

Research Article

Spectroscopic Characteristics of Treated-Color Natural Diamonds

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With the increasing availability of treated-color diamonds on the market, their characterization is becoming more and more critical to the jewelry testers and customers. In this investigation, ten color diamonds treated by irradiation (4 pieces), HPHT (3 pieces), and multiprocess (3 pieces) were examined by spectroscopic methods. These diamonds are classified to be type Ia according to their FTIR characteristics. Using microscope and DiamondView, the internal features (such as distinctive color zoning and graphitized inclusions) and complex natural growth structures were observed, which show that the samples are more likely artificially colored natural diamonds. Through photoluminescence spectroscopy, a combination of optical centers was detected, including N-V⁰ at 575 nm, N-V⁻ at 637 nm, H3 at 503 nm, H2 at 986 nm, and GR1 at 741 and 744 nm. Combining with the previous studies, treatment conditions for the studied diamonds were estimated depending on the presence and/or absence of the optical centers. In addition, the coloration mechanism of the samples (blue, green, and red) during the treatment process was also discussed. It is suggested that a number of techniques should be combined in order to make a reliable identification for such diamonds.

1. Introduction

Diamonds, one of the most precious gemstones, have been very popular on the jewelry market, especially the fancy color gem-quality diamonds. However, most natural diamonds show brown hue in color and have some internal or external defects, and only a few of them are suitable for using as gemstones [1]. Therefore, considerable scientific work has been continuously done to enhance the color of diamonds so as to make them exhibiting fancy color, in order to offset the scarcity of natural diamonds and to satisfy the demand for color gem-quality diamonds of the jewelry market.

Generally, the gemologists have begun to enhance the color of diamond since the 1930s [2] and diamond treatments in the modern era mostly involve high-energy irradiation, high pressure and high temperature (HPHT) treatment, low pressure and high temperature (LPHT) annealing, and combination of these treatments [3–11]. Such as Vins [12] reported that natural diamonds with brown hue could be altered to display purple to red color, through multiprocess treatments including HPHT treatment (6–7 GPa at over

2150°C), high-energy irradiation, and LPHT annealing (lower than 1100°C).

With the increasing availability of the treated-color diamonds in the jewelry market, characterization of them becomes more and more critical to the gem testers and customers. However, by far, there are not enough works for systematically studying the treated-color diamonds and most of them are focused on examining the diamonds treated by the same method or that from the same company [13–15]. This study attempts to characterize the natural diamonds treated by different process (irradiation, HPHT, and multiprocess) using spectroscopic methods, to present the coloration mechanism of them during treatment, and to provide more data of the identification and the treatment method for the gemologists and the jewelry market.

2. Materials and Methods

Ten treated-color natural diamonds were collected for this investigation (4 irradiation-treated, 3 HPHT-treated, and 3 multiprocess-treated diamonds, see Table 1 and Figure 1).

TABLE 1: Description of the treated-color natural diamonds used in this study.

	Sample number	Color	Weight (ct)	Clarity	Fluorescence to long-wave UV	Fluorescence to short-wave UV
Treated-irradiated	TR-1	Blue	0.4	SI ₂	Very weak blue, chalky	Invert
	TR-2	Dark green	0.24	SI ₁	Moderate green, chalky	Invert
	TR-3	Blue	0.24	VVS ₂	Invert	Invert
	TR-4	Dark green	0.36	VS ₁	Invert	Invert
Treated-HPHT	TR-5	Yellowish green	0.38	VS ₁	Greenish yellow	Moderate greenish yellow
	TR-6	Yellow	0.42	SI ₁	Weak blue, chalky	Invert
	TR-9	Greenish yellow	0.29	SI ₂	Blue, chalky	Greenish yellow
Treated-multiprocess	TR-7	Dark purplish pink	0.39	I ₁	Pink, chalky	Moderate orange
	TR-10	Dark purplish pink	0.35	SI ₂	Weak pink, chalky	Weak orange
	TR-11	Slight dark red	0.30	SI ₁	Very weak blue	Invert

