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DIAMONDS

A natural diamond with very high Ni content. Nickel in diamond (as point defects and nickel-nitrogen complexes) is mainly known in synthetics that are grown from a Ni-containing catalyst. These synthetic diamonds may contain a large number of Ni-related absorption features in a wide region of the spectrum, from the UV to the NIR (S. C. Lawson, and H. Kanda, "An annealing study of nickel point defects in high-pressure synthetic diamond," *Journal of Applied Physics*, Vol. 73, No. 8, 1993, pp. 3967–3973). The presence of trace Ni impurities in natural diamonds has been known for years, but little has been published on the associated spectral features. K. Iakoubovskii and G. J. Adriaenssens ("Optical characterization of natural Argyle diamonds," *Diamond and Related Materials*, Vol. 11, 2001, pp. 125–131) and others have attributed a number of photoluminescence features detected in natural diamonds to nickel. More recently, the UV-Vis-NIR optical centers related to Ni and nickel-nitrogen complexes in a natural diamond were published by J.-P. Chalain (see the Winter 2003 Gem News International section, pp. 325–326).

Figure 1. This 1.33 ct orangy yellow natural diamond displayed unusual Ni-related absorption features. The stone contains numerous hollow etch channels (see inset; magnified 25×), some of which appear dark in the photo of the diamond. Photos by F. Notari.

The present contributors recently analyzed a saturated orangy yellow 1.33 ct natural diamond (figure 1) that contained elevated contents of Ni and exhibited very interesting properties. The diamond fluoresced pinkish orange to both long- and short-wave UV excitation, which is a very rare emission color for diamond. Yellow phosphorescence lasting several seconds also was observed, which was more distinct after short-wave UV excitation.

Internal features consisted of fractures and distinct etch channels, some with a tabular appearance (figure 1, inset). The morphology of these etch channels resembled that of the metallic flux inclusions in some HPHT-grown synthetic diamonds. These inclusions are sometimes dissolved during particular post-growth conditions, leaving behind hollow channels.

Infrared spectroscopy revealed that this was a low-

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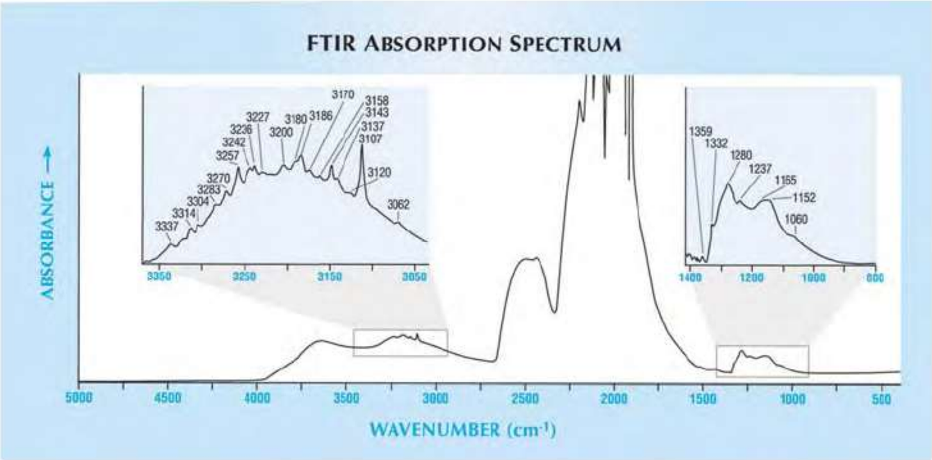


Figure 2. The FTIR spectrum indicates that the sample is a low-nitrogen type IaA natural diamond with a distinct Ib character, as shown by peaks at 1359 and 1237 cm^{-1} and several sharp absorptions between 3270 and ~3000 cm^{-1} (see insets). The spectrum proves natural origin, since most of these features are unknown in synthetic diamonds.

nitrogen type IaA diamond with a very distinct Ib character, as shown by peaks at 1359 and 1237 cm^{-1} and several sharp, weak absorptions between 3270 and ~3000 cm^{-1}, with main features at 3180 and 3143 cm^{-1} (figure 2; see G. S. Woods and A. T. Collins, "Infrared absorption spectra of hydrogen complexes in type I diamonds," *Journal of Physics and Chemistry of Solids*, Vol. 44, No. 5, 1983, pp. 471–475). This spectrum indicated natural origin, since most of the features recorded are unknown in synthetic diamonds.

