On unusual deep-violet microcrystals of diamonds from placers of Ukraine

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Abstract: A distinctive feature of Ukrainian deep-violet diamond microcrystals is a broad absorption band centered at about 560 nm (17850 cm^{-1} or 2.21 eV). In the Ukrainian samples, the intensity of this band is almost two orders of magnitude greater than in a light-rose diamond from Yakutia. Previously (Taran *et al.*, 1998), the band was attributed to the N-V center because the absorption spectrum of the negative N-V center in irradiated and annealed type Ib diamonds is known to have an absorption band with a maximum at a similar wavelength. However, this assignment is not confirmed by vibrational spectroscopy and low temperature optical absorption spectroscopy in all crystals studied. In addition, at ~77 K the band 17850 cm^{-1} displays no fine structure that unambiguously evidences that it can not be the band at ~2.2 eV, commonly attributed to the N-V center.

Key-words: diamond, electronic and vibrational spectroscopy.

Introduction

Tiny crystals of diamond, less than 0.5 mm in diameter, are rather abundant in sedimentary rocks of various geologic ages in Ukraine. Tens of thousands of these microdiamonds have been found in fine-grained Neogenic sands (dated at less than 25 million years old) of the northeastern slope and the central part of the Ukrainian shield, and on the northeastern flank of the Dniepro-Donets depression. Many finds were made in the alluvium of Dniepro and other rivers, and on the coasts of the Azov and Black seas, where diamonds were very likely transported from the Neogenic sands.

The primary sources of these Ukrainian diamonds are not yet known. It is believed, however, that among the crystals, which have been found, almost all known genetic types of diamond (*e.g.*, lamproitic-kimberlitic, metamorphic, impact and condensed) are present (Kvasnytsya *et al.*, 1999).

The color of these alluvial diamonds varies widely from light pink, rose and violet to greenish, yellow-greenish, yellow and brown through various intermediate colors and hues (Taran *et al.*, 1998). The most impressive are deep-violet microcrystals mainly of cubic-shaped and, with a smaller abundance, octahedral or cubic plus octahedral combination forms. Such diamonds appear to be unique in the world in terms of their extremely strong color intensity in spite of their small size.

Eremenko & Polkanov (1969) first studied the electronic absorption spectra of variously colored Ukrainian diamonds, but they reported somewhat ambiguous results. Taran *et al.* (1998) conducted a more recent study. These authors reported an extraordinary high intensity of violet color of some samples, which they suggested to be caused by N-V-centers in the diamond structure. They also proposed that these violet diamond crystals might have been irradiated during their geological history.

Because of the extremely intense color of the Ukrainian deep-violet diamonds, any further characterization of this unique material seemed important. Here, we present new results on deep-violet diamonds from Samotkan' littoral titanium-zirconium placer (Middle Dniepro region) by means of electronic and vibrational spectroscopy as well as by scanning electron microscopy.

Experimental methods

Unpolarized electronic absorption spectra were scanned in the range from 330-1000 nm with a single-beam microspectrophotometer, which comprises a highly modified mineralogical polarizing microscope MIN-8, a stabilized light source (changeable Xe-arc or W-lamp, both of 70 W), a SpectraPro 275 triple-grating monochromator and a PC IBM 486. The microscope is equipped with a photometric device consisting of variable entrance- and changeable exit diaphragms and two changeable photomultiplier tubes for spectral ranges 300-750 nm and 730-1100 nm, respectively.

