

Identification of GE POL diamonds: a second step

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ABSTRACT: An identification method for GE POL treated diamonds in two steps is proposed. First, as almost all GE POL diamonds are type IIa, near colourless type IIa diamonds are separated from other diamonds of similar colour using the SSEF Type IIa Diamond Spotter. Second, a Raman spectrum of these IIa stones is obtained using the 514 nm laser line of a Raman spectrometer. If a luminescence pattern at 3760 cm⁻¹ is observed, this proves the presence of a small number of N-V centres in the stones. This is believed to be characteristic of the material used for the GE process, as all studied GE POL diamonds exhibit this emission. Hence, a near-colourless type IIa diamond showing a N-V centre emission is likely to be a GE POL treated diamond. Further samples are necessary to confirm this preliminary criterion.

Keywords: GE POL, HPHT diamond treatment, type IIa, N-V centres (637 nm), luminescence, Raman spectrum

Introduction

General Electric (GE) currently treats certain brownish diamonds to make them more colourless, up to D colour. GE applies this high pressure and high temperature process on essentially type IIa diamonds, which are rare on the diamond market (approximately 1%, only) (Anthony and Casey, in Moses, 1999).

Since April 1999, these treated diamonds have been marketed by Pegasus Overseas Limited (POL) in Antwerp, a subsidiary of a sight holder based in New York City, Lazare Kaplan International (LKI). These stones are known in the trade as Pegasus diamonds, GE POL diamonds and more recently as Monarch™ diamonds (Schmetzer, 1999). LKI

markets them at the same price as their untreated counterparts because the treatment is claimed to be undetectable and remain so in the future. While GIA discloses on reports that these diamonds have been only 'processed', CIBJO laboratories disclose 'treated diamonds' in accordance with a CIBJO directive dated May 1999.

GE POL has been subsequently inscribed on the girdle of these diamonds to make them easily identifiable. But unfortunately, GIA has recognised a few GE POL diamonds that were resubmitted for certificates after a repolish of the 'GE POL' inscription. Until now, no gemmological criterion has been proposed to identify this treatment with certainty, thus it is an ongoing challenge for all gemmologists.



Type IIa diamond samples

A first article from our team described observations under magnification of two GE POL diamonds, as well as some fluorescence bands triggered by the laser of the Raman spectrometer; one of these bands has been attributed to the presence of N-V centres (Chalain *et al.*, 1999). This article demonstrates how this emission may be used for identification of GE POL diamonds. It also describes the SSEF Type IIa Diamond Spotter, a new simple device for a quick identification of all type IIa diamonds and type IaB, an even rarer type.

As the vast majority of GE POL diamonds are type IIa, it is important for the trade to be able to separate these near-colourless diamonds, potentially GE POL treated, from those of other types. Laboratories do this on the basis of infrared absorption; however, most jewellers do not have an infrared spectrometer. In addition, the original definition of type I and type II diamonds is based also on transparency to shortwave ultraviolet radiation (SWUV; Robertson *et al.*, 1934). When putting a diamond on top

Method of study

The aim of the current study is to present, compare and discuss the spectra obtained on a Raman spectrometer of these fifteen diamonds. For each diamond of the three groups, the following tests were performed, besides classical gemmological observations (which are not discussed further here, as they did not prove diagnostic in all cases):

- FTIR spectrum to verify that the diamond is indeed type IIa by the infrared spectrum pattern as well as the ultraviolet;
- Raman spectra were obtained at room temperature.

