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Micro-Raman Spectroscopy Study of Gem-Quality Diamond-Like Nexus Labs Stone and its Comparison to Natural and Synthetic Polished Diamonds

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Dispersive (visible) confocal micro-Raman spectroscopy (DCμRS) was non-destructively performed on a gem-cut diamond-like nexus labs stone, which is the most popular gem on the market today to characterization and identification. The observed Raman bands were compared and contrasted to the natural mined diamond and synthetic produced chemical vapour deposotion diamond in order to distinguish them from one another. A total 9 of Raman bands were observed in the spectra of the representative diamond-like nexus labs stone which was firstly synthesized from the elements C, S, Ca, Fe, Co, Ni, Y, Zr, Gd, and Hf. Then covered by corundum and related material composite. They showed bands at 170, 312, 520, 727, 918, 1079, 1112, 1332 and 1523 cm^{-1} in a range between 50 and 1600 cm^{-1} and they are characteristic for this stone, which is fully colourless. In addition, possible causes of these bands were assigned to some crystalline defects. It can be stated that only one Raman band at 1332 cm^{-1} can be related to the characteristic crystalline diamond band, since the strong characteristic carbon Raman band representing a covalent bonding at 1332 cm^{-1} in the natural and synthetic diamonds. Additionally, one weaker characteristic Raman band also appear at 1349 cm^{-1} in the synthetic chemical vapour deposition pure-carbon lab-created diamond, which is yellowish only. Moreover, the weak band is due to the ionic bonded [AlO_4] centre which composed of corundum covering.

Key Words: Diamond nexus stone, Natural diamond, Synthetic CVD diamond, Dispersive confocal micro-Raman spectroscopy (DCμRS), Characterization.

INTRODUCTION

Diamond-like transparent gemstones, the origin of which is kept secret so that everyone believe that they are real, have been used in the jewellery sector for a long time. However, one stone has been more and more popular in recent years. This is diamond-like nexus labs stone[1]. Actually, this stone, after being synthesized, is coated with some diamond-like materials. Thus, the coating facility enables the Nexus stone to have important measurable physical characteristics[1]. However, the diamond Nexus labs produce a range of pure-carbon lab-created diamonds, which duplicate the chemical properties of earth-mined diamonds as well as the optical and the physical properties. But, this study does not include pure carbon gemstones, which are available in yellow, pink and blue. Even though a pure carbon crystal up to 10 carats can be grown, the crystal, however, at this point has a tinge of colour to it and cannot be used as a colourless stone[1].

The Raman effect was predicted by Smekal in 1923 and later observed experimentally by Raman and Krishnan in 1928[2]. FT-Raman and/or dispersive (visible)-Raman spectroscopy are spectroscopic techniques used in condensed matter physics and chemistry to study vibrational, rotational and other low-frequency modes in a system. In any case, Raman spectroscopy is nowadays an even more powerful tool to analyze the structure, symmetry and short range order at nano-scale[3]. Moreover, the Raman signature of a covalent-bonded structure can be described as that of the covalent entities constituting the structure (BO_6 octahedron). The other ions are highly ionic and contribute with the translation oscillation modes (T') (low energy, below *ca.* 250 cm^{-1}), which couple themselves with other vibrational modes of the neighbouring entities: translations (T') and rotations/librations (R') of the iono-covalent BO_6 entity leading to the wavenumber shifts. A low wavenumber region (250-100 cm^{-1}) mainly involves a cationic network and the lattice modes, while a 800 to 250 cm^{-1} spectral range reveals the bending and stretching modes of the covalent-bonded octahedron[4,5]. Every conventional characterization technique is not suitable for this purpose, but Raman spectroscopy has

TABLE-1
SIMILARITY AND CONTRASTING OF SOME PHYSICAL-CHEMICAL FEATURES OF A DIAMOND-LIKE NEXUS LABS STONE WITH NATURAL AND SYNTHETIC DIAMONDS USED IN THIS STUDY. SOME DATA WERE COMPILED FROM DIAMOND MINERAL DATA (2011), DIAMOND NEXUS STONE (2011) AND ELEMENTSIX (2011)