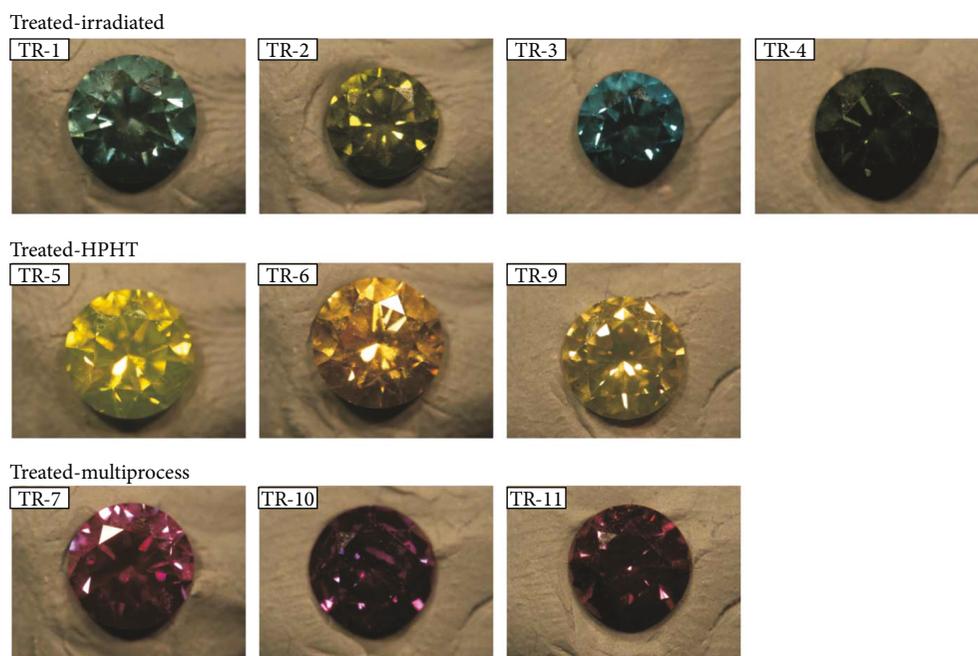


FIGURE 1: These faceted diamonds are treated by irradiation, HPHT, and multiprocess treatments, respectively, and they range in size from 0.24 to 0.42 ct.

All the faceted samples are round brilliants and range in size from 0.24 to 0.42 ct. Using a standard gemological binocular microscope, the internal features of all diamonds were examined. The reactions to ultraviolet (UV) light were checked with a conventional four-watt combination long-wave (365 nm) and short-wave (254 nm) lamp (Table 1). In addition, we recorded the fluorescence and phosphorescence images by the Diamond Trading Company (DTC) DiamondView instrument (illumination wavelengths < 230 nm, Welbourn et al. [16]) in the laboratory of National Gems & Jewelry Technology Administrative Center (NGTC) in Beijing, and which could also reveal the internal growth features of the samples.

Two other spectroscopic analyses were conducted on most of the samples at NGTC laboratory. Infrared absorption spectra in the midinfrared ($4000\text{--}400\text{ cm}^{-1}$, 2 cm^{-1} resolution)

were measured by a Thermo Nicolet Nexus iN10 Fourier-transform infrared (FTIR) spectrometer, furnished with KBr and quartz beam splitters. A total of 64 scans were collected for each sample. A Renishaw InVia Raman confocal microspectrometer was used to acquire the low temperature photoluminescence (PL) spectra, with the samples cooled by submerging in liquid nitrogen. To activate various types of defects in these treated-color natural diamonds, three different excitation wavelengths (473, 532, and 785 nm) were employed.

3. Results

3.1. Microscopic Characteristics. Viewing with the binocular gemological microscope, natural mineral inclusion and internal growth graining were observed in some of the treated-

color diamonds, which indicated that they had grown naturally, as shown in Figures 2(a) and 2(b). Some of them display color zoning, as the most characteristic feature of the treated diamonds (Figure 2(c)). In addition, other evidences of treatment were also noted, such as one diamond exhibited etched facet near to the girdle which was not removed during polishing (Figure 2(d)) and some graphitized inclusions formed during the HPHT treatment were also shown (Figure 2(e)). Besides, under magnification with crossed polarizer, anomalous birefringence with high interference colors caused by residual internal strain was observed in all treated diamonds (Figure 2(f)).

3.2. DiamondView Imaging. When exposed to the high-intensity ultrashort wavelengths of the DTC DiamondView, the treated-color diamonds exhibited strong green, blue, orange, and orangey red fluorescence (Figure 3). In general, one sample could display two or more different fluorescence color. For example, numerous red, orangey red, blue, and slight green fluorescence lines were simultaneously present in the TR-10 sample (Figure 3(h)). The TR-6 sample with blue fluorescence displayed some irregular green regions as shown in Figure 3(e). In addition, the luminescence images of the examined diamonds revealed complex growth patterns, which is a typical reflection of complex growth history and also the natural origin.

