never appeared alone, and if there is a peak at 3143 cm⁻¹, there must be a relatively stronger peak at 3107 cm⁻¹. However, in the HPHT-treated synthetic diamonds, even though the content of aggregated nitrogen is relatively high, there was no detectable absorption peak at 3143 cm⁻¹.

We proposed a model for the 3143 cm⁻¹, including a 3107 cm⁻¹ defect and a single nitrogen atom, which is maybe N₃V-H-C-N. The carbon atom plays the connection role between the single nitrogen atom and the 3107 cm⁻¹ defect, which explains why the 3143 cm⁻¹ is only observed in diamonds with the 3107 cm⁻¹ defect and single nitrogen simultaneously. We need further experiments to understand the specific structure of the 3143 cm⁻¹ defect in more detail.

4. Conclusions

Hydrogen is a common impurity in natural diamonds. However, only a small amount of hydrogen is optically active, and the absorption line at 3107 cm⁻¹ is one of the most frequently observed hydrogen-related defects. Based on the above analysis, this paper further shows that the 3107 cm⁻¹ defect is related to aggregated nitrogen, and the 3143 cm⁻¹

defect is not only related to isolated nitrogen but also related to aggregated nitrogen. The 3143 cm^{-1} only appears in diamonds containing isolated nitrogen and a certain amount of aggregated nitrogen. We proposed a model for the 3143 cm^{-1} including a 3107 cm^{-1} defect and a single nitrogen atom, which is $\text{N}_3\text{V-H-C-N}$.

High-temperature annealing alters the form of both nitrogen and hydrogen in diamonds and then changes the strength of 3107 and 3143 cm^{-1} . In the natural diamond mainly containing single nitrogen, the 3143 cm^{-1} defect will develop from none to weak when annealed at a high-temperature process. However, no 3143 cm^{-1} is created in synthetic diamonds, even those which experienced higher temperature when strong 3107 cm^{-1} absorption occurred. Whether the 3143 cm^{-1} absorption can occur in HPHT-treated synthetic diamonds is as yet unclear and requires further investigation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12101352/s1>, Figure S1: The linear relationship of peak area between 3107 and 1405 cm^{-1} , the slope value is 0.19 . Figure S2: There was no strict linear relationship about the peak area between the 3107 and 3143 cm^{-1} defects. The absorption intensity of 3143 cm^{-1} is much weaker than that of 3107 cm^{-1} . Generally, the stronger the absorption of 3107 cm^{-1} , the stronger the absorption of 3143 cm^{-1} is. Figure S3: If there is 3107 cm^{-1} defect in the diamond, the higher the total nitrogen, the more the 3107 cm^{-1} defect. However, the 3143 cm^{-1} defect do not related to the total nitrogen concentration. Figure S4: There is a similar relationship between the A center and the total nitrogen concentration with the 3107 and 3143 cm^{-1} defects. Figure S5: There was no correlation between the C center concentration and the 3107 , 3143 cm^{-1} defects. Figure S6: the color change of DIAM 10703 before and after high temperature annealing.

Author Contributions: Conceptualization, analysis of data, writing the manuscript, Z.S.; discussion, J.S. and T.L.; revising the manuscript, T.L.; measurements, Y.W., W.Z. and S.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by NGTC20200300 and NGTC20210100.

Data Availability Statement: All data are contained within the article and Supplementary Tables.

Acknowledgments: This study was supported by the NGTC Research Foundation (grant no. NGTC20200300, 20210100) and partially by the China National Nature Science Foundation (grant nos. 42073008). We thank Alan Collins for helping correct this manuscript and for supplying helpful information.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Collins, A.T. The colour of diamond and how it may be changed. *J. Gemmol.* **2001**, *27*, 341–359. [[CrossRef](#)]
2. Sideras-Haddad, E.; Connell, S.H.; Sellschop, J.; Machi, I.Z.; Rebuli, D.; Maclear, R.D.; Doyle, B.P. Hydrogen and oxygen chemistry and dynamics in diamond studied by nuclear microscopic techniques. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2001**, *181*, 419–425. [[CrossRef](#)]
3. Khan, R.U.; Martineau, P.M.; Cann, B.L.; Newton, M.E.; Twitchen, D.J. Charge transfer effects, thermo and photochromism in single crystal CVD synthetic diamond. *J. Phys. Condens. Matter* **2009**, *21*, 364214. [[CrossRef](#)] [[PubMed](#)]
4. Glover, C.; Newton, M.E.; Martineau, P.M.; Quinn, S.; Twitchen, D.J. Hydrogen incorporation in diamond: The vacancy-hydrogen complex. *Phys. Rev. Lett.* **2004**, *92*, 135502. [[CrossRef](#)] [[PubMed](#)]
5. Shaw, M.J.; Briddon, P.R.; Goss, J.P.; Rayson, M.J.; Kerridge, A.; Harker, A.H.; Stoneham, A.M. Importance of quantum tunneling in vacancy-hydrogen complexes in diamond. *Phys. Rev. Lett.* **2005**, *95*, 105502. [[CrossRef](#)] [[PubMed](#)]
6. Fritsch, E.; Hainschwang, T.; Massi, L.; Rondeau, B. Hydrogen-related optical centers in natural diamond: An update. *New Diam. Front. Carbon Technol.* **2007**, *17*, 63–89.
7. Woods, G.S.; Collins, A.T. Infrared absorption spectra of hydrogen complexes in type I diamonds. *J. Phys. Chem. Solids.* **1983**, *44*, 471–475. [[CrossRef](#)]
8. Goss, J.P.; Briddon, P.R.; Hill, V.; Jones, R.; Rayson, M.J. Identification of the structure of the 3107 cm^{-1} H-related defect in diamond. *J. Phys. Condens. Matter* **2014**, *26*, 145801. [[CrossRef](#)]
9. Fuchs, F.; Wild, C.; Schwarz, K.; Müller-Seibert, W.; Koidl, P. Hydrogen induced vibrational and electronic transitions in chemical vapor deposited diamond, identified by isotopic substitution. *Appl. Phys. Lett.* **1995**, *66*, 177–179. [[CrossRef](#)]
10. Kiflawi, I.; Fisher, D.; Kanda, H.; Sittas, G. The creation of the 3107 cm^{-1} hydrogen absorption peak in synthetic diamond single crystals. *Diamond Relat. Mater.* **1996**, *5*, 1516–1518. [[CrossRef](#)]