The Renishaw 1000 Raman spectrometer used is equipped with a Peltier-cooled CCD detector and ionised argon laser, with a green ray at 514 nm (Hänni *et al.*, 1997). It is calibrated with the 1332 cm^{-1} diamond peak of a reference diamond prior to each analysis. For better consistency of the results each diamond is set under the laser beam of the Raman microprobe by the same operator who always follows the same procedure. The table of the diamond is rubbed on a clean and dry white sheet of paper to ensure that no grease is present. The diamond is then placed on a glass

support and held up by two small pieces of Blutack[®] placed between the glass and the pavilion of the diamond. The Blutack[®] is set as far back as possible from the area of interest, because it might induce a non negligible fluorescence. Then, the laser beam is focused on the table using a x20 magnification lens (Olympus: MS Plan 20; 0.46), the beam being perpendicular to the table of the stone. Finally, both sample and Raman microprobe are wrapped in an opaque black fabric to avoid any interference from external lighting. The particular experimental instrument set up parameters are saved in a computer file and loaded before each analysis, so that experimental conditions are always identical. This experimental procedure uses a 25 mW laser power, in the Renishaw 'extended and continuous mode', as well as the 'Gain and Cosmic Ray elimination mode'. Five scans are averaged in the range 100 cm^{-1} to 6500 cm^{-1} . This procedure takes approximately 25 minutes per stone.

Raman spectra were obtained at room temperature on two diamonds in various zones, to ensure that the whole stone is sample tested in a comprehensive way.

of the SSEF Type IIa Diamond Spotter (Figure 1), and illuminating it with SWUV, type IIa stones will transmit the radiation, exciting a green fluorescent screen placed underneath the stones. If the screen remains inert, the stone is not type IIa. This is a quick and easy way of recognising type IIa stones without infrared absorption.

Since October 1999, ten diamonds of type IIa, both colourless and brownish, have been recognised by staff of the SSEF laboratory thanks to several diamond dealers who kindly sent them to SSEF for one day. The identification of IIa diamonds is done with the SSEF Type IIa Diamond Spotter. They were further divided into two groups. Group 1 is composed of seven untreated colourless diamonds, all D colour (see Table I). Group 2 consists of three untreated diamonds of a brown to brownish hue (see Table II). Group 3 is composed of the GE POL diamonds that were submitted to SSEF for research (see Table III).

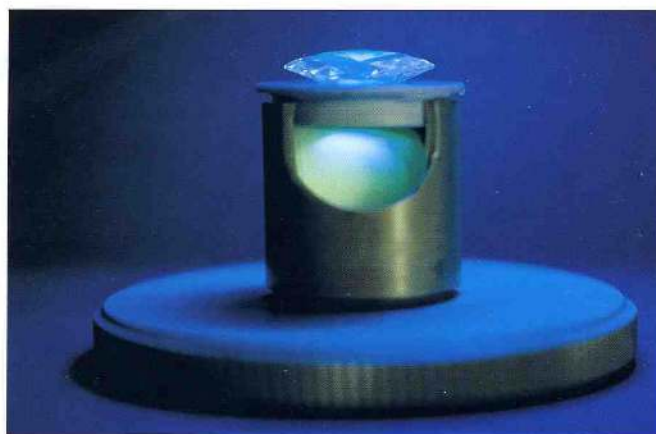


Figure 1: The SSEF Type IIa Diamond Spotter.

Results

All the spectra obtained showed of course the first order (1332 cm^{-1}) and second order (2000 to 2665 cm^{-1} approximately) Raman spectrum of diamond. Additional weak

Table I: Group 1: Untreated near-colourless type IIa diamonds

Reference	Weight (ct)	Shape & Cut	Colour	N-V centre ($3760\text{ cm}^{-1}/637\text{ nm}$)	Other noticeable bands (cm^{-1})
ma048	0.468	marquise, modified brilliant	D	no	3076
ma354	3.54	marquise, modified brilliant	D	no	3073
ma202	2.02	marquise, modified brilliant	D	no	none
pea175	1.751	pear-shaped, modified brilliant	D	no	5966
pea180	1.808	pear-shaped, modified brilliant	D	no	none
pea202	2.028	pear-shaped, modified brilliant	D	no	none
ma161	1.613	marquise, modified brilliant	D	no	none

Table II: Group 2: Untreated brownish to brown type IIa diamonds

Reference	Weight (ct)	Shape & Cut	Colour	N-V centre ($3760\text{ cm}^{-1}/637\text{ nm}$)	Other noticeable bands (cm^{-1})
RD465	4.650	round, rose cut	L(brown)	yes	4276
ma354	5.838	marquise, modified brilliant	M-Q (brown)	yes	794 4284 2065
rou903b2	9.03	rough, flat	faint brown	yes	5960

