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FTIR Spectra of faceted diamonds and diamond simulants

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Abstract

FTIR spectra of faceted diamonds and diamond simulants collected by diffuse reflectance, transflectance, and specular reflection techniques were compared. The transflectance technique exploited total internal reflection phenomenon within the faceted diamond for the spectral acquisition. The transflectance spectra were similar to the well-accepted diffuse reflectance spectra with equal or better spectral qualities. Based on the observed spectral features of the faceted diamond, classification of the diamond, determination of defects, impurities, and treatment process (i.e., irradiation and high pressure and high temperature) can be performed.

Keywords: Faceted diamond; Diamond simulant; Infrared spectroscopy; Diffuse reflectance; Transflectance; Specular reflection

1. Introduction

In the recent years, synthetic gemstones with the same chemical composition as the natural gemstones were encountered. In many cases, they cannot be differentiated from their natural counterparts by the conventional characterization techniques such as refractive index, hardness, color, specific gravity, and light dispersion measurements. Beside the synthetic gemstones, there are various gemstone simulants of different chemical composition with similar appearances to those of the natural gemstones. Moreover, various treatments (i.e., irradiation, heat, and high pressure-high temperature (HPHT) treatments) were normally applied to the low quality gemstones in order to improve their appearances (i.e., eliminate inclusion, enhance color, and improve clarity) [1-3]. Due to their distinct commercial values, it is important for gemologist to correctly identify synthetic, natural, and treated gemstones.

Owing to its mystic belief, popularity and commercial value, diamond is probably the most imitated of all

gemstones. Common diamond simulants included cubic zirconia (CZ), colorless synthetic corundum (sapphire), synthetic spinel, strontium titanate, yttrium aluminium garnet (YAG), gadolinium gallium garnet (GGG), and synthetic moissanite. Some of the simulants can be identified by standard gemological characterization techniques, others cannot [4]. HPHT treatment, where diamond color is altered due to changes of defects in the diamond crystal lattice, has brought a completely new threat to the gems and jewelry industry [1,3]. Detection of the treatment processes has become a major task for diamond grading laboratories, especially faceted diamonds where nondestructive characterization techniques are required. Advance analytical techniques providing information associated with chemical structures and compositions such as Fourier transform infrared (FTIR) spectroscopy [5-8], Raman spectroscopy [9], electron spin resonance (ESR) spectroscopy [10,11], and photoluminescence spectroscopy [8,12-14] are necessary for gemstone characterization.

FTIR spectroscopy is well known for its molecular related spectral information. FTIR spectral fingerprints provide information directly related to chemical structure, chemical compositions and impurities in the analyzed materials. The technique was employed for diamond

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classification based on impurities (i.e., nitrogen, hydrogen and boron) in the diamond crystal lattice [5,7]. It was also employed for differentiating diamond simulants from natural diamonds as well as determining the treatment processes applied onto the diamonds [15,16]. However, conventional infrared characterization techniques encountered several problems that make them unsuitable for routine analysis of faceted diamond. The classical transmission measurement using a thin slab of diamond [5-8] is not suitable for faceted diamonds due to its destructive nature and complex reflections of the cut and polished surfaces. Transmission measurement of a faceted diamond using beam condenser is complicated by sample arrangement where the coupled infrared radiation must pass through girdle [17,18]. Diffuse reflectance measurements of faceted diamonds tend to be non-reproducible since the spectral intensity depends strongly on the diamond orientation within the sample holder [5,19].

In order to solve the problems associated with characterization of faceted diamond and diamond simulants, a novel nondestructive transflectance technique for FTIR spectral acquisition using an infrared microscope was developed. The transflectance spectra were compared to the well-accepted diffuse reflectance and specular reflectance spectra. Spectral features associated with structures, impurities, and treatment processes were discussed.

