Identification of Diamond and its Imitators with Using Excilamp

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Abstract – Optical transmission and photoluminescence spectra of man-made and natural samples of corundum, diamond and fianite were investigated. A photoluminescence excitation carried out by barrier-discharge KrCl excilamp with spectral maximum at 222 nm. It was suggested to use a KrCl excilamp for nondestructive identification of diamond and its imitators.

1. Introduction

Diamonds are known at least from three thousand years B.C. In all times an identification of diamonds was relevant. Nondestructive methods are most important and developing to present day. New devices of express-analysis of diamond identity constantly appear in the market known as diamond-testers [1].

Principle of its operation is based on measuring of one or two sample properties like thermal conductivity, refraction coefficient, transmission spectrum and permittivity.

Rapid development of material science leads to appearance of new diamond imitators. Some of its properties became very close to same property of diamond. In this case, for express identification of diamond it is necessary to measure more than one of properties mentioned above.

Moreover, a fast evolution of man-made diamond synthesis of large size and jewelry quality leads to further complication of express-analysis. In this connection, a development of diamond-testers based on measuring of optical transmission (OT) and photoluminescence (PL) is very perspective. After accumulation of enough digital spectra database it is possible to determine not only class of sample material, and even type and origin.

In the recent years new light sources – excilamps have been developed [2]. These lamps are based on a radiation of dimmers and halides of inert gases in different kinds of gas discharges. A KrCl excilamp produces UV light at 222 nm with average power tens of mW/cm². This wavelength is located at the edge of fundamental absorption range of diamond. An UV radiation at 222 nm excites a PL in all of diamonds practically.

In the present work PL and OP spectra of natural and man-made diamonds, and its imitators – corundum and fianite (cubic stabilized zirconia) were investigated. Some spectral differences of samples were demonstrated. We have suggested using a KrCl-lamp to measure a PL and OP spectra with aim of identification of diamond and its imitators.

2. Samples and experimental methods

In present work, optical properties of three samples of corundum, two natural and one man-made diamonds, and a fianite were investigated. Short characteristics and dimensions of samples are presented in Table 1.

PL of samples was excited by a sealed-off barrier-discharge KrCl excilamp (1 in Fig. 1). PL emission of sample 2 and emission of KrCl excilamp passed through light filter 3 and optical fiber 4, then analyzed by EPP-2000C spectrometer 5 (Stellar-Net Inc.). Signal was accumulated during 1–20 s and presented on PC 6 by spectrum.

Transmission spectra of samples were measured in two spectral region: using KrCl excilamp in 200–300 nm region and using halogen lamp in 300–850 nm region. During transmission measuring light filter 3 was not used. Signal was accumulated during not more than 1 s.

Table 1. Numbers, dimensions and description of samples

<table>
<thead>
<tr>
<th>N sample</th>
<th>Dimensions, mm</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15×11×8</td>
<td>Synthetic faceted corundum of saturated red color</td>
</tr>
<tr>
<td>2</td>
<td>6×6×4</td>
<td>Synthetic faint-colored faceted corundum</td>
</tr>
<tr>
<td>3</td>
<td>11×9×7</td>
<td>Synthetic faint-colored faceted corundum</td>
</tr>
<tr>
<td>4</td>
<td>Ø5×0.25</td>
<td>Plane-parallel disk of natural Hla-type diamond</td>
</tr>
<tr>
<td>5</td>
<td>Ø5</td>
<td>Natural round-faceted diamond of 0.43 carat</td>
</tr>
<tr>
<td>6</td>
<td>10×10×0.5</td>
<td>Plane-parallel plate of man-made CVD diamond</td>
</tr>
<tr>
<td>7</td>
<td>6×6×4</td>
<td>Faceted fianite (cubic stabilized zirconium oxide)</td>
</tr>
</tbody>
</table>
3. Results and discussion

In the first place, all samples were checked by diamond/moissanite DN1 Tester (Oris Nelson Enterprise, Inc.). Samples 4, 5, 6 were identified like diamonds. The device was not responded to samples 1, 2, 3, 7.

OP spectra of three man-made faceted samples of corundum shown in Fig. 2, a. One of them had the most deep red color and demonstrated spectrum 1 in Fig. 2, a. There was an intensive absorption band in the range 500–600 nm. Besides, in the spectrum there were intensive R-lines of chrome PL with contour maximum at 693 nm. There were S- and N-lines of chrome PL to short- and longwave sides from the dominant [3]. A PL of corundum was stimulated by broad emission of halogen bulb. Two other samples of corundum had a pale pink color and demonstrated spectrum 2, 3 in Fig. 2, a. These samples showed an absorption band in the range 500–600 nm also.

