Raman Spectroscopy Study on the Surface of High Temperature and High Pressure Diamond Crystal in Geology, Rock and Minerals

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Abstract. This paper analyses the colour origin and colour change mechanism of high temperature and high-pressure synthetic diamonds through experiments. In this paper, ultraviolet-visible absorption spectroscopy, infrared spectroscopy, photoluminescence spectroscopy, three-dimensional fluorescence spectroscopy, laser Raman spectroscopy and X-ray rocking curve were used for analysis. The results show that it is easy to identify genuine and fake gemstones based on Raman testing of the gemstone itself. The measurement of tiny inclusions with a confocal microscope system can provide information on whether the gemstone is natural or artificially improved, and even trace the origin of the gemstone. Width at half maximum of the Raman spectrum. Phonon "lifetime" can provide information on whether the gemstone is natural or synthetic. The photoluminescence spectrum of gemstones can also provide valuable information about the sample. This article can also identify natural gemstones or synthetic gemstones accordingly.

Keywords: Geological rock and mineral; high temperature and high pressure; diamond crystal; Raman spectroscopy.

1. Introduction

Since the 1990s, gem-quality synthetic diamonds with commercial value have been discovered in domestic and foreign diamond markets. After the unremitting efforts of researchers in recent years, Chinese synthetic diamond technology has been improved day by day. Among them, the clarity and size of high-temperature and high-pressure synthetic diamonds can basically reach gem-level, but the yellow tone of its difficult-to-remove features seriously affects the appearance and the market. value. Since the National Jewellery Quality Supervision and Inspection centre first detected jewellery inlaid with high temperature and high-pressure synthetic diamonds in 2012, many laboratories around the world have successively discovered undisclosed small particles of high temperature and high-pressure synthetic diamonds. In order to maintain the stable development of the diamond industry, it is necessary to conduct sufficient research on high-temperature and high-pressure synthetic diamonds, summarize their common characteristics, and establish a detection technology for rapid and effective identification of synthetic diamonds [1]. The predecessors have carried out related research on high-temperature and high-pressure synthetic diamonds grown under different conditions. High-temperature and high-pressure synthetic diamonds often contain boron and nitrogen elements, and nitrogen elements mainly exist in the form of lone nitrogen atoms, which can be partially aggregated into A set after high temperature annealing treatment. body, resulting in its characteristic infrared and ultraviolet spectra. Different raw materials and catalysts lead to differences in lattice defects in synthetic diamonds, but the luminescence peaks of nickel and nitrogen can be detected, and the luminescence peak of silicon can also be seen in some samples. This paper focuses on the main work we have done in gemstone identification using Raman spectroscopy in recent years: gemstone

composition, gemstone fillings, synthetic gemstones, identification of natural gemstone growth ages, etc.

2. Experimental part

2.1. Sample introduction

The samples selected in this paper are 5 high-temperature and high-pressure synthetic rough diamonds. The sample is in the shape of cube and octahedron, which is the typical crystal shape of synthetic diamond. All are yellow, with slight yellow and green tones, transparent and clean inside. The sample numbers are H_1, H_2, H_3, H_4, H_5, and the sample size is smaller, and it is synthesized under the same conditions. The high temperature and high-pressure method are used to remove the yellow tint of the high temperature and high-pressure diamond to improve the transparency and colour grade [2]. By setting different experimental parameters, parameters of different degrees of yellow fading are obtained. Three samples with obvious fading effect were selected for analysis. The sample size is 3mm×3mm×1mm, the processing pressure is 5-6GPa, the processing temperature range is 1500-1700℃, the heating time is 200s, and the cooling time is 400s

2.2. Test equipment and test conditions

Ultra-depth-of-field microscope: It is mainly used to observe the surface topography characteristics of the sample. Gemmological microscope: observe the internal features of a sample. Diamond Observer: Observe the fluorescence, phosphorescence, growth structure of the sample under the ultra-short-wave ultraviolet (<220nm) light source, this instrument is produced by DeBeers Company. X-ray spectrometer: analyses the elemental composition of inclusions in the sample. Test apparatus: Thermo Scientific QUANT'X X-ray spectrometer. Test conditions: voltage 20kV, current 1.98mA, filter PdThin, test time 100s. Micro-infrared spectroscopy: Micro-infrared spectroscopy of the test samples to quantify the boron content in the colourless samples and the nitrogen content of different structures in the yellow samples. Testing Instrument: Thermo Nicole tin 10MX Fourier Transform Infrared Microscope. Test conditions: transmission method, scanning range 650-6000cm^{-1}, resolution 4cm^{-1}, scanning times 64 times. Photoluminescence Spectroscopy: Analysis of impurity elements in samples and their occurrence modes, defect types. Test equipment: Laser Raman spectrometer. Tests were performed with 473nm, 532nm and 785nm lasers, respectively.