2. Experimental

The measured samples were gems quality faceted diamonds (0.105 ct type IaB, 0.207 ct type IaA, 0.078 ct HPHT-treated and 0.144 ct irradiated and annealed diamonds) and diamond simulants (0.150 ct synthetic moissanite, 1.880 ct CZ, 2.010 ct GGG, 1.480 ct YAG, 1.780 ct strontium titanate, 1.100 ct synthetic sapphire, 1.350 ct synthetic rutile, and 1.250 ct synthetic spinel). The gemstones were characterized as received without an additional sample preparation except cleaning. All FTIR spectra were acquired by a Nicolet Magna 750 FTIR spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. A spectral resolution of 4 cm⁻¹ with 512 co-addition scans was employed. The observed spectra (6000–650 cm⁻¹) were baseline corrected before further analysis.

A commercial diffuse reflectance accessory (Collector, Spectra-Tech Inc., USA) was employed for all diffuse reflectance measurements. A faceted gemstone was placed on the sample holder with the table facet faced down, the infrared radiation was coupled into the gemstone at a near normal angle of incidence. The diffuse reflected radiation was then collected while the absorption of the gemstone was expressed in terms of Kubelka-Munk unit [20,21]. Since the observed diffuse reflectance spectrum



Fig. 1. FTIR spectra of a 0.105 ct round brilliant cut type IaB natural diamond acquired by (A) diffuse reflectance, (B) transflectance, and (C) specular reflection techniques.

was greatly influenced by the gemstone arrangements, several spectra with different gemstone arrangements were collected. The observed spectrum with the best signal-to-noise ratio was employed for further spectral analysis. The transflectance and specular reflection spectra of the same gemstone were collected by a NICPLAN infrared microscope attached to the FTIR spectrometer. The microscope was also equipped with an MCT detector. A homemade accessory was employed for all spectral acquisitions



Fig. 2. FTIR spectra of round brilliant cut diamond simulants acquired by diffuse reflectance technique.

using the microscope. The faceted gemstone was placed on the sample holder with the table facet faced up perpendicularly to the infrared radiation from the built-in 15X Cassegrainian objective. The incident radiation is coupled into the gemstone while the reflected radiation from the gemstone is collected by the objective. The specular reflection spectrum at the table facet was collected from the reflected radiation while the transflectance spectrum was collected from the total internal reflected radiation at the normal angle of incidence.



Fig. 3. FTIR spectra of round brilliant cut diamond simulants acquired by transflectance technique.

3. Results and discussion

Spectra of a 0.105 ct type IaB round brilliant cut diamond are shown in Fig. 1. The diffuse reflectance and transflectance spectra clearly reveal the three principle absorption bands of diamond (i.e., three-phonon absorption at $3900-2650 \text{ cm}^{-1}$, two-phonon absorption at $2650-1500 \text{ cm}^{-1}$, and one-phonon absorption at $1400-900 \text{ cm}^{-1}$) [22]. The high noise level at the peak maxima of the two-phonon region indicates saturated absorption. This is due to the high



Fig. 4. FTIR spectra of round brilliant cut diamond simulants acquired by specular reflection technique.

absorption coefficient of diamond in that region. The absorption bands associated with hydrogen impurity and nitrogen impurity in the diamond crystal structure are clearly observed in diffuse reflectance and transflectance spectra. The hydrogen-impurity-related absorptions at 4495, 3107, 2786 and 1405 cm⁻¹ are assigned to the vinylidene group. The weak absorptions at 1330, 1172 and 1013 cm⁻¹ are due to B-nitrogen complex [8]. An associated absorption band at 1360 cm⁻¹, which referred to the extended-planardefect platelets, could also be noticed. The specular reflection spectrum, on the other hand, does not show any prominent absorption feature. It should be noted that the absorptions of water vapor (3900–3500 and 1800–1400 cm⁻¹) and carbon dioxide gas (2400–2300 cm⁻¹) can be noticed in all measured spectra. The variations of the absorption magnitudes are due to the fluctuation of the ambient air during the spectral acquisition.