3.3. Infrared Absorption Spectroscopy. As shown in Figures 4(a) and 4(b), all the irradiation-treated diamonds are assigned to be type IaAB according to their infrared spectra. The absorption from the H1a defect (the $\langle 001 \rangle$ dinitrogen split interstitial N_{2i} ; [17]) at 1450 cm^{-1} is observed in all the irradiated diamonds, which points out that they have been irradiated or irradiated with subsequently annealing at relatively low temperatures ($\sim 300^\circ\text{C}$; Clark et al. [18]). The absence of band of 2800 cm^{-1} in the blue diamonds is another evidence for the existence of irradiation. Absorption peaks located at near $1356\text{--}1380\text{ cm}^{-1}$ are related to C-C platelets, which represent for the layers of interstitial carbon atoms generated as a byproduct of nitrogen aggregation [19]. In addition, the intensity of band of 1405 cm^{-1} is found to be positive related to that of 3107 cm^{-1} , indicating that both of them may originate from the same VN_3H defect [20]. The peak at 2785 cm^{-1} was reported to be produced by the vibrations of 1405 and 3107 cm^{-1} [21]. Besides, the double peak at ~ 2926 and $\sim 2854\text{ cm}^{-1}$, attributing to C-H stretch [22], is observed in all the samples. Unknown weak or sharp bands of the two dark green diamonds are also detected at $3254, 3236, 3069, 3056, 2812, 2785, 1553, 1524, 1528, 1499,$ and 1435 cm^{-1} , and we speculate that some of them may arise from the hydrogen in diamonds.

The FTIR spectra of the HPHT-treated samples display typical features of type Ia, with various aggregation states of nitrogen. As represented in Figures 4(c) and 4(d), the TR-6 sample shows stronger A-aggregate absorption while the other two show stronger B-aggregate features. The occurrence of 1331 cm^{-1} , associated with the positive charge state of the single substitutional nitrogen defect (N_s^+), may indicate that the diamonds have been treated by HPHT process

which can create isolated nitrogen [23]. Additionally, the two TR-5 and TR-9 samples also exhibit absorption related to hydrogen impurities at 3107 cm^{-1} .

The multiprocess-treated diamonds are proved to be type IaAB (Figures 4(e) and 4(f)), where the concentration of A-aggregates is stronger than that of B-aggregates. Weak absorptions at 1344 and 1331 cm^{-1} attributed to isolated nitrogen impurities are recorded in all the samples. In addition, the H1a defect due to irradiation is observed in this group of samples. Other weak and broad features also occurred in some of them, including peaks at $3107, 1502,$ and 1405 cm^{-1} , where the 1502 cm^{-1} center was suggested to be related to the H1a center according to their positive correlation in intensity [24].

3.4. Photoluminescence Spectroscopy. Low temperature photoluminescence spectra were collected for most of the samples using three laser excitations with wavelengths of $473, 532,$ and 785 nm . The major PL emission lines are illustrated below based on each laser excitation.

As illustrated in Figures 5(a)–5(c), when the 473 nm laser excitation is employed, all the treated diamonds display the H3 (503.2 nm) defect, with side bands between ~ 512 and $\sim 553\text{ nm}$, and with various intensity between different samples. A faint emission line at 496 nm , assigned to be H4 center, occurs in the irradiation-treated and multiprocess-treated diamonds. At the same time, a set of emissions at $484, 486,$ and 491 nm are present in some of the samples in these two groups; however, it is unknown whether they are related with the H4 defect or not. Besides, the 3H defect (a radiation center of diamond [22, 25]) is not found in the irradiation-treated diamonds, which needs further exploration. Nitrogen-vacancy centers ($NV^0/-$), with zero-phonon lines at 575 and 637 nm , are obvious in the multiprocess-treated diamonds. However, they are absent in the HPHT-treated diamonds and only one of the irradiation-treated diamonds shows very weak NV^0 center. In addition, one spectrum of the HPHT-treated diamonds displays an intense peak at 478.9 nm (not shown), which was suggested to be an indicator of possible HPHT treatment [26]. The 588 nm emission, considered as an evidence of multiprocess treatment [26], is observed in the multiprocess-treated diamonds. These spectra also reveal peaks at 634.4 nm in the HPHT-treated diamonds, at $489.1, 558.1, 613.5, 647.1,$ and 657.9 nm in the irradiation-treated diamonds, and at 600.2 nm in the multiprocess-treated diamonds.

The PL spectra taken with 532 nm laser excitation reveal sharp NV center emission systems in most of the treated samples, with the intensity of the 637 nm ZPL more intense than that of 575 nm ZPL. Another band is detected at $\sim 658\text{ nm}$ in most of the samples, which was suggested to be created at high temperatures and then destructed by HPHT treatment [27]. Strong doublet emissions at 741.4 and 744.7 nm , attributed to GR1 center, are observed in the irradiation-treated diamonds. In addition, numerous emission lines at $536.0, 539.7, 542.9, 551.0, 558.2, 588.1, 563.6, 603.5, 609.3, 612.5, 640.0, 647.3, \sim 680, \sim 715, \sim 723, \sim 757, \sim 787,$ and $\sim 800\text{ nm}$ are detected in the spectra of the irradiation-treated diamond. Other features are also recorded