3. Results and Discussion

3.1. Infrared spectroscopy

The infrared spectra and Raman spectra of the five samples after growth were tested (Fig. 1). The infrared spectra of each sample are roughly the same in peak position, but there are certain differences in intensity. In the Raman spectrum, most of the samples have a broadband around 1420cm^{-1}, indicating that there are amorphous carbonaceous components in the samples, only two samples H-4 and H-5 show a broadband around 1580cm^{-1}, indicating that Graphite components are present in the sample. It can be seen from Figure 1 and Figure 2 that the infrared absorption peaks at 1465cm^{-1} and 2955cm^{-1} appeared in the samples after growth, while the infrared absorption peaks at 2850cm^{-1} and 2920cm^{-1} were significantly stronger than those before growth [3]. The 2850cm^{-1} infrared absorption peak is related to the symmetric stretching vibration of sp_3-CH^{2-} in diamond, and the 2920cm^{-1} infrared absorption peak is related to the antisymmetric stretching vibration of sp_3-CH^{2-} in diamond. The 1465cm^{-1} infrared absorption peak that appears after growth may be related to the bending vibration of sp_2-CH^{2-} in diamond, and the 2955cm^{-1} infrared absorption peak may be related to the stretching vibration of sp_2-CH^{2-} in diamond. This pair of infrared absorption Peaks are commonly found in HPHT synthetic diamonds.