Spectra of faceted diamond simulants acquired by diffuse reflectance, transflectance and specular reflection techniques, respectively, are shown in Figs. 2-4. The spectral envelops of the transflectance spectra are similar to those of the diffuse reflectance spectra. In the lower wavenumber region, saturation is observed in the diffuse reflectance and transflectance spectra. The specular reflection spectra, on the other hand, show refractive-index type spectral features. This is due to the high absorption coefficient of the gemstones in the low wavenumber region. Although the exact positions of the absorption maxima in that region cannot be identified from the diffuse reflectance nor transflectance spectra, they can be noticed from the specular



Fig. 5. FTIR spectra of round brilliant cut diamonds acquired by transflectance technique: (A) a 0.207 ct natural diamond, (B) a 0.144 ct irradiated and annealed diamond, and (C) a 0.078 ct HPHT-treated diamond.

reflectance spectra. It should be noted that Kramers-Kronig transformations of the specular reflection spectra cannot be performed since the absorption maxima are too close to the low wavenumber end of the observed spectra. The weak absorption bands in the high wavenumber region are clearly observed in the diffuse reflectance and transflectance spectra. Although the absorption bands of the synthetic moissanite in the 2500-2200 cm⁻¹ are interfered by that of carbon dioxide gas, their absorption maxima are clearly identified. Spectral quality of the transflectance spectra seem to be better than that of the diffuse reflectance spectra. Two small absorption bands of the synthetic moissanite at 3157 and 3071 cm⁻¹ can be noticed in the transflectance spectra while the same bands could not be observed in the diffuse reflectance spectra. Peak positions of the absorption bands of diamonds stimulants deduced from the experimentally observed spectra in Figs. 2-4 are conformed to those reported elsewhere [6].

FTIR spectra of natural, HPHT-treated, and irradiated and annealed diamonds are shown in Fig. 5. The absorption bands unique to type of diamond and treatment processes are clearly observed. All diamonds exhibited an absorption band associated with defect-induced one-phonon absorption caused by nitrogen impurities. According to the spectral envelop and the main absorption at 1280 cm⁻¹, the diamond in Fig. 5A was classified as type IaA diamond. Since the spectral features are associated with an A-centered defect (i.e., a defect consists of a pair of adjacent substituting nitrogen atoms in the diamond crystal lattice) [22].

Due to the saturation in the one-phonon region associated with high concentration of nitrogen, classification of the irradiated and annealed diamond in Fig. 5B was not possible. Since absorptions in the high wavenumber region (4000-5000 cm⁻¹) are clearly observed, the associated defect centers could be employed for characterization purpose. It should be noted that absorption bands in this region are not observed in un-irradiated type I natural diamonds. The H1a absorption at 1450 cm⁻¹ involves the creation of a local vibrational mode due to interstitial nitrogen. The H1b absorption at 4931 cm⁻¹ seen in type IaA diamonds is related to the A-center. The absorption centers, H1a and H1b, are unique to the irradiated and annealed type I diamond [16,23-25]. The sharp absorptions associated with the vibration of the vinylidene group at 3107 cm⁻¹ and 1405 cm⁻¹ and that with NH stretching at 3236 cm⁻¹ are clearly observed [26].

The absorptions in the one-phonon region of the HPHTtreated diamond in Fig. 5C indicates that the diamond was type Ib. Absorptions at 1342 and 1128 cm⁻¹ are typical for HPHT-treated diamond and are attributed to defect center with a single substituting nitrogen atom [5,7,27]. It should be pointed out that the weak absorptions at 2920 and 2849 cm⁻¹ in Fig. 5B and C are due of aliphatic hydrocarbon on the surfaces of the faceted diamond. The absorption bands were disappeared when the faceted diamond were carefully cleaned (see Fig. 5A).