OP spectra of natural IIa type and man-made CVD diamonds were coincided (spectra 4 and 6 in Fig. 2, b, correspondingly). There was only a difference in the range 230–300 nm. Both spectra demonstrated definite fundamental absorption edge. Natural diamond 4 contained nitrogen N3-defects [4, 5]. A N3-defect in diamond is three nitrogen atoms in neighboring substitutional site and “bonded” with a vacancy. HOWEVER, N3 defect concentration was too low to observed N3 system in OP. The man-made diamond was characterized by a high quality and concerned to type IIa in term of standard physical classification of diamonds [6]. OP spectrum 5 of natural faceted Ia diamond shown in Fig. 2, b. It demonstrated a secondary absorption edge from ~308 nm and an intensive N3 system.

OP spectrum 7 of faceted fianite had not any peculiarities and demonstrated a broad structureless absorption band in the visible range from 300 nm.

PL spectra of corundum samples showed an intensive chrome R-lines at 693 nm, S- and N-lines to short- and longwave sides (spectra 1, 2, 3 in Fig. 3, a). The intensity ratio of R-lines to S/N-lines was 0.17–0.34 for chrome enriched sample 1 and 0.02–0.05 for sample 2 and 3. Lines at 725 and 740 nm in spectra 2 and 3 associated with discharge plasma emission of KrCl exilamp.

PL spectra of natural and man-made diamonds (spectra 4, 5, 6 in Fig. 3, b) consisted in a broad structureless band-A with maximum in the range 420–450 nm. In according with [7] band-A associated with dangling bonds in dislocation cores. In [8], it was reported that band-A connected with amorphous carbon in grain boundaries of CVD diamond. Thus, band-A associated with intrinsic defects and observes both in natural and man-made diamonds.

The N3 system with zero-phonone line (ZPL) at 415.2 nm and phonon replicas in the range 420–460 nm superimposed on band-A in the PL spectrum of sample 4. Same situation was observed for this sample in [4, 5]. However an absorption N3 system with ZPL at 415.2 nm and phonon replicas in the range 350–410 nm was observed in the PL spectrum of Ia diamond sample 5. In spite of rather high N3-defect concentration (~5 \cdot 10^{17} \text{ cm}^{-3}), the PL spectrum of the stone 5 not consisted in the N3 system.

![Fig. 2. OP spectra of samples. Numbers of spectra coincide to numbers of samples in Table 1](image-url)
Fig. 3. PL spectra of samples at excitation of KrCl excilamp. Numbers of spectra coincide to numbers of samples in Table 1.

It possible to suggest, that sample 5 consisted in another kind of defects, which effectively quenched a N3 emission. Usually samples with high concentration of A-defects not demonstrated a N3 emission. An A-defect in diamond is two nitrogen atoms in neighboring substitutional site.

On the other hand, a KrCl excilamp emitted a dominant line at 222 nm. The wavelength is located in the range of fundamental absorption of diamond ($E_g \approx 5.5$ eV $\approx 226$ nm). The absorption coefficient of diamond at 222 nm is about 300–400 cm$^{-1}$ [6]. The mean free pass of 222 nm photon is 25–30 $\mu$m. So, a PL band-A is excited in a thin layer and passing through a 5-mm thick diamond weakened in absorption on N3-defects in the range 350–418 nm. Thus, we observed the absorption N3 system in the PL spectrum of sample 5.

Note that a PL intensity of sample 5 was 20 times higher than of sample 4. In Fig. 3, b an intensity of spectrum 4 was increased in 10 times for a simple comparison.

A PL spectrum of sample 6 was increased in 100 times due to very low intensity. Sample 6 demonstrated only structureless band-A without any peculiarities. Lines at 555 and 585 nm associated with discharge plasma of KrCl excilamp.

PL spectrum 7 of fianite in Fig. 3, b consisted in a broad structureless band with maximum at ~500 nm and had not any sharp-line peculiarities. Same spectra were observed for many fianite with different stabilized compounds [1, 9].

4. Conclusion

In the present work OP and PL spectra of man-made corundum samples, natural and man-made diamonds and a fianite were investigated.

Chrome PL at 693 nm was observed both in OP and PL spectra of corundum samples. This PL never observed in diamonds of different origin.

The fianite demonstrated specific broad yellowish PL band with maximum at 500 nm without any sharp-line peculiarities.

The system N3 was observed both in OP and PL spectra of natural diamonds. Man-made diamonds had not showed the system N3 usually, with exception of nitrogen-enriched samples annealed at high temperature and high pressure [10].

Thus, we sure that it is possible to develop devices based on OP and PL measuring, equipped a KrCl excilamp, and able to identify a diamond and its imitators.

References