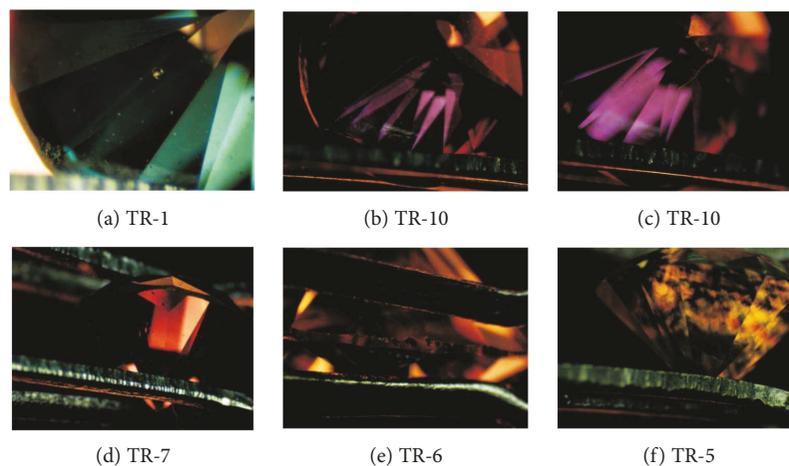


FIGURE 2: A broad range of internal characteristics were noted with magnification, including natural mineral inclusions and some graphitized inclusions, as well as color zoning and etched facet near to the girdle. In addition, anomalous birefringence with high interference colors was also observed.

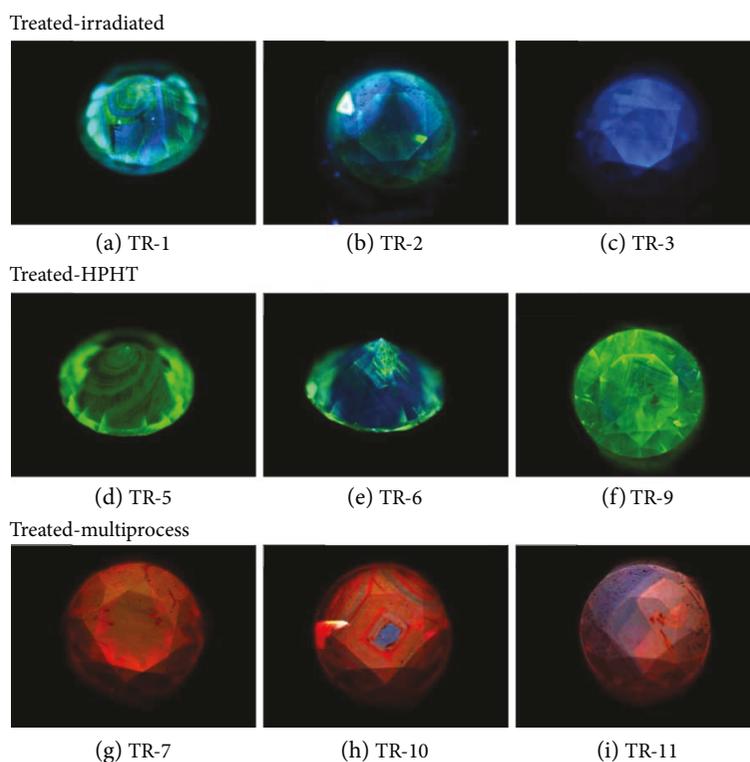


FIGURE 3: DiamondView images showed complex growth patterns of the treated-color diamonds, which revealed the natural origin. The dominant luminescence was strong green, blue, orange, and orangey red, and while one sample usually displayed two or more different fluorescence.

in the HPHT-treated diamond, including peaks at 536.1, 539.8, 555.3, 565.3, 566.2, and 601 nm. The defects responsible for most of these emission lines have not been identified.

Infrared laser excitation at 785 nm produces two emission features (876.4 nm, the first order diamond Raman line, and 986.2 nm, the H2 center) in the HPHT-treated diamonds.