4. Conclusions

FTIR spectra of faceted diamonds and diamonds simulants measured by three different techniques were compared. The transflectance technique provides spectrum with an equal or better spectral qualities to that of the wellaccepted diffuse reflectance technique. An infrared microscope can be utilized for a nondestructive transflectance spectral acquisition of faceted diamonds and diamond simulants. The observed spectra can be employed for classification purpose as well as for identification the treatment processes applied onto the diamonds. Due to the nondestructive nature, short measurement time, simplicity, and spectral information directly related to chemical structures and compositions, transflectance technique could be employed for routine analysis of faceted diamond. Although the shown results are those of the round brilliant cut diamonds, the techniques are applicable for other types of diamond cuttings and/or gemstones.

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References

- [1] A. Petkewich, Anal. Chem. 75 (2003) 71A.
- [2] A. Jayaraman, Curr. Sci. 79 (2000) 1555.
- [3] J.E. Shigley, Curr. Sci. 79 (2000) 1566.
- [4] K. Nassau, Curr. Sci. 79 (2000) 1572.
- [5] N. Ferrer, J.M. Jogués-Carulla, Diamond Relat. Mater. 5 (1996) 598.
- [6] S. Fernandes, M. Khan, G. Choudhary, Aust. Gemmol. 1Q (2003) 361.
- [7] M.J. Mendelssohn, H.J. Milledge, Int. Geol. Rev. 37 (1995) 95.
- [8] K. Iakoubovskii, G.J. Adiaenssens, Diamond Relat. Mater. 11 (2002) 125.
- [9] A.L. Jenkins, R.A. Larsen, Spectroscopy 19 (2004) 20.
- [10] C.J. Noble, Th. Pawlik, J.M. Spaeth, J. Phys., Condens. Matter 10 (1998) 11781.
- [11] P.F. Lai, S. Prawer, C. Noble, Diamond Relat. Mater. 11 (2002) 1391.
- [12] I.N. Kupriyanov, V.A. Gusev, Y.M. Borzdov, A.A. Kalinin, Y.N. Palyamov, Diamond Relat. Mater. 8 (1999) 1301.
- [13] J. Lindblom, J. Hölsä, H. Papunen, H. Häkkänen, J. Mutanen, Opt. Mater. 24 (2003) 243.
- [14] A.T. Collins, Diamond Relat. Mater. 9 (2000) 417.
- [15] F. de Weerdt, J. van Royen, Diamond Relat. Mater. 10 (2001) 474.
- [16] I. Kiflawi, G. Davies, D. Fisher, H. Kanda, Diamond Relat. Mater. 8 (1999) 1576.
- [17] G.S. Woods, A.T. Collins, J. Phys. C. Solid State Phys. 15 (1982) L949.
- [18] I.M. Reinitz, E. Fritsch, J.E. Shigley, Diamond Relat. Mater. 7 (1998) 313.

- [19] L.I. Tretyakova, N.B. Reshetnyak, Y.V. Tretyakova, J. Gemmol. 25 (1997) 532.
- [20] R.G. Messerschmidt, Appl. Spectrosc. 39 (1985) 737.
- [21] M.P. Fuller, P.R. Griffiths, Anal. Chem. 50 (1978) 1906.
- [22] C.D. Clark, A.T. Collins, G.S. Woods, in: J.E. Field (Ed.), The Properties of Natural and Synthetic Diamond, Academic Press, London, 1992, p. 35, Chapter 2.
- [23] I. Kiflawi, A. Mainwood, H. Kanda, D. Fisher, Phys. Rev., B 54 (1996) 16719.
- [24] G.S. Woods, A.T. Collins, J. Phys. C. Solid State Phys. 15 (1982) L949.
- [25] A.T. Collins, G. Davies, G.S. Woods, J. Phys. C 19 (1986) 3933.
- [26] F. de Weerdt, Y.N. Palyanov, A.T. Collins, J. Phys., Condens. Matter. 15 (2003) 3163.
- [27] A. Yelisseyev, Yu. Babich, V. Nadolinny, D. Fisher, B. Feigelson, Diamond Relat. Mater. 11 (2002) 22.