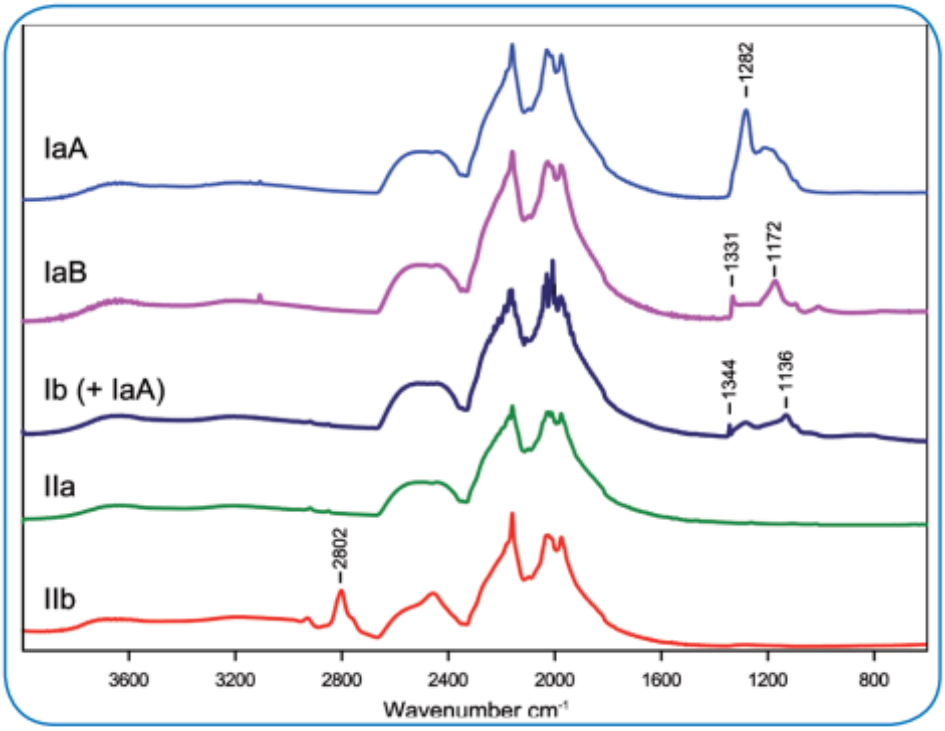

Figure 1. Infrared spectrum of the sample after growth

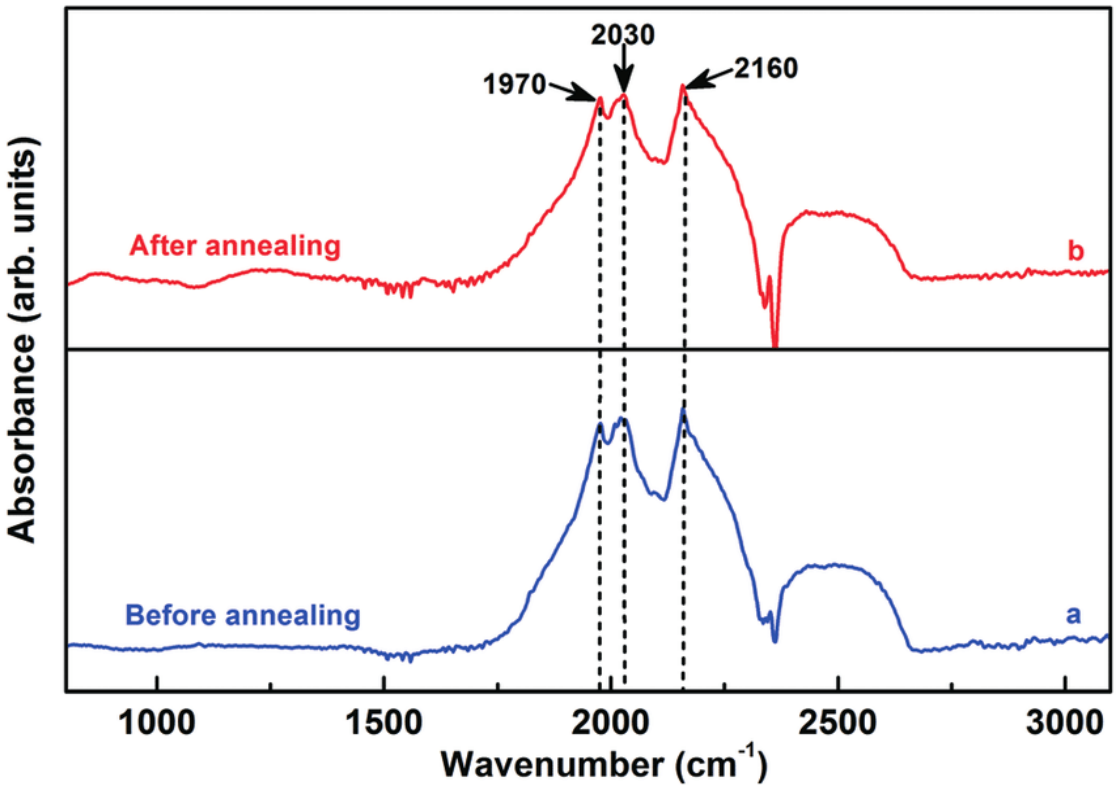

Figure 2. Infrared spectra of sample H-5 before and after growth

In synthetic diamonds, sp_3-CH^{2-} is a common defect caused by incomplete dehydrogenation of hydrocarbon groups during growth. From the infrared absorption spectra of the samples before and after growth, it can be seen that the infrared absorption peak intensity of sp_3-CH^{2-} of the grown samples is much stronger than that of the samples before growth. Combined with the Beer-Lambert law A=εcd, where A is the absorbance, c is the concentration of the substance, d is the thickness of the sample, and ε is the molar absorption coefficient, which is a function of wavelength [4]. The

infrared absorption peak of the sp_3-CH^{2-}antisymmetric stretching vibration with greater intensity is selected as the research object to explore the relationship between the concentration of C-H defects in diamonds and the growth conditions.

Compared with absorption spectroscopy, photoluminescence spectroscopy is a more sensitive analytical method to defects. PL spectroscopy was performed using excitation wavelengths of 532 and 633 nm, respectively. The change trends of the three samples before and after treatment are basically similar, and the sample H-2 is taken as an example for comparative analysis [5]. The PL peak measured at the excitation wavelength of 532 nm was normalized with the intensity of the diamond Raman peak at 573 nm as the standard. The comparison of the spectral peak intensity before and after treatment is shown in Figure 3(a). The spectral peaks measured at this excitation wavelength may appear fluorescence packets at different peak positions, such as the fluorescence packets cantered at 660 nm, where the fluorescence peaks are related to the zero-phonon sideband of the NV-centre in diamonds. After treatment, the intensity of the fluorescence peaks cantered at 660 and 683 nm was significantly weakened, and the intensity of the peak at 575 nm increased, which was related to the centre of NV0, and the intensity of the peak at 637 nm was weakened, which was related to the centre of NV-. The intensity of spectral peaks can reflect the defect ratio to a certain extent, indicating that the proportion of NV-defects in high temperature and high-pressure diamonds decreases after high temperature and high-pressure treatment. The PL spectrum measured at the excitation wavelength of 633 nm was normalized with the intensity of the diamond Raman peak at 691 nm as the standard. After treatment, the spectral peak at 737 nm was significantly enhanced, which was related to SiV-center, indicating that the proportion of SiV-center defects increased after treatment.

