

# A Diamond with a Transient 2804 cm<sup>-1</sup> Absorption Peak

*Jianjun Li, Chengxing Fan, Shuxiang Chen and Guihua Li*

The National Gold & Diamond Testing Center (NGDTC) in Shandong, China, recently encountered a colourless 0.08 ct diamond with strong greenish blue phosphorescence in the DiamondView. Such phosphorescence is often found in HPHT-grown synthetic diamonds from Russia and China. However, the sample proved to be a near-type-IIa natural diamond with weak A and B centres and a subtle type IIb component detectable in the infrared spectrum. The DiamondPlus indicated 'Pass', confirming it was an untreated natural diamond. Notably, while the diamond phosphoresced, the infrared spectrum displayed a transient ~2804 cm<sup>-1</sup> absorption peak associated with boron. This is the first evidence of charge transfer at boron acceptors being directly linked to phosphorescence in diamond.

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## Introduction

In recent years, synthetic diamonds grown by chemical vapour deposition (CVD) and high-pressure, high-temperature (HPHT) techniques have been more commonly encountered in gem testing laboratories. Especially in the last two years, a considerable number of melee-size (less than 0.20 ct) synthetic diamonds have entered the Chinese market, and most are HPHT synthetics from China and Russia. Nearly all show greenish blue phosphorescence that is similar in colour to Sleeping Beauty turquoise. Therefore, when a parcel of melee diamonds undergoes screening at NGDTC, the first step is to separate for further testing those specimens showing this phosphorescence.

Phosphorescence is rare in most natural diamonds, although it is frequently observed in

type IIb stones, as well as in some that do not show the type IIb-related absorption at ~2800 cm<sup>-1</sup> in their infrared spectra. For the latter diamonds, the boron concentration is below the level of detection, so they are nominally type IIa diamonds (see, e.g., Eaton-Magaña and Lu, 2011).

Recently during routine testing, the NGDTC laboratory encountered a natural diamond with strong greenish blue phosphorescence. Further analysis demonstrated that this unique diamond showed different infrared spectral features before and after the disappearance of its phosphorescence.

## Methods

The 0.08 ct round brilliant diamond was tested and graded by standard gemmological methods. Testing also was performed on the DiamondSure, DiamondView and DiamondPlus verification

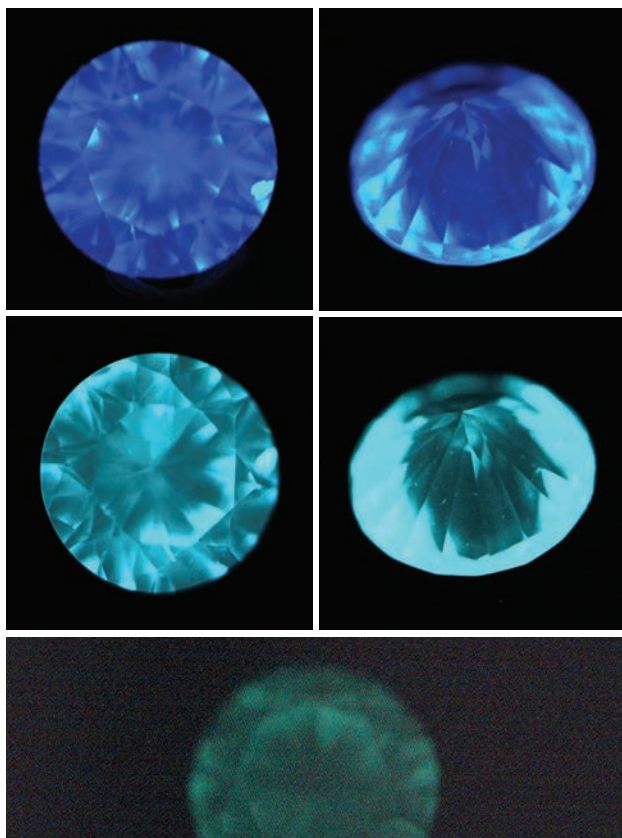


Figure 1: In the DiamondView, the 0.08 ct diamond displays vivid blue fluorescence (top) and strong slightly greenish blue phosphorescence (centre, as captured with the DiamondView's imaging system). When the hatch of the DiamondView was opened, greenish phosphorescence was visible to the naked eye (bottom). Images by Li Jianjun.