The spectra were measured on naturally faced crystals without any additional treatment such as polishing. For this purpose, transparent homogeneously colored samples with two parallel smooth faces were selected under a binocular microscope. To diminish, at least partly, the scattering of light by surface imperfections, the crystals were embedded
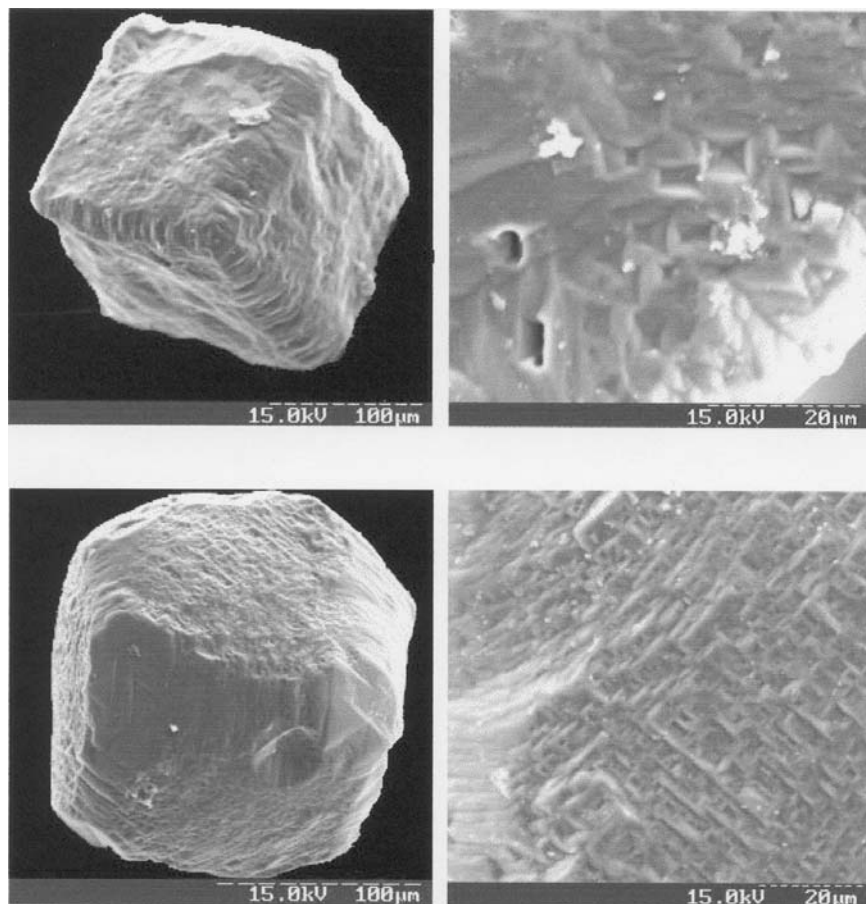
Fig. 1. Two cube-shaped deep-violet diamond microcrystals and details of their surfaces.

in a drop of glycerin between a supporting glass plate and a thin glass cover slide. Then they were fixed in a position most suitable for microscope-spectrophotometric measuring, *i.e.* with the chosen pair of faces perpendicular to the light beam. The position of the reference beam was always taken just near the sample so that all conditions of registering both the sample and reference beams were nearly identical. The diameter of the beam size varied, depending on dimension and quality of the crystal studied, from 50 to 200 µm.

Optical absorption spectra at liquid nitrogen temperature (~77 K) were measured using a home-made miniature cryostat attached to the microspectrometer. The samples were placed on a transparent supporting plate prepared from synthetic high-quality single-crystal sapphire. Since at low temperature the thermal conductivity of Al_2O_3 is almost two times higher than that of annealed pure copper (Volkov *et al.*, 1981) it provides a good thermal conductivity between the samples and sample holder of the cryostat. To maintain thermal contact, the sample was attached to the supporting plate and the latter to the cooled sample holder with vacuum grease.

The cryostat was evacuated to pressure $\sim 10^{-5}$ torr, low enough to prevent any moisture condensation on the external surfaces of the cryostat windows.

Infrared spectra of the diamonds were measured in the range 700-4000 cm^{-1} by means of a FTIR-spectrometer (Bruker IFS 66) with KBr beam-splitter and attached IR-micro-

scope equipped with mirror optics and an LN_2-cooled MCT detector. 200 scans were averaged for every measurement.

Enlarged images of the crystals were obtained with a PEM-101M scanning electron microscope (SEM) with a resolution in secondary electrons of less than 5 nm.