Features	Imitation Diamond (Nexus Stone)	Natural Diamond (Mined Diamond)	Synthetic Diamond (CVD Diamond)
Colour	Colourless	Almost colourless	Almost colourless
Clarity	Internally flawless	Small flaws	Very very small flaws
Shape and cut	Round, Full-cut brilliant	Round, Full-cut brilliant	Round, Full-cut brilliant
Chemical composition	C, S, Ca, Fe, Co, Ni, Y, Zr, Gd, Hf (Carbon, Sulphur, Iron, Calcium, Cobalt, Nickel, Yttrium, Zirconium, Gadolinium, Hafnium)	C	C
Specific gravity	7.78	3.52	3.52
Hardness	Over 9	10	~10
Crystal system	Cubic	Cubic	Cubic
Refractive indexes	Isotropic, N: 2.20	Isotropic, N: 2.42	Isotropic, N: 2.42
Double refraction	None	None	None
Lustre	Adamantine	Adamantine	Adamantine
Porosity	0.097	0.096	0.096
Dispersion	0.046	0.044	0.044
Cleavage	None	Perfect	Perfect
Fracture	Conchoidal	Conchoidal	Conchoidal
Luminescence	Weak blue	Strong blue	Weak blue
Appearance	Perfect lustre and brilliance	Perfect lustre and brilliance	Dull lustre and brilliance

already been proved as powerful tool[6]. For quite a long time this technique was mainly devoted to fundamental research, but instrumental progress has rendered it for a general characterization method[6-8].

Dispersive confocal micro-Raman spectroscopy (DCμRS) is one of the well-known non-destructive and non-invasive methods for the characterization of gem minerals[9]. Therefore, the DCμRS can be used in the identification and determination of a diamond-like gemstone.

This study aims to characterize a gem-cut diamond-like nexus labs stone (DNL), which is fully colourless using the confocal micro-Raman spectroscopy and compare and contrast with those of the natural mined diamond and synthetic diamond produced by a chemical vapour deposition (CVD) method.

EXPERIMENTAL

During this study, three materials were used for representing the imitation, natural and synthetic gem-cut stones. The main investigation material is a diamond-like imitation stone created by the diamond Nexus labs (USA). This stone was obtained from the jewellery market in Turkey. It is 1.23 carats in weight and is fully colourless (D colour regarding the GIA scale) and also cut as round, full-cut brilliant, with a perfect appearance.

In the case of the comparison stones, first, a natural diamond was obtained from the jewellery market in Turkey. It is 2.02 carats in weight and is almost colourless (I colour regarding the GIA scale) and also cut as round, full-cut brilliant, with a perfect appearance. Second, a synthetic chemical vapour deposition diamond was obtained from the Element Six Co. (a subsidiary of De Beers) (Luxemburg), having a code SC Plate 1b 30-30-05 < 100 > PL. It is 0.35 carats in weight and is almost colourless (J colour regarding the GIA scale) and also cut as round, full-cut brilliant, with a dull lustre.

In order to verify, some non-destructive mineralogical characterization tests were carried out on these three representative samples. The tests were performed in the Dokuz Eylul Gemmological Testing Laboratory of Dokuz Eylül University. First, it measured the average specific gravity values of the three representative samples using an electronic balance scale (measurement sensitivity of 0.001) with an SG kit, based on the formula ($SG = W_{air}/W_{air} - W_{water}$). Second, the average refractive index values of these representative samples were determined in order to establish the optical character and optical sign using an Eickhorst SR/XS standard refractometer device with an optical contact liquid of 1.79 RI and a quartz lamp with a wavelength of 589 nm. Third, ultraviolet (UV) luminescence excitation of these representative samples was observed using a System Eickhorst UV 240 shortwave (255 nm) and long wave (366 nm) 4W UV lamp. Finally, other gemmological and mineralogical features of these representative samples were obtained with well-known, non-destructive investigation methods. The results were given in Table-1.

The dispersive confocal micro-Raman spectra of these representative samples were recorded against a dark background at room temperature using a HORIBA Jobin Yvon Scientific XPLORA dispersive (visible) confocal micro-Raman spectrometer with a high throughput integrated spectrograph, which also includes a monochromator, a filter system and a charge-coupled device (CCD) (Fig. 1). Raman spectra were excited by a He-Ne laser (532 nm) at a resolution of 1 cm^{-1} in the range between 4000 and 50 cm^{-1}. The micro-Raman analyses were performed on a dark background at room temperature. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectral manipulation as a baseline adjustment was carried out using the software of the device. The Raman analysis was carried out in the Gemmological Testing Laboratory at the Izmir Multidisciplinary Vocational School of Dokuz Eylül University-Izmir (Turkey).