instruments manufactured by the International Institute of Diamond Grading & Research (IIDGR; De Beers Group of Companies). Ultra-violet-visible-near infrared (UV-Vis-NIR) spectroscopy was performed using a GEM-3000 instrument made by Biaoqi Scientific (China) Corp., and an integrating sphere was used to collect the internal reflectance spectra. (The incident light on the crown of a round brilliant diamond is internally reflected back through the crown by the pavilion facets, so the internal reflectance spectrum is a combination of reflection and transmission signals.) Fourier-transform infrared (FTIR) transmission spectra were collected using a Nicolet iS5 spectrometer with a Pike Technologies UpIR diffuse reflectance accessory, both during phosphorescence and after it disappeared. The spectra were scanned cumulatively four times while the diamond displayed phosphorescence and 32 times after the phosphorescence disappeared, and the resolution was set to  $8\text{ cm}^{-1}$ .

## Results

### Standard Testing

The 0.08 ct diamond had a colour grade of F and clarity grade of SI<sub>1</sub> (due to a small brown feather). In addition, a small colourless transparent inclusion was visible at about 30×–40× magnification. The sample was inert to both long- and short-wave UV radiation.

### Reactions to Verification Instruments

The DiamondSure indicated the sample was a type II diamond and referred it for further testing. The DiamondPlus showed 'Pass' when the sample was tested in liquid nitrogen.

In the DiamondView, the sample showed vivid blue fluorescence and strong phosphorescence in slightly greenish blue, but no strain pattern was visible (Figure 1). The phosphorescence lasted for a few seconds after the radiation source was turned off. Slightly greenish blue phosphorescence is often observed in synthetic diamonds in the DiamondView (D'Haenens-Johansson et al., 2015), so the sample was tested further to rule out a lab-grown origin.

### UV-Vis-NIR Spectroscopy

The UV-Vis-NIR spectrum (Figure 2) displayed no significant absorption from 250 to 1000 nm, but it did show the strong 225 nm feature caused by the diamond energy bandgap at 5.47 eV.

Figure 2: The UV-Vis-NIR spectrum of the diamond shows strong absorption at 225 nm initiated by the diamond energy bandgap at 5.47 eV. The weak, broad absorption at 350 nm is likely an instrumental artefact.