Results and discussion

Enlarged SEM images of two deep-violet cube-shaped microcrystals are shown in Fig. 1. In both crystals, small octahedral faces on the vertices and rhombo-dodecahedral faces on the edges complicate the cubic-shaped habit. The cubic faces are ornamented by quadrangular cavities which were formed either during growth, or afterwards due to dissolution. Only the octahedral faces are true faces because they have their own growth pyramids, whereas the rhombododecahedral ones appear due to degradation of the octahedron. The origin of the cube {100}-faces is not clear. Either they may appear due to degradation of the octahedral faces (tangential growth), or they may be formed by the fibrous growth mechanism. In any case, such a habit suggests that the diamonds grew rapidly under supersaturation of the crystallization medium, which promoted the incorporation of substitutional and interstitial nitrogen atoms into the structure (Lupashko *et al.*, 1999). Investigation of the photoluminescence of such crystals showed that they contain a set of different nitrogen-bearing luminescence
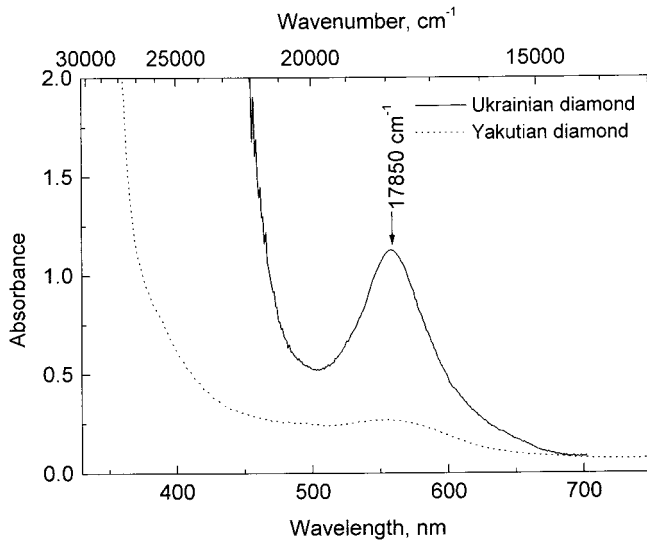
Fig. 2. Optical absorption (electronic) spectra of deep-violet (Samotkan' placer, Ukraine) and light-rose (Udachnaya kimberlite pipe, Yakutia) diamonds. The samples are ~0.25 mm and ~2 mm thick, respectively. For the sake of clarity the spectrum of the Ukrainian sample was shifted down by 1.3 absorbance units.

centers such as 575 nm, 503.4 nm (H3), 465 nm and 409 nm (Lupashko *et al.*, 1999). Here, the wavelengths indicate sharp lines of luminescence caused by no-phonon vibronic transitions of the centers.

Electronic absorption spectra in the range 330-750 nm of a Ukrainian deep-violet cubic-shaped microcrystal (~0.25 mm thick) and, for comparison, of a typical pale rose octahedral crystal (~2 mm thick), from the Udachnaya kimberlite pipe (Yakutia, Russia), are shown in Fig. 2. The range 750-1000 nm is omitted because it contains no absorption bands.

Due to internal imperfections of the investigated crystals and, especially, due to the typical fine morphologic structure of their faces (see again Fig. 1), optical absorption spectra of all Ukrainian diamonds contain a strong absorption background caused by the scattering of light by the imperfections. This complicates significantly the measurement of the spectra and causes their ordinate to shift upwards by 0.8-1.5 absorption units. (In Fig. 2, in particular, for the sake of clarity the spectrum of the Ukrainian sample was shifted down by 1.3 absorption units). It is known that scattering by small imperfections increases with decreasing wavelength of light. In some cases, this can even cause bands of pseudoabsorption in the UV-range (*e.g.* Khomenko *et al.*, 2002, 2003). Therefore, the imperfections of the surfaces cause not only the wavelength-independent background, which is responsible for the uniform shift of spectral curves, but may also significantly contribute to the short-wave absorption edge, which is shifted to lower energies in the spectrum of the Ukrainian diamond microcrystal compared to the Yakutian crystal (Fig. 2).

It is evident from Fig. 2, that in spite of different intensities of the absorption features, which are much stronger in the Ukrainian than Yakutian sample, the two spectra are rather alike. They both consist of a short-wave absorption edge, and a broad band of nearly Gaussian form with a maximum at ~17850 cm^{-1} (560 nm) and a half-width, FWHM, of ~1500

cm^{-1}. The most significant difference occurs in the intensity of the band, which is much higher in the Ukrainian compared to the Yakutian material. As was quantitatively evaluated from the spectra normalized to equal thickness of the two samples, in the Ukrainian diamond this band is nearly two orders of magnitude stronger than in the Yakutian one.