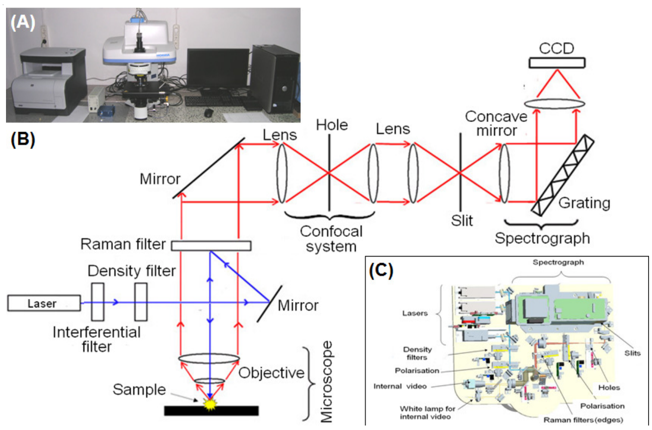
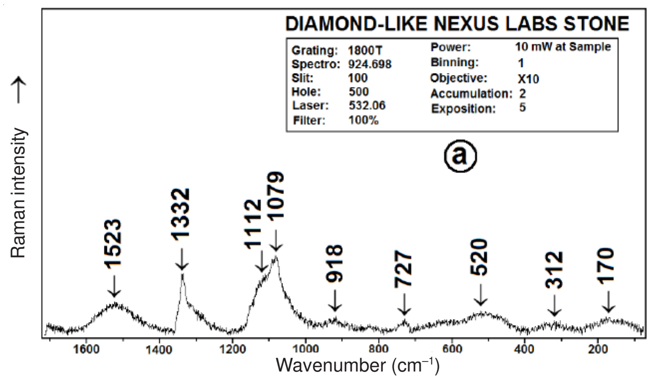


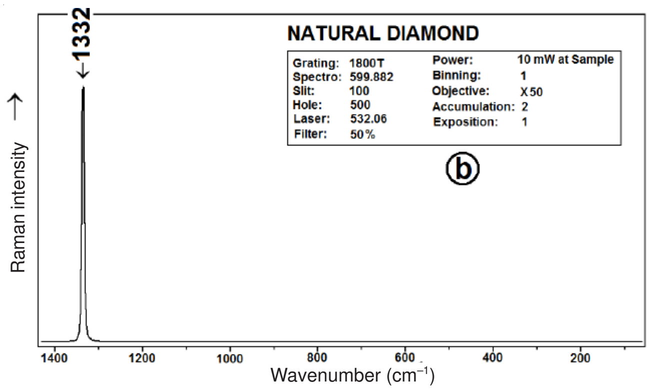
Fig. 1. Dispersive confocal micro-Raman spectrometer used in this study (A), its schematic diagram (B) and description (C). In Raman spectroscopy, the sample is irradiated with a strong monochromatic light source (532 nm laser)

RESULTS AND DISCUSSION

Comparative showing of the dispersive confocal micro-Raman bands in the range between 50 and 4000 cm^{-1} of a gem-cut diamond-like fully colourless nexus stone created by the Diamond Nexus Labs, a gem-cut, natural, nearly colourless diamond and a gem-cut, synthetic, nearly colourless diamond of the chemical vapour deposition (CVD) method produced by the Elementsix Co., is given in Fig. 2.

Main interest was given to the diamond-like nexus stone which is fully colourless, except for the pure-carbon lab-created diamond which is yellowish, since its Raman spectra is very distinctive (Fig. 2a). A total of 9 micro-Raman bands were established. They have strong and weak bands and are peaked at 170, 312, 520, 727, 918, 1079, 1112, 1332 and 1523 cm^{-1} in the range between 50 and 1600 cm^{-1}. Development





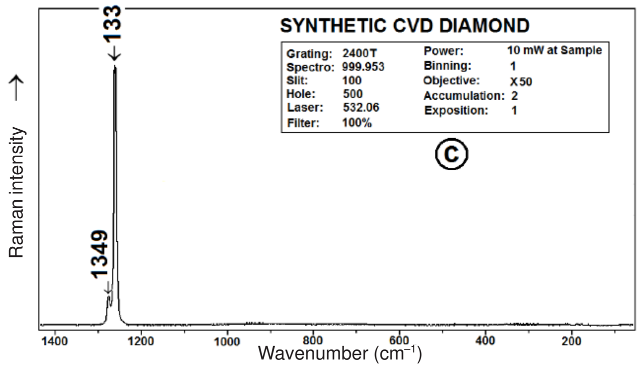


Fig. 2. Comparative showing of the dispersive confocal micro-Raman bands of a gem-cut diamond-like nexus stone created by the Diamond Nexus Labs (DNL) (a), a gem-cut natural earth-mined diamond (b) and a gem-cut synthetic diamond of the chemical vapour deposition (CVD) method produced by the Elementsix Co. Spectral details are labelled on spectra