We also observe another weak peak at 959.7 nm in one of these samples. In the irradiation-treated diamonds, many weak and sharp peaks are recorded, including those at 795.3, 799.2, 802.5, 805.4, 806.4, 839.7, 890.5, 900.6, 926.3, 936.7, 948.6, 960.3, and 986.4 nm. The spectra of the multiprocess-treated diamonds reveal several features at 789.9, 805.1, 815.9,

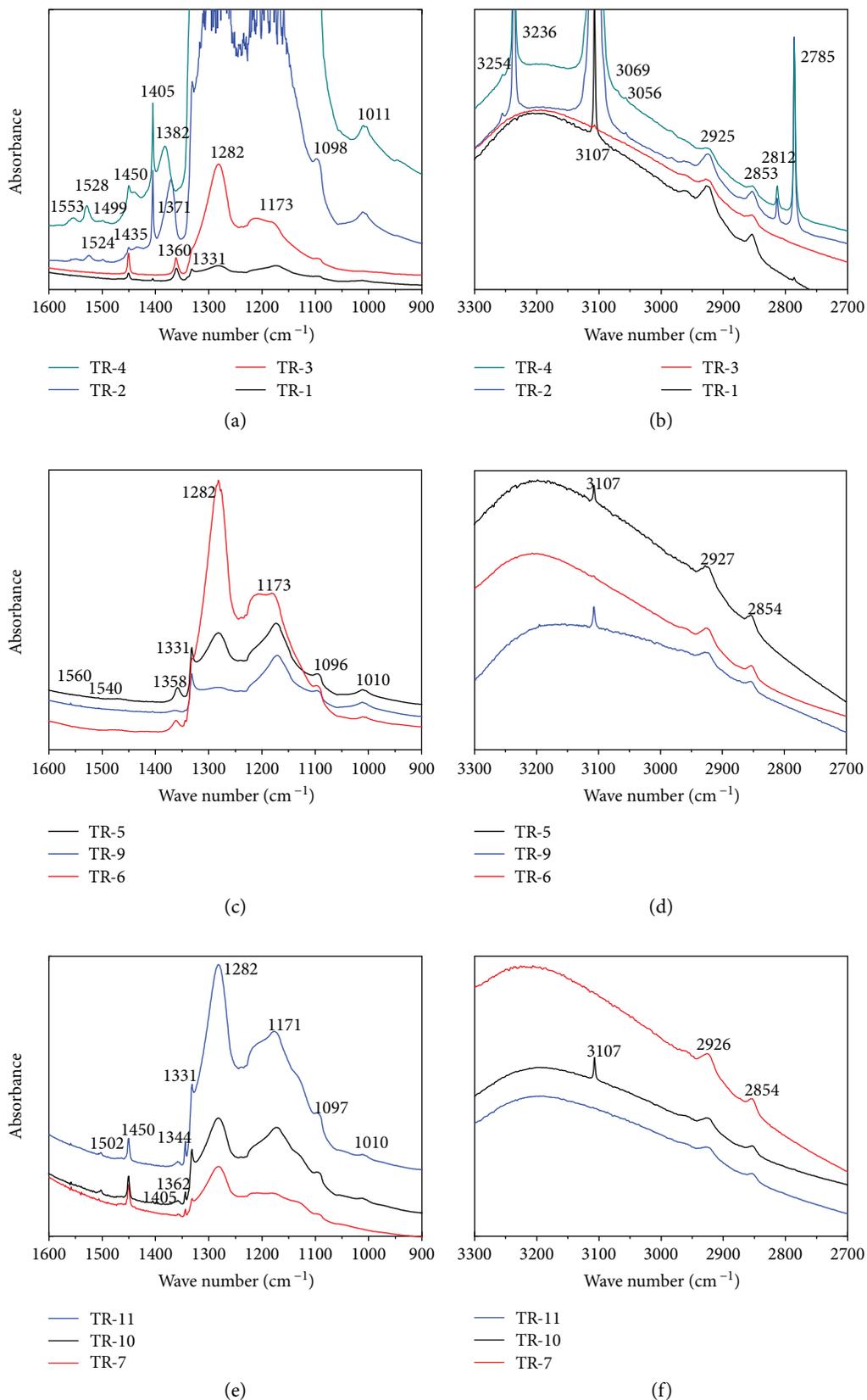


FIGURE 4: The FTIR spectra of the treated-color diamond collected in the midinfrared range reveal typical features of type Ia diamonds, with various aggregation states of nitrogen. The H1a absorption at 1450 cm^{-1} and the isolated nitrogen-related peaks (1344 and 1331 cm^{-1}) were also observed in some of them.