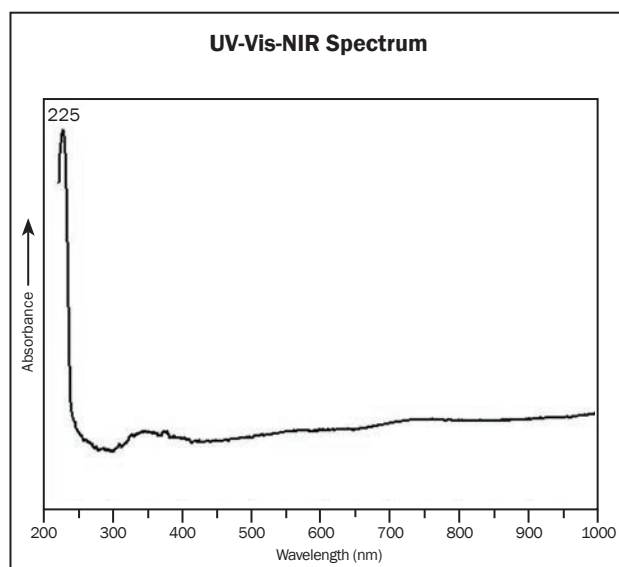
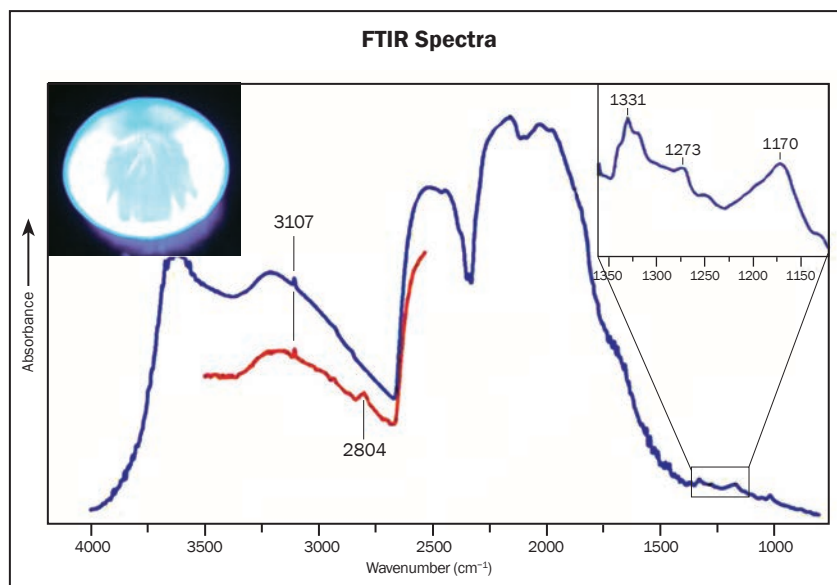


Figure 3: FTIR spectroscopy shows that the diamond is near type IIa with a  $3107\text{ cm}^{-1}$  feature due to hydrogen; the weak bands at  $1331$ ,  $1273$  and  $1170\text{ cm}^{-1}$  (see inset) indicate the diamond also contains A and B centres and possibly  $N_s^+$  (blue line). After the sample was excited using the DiamondView, it displayed strong greenish blue phosphorescence, and the resulting spectrum (red trace) shows an absorption peak at  $\sim 2804\text{ cm}^{-1}$  related to neutral substitutional boron.



eV. A broad, weak absorption band centred at  $350\text{ nm}$  may have been an instrumental artefact. There was no  $270\text{ nm}$  absorption related to single nitrogen (Zaitsev, 2001). The absence of significant extrinsic absorption in the visible and ultraviolet regions suggested that the diamond is type IIa.

### FTIR Spectroscopy

FTIR spectroscopy (Figure 3) confirmed that the sample was a near-type-IIa diamond. The spectra showed a sharp, weak band at  $3107\text{ cm}^{-1}$  related to hydrogen (Woods and Collins, 1983; Field, 1992; Kiflawi et al., 1996; Goss et al., 2014). In the  $1400\text{--}1100\text{ cm}^{-1}$  range (see Figure 3, inset), absorption bands were recorded at  $1330/1331$ ,  $1273$  and  $1170\text{ cm}^{-1}$ . These bands (and the  $2804\text{ cm}^{-1}$  feature mentioned below) are usually reported as occurring at  $1332$ ,  $1282$ ,  $1175$  and  $2803\text{ cm}^{-1}$ , respectively. As all these bands are very weak in this sample, the presence of noise might explain the apparent shift in the peak positions.

The absorption feature at  $1273\text{ cm}^{-1}$  correlates to nearest-neighbour substitutional pairs of nitrogen (A centres), and the  $1170\text{ cm}^{-1}$  band is attributed to nitrogen aggregates (B centres), that is, four nitrogen atoms symmetrically surrounding a vacancy. These spectral characteristics show that the diamond is natural in origin. The  $1331\text{ cm}^{-1}$  peak is mostly related to B-centres (see, e.g., Breeding and Shigley, 2009) and/or might also indicate the diamond contains the positively charged state of the single substitutional

nitrogen centre ( $N_s^+$ ). Therefore, the sample may be classified as near type IIa with a low IaAB component. Combined with the results of the DiamondPlus and the UV-Vis-NIR spectrum, the sample was confirmed as untreated natural diamond.