of these distinctive confocal micro-Raman bands in the diamond-like nexus labs stone is related to its rich chemical composition [mixing of the elements in order of atomic weights, carbon (C^6), sulphur (S^{16}), calcium (Ca^{20}), iron (Fe^{26}), cobalt (Co^{27}), nickel (Ni^{28}), yttrium (Y^{39}), zirconium (Zr^{40}), gadolinium (Gd^{64}), hafnium (Hf^{72})][1] and the production process. The production of a diamond nexus labs stone is carried out in a ceramic and carbon-fibres crucible, which is lined with a technical advanced phase-change material that is necessary to handle the enormous heat (approaching 4000 ºC) and pressure (approaching 90.000 atmosphere)[1]. However, the most important factor in the production of the micro-Raman bands can be due to the coating with corundum (Al_2O_3) and some proprietary materials of the diamond nexus labs stone[1]. The coating seals the stone's surface greatly lowering porosity and makes the nexus stone impervious to outside contaminants as well as increases its hardness and scratch resistance. On the other hand, because this coating process is not fully transparent, the slight opaque and blue phase band imparted brought the reflective and refractive index (called brilliance and dispersion) of the stone almost exactly in line with a natural diamond[1]. Ultimately, it is also reported that the coating gave the slightest hint of fluorescence[1].

The collective spectra (Fig. 2) reveal stretching and bending modes equivalent to those of polyhedral (mostly tetrahedral or octahedral) isolated molecules. The difference arises from the cations generating Ti (translational) and Ri (rotational) libration modes. A given stretching or bending vibration always appears in the same region, its exact position imparting information about the local environment of the corresponding bonds, both in the crystalline and amorphous states[7,10].

However, micro-Raman bands of natural and synthetic diamonds (Figs. 2b and 1c) were also established for comparison with those of imitation diamonds. It is well-known that natural and synthetic diamonds give a very distinctive micro-Raman band peaked at 1334 cm-1 which represents the characteristic crystalline carbon band[3]. However, it was clearly observed that one weaker characteristic Raman band is also peaked at 1349 cm^{-1} in the synthetic chemical vapour deposition diamond only (Fig. 2c). This band can be dependably used in the identification of a synthetic chemical vapour deposition diamond. Development of this additional Raman band in the synthetic chemical vapour deposition diamond is related to its production process. For a single crystal chemical vapour deposition diamond, the substrate needs to be a single crystal diamond and the new diamond film grows epitaxially, with the deposited film taking on the lattice structure and orientation identical to those of the substrate. For a polycrystalline diamond, a non-diamond substrate is used. A variety of materials can be used in this context; primarily silicon, silicon carbide and a range of carbide forming metals including molybdenum and tungsten.

It can be proposed that only one Raman band at 1332 cm^{-1} can be related to the characteristic crystalline diamond band, since the strong characteristic carbon Raman band representing a covalent bonding is observed at 1332 cm^{-1} in the natural and synthetic diamonds. Additionally, one weak characteristic Raman band also appeared at 1349 cm^{-1} in the synthetic chemical vapour deposition pure-carbon lab-created diamond which is yellowish only. Moreover, the weakness of this band is cause of the ionic bonded [AlO_4] centre which composed of corundum covering.

On the other hand, in the spectrum of the nexus stone (Fig. 2a), the Raman bands at 1523, 1332, 1112, 1079 and 918 cm^{-1} were assigned to ν_1 symmetric stretching modes[10]. The Raman bands at 727 and 520 cm^{-1} were assigned to ν_2 symmetric bending modes[10]. The Raman band at 312 cm^{-1} was assigned to rotational libration[10] and finally the Raman band at 170 cm^{-1} was assigned to translational libration[10].

Fig. 2 shows that only one micro-Raman band at 1335 cm^{-1} can be related to the characteristic carbon band at 1334 cm^{-1}. The colourless nexus stone has many features of natural and synthetic diamonds. Therefore, Table-1 shows the similarity and contrast of some physical-chemical features of diamond-like nexus labs stone, earth-mined natural diamond and synthetic chemical vapour deposition diamond. As a result, it can be stated that the nexus stone is a near perfectly created stone of the diamond-like colourless gemstones similar to moissanite, CZ, GGG, YAG, fabulite and strontium titanate.

Conclusion

An application of dispersive (visible) confocal micro-Raman spectroscopy (DCµRS) with a silicon CCD array was carried out as a non-destructive and non-invasive method to reveal the vibrational characterization of the diamond-like nexus stone and to distinguish it from other natural and synthetic diamonds.

Characteristic Raman bands of the diamond-like nexus stone were assigned some vibrational causes. Firstly, the Raman bands peaked at 1523, 1332, 1112, 1079 and 918 cm^{-1} were assigned to ν_1 symmetric stretching modes. The Raman bands peaked at 727 and 520 cm^{-1} were assigned to ν_2 symmetric bending modes. The Raman band peaked at 312 cm^{-1} was assigned to rotational libration and finally the Raman band peaked at 170 cm^{-1} was assigned to translational libration.

It is revealed that diamond-like nexus stone is exactly distinguished in a few seconds from the natural and synthetic diamonds using a dispersive confocal micro-Raman spectrometer as well as a specific gravity test because of its higher specific gravity value of 7.78.

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