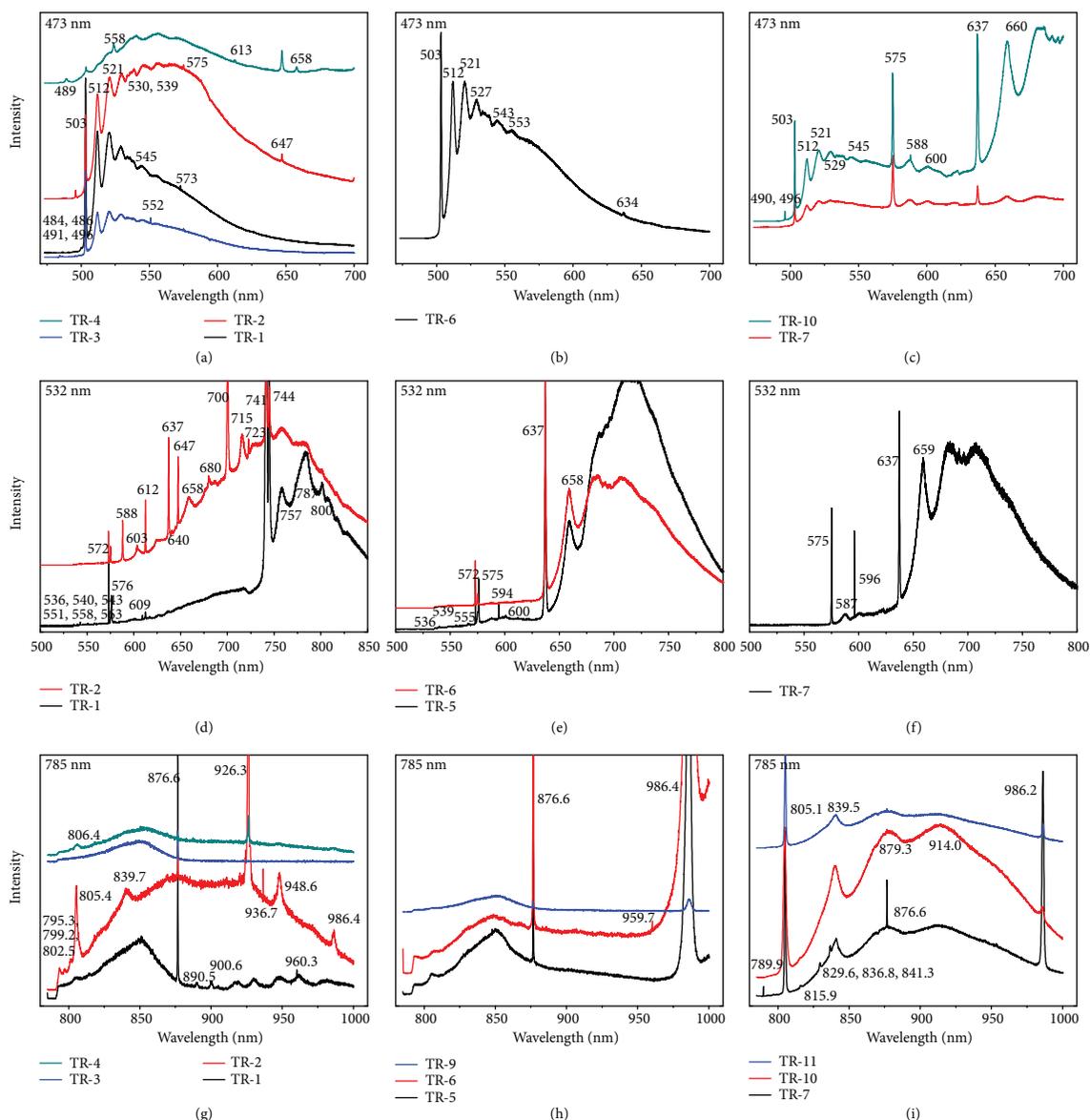


FIGURE 5: Photoluminescence spectra were taken at liquid-nitrogen temperatures for most of the samples using three laser excitation wavelengths of 473, 532, and 785 nm. Strong H3 center, NV center, GR1 center, and H2 center were observed in some of these treated-color diamonds. The presence and/or absence of these centers have an indicative role to determine the type of treatment and the process of the treatment.

829.6, 836.8, 839.5, 841.3, and 986.2 nm. Unfortunately, the assignments for most of them are not sure.

4. Discussions

4.1. Spectroscopic Features and Related Treatment. Usually, the condition of treatment correlates with the presence and/or absence of the optical centers, and thus analysis of the optical centers may contribute to reveal the condition of treatment. The variations of some optical centers with different treatment processes and conditions in previous works are reviewed as followed.

4.1.1. H3 and H2 Centers. The H3 (503.2 nm) and H2 (986.2 nm) centers are related to the nitrogen-vacancy-

nitrogen (NVN) defect in neutral and negative charge state, respectively. Commonly, the H3 center has been observed in diamonds involving with irradiation and high temperature annealing (or HPHT annealing) [28–30] or been directly created in plastically deformed brown diamonds through heating at high temperature [31, 32], while various concentrations of the H3 defect can also occur in some natural diamonds [33–36]. In nitrogen-containing diamonds, high-energy irradiation followed by annealing at temperatures over 500°C could result in the formation of H3 center [26]. Collins [37] reported that the H3 center had maximum intensity at approximately 800°C and annealed out at temperatures above 1500°C in irradiated diamonds. In terms of the HPHT annealing treatment for the irradiated type Ia diamonds, the H3 absorption just began to decrease after 1650°C

[28] or reduced largely or disappeared after high pressure annealing at 2300°C [29]. While in most of the HPHT-treated diamonds, the H3 center may form in brown plastically deformed type IaA and IaB diamonds when annealed at a temperature 1800°C at 7.0 GPa and then its concentration increased up to about 2150°C [32, 38] or decreased considerably at temperatures above 2100°C [39, 40].