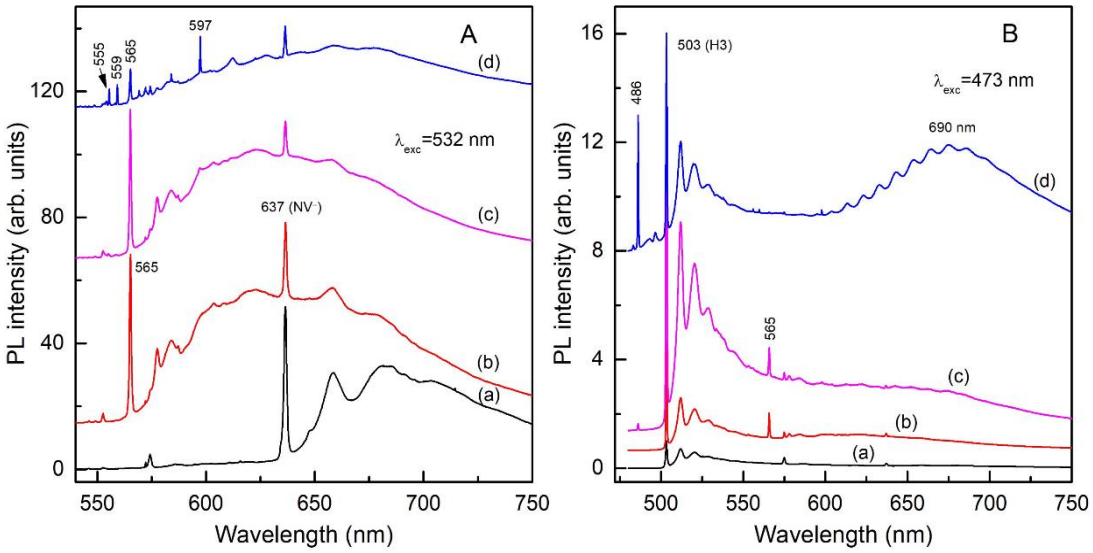

Figure 3. Near-infrared absorption spectra of samples before (a) and after (b) treatment

3.2. 3D Fluorescence Spectroscopy

The fluorescence spectrum can reflect the change of defect fluorescence before and after high temperature and high-pressure diamond processing. After treatment under different conditions, the change rules of the fluorescence spectra of the samples before and after treatment are similar. Taking sample H-2 as an example, the contour line display level of the three-dimensional fluorescence spectra before and after treatment is set to the same value, as shown in Figure 4 (a-d) shown. Fluorescence spectrum has lower excitation energy than PL spectrum, but can reflect the change of fluorescence intensity with excitation wavelength and emission wavelength [6]. The X, Y, and Z axes in the coordinate system of the isometric three-dimensional projection map represent the emission wavelength, excitation wavelength and fluorescence intensity, respectively, as shown in Figure 4(a, c), mainly to observe the height of the fluorescence peak. In the contour map, the horizontal axis X of the plane coordinate system represents the emission wavelength, the vertical axis Y represents the

excitation wavelength, and the contour lines on the plane represent the fluorescence intensity, as shown in Figure 4(b, d), mainly observe the position of the fluorescence peak.