A low-temperature Vis-NIR spectrum in the 400–1000 nm range was recorded to detect possible color treatment (figure 3). This spectrum was very unusual and exhibited at least 36 absorptions, with multiple oscillations between 600 and 720 nm. These oscillations are apparent as two distinct groups of absorptions with individual peaks that show regular spacing (i.e., 6–9 nm for the first group [610–647 nm] and about 8–9 nm for the second group [686–720 nm]). The oscillating nature of the second group is clearer than the first, which has rather variable spacing, intensity, and curve shapes (see figure 3, inset). Such spectral properties in diamond have been reported before, and the oscillating nature of the defects has been documented by I. M. Reinitz et al. ("An oscillating visible light optical center in some natural green to yellow diamonds," *Diamond and Related Materials*, Vol. 7, 1998, pp. 313–316). Those authors indicated that such a spectrum is extremely rare and possibly due to vibronic interactions of some unknown molecular species, particularly in green diamonds. In contrast, the saturated orangy yellow color of the 1.33 ct diamond described here can be explained by the absence of the two broad bands centered at ~700 and 600 nm, as seen in the spectrum of a green diamond published by Reinitz et al. The transmission window in the green part of the spectrum of the 1.33 ct diamond is distinctly weaker, so the stone appears yellow. There is no indication that the color of this diamond resulted from a treatment process.

A strong absorption at 891 nm (not mentioned by Reinitz et al., since their spectra did not extend above 850 nm) appeared to be a "normal" zero-phonon line, and thus

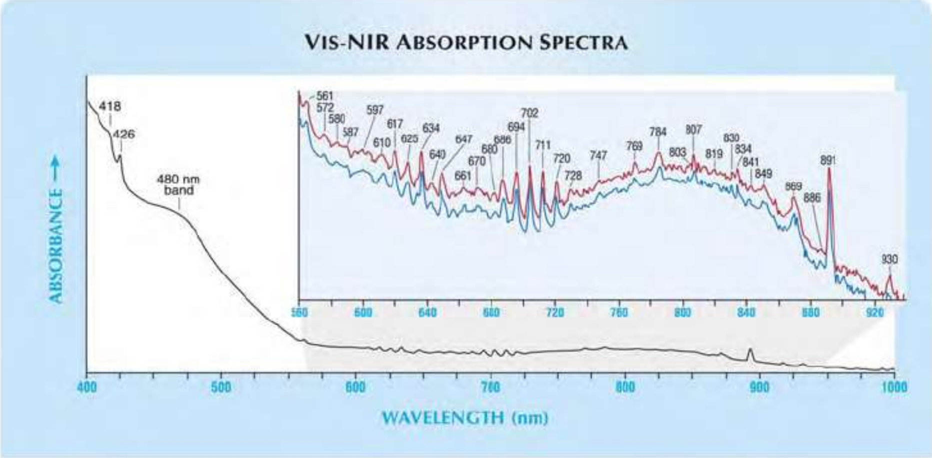


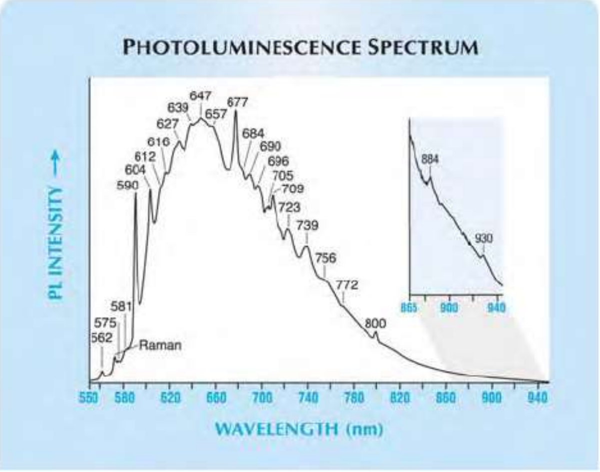
Figure 3. Numerous absorptions are evident in this low-temperature Vis-NIR spectrum of the diamond. The inset view of the 560–940 nm region shows two separately recorded spectra from this sample to demonstrate the reproducibility of the small absorptions. Besides the possibly oscillating nature of the defect(s) responsible for the 600–720 nm absorptions, the vibronic nature of the broad band at 800 nm with its zero phonon line at 891 nm is apparent.

the broad band centered at approximately 800 nm can be interpreted as the vibronic structure of this defect (again, see figure 3). To our knowledge, this is the first time that the 891 nm system has been documented in any diamond, natural or synthetic.