It is notable that while the diamond displayed phosphorescence, it showed a  $\sim 2804\text{ cm}^{-1}$  absorption feature related to neutral substitutional boron (i.e. uncompensated boron: Collins and Williams, 1971; Fisher et al., 2009; Gaillou et al., 2012; D'Haenens-Johansson et al., 2014). To verify this phenomenon, we scanned the sample in the region  $3500\text{--}2500\text{ cm}^{-1}$  after exciting it in the DiamondView until it displayed strong greenish blue phosphorescence. After the sample was removed from the DiamondView, the absorption spectrum was quickly measured using the diffuse reflectance accessory (Figure 3, red trace) while we could still see significant phosphorescence. According to the Omnic software, the scanning time was 3.95 seconds.

To obtain a higher signal-to-noise ratio, we attempted to accumulate eight scans of the phosphorescing diamond (Omnic software recorded a scanning time of 7.90 seconds), but we found that the  $\sim 2804\text{ cm}^{-1}$  absorption feature had disappeared after about six or seven scans.

Repeated testing as described above (i.e. exciting the sample in the DiamondView and then collecting the FTIR spectrum by accumulating four to eight scans) confirmed that the  $\sim 2804\text{ cm}^{-1}$  feature only lasted for a few seconds; as the phosphorescence disappeared, the absorption

band became extinct. Thus, the  $\sim 2804\text{ cm}^{-1}$  feature was only recorded while the diamond phosphoresced (i.e. for about 4–8 seconds).

The current understanding of the phosphorescence process in diamond is in terms of a charge transfer between the boron acceptor and a deep donor (Watanabe et al., 1997), changing the charge state of boron from compensated to uncompensated and back again. There are other instances in which a short-lived charge-transfer effect has been observed in diamond, such as  $\text{SiV}^{-/0}$  in highly silicon-doped CVD synthetic diamond (D'Haenens-Johansson et al., 2011). To our knowledge, however, this is the first record of a transient  $\sim 2804\text{ cm}^{-1}$  absorption peak observable only during the process of phosphorescence. Compared with the  $2803\text{ cm}^{-1}$  peak in the spectra of diamonds containing more boron, this is the most direct evidence of charge transfer at boron acceptors being immediately linked to phosphorescence in diamond.

## Conclusions

A 0.08 ct round brilliant displaying greenish blue phosphorescence in the DiamondView was verified as a near-type-IIa natural untreated diamond of a mixed type that contained a low IaAB component and a IIB boron content near the detection limit of infrared spectroscopy. Infrared spectra recorded while the diamond phosphoresced displayed an absorption feature at  $\sim 2804\text{ cm}^{-1}$  related to boron. This is the first instance of UV radiation inducing a characteristic IR absorption feature during phosphorescence in diamond. The specimen provides evidence that charge transfer (from negative to neutral) at boron acceptors is directly linked to phosphorescence in diamond.

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## The Authors

### Jianjun Li

National Gold & Diamond Testing Center and Shandong Provincial Key Laboratory of Metrology and Measurement, Shandong Institute of Metrology, 28 Qianfoshandong Road, Lixia District, Jinan 250014, Shandong, China  
Email: geoli@vip.sina.com

### Chengxing Fan

National Jewellery Quality Supervision and Inspection Center of China, Fourth Floor South, West Building, Weiping Plaza, 2109 Cuizhu Road, Luohu District, Shenzhen 518020, Guangdong, China

### Dr Shuxiang Chen

School of Material Science and Engineering, Qilu University of Technology, 3501 Daxue Road, Changqing District, Jinan 250353, Shandong, China

### Dr Guihua Li

National Gold & Diamond Testing Center, 28 Qianfoshandong Road, Lixia District, Jinan 250014, Shandong, China

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