Table III: Group 3: GE POL type IIa diamonds

Reference	Weight (ct)	Shape & Cut	Colour	N-V centre (3760 cm ⁻¹ /637 nm)	Other noticeable bands (cm ⁻¹)
GE POL001	0.75	round, brilliant	E	yes	none
GE POL002	0.56	marquise, modified brilliant	F	yes	794 2073
GE POL003	0.79	pear-shaped, modified brilliant	E	yes	794
GE POL004	0.94	oval, modified brilliant	D	yes	none
GE POL005	0.72	round, brilliant	F	yes	786

signals, interpreted as luminescence on the basis of their already known energy position and associated vibronic structure, are also of interest.

Untreated colourless diamonds

The seven untreated colourless diamonds of Group 1 were confirmed to be type IIa by infrared spectroscopy. None of these diamonds shows the fluorescence of an N-V centre in the Raman spectrum. The corresponding spectra are presented in Figure 2 and some of their properties are summarised in Table I.

Untreated brown to brownish diamonds

Infrared spectrometry confirmed that the three untreated brown diamonds of Group 2 are indeed type IIa. The colour of these three stones ranges from L on the GIA colour grading scale to faint brown. Their Raman spectra reveal the presence of a peak at 3760 cm⁻¹ (Figure 3). The laser emits at 19435 cm⁻¹ (514 nm); the apparent Raman shift therefore corresponds to an emission at 19435 - 3760 = 15675 cm⁻¹ (637 nm). This is the position of the characteristic line of the N-V centre, therefore this defect is present in each of the three stones.

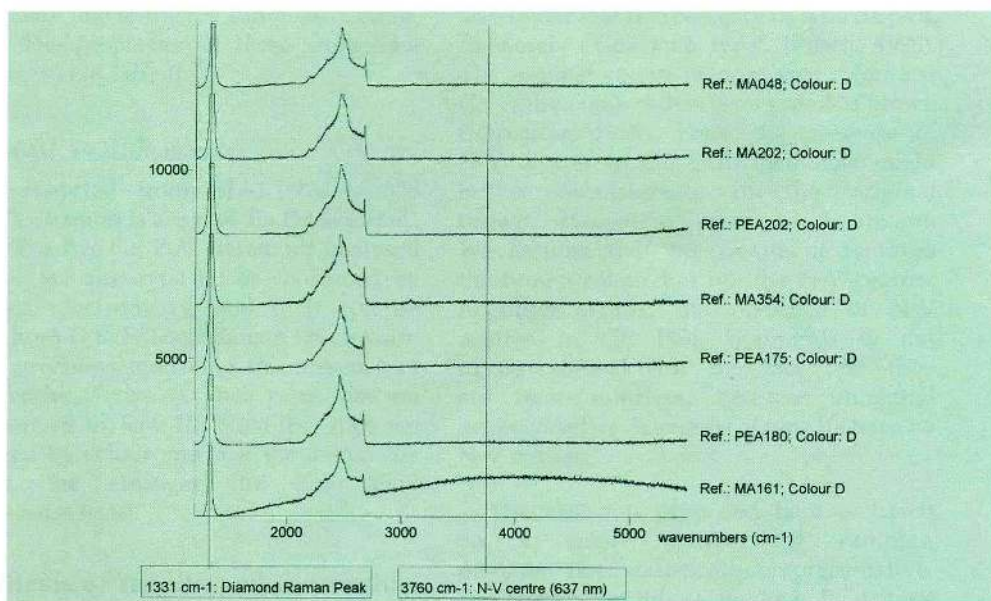


Figure 2: Raman spectra of seven type IIa near-colourless diamonds. No emission is observed at 3760 cm⁻¹