In our experience, the general appearance and positions of several absorptions in this spectrum have distinct similarities to the spectra of certain synthetic diamonds grown with a Ni catalyst, especially after annealing at high temperature. We have recorded Vis-NIR spectra of high-Ni synthetic diamonds with up to 25 sharp absorptions between 470 and 819 nm. Some of the absorptions seen in the spectrum of the 1.33 ct orangy yellow diamond were detected by us in a Ni-rich dark yellow-brown Gemesis synthetic diamond (i.e., at 572, 610, 617, 647, 661, 670, 694, 711, 747, and 819 nm). In contrast, the combination of bands at 426 and 480 nm is known in natural diamonds exhibiting a thermochroic and photochroic color change, the so-called "chameleon" diamonds (E. Fritsch, et al., "Examination of the twenty-two carat green chameleon diamond," in D. J. Content, Ed., *A Green Diamond: A Study of Chameleonism*, W. S. Maney & Son, Leeds, England, 1995, p. 25). Such diamonds also exhibit an 800 nm band, although they lack the vibronic structure seen in the spectrum of this sample. The 426 nm band provides additional proof that this is a natural diamond.

The low-temperature photoluminescence spectrum of the diamond provided further evidence of Ni-related defects (figure 4). The PL spectrum was very similar to those of chameleon diamonds analyzed by these contributors, and many of the observed emissions correspond to known features that are assigned to Ni point defects and nickel-nitrogen complexes. The features at 639, 657, 677, 690, 705, 723, 739, 800, and 884 nm seen in this diamond have been identified in Ni-catalyst synthetic diamonds and attributed to nickel defects (A. M. Zaitsev, *Optical Properties of Diamond: A Data Handbook*, Springer-Verlag, Berlin, 2001, pp. 140–197). In addition to these, the present authors know of emissions at 581, 590, 604, 616, 647, and 756 nm in synthetic diamonds grown from a Ni-containing catalyst.

Figure 4. The low-temperature photoluminescence spectrum of the diamond exhibits several emissions that appear to be Ni-related. The inset shows the weak Ni-related feature at 884 nm plus a weak 930 nm peak of unknown origin.



EDXRF spectroscopy of the diamond revealed distinct peaks for both Ni and Fe. From the spectrum we estimated the Ni content of the diamond at 30–50 ppm. While the Fe content was not too unusual for a natural diamond, the detection of Ni by EDXRF spectroscopy has so far been restricted to synthetic diamonds grown by the temperature gradient method using a Ni-containing catalyst (J. E. Shigley et al., "Gemesis laboratory-created diamonds," Winter 2002 *Gems & Gemology*, pp. 301–309). In natural diamonds, the Ni content is generally far too low to be detected by this method.

The same holds true for UV-Vis-NIR absorption spectroscopy, by which Ni point defects and nickel-nitrogen complexes can be identified in synthetic diamonds; in contrast, Ni-related features in natural diamonds are very rarely detected by this method. The only nondestructive method to effectively detect extremely low Ni contents in diamond is photoluminescence spectroscopy (see Zaitsev, 2001).

The complex Vis-NIR and PL spectra of this diamond are explained with high probability by the presence of an unusually high concentration of Ni-related defects. Our observation of many absorptions at approximately equal positions in the Vis-NIR and PL spectra of Ni-catalyst synthetic diamonds, combined with the detection of remarkable amounts of Ni in the 1.33 ct stone by EDXRF, lead us to propose that at least some of the many peaks in these spectra are due to naturally occurring Ni and/or nickel-nitrogen complexes. It would be very surprising *not* to detect Ni-related optical absorptions in the PL and Vis-NIR spectra of a diamond with such elevated Ni content, especially after the natural annealing this stone must have experienced, since substantial amounts of its nitrogen were aggregated. Further chemical analyses of diamonds exhibiting these spectral features will be performed to confirm these findings as we encounter the appropriate samples.

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