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Residual radioactivity of treated green diamonds

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ABSTRACT

Treated green diamonds can show residual radioactivity, generally due to immersion in radium salts. We report various activity measurements on two radioactive diamonds. The activity was characterized by alpha and gamma ray spectrometry, and the radon emanation was measured by alpha counting of a frozen source. Even when no residual radium contamination can be identified, measurable alpha and high-energy beta emissions could be detected. The potential health impact of radioactive diamonds and their status with regard to the regulatory policy for radioactive products are discussed.

1. Introduction

In 2013, the GGTL Laboratories Switzerland received three green diamonds set in ring and earrings for gemmological characterization. After analysis, it turned out that the colour of these diamonds was due to irradiation and that one of them appeared to be radioactive. This was not the first time that GGTL Laboratories Switzerland was faced with irradiated gemstones, and this shows that the traffic of radioactive diamond is still an actual problem. Previous measurements of these radioactive samples were undertaken by gamma-ray spectrometry (Ashbaugh, 1992), and alpha-ray measurements were also performed on five radioactive samples. Some high radioactivity levels were recorded, with a maximum of about 20 kBq for one specimen. From this it was concluded that these stones had been treated with radioactive salts, probably $RaBr_2$, to change their colour.

GGTL Laboratories Switzerland contacted LNHB, the French National Metrology Institute for radioactivity measurements, in order to precisely characterize the activity and properties of two treated green diamonds.

2. Historical background

Treated green diamonds have frequently been mentioned in the gemmological literature. Today, these stones are typically treated with fast electrons generated by electron accelerators or with neutrons in nuclear reactors (Collins, 1982). Decades before these techniques were available, the method used to turn diamonds to green involved direct contact of diamonds with radioactive salts of radium bromide or with radon gas (Crookes, 1904, 1914) and later using americium oxide (Reinitz and Johnson, 1994).

Sir Crookes was the first to discover radiations effects on the colour of diamond: he treated diamond crystals by contact with radium salts and observed that then they turned to green after a few months. He donated one of these crystals to the British Museum in London in 1914. The sample exhibits an almost uniform green surface coloration simulating a green body colour and it is still radioactive.

The technique consisting in irradiating diamonds with radioactive substances like radium or americium salts was quickly abandoned since diamonds treated with these radioactive elements exhibit long-lasting residual radioactivity which make them unwearable.

3. Materials and methods

Although several radioactive green diamonds, ranging from 0.11 carat (ct, a carat equals 0.2 g) to 12.86 carats, were analyzed at GGTL Laboratories Switzerland, this paper will focus on two specimens: a small 0.5 ct dark-green diamond (Fig. 1) and an over 7 ct pale-green diamond initially set in a ring (Fig. 2).

Initial gemmology characterization and routine testing for radioactivity was performed with a Geiger-Müller counter. More detailed radioactivity measurements were performed at Laboratoire National Henri Becquerel, CEA Saclay in France, with a high-purity germanium

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Fig. 1. Photography of the 0.5 ct diamond.

Fig. 2. Photography of the 7 ct diamond mounted on a ring.

detector (HPGe), an alpha spectrometer and an absolute radon measurement instrument, based on alpha counting in a defined geometry on a cold spot at 80 K.

4. Gemological optical testing

The green colour of the diamonds is apparently distributed on the surface or penetrating only into the subsurface (few tens of μm) of the diamonds. Magnification revealed the presence of irradiation stains (Fig. 3) on the surface. These green marks showed strongly irregular and coma-shape associations in contrast to the normally relatively round regular shape (usually with more blurred outline) of the natural green spots (Fig. 4) found at the surface of many rough diamonds (Koivula, 2000). Sometimes, the green stains coalesce to form a continuous green surface coloration called a “green skin”.

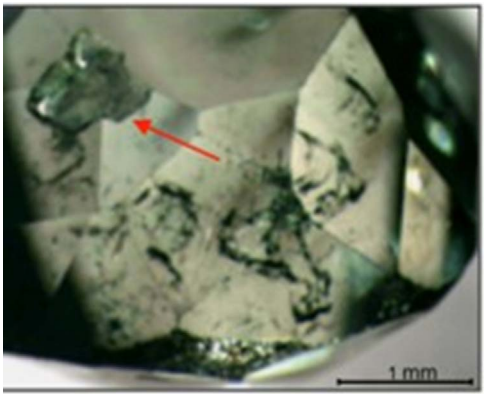

Fig. 3. Irregular, coma-shaped dark green stains on the polished surface of the 0.5 ct diamond. The red arrow points to a fracture containing residual radium salts. Micrograph F. Notari. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Until about 25 years ago, the presence of green stains usually situated on the girdle or pavilion of polished diamonds, was considered as an indicator of natural irradiation and there are also examples of near-colourless rough and cut diamonds with natural green stains. However, Crookes' diamond octahedra and the faceted examples examined here remind us that green spots and skins can also be generated by artificial alpha irradiation of rough and polished diamond surfaces as well. Faceted diamonds are the main targets for radium salt exposures and show green stains on the facets of crown and pavilion.

5. Fourier-transform infrared and near-infrared absorption spectroscopy

All tested diamonds are of type IaAB with nitrogen impurities aggregates, which is an unusual type for natural green diamonds, which are usually of type IIa, without detectable nitrogen or boron, by infrared spectroscopy. The infrared spectra (Fig. 5), does not reveal the presence of the absorption peak H1a, which is generally observed on bulk irradiated diamonds. This is probably a consequence of the small thickness of the irradiated zone, due to the small path length of alpha particles in condensed matter.

6. Visible and near infrared spectroscopy

The Vis-NIR spectrum of the 0.5 ct diamond (Fig. 6, red trace) recorded at 77 K indicates an irradiation at ambient temperature, as no nitrogen-vacancy centres indicating annealing were detected. The spectrum mainly consists of a strong absorption band in the 750–510 nm region. This wide absorption band induces the green colour. Besides the GR1 system with its zero phonon line (ZPL) in the 740.9–744.4 nm range, only the 3H absorption is apparent in the spectrum, with a distinct ZPL at 503.4 nm, and a vibration sideband at 491 nm. Both absorption systems are superimposed on a general absorption continuously rising from about 950 nm to the ultraviolet region, which induces a yellowish colour component.

7. Preliminary radioactivity measurement

For the 0.5 ct diamond, the apparent radioactivity measured with the Geiger-Müller counter revealed a high value in the direction of the pavilion for an analyzed surface of approximately.

1.5 mm^2 at a distance of about 6 mm from the detector. Despite the arbitrary readings of a GM counter, the observed count rate was unusually high considering the small size of the sample. This count rate was one order of magnitude greater than those of all observed gems at GGTL Laboratories Switzerland. This is why this stone deserved a more precise activity measurement and also a measurement of its radon emanation.

8. Gamma ray spectrometry

The 0.5 ct diamond was placed in a polymer container and measured with an HPGe detector at LNHB, in its calibration position, i.e. at a distance of 10 cm from the detector window. The spectrum recorded during an acquisition time of 20 000 s is presented in Fig. 7.

The observed peaks can be related to the gamma ray emission of ^{226}Ra and the radionuclides of its decay chain.

The activity was deduced from the net peak areas of the gamma lines of ^{226}Ra, ^{214}Po and ^{214}Bi, using the efficiency calibration curve obtained with standard point sources. The activities are presented in Table 1.

The 7 ct diamond was measured with an HPGe detector, the table