By energy the band at 17850 cm^{-1} in the spectra of Fig. 2 is close to the broad band with maximum near 2.2 eV (564 nm, or ~17700 cm^{-1}), which appears in spectra of diamonds after irradiation and thermal annealing. In the literature, this band is attributed to electronic transitions of negative N-V centers, which are believed to consist of an impurity nitrogen atom coupled with a carbon vacancy (*e.g.* Clark *et al.*, 1979; Vavilov *et al.*, 1985; Bokij *et al.*, 1986). At low temperature, the band acquires a complicated shape, being structured by a series of sharp narrow lines of vibronic transitions of the N-V center (*e.g.* Collins, 1982; Clark *et al.*, 1992; Vavilov *et al.*, 1985). Taking into consideration the energy of the 17850 cm^{-1} band in Ukrainian deep-violet diamonds, close to the band at ~2.2 eV in spectra of irradiated and annealed diamonds, Taran *et al.* (1998) assumed that it may be caused by the N-V center. In such case, admitting that the extraordinary strong intensity of the band at 17850 cm^{-1} in spectra of deep-violet Ukrainian diamonds is evidence of a high concentration of single nitrogen atoms in their structure, one should expect the appearance of intense absorption bands caused by this impurity in the infrared spectra of the samples. We have studied the vibrational spectra of more than two hundred differently colored diamond microcrystals from Ukrainian placers. Analysis of the spectra shows, first of all, that, in fact, none of them, including violet varieties, belong to the Ib type[1]. It should be kept in mind that just diamonds of this type acquire their rose color, caused by the band at ~2.2 eV, by irradiation and thermal treatment (Clark *et al.*, 1992). Further, we found that there is no correlation between color and vibrational spectra of the diamonds studied. For illustration, typical NIR spectra of four deep-violet samples, scanned in the range 700-4000 cm^{-1}, are shown in Fig. 3. As seen from this figure, besides the characteristic bands of vibrations of the diamond lattice itself (1970-2550 cm^{-1}) (*e.g.* Kurdyumov *et al.*, 1994), marked by the light gray area in the figure, there are a number of absorption bands and lines caused by various imperfections of the structure which indicate a diverse impurity content of Ukrainian diamonds. In the literature, some of these bands are quoted and attributed to certain defects, others are, as far as we are aware, not yet described. Here we dismiss ourselves from discussing the NIR-spectra in detail. We only want to emphasize that neither a band of remarkable intensity at 1130 cm^{-1} nor a sharp line at 1344 cm^{-1} correlated with the first, which are both regarded by Clark *et al.* (1992) as "a direct measure of the single substitutional nitrogen concentration", are found in the samples studied. The spectrum in the range 1110-1340 cm^{-1} of sample 2 resembles, in a way, that of synthetic diamonds of Ib type (*e.g.* Kurdyumov *et al.*, 1994), although the weak bands at 1145 cm^{-1} and 1332 cm^{-1}, marked by arrows, are not of the same energy as found by Clark *et al.* (1992) (see above). Relatively intense bands, which are seen