The H2 center, with negative charged state, is usually observed in diamonds containing defects which can act as donors. In irradiated type IaA diamonds, the absorption of the H2 center started to increase after annealing at around 1250°C and reached a maximum at 1600°C or disappeared when annealed at 2300°C and high pressure [28, 29]. Through HPHT annealing with temperatures above 1800/1900°C, in type IaA/IaB diamond with plastic deformation, the absorption of the H2 center appeared and increased with increasing temperature and then began to decrease at 2150/2200°C [38, 39].

4.1.2. GR1 Center. The GR1 center is attributed to the neutral isolated vacancy (V^0), located at 741 and 744 nm. Weak line at 741 nm has been found in a few natural diamonds [41, 42]. Through high-energy irradiation (electrons, gamma-rays, neutrons, and ions), the GR1 center could be artificially created in most of diamonds [22, 26]. Kiflawi et al. [43] reported that there was an initial reduction in the strength of the GR1 absorption at 390–410°C followed by sharp decrease beyond 700°C in the irradiated diamonds. In addition, the GR1 center is completely destroyed in high-nitrogen diamonds when heated at 800°C for 1 h, whereas heating above 900°C was required in low-nitrogen specimens [28, 44]. The GR1 center was absent in irradiated diamonds upon HTHT treatment at 1000°C [26].

4.1.3. NV Center. One of the nitrogen-vacancy defects locates at 575 nm in neutral charge state (NV^0), and the other one locates at 637 nm in negative charge state (NV^-). In irradiated diamonds, the 575 nm center annealed out at approximately 1400°C; however, in some cases, it was still stable at temperatures above 1600°C and it could survive to about 2000°C when the diamonds were heated under high pressure [22, 25]. Vins and Eliseev [38] suggested that the A defects began to dissociate and some C defects (isolated nitrogen impurities) were formed in brown type IaA diamond after HPHT annealing at 2100°C, and a weak absorption of the NV defects simultaneously appeared.

The 637 nm center in electron irradiation type Ia diamonds began to develop after annealing at 800°C [5] and may anneal out at about 1500°C [25]. In addition, when the irradiated type Ia diamonds are subjected to 2300°C at 5.0 GPa, the 637 nm absorption is extremely weak or undetectable [29]. In type Ia brown diamonds, the NV^- center was produced by HPHT treatment at 2000°C and above [4, 34] and could be rather strong through a few minutes of HPHT treatment at a temperature of 2300°C [45].

4.1.4. Other Features. The 3107 cm^{-1} center is attributed to H-related vibration and is assigned to be mode of VN_3H [20, 46]. In general, the behavior of the 3107 cm^{-1} during

treatment is complex. After electron irradiation and subsequent prolonged annealing at 1200°C for 24 h, the intensity of the 3107 cm^{-1} absorption in type Ia diamonds can be considerably reduced or even disappeared [47]. The study of De Weerd and Kupriyanov [48] showed that the 3107 cm^{-1} absorption was stable in type IaA/B diamonds when annealing at 1900°C and 7.0 GPa. As summarized by Dobrinets et al. [26] and Vins and Yelissev [39], HPHT treatment could strongly reduce the intensity of the 3107 cm^{-1} in 80% of cases. The C center is related to the isolated nitrogen, located at 1344 and 1131 cm^{-1} . Usually, the presence of C center in the FTIR spectrum of type IaAB is an indication of possible HPHT treatment. After HPHT treatment performed at 2000°C and above, the C defects with detectable concentration appeared [38, 45, 49].

Combining the above data with the presence and/or absence of the optical centers in the diamonds of this study, it can be inferred that the irradiation-treated diamonds were irradiated without annealing or the annealing temperature was very low, the minimum annealing temperature was $\sim 2000^\circ\text{C}$ for the HPHT-treated diamonds and the annealing temperature for the multiprocess-treated diamond was between 2000 and 2300°C.

4.2. Cause of Color

4.2.1. Blue. In natural diamonds, the blue color is rare. The type IIb diamonds owe their blue color to the absorption of the boron acceptors [22, 50, 51]. Some natural type Ia diamonds can also show the blue-gray color, which is caused by the high concentration of hydrogen [52, 53]. Moreover, the GR1 center produced by irradiation is another origin of the blue color. A few diamonds are naturally irradiated to display blue color [22], and a similar color can also be induced by artificial irradiation [28, 54]. The blue diamonds in this study were artificially irradiated, which give rise to strong GR1 center.