11. Weerdt, F.D.; Collins, A.T. Optical study of the annealing behaviour of the 3107 cm⁻¹ defect in natural diamonds. *Diamond Relat. Mater.* **2006**, *15*, 593–596. [[CrossRef](#)]
12. Charles, S.J.; Butler, J.E.; Feygelson, B.N.; Newton, M.E.; Carroll, D.L.; Steeds, J.W.; Darwish, H.; Yan, C.S.; Mao, H.K.; Hemley, R.J. Characterization of nitrogen doped chemical vapor deposited single crystal diamond before and after high pressure, high temperature annealing. *Phys. Status Solidi A* **2004**, *201*, 2473–2485. [[CrossRef](#)]
13. Lai, M.Y.; Breeding, C.M.; Stachel, T.; Stern, R.A. Spectroscopic features of natural and HPHT-treated yellow diamonds. *Diamond Relat. Mater.* **2020**, *101*, 107642. [[CrossRef](#)]
14. Kiflawi, I.; Mayer, A.E.; Spear, P.M.; Van Wyk, J.A.; Woods, G.S. Infrared absorption by the single nitrogen and a defect centres in diamond. *Philos. Mag. B* **1994**, *69*, 1141–1147. [[CrossRef](#)]
15. Boyd, S.R.; Kiflawi, I.; Woods, G.S. The relationship between infrared absorption and the A defect concentration in diamond. *Philos. Mag. B* **1994**, *69*, 1149–1153. [[CrossRef](#)]
16. Lawson, S.C.; Fisher, D.; Hunt, D.C.; Newton, M.E. On the existence of positively charged single-substitutional nitrogen in diamond. *J. Phys. Condens. Matter* **1998**, *10*, 6171–6180. [[CrossRef](#)]
17. Hainschwang, T.; Fritsch, E.; Notari, F.; Rondeau, B.; Katrusha, A. The origin of color in natural C center bearing diamonds. *Diam. Relat. Mater.* **2013**, *39*, 27–40. [[CrossRef](#)]
18. Song, Z.; Tang, S.; Zhu, W.; Gao, B.; Li, Y.; Lu, T. Spectral characteristic of natural and HPHT-Grown type Ib diamond. *J. Gems Gemol.* **2021**, *23*, 51–57.
19. Zedgenizov, D.; Bogush, I.; Shatsky, V.; Kovalchuk, A.; Kalinina, V. Mixed-habit type ib-iaa diamond from an udachnaya eclogite. *Minerals* **2019**, *9*, 741. [[CrossRef](#)]
20. Davies, G.; Collins, A.T.; Spear, P.M. Sharp infrared absorption lines in diamond. *Solid State Commun.* **1984**, *49*, 433–436. [[CrossRef](#)]
21. Eaton-Magana, S.; Ardon, T.; Breeding, C.M.; Shigley, J.E. Natural-color fancy white and fancy black diamonds: Where color and clarity converge. *Gems Gemol.* **2019**, *55*, 320–337. [[CrossRef](#)]
22. Hainschwang, T.; Notari, F.; Fritsch, E.; Massi, L. Natural, untreated diamonds showing the A, B and C infrared absorptions (“ABC diamonds”), and the H2 absorption. *Diam. Relat. Mater.* **2006**, *15*, 1555–1564. [[CrossRef](#)]
23. Hainschwang, T.; Notari, F.; Fritsch, E.; Massi, L.; Rondeau, B.; Breeding, C.M.; Vollstaedt, H. HPHT treatment of CO₂ containing and CO₂-related brown diamonds. *Diam. Relat. Mater.* **2008**, *17*, 340–351. [[CrossRef](#)]
24. Kazuchits, N.M.; Rusetsky, M.S.; Kazuchits, V.N.; Korolik, O.V.; Kumar, V.; Moe, K.S.; Wang, W.; Zaitsev, A.M. Comparison of HPHT and LPHT annealing of Ib synthetic diamond. *Diam. Relat. Mater.* **2019**, *91*, 156–164. [[CrossRef](#)]
25. Kiflawi, I.; Bruley, J. The nitrogen aggregation sequence and the formation of voidites in diamond. *Diam. Relat. Mater.* **2000**, *9*, 87–93. [[CrossRef](#)]
26. Jones, R.; Goss, J.P.; Pinto, H.; Palmer, D.W. Diffusion of nitrogen in diamond and the formation of A-centres. *Diam. Relat. Mater.* **2015**, *53*, 35–39. [[CrossRef](#)]
27. Breeding, C.M.; Eaton-Magana, S.; Shigley, J.E. Naturally Colored Yellow and Orange Gem Diamonds: The Nitrogen Factor. *Gems Gemol.* **2020**, *56*, 194–219. [[CrossRef](#)]