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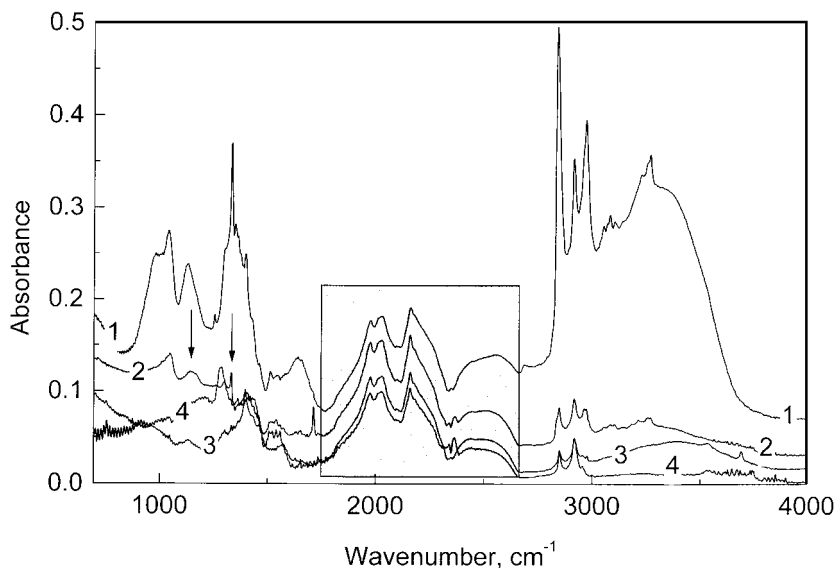[1] Among natural diamonds only ~0.1 % are of the Ib type (Kurdyumov *et al.*, 1994).

Fig. 3. Typical infrared spectra of deep-violet diamond microcrystals from Ukrainian placers. The arrows indicate the bands at 1145 cm^{-1} and 1332 cm^{-1} in Sp. 2, which may be caused by single nitrogen atoms in the structure. The light gray area indicates the range of absorption caused by vibrations of the diamond lattice itself.

in this spectral range in many samples studied (they are intense, for instance, in sample 1, Fig. 3), certainly belong to the systems of correlated bands which are very likely caused by vibrations of C-H-bonds and water molecules in some not yet identified defects or impurities. The latter may be natural or/ and technical contamination of porous surfaces of the samples, which are all covered by numerous microscopic rectangular cavities (Fig. 1).

In consequence, we should emphasize that the assignment of the band at 17850 cm^{-1} in spectra of Ukrainian deep-violet diamonds to the N-V center by Taran *et al.* (1998) is not consistent with the above-mentioned observations. The results of low-temperature optical absorption spectroscopy also do not confirm such assignment either. Indeed, comparing with the room temperature experiments no significant changes occur in spectra of the deep-violet microcrystals at ~77 K: the short-wave absorption edge shifts slightly to higher energies, whereas the band at 17850 cm^{-1} becomes narrower, FWHM ≈1350 cm^{-1} *versus* ~1500 cm^{-1} at room temperature, and better resolved, showing, however, no fine structure. Thus, the band significantly differs from the broad band at 2.2 eV of the N-V center, which displays a distinct characteristic fine structure at low temperature (*e.g.* Collins, 1982).

It should be noticed that among the microdiamond samples available we have found a transparent fragment of *ca.* 0.2 mm in size, whose lilac color is practically indistinguishable from the deep-violet color of all other samples studied. However, as seen from Fig. 4, the absorption spectrum of this fragment is different from that of the deep-violet crystal in Fig. 2: though it also contains a broad band with a smooth maximum at around 550 nm (18200 cm^{-1}) partly overlapped by the high-energy edge, the half-width of the band, FWHMΔ ≈2800 cm^{-1}, is significantly larger than that of the band at 17850 cm^{-1} in deep-violet diamonds (*cf.* Fig. 2 and 4). Besides, even at room temperature the broad band in Fig. 4 displays a fine structure, which becomes more intense and distinct at 77 K. The shapes, positions and intensity ratio of two characteristic absorption lines at 638 nm (15680 cm^{-1}) and ~616 nm (16240 cm^{-1}), as well as the

whole shape of the absorption envelope in Fig. 4 undoubtedly evidence that this is the band commonly attributed of the N-V center (*e.g.* Collins, 1982). Note that in contrast to the formerly published data, where the fine structure of such band was observed only at low temperature (*e.g.* Collins, 1982), in this sample we can see it even at room temperature. Cooling to ~77 K results in intensification and better resolution of the absorption features (Fig. 4), however, no other absorption lines, expected for the N-V-center spectrum (*e.g.* Collins, 1982), were revealed. Perhaps, their absence in the low temperature spectrum in Fig. 4 may be due to a relatively low spectral resolution (Δλ ≈ 1.5 nm) of the spectrophotometer used.