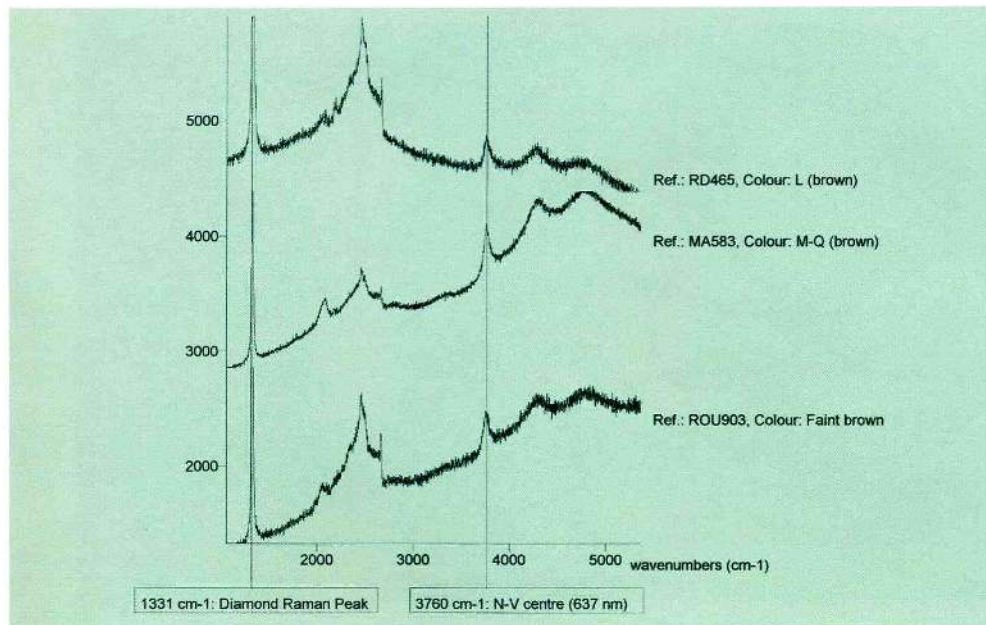


Figure 3: Raman spectra of three brown type IIa diamonds. They all show an emission at 3760 cm^{-1} , due to the N-V centre.

The weak band observed around 2060 cm^{-1} corresponds to an emission at 17375 cm^{-1} (575.5 nm) which is a known companion line to the 637 nm peak (Collins, 1982). The properties of these stones are summarised in *Table II*.

Treated GE POL diamonds

As reported from GIA, 99% of 858 GE POL diamonds are type IIa (Moses *et al.*, 1999). The five GE POL diamonds analysed at SSEF are also type IIa as confirmed by infrared spectrometry, and their colours range from D to F. Their Raman spectra also show emissions indicating the presence of N-V centres (*Figure 4*). Their properties are summarized in *Table III*. Note that they are arranged by colour and that the darker the colour, the stronger the 3760 cm^{-1} fluorescence band.

Synthesis of results and discussion

All seven untreated near-colourless diamonds of type IIa show no N-V

luminescence. On the other hand, both GE POL and brown diamonds of type IIa all show N-V emission. This luminescence is also found in a rare category of type IIa pink diamonds ('Golconda type', Fritsch, 1998). The original colour of now near-colourless GE POL diamonds has been stated as brown (Rapaport, 1999). Thus, the presence of N-V centres in GE POL diamonds might be a characteristic of the original brown diamonds, prior to treatment. We assume that the treatment removes the brown colour but not the N-V centres. In other words, the presence of N-V centres in GE POL diamonds is not in agreement with the fact that they are near-colourless, because untreated near-colourless diamonds of type IIa have no N-V centres.

The criterion proposed here is based on a small number of samples, perhaps not statistically representative. The reason for this is twofold. First, type IIa diamonds are rare (1% approximately). Second, the work is at a preliminary stage.