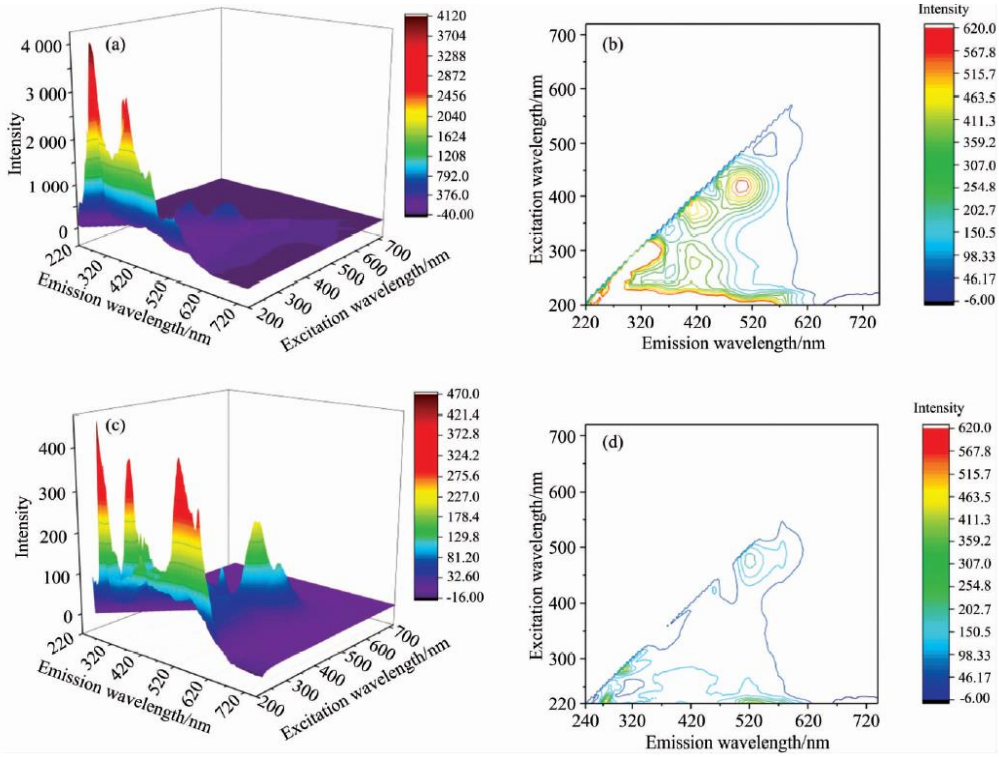

Figure 4. Three-dimensional fluorescence spectra of sample H-2 before and after treatment

4. Discussion

After the high temperature and high-pressure synthetic diamond is acid washed, the metal catalyst and graphite will be dissolved and removed, and the diamond will not be corroded and affected. The locations where stress and defects exist on the surface and inside of the crystal are often enriched regions of impurities. After pickling treatment, these stress locations and defects are exposed, leaving a characteristic fine structure [7]. The most common are some point-like and line-like structures, which are usually growth defects caused by graphite and metal catalysts on the diamond surface. In addition, stepped structural features are also very common in HPHT synthetic diamonds, and are often accompanied by an included angle of 60° or 120°. In addition, on the surface of high-temperature and high-pressure synthetic diamonds, there are often linear or curved strip structures, which are approximately parallel in one or two directions. The interior of these strip ravines is smooth and has no stepped structural features. It is speculated that the formation of this structure is due to the continuous phase transition between the graphite phase and the diamond phase in the growth cavity, and the density of the two phases is different, so the volume of the growth cavity is continuously compressed during the growth process, and the diamonds in the cavity are continuously compressed. Contact displacement occurs, leaving many wire-like structures on the original crystal plane.

The atoms in the crystal are restrained by the surrounding atoms, and generally can only vibrate in the equilibrium position. When heated to a certain temperature, the heat energy provided by it reaches the defect formation energy μ of a certain defect, and the corresponding defect is generated, and its concentration is $C=Aexp(-\mu/kT)$ (where A, k is constants), that is, the equilibrium concentration of point defects changes exponentially with temperature. It can be seen from this formula that at the same temperature, the defect concentration with smaller defect formation energy is higher, so the movement of particles or defects in the lattice will preferentially be carried out in the way of least energy consumption. At the same time, the crystal has the smallest internal energy, so the movement of the particles in the lattice also tends to form a combination that makes the internal

energy of the lattice smaller. The transformation of defects is regarded as the result of the movement of point defects. This paper believes that there are two main ways of movement of point defects: one is the generation and recombination of vacancies and interstitial atoms, and the other is the climbing movement of point defects. The way is related to temperature. in the high temperature and high-pressure process.

5. Conclusion

In this paper, five yellow high-temperature and high-pressure synthetic diamonds were subjected to high-temperature and high-pressure colour-changing experiments, and the infrared spectra, photoluminescence spectra and Diamond View TM images of the samples before and after colour-changing were analysed. The high-temperature and high-pressure method used in this paper contains many defects. In addition to stress defects, it also contains many holes and impurity atoms, such as N, Ni, etc., which have a great impact on the quality and colour of synthetic diamonds.

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