It should be noted that the linear absorption coefficient of the N-V-center band in the spectrum in Fig. 4, ~15 cm^{-1}, is at least one order of magnitude higher than in artificially irradiated diamond studied so far, thus indicating a relatively high concentration of this center in our sample studied. This result evidences that the N-V center appears in natural Ukrainian diamonds, in some of them even with an extremely high concentration. Up to now the N-V-center band system has not been observed in natural untreated diamonds, but it can be generated in natural or synthetic crystals (*e.g.* Collins, 1982; Mita, 1996) of 1b type by irradiation and subsequent thermal treatment. Therefore, a high content of the N-V center in some Ukrainian samples may be considered as evidence that they may have been irradiated (and then annealed) during their geological history.

All above results undoubtedly evidence that the intense unstructured band at ~17850 cm^{-1} in spectra of Ukrainian deep-violet diamonds (Fig. 2) is not the band at ~2.2 eV of the N-V center, as it was previously assumed by Taran *et al.* (1998). A similar band appears in spectra of pink diamonds from the Argyle mine (Australia): King *et al.* (2002) reported a broad band at 550 nm (18200 cm^{-1}), *i.e.*, at a somewhat higher energy than the band at 17850 cm^{-1} in our samples. It is also believed that in the Australian diamonds the band at 550 nm correlates with a broad band at 390 nm (King *et al.*, 2002). In our samples the latter is, probably, not
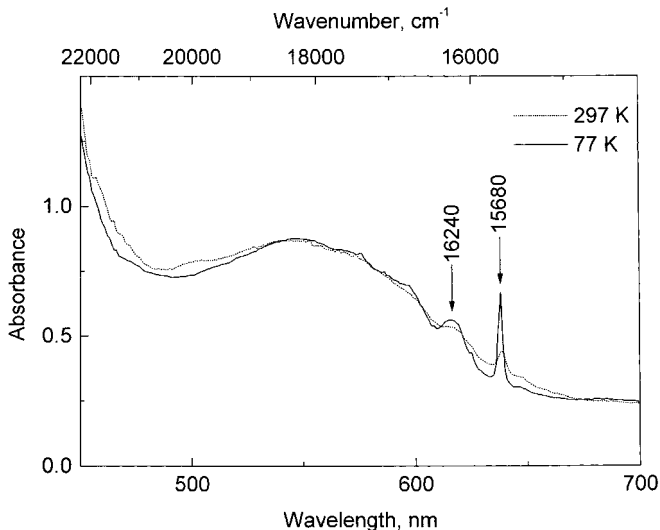
Fig. 4. Optical absorption spectrum of a fragment of lilac microdiamond at room and liquid nitrogen temperature. The sample is ~0.2 mm thick. A distinct fine structure of the broad band with maximum around 550 nm and two lines of absorption at 15680 and 16240 cm^{-1} are characteristic for the N-V center.

seen because of masking influence of the strong absorption edge. Note, that a number of investigators attribute the band ~550 nm to a color center of unknown structure related to "plastic deformation" (Raal, 1958; Collins, 1982; Fritsch, 1998). Such "plastic deformation" frequently appears morphologically on octahedral, dodecahedral or rhombo-dodecahedral faces of transparent crystals. As in our case the violet color appears in the cubic-shaped diamonds, no evidence of plastic deformation can be seen because of imperfection on the cube faces.

The nature of deep-violet color of Ukrainian diamonds is, therefore, not clear and needs further investigations. EPR-spectroscopy and luminescence might be useful for this purpose, although in this case their application is highly complicated because of the small amount of the material available and small dimensions of individual samples.

Summary

A broad optical absorption band 17850 cm^{-1} (560 nm) is extraordinary strong in the spectra of deep-violet Ukrainian diamond microcrystals. Optical absorption spectra, measured at liquid nitrogen temperature, evidence that it can not be attributed to electronic transitions of the N-V center (*i.e* impurity nitrogen atom, neighboring a carbon vacancy), as was previously assumed by Taran *et al*. (1998). IR-spectra of variously colored microdiamonds from Ukrainian placers are also not consistent with such interpretation as they indicate only low, if any, contents of "isolated" nitrogen in them. Probably, this band is caused by "plastic deformation", typical of pink diamonds from Argyle (Australia).

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