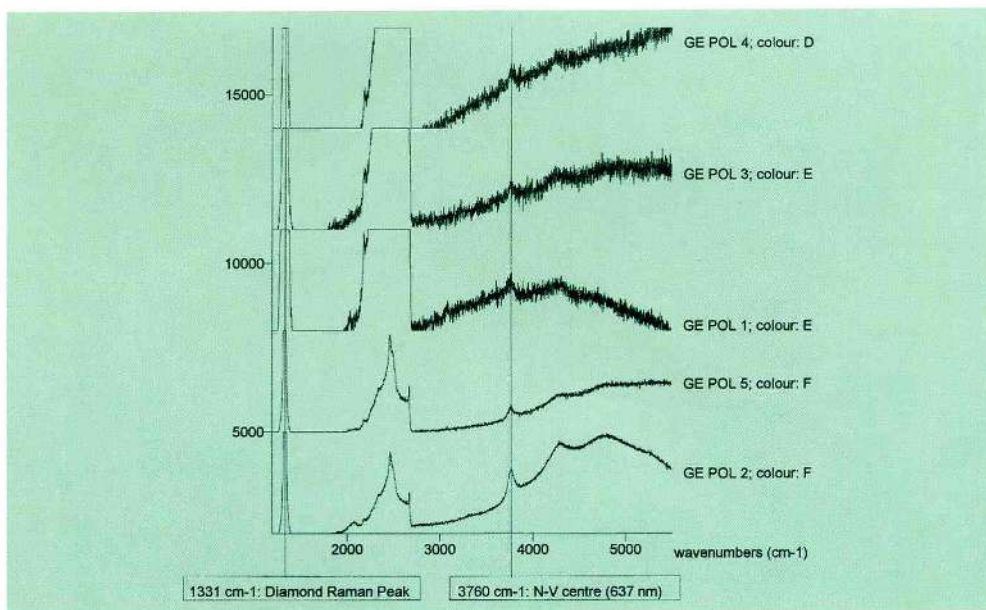


Figure 4: Raman spectra of five GE POL diamonds, all exhibiting emissions at 3760 cm^{-1} , due to the N-V centre.

SSEF will continue to study a selection of type IIa untreated diamonds, both colourless and brown, and endeavour to obtain more GE POL diamonds for comparison.

Conclusion

Five GE POL diamonds and ten untreated diamonds, all type IIa, have been studied. We have shown here that the presence of N-V centres might not be consistent with the fact that GE POL diamonds are colourless. Hence, the presence of a small number of N-V centres, luminescing under the excitation of the 514 nm line of a Raman spectrometer, might indicate that a colourless type IIa diamond has been treated by the GE process. However, because of the scarcity of type IIa untreated and treated diamonds, this identification criterion based on fluorescence spectroscopy must only be considered as a promising hypothesis. But we believe that, if confirmed, this method could be of considerable benefit for the diamond trade.

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References

- Chalain, J-P., Fritsch, E., and Hänni, H.A., 1999. Detection of GE POL diamonds: a first stage, *Revue de Gemmologie AFG*, **138-9**, 30-3
- Collins, A.T., 1982. Colour centres in diamonds, *Journal of Gemmology*, **18**(1), 37-75
- Fritsch, E., 1998. *The nature of diamonds*. G.E. Harlow Ed. Cambridge University Press & American Museum of Natural History, Cambridge, U.K. pp. 38-40
- Hänni, H.A., Kiefert, L., Chalain, J.P., and Wilcock, I.C., 1997. A Raman microscope in the gemmological laboratory: first experiences of application. *Journal of Gemmology*, **25**(6), 394-406
- Moses, T.M., Shigley, J.E., McClure, S.F., Koivula, J.I., and Van Daele, M., 1999. Observations on GE-processed diamonds: a photographic record. *Gems & Gemology*, **35**, 14-22
- Rapaport Diamond Report 1999. <http://www.diamonds.com> Consulted from March 1999 to January 2000
- Robertson, R., Fox, J.J., and Martin, A.E., 1934 *Philosophical Transactions*, A232, London, pp. 463-535
- Schmetzer, K., 1999. Behandlung natürlicher Diamanten zur Reduzierung des Gelb- oder Braunsättigung. *Goldschmiede Zeitung*, **97**(5), 47-8