4.2.2. Yellow to Green. In natural diamonds, the yellow color is usually caused by the absorption of the N3 and N2 optical centers (“cape-yellow”) and/or the C defects (canary-yellow). The green hue of some natural diamonds is due to the GR1 center produced by natural irradiation [26, 54]. HPHT treatment is a common method to induce yellow/green color to the diamonds. After HPHT annealing at 1800°C, a yellow hue due to the C center was created in brown type Ia diamonds [49, 55]. With increasing temperature, the H2 center—additional green color modifier—was produced [25, 26, 56]. In general, the resulting green/yellow color is a combination of the absorptions of H3, H2, and C defect in the spectrum and also the same as the HPHT-treated diamonds in this study. Strong GR1 center created by artificial irradiation can also give rise to dark green color, such as the sample TR-2 and TR-4.

4.2.3. Red. Pure red diamond is extremely rare in nature, and some pink diamonds with moderate brightness and high saturation can display red color [54]. After multiprocess treatment, the diamonds could also show red color. Usually, the type IaAB natural diamonds are chosen to be treated to

induce the red color [9, 12]: firstly, HPHT annealing is performed at over 2150°C to achieve high concentration of C center and then the diamonds are irradiated with 2–4 MeV energy to create enough isolated vacancies; finally, the diamonds are annealing at a temperature exceeding 1100°C in order to combine the C defects with the vacancies into NV centers; after these, the purple to red color could be obtained. The main reason for the red color is the absorption of N-V centers at 575 and 637 nm, with some influence from other absorption features [15, 26, 35]. It is obvious that the red color of the diamonds in this study has been induced by a similar process, because the N-V centers at 575 and 637 nm were also observed in these multiprocess-treated diamonds.

4.3. Identification Features. Generally, a number of techniques should be combined to identify a certain diamond, as it is difficult to be identified just by means of a single feature [57]. Combination of the presence of internal growth graining and the absence of growth structures typical of HPHT- and CVD-grown diamonds is a common feature of the diamonds in this work, which could confirm that they have grown in nature. Usually, after HPHT treatment, some of the diamonds could display obvious color zoning (especially around the culet or girdle), etched facet near to the girdle which was not repolished, and some graphitized inclusions along fracture surfaces.

The absorption caused by H1a at 1450 cm⁻¹ in the spectra of FTIR is observed in all the irradiated samples of this study (Figure 4). Besides, the GR1 center related to the isolated neutral vacancies is another common center in irradiated diamonds; however, it easily disappears after high temperature annealing (Figure 5).

Fisher [23] suggested that aggregation of nitrogen in natural diamonds tended to follow a progression: firstly, the single nitrogen aggregates to form pairs, and only after this transformation is completed, the A centers will aggregate further to form B centers. It is rare to find a normal color untreated diamond simultaneously exhibiting strong absorption from both single nitrogen and B centers, and therefore the occurrence of isolated nitrogen associated with the B centers could be considered as a possible indicator of HPHT treatment. It is true that various aggregation states of nitrogen (C, A, and B centers) are observed in the FTIR spectra of the HPHT-treated samples in this work. Similarly, the formation of H2 center requires for the existence of the donors (e.g., the C center), and therefore the existence of isolated nitrogen together with H3 and H2 centers is another possible property related to HPHT treatment [55, 58]. Although the intensity of the 637 nm is found to be stronger than that of 575 nm for the HPHT-treated diamonds in this work, which is considered to be a typical characteristic of HPHT treatment in previous works [4, 49, 59, 60], however, Collins [34] suggested that it is just a rough criterion and works well for approximately 75% of the HPHT-treated diamonds.

5. Conclusions

Recently, the color diamonds have become highly popular and gotten a great value in the jewelry market. Through

high-energy irradiation, HPHT treatment, LPHT annealing, and combination of these treatments, many industries and researchers have continuously focused on enhancing the color of diamonds so as to achieve a fancy color. Therefore, the study of these treated-color diamonds appears particularly important for the jewelry testers and customers. In this work, we collected ten treated-color diamonds with different treatment process and characterized them through the most widely used optical gemological and spectroscopic techniques (IR absorption spectrum, PL spectra, and Diamond-View). The possible conditions of the treatment and the coloration mechanism of these samples (blue, green, and red) were discussed. It is suggested that the conclusive identification of these treated-color diamonds should be made by a combination of gemological and spectroscopic properties, such as their distinctive growth patterns, color zoning, and absorption features in the IR and PL spectra.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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