3-D microspectroscopy of optical centers in color natural diamonds

© *E.N. Rimskaya*[1], *E.V. Kuzmin*[1], *P.A. Danilov*[1], *G.Yu. Kriulina*[2], *D.A. Pomazkin*[1], *S.I. Kudryashov*[1]

[1] Lebedev Physical Institute, Russian Academy of Sciences,
119991 Moscow, Russia
[2] Lomonosov Moscow State University,
119899 Moscow, Russia

e-mail: romehelen@gmail.com

A study of three-dimensional photoluminescence of natural diamonds of two types, differing in morphology and absorption in the infrared range, was carried out. It is shown that, depending on the type and concentration of nitrogen defects in natural diamond, the position of the absorption band maximum can shift, which determines the pink or brown color of diamonds. The results of the study were carried out photoluminescence spectra at two pump wavelengths (488 and 532 nm), which make it possible to determine the optical centers that contribute to the color of diamonds. It is shown that complex nitrogen defects appear in natural colored diamonds as a result of plastic deformation, which determine the properties of the diamond.

Keywords: natural diamonds, color centers, photoluminescence, crystal defects.

DOI: 10.61011/EOS.2023.02.55775.4-23

Introduction

Inscribing of unique photoluminescent micro-mark (QR-code) in diamonds and gemstones is in great demand with manufacturers worldwide to ensure protection against fakes and for tracking [1]. Ultra-short laser pulses make it possible to mark transparent materials, however, a security concern in terms of natural diamond microstructure still exists [2]. Many main physical questions regarding the origin and growth of microstructures inside the diamond crystals still require more in-depth study. Besides the diamond structure itself, the diamond properties are greatly influenced by the distribution of natural color centers, defects and inclusions existing both on the surface and in the bulk of the diamond. One of the main issues is the unknown initial distribution of nitrogen impurities that may be both low and highly aggregated and may be characterized simultaneously by different spectroscopy methods (optical, infrared, Raman scattering (RS), electron paramagnetic resonance, etc.).

Photoluminescence (PL) is currently the most informative and popular gemological analysis method. Therefore, identification of color center, crystal lattice defects, inclusion distribution patterns within the diamond and transformation mechanisms is an crucial challenge. In PL spectra, color centers form specific spectral bands which are unique for each center and, thanks to strong laser emission exposure, optic center association/dissociation processes may occur [3] allowing to control „spectral imprint " of the diamond and to have multiple applications. Thus, NV center existing in the diamond can be used as a quantum bit because it has two steady states with possibility of controlled transition between each other [3–5].

Since the natural diamond grows for a long period of time and is subjected to several stages, the resulting gem usually has many individual features (lattice defects, inclusions, etc) that form zones which respond to laser exposure differently [3,5,6]. Thus, initial diamond characterization is one of the most important diamond application stages. Two types of natural diamonds are used as specimens herein: diamonds in the form of dodecahedral habit with negligible signs of dissolution having high nitrogen fraction in the form of *B* defects (pink diamond „8−1" and brown diamond „31−1") and in the form of strongly dissolved dodecahedron with low fraction of *B* defects (pink diamond „24−2").

Color centers were studied by optical methods and scanning confocal 3D Raman microspectroscopy at two exciting wavelengths (488 nm and 532 nm).

Experimental

Primary characterization of specimens (Figure 1) performed by infrared (IR) spectroscopy methods (Vertex V-70, Bruker) allowed to define the optical centers existing in the diamonds and to classify the types of studied diamonds. For 3D RS/PL scanning of diamonds, two pump wavelengths were used — 488 (Alpha 300 AR, WITec) and 532 nm (Confotec MR350, SOL Instruments), which allowed to expand the studied spectral range and revise the results.

Nitrogen concentration in „8−1" pink diamond in the form of *A* defects achieves $[A(2N)] \sim 653$ ppm, in the form of *B* defects achieves $[B1(4NV)] \sim 910$ ppm and corresponds to type IaAB. Band absorption factor at
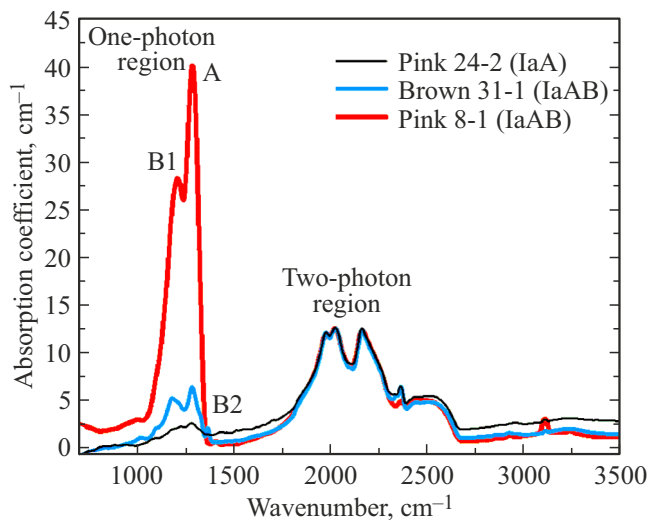
Figure 1. IR absorption spectra of the test diamonds.

Maximum/minimum PL signal ratio

Diamond	I_{max}/I_{min} to 488 nm	I_{max}/I_{min} to 532 nm
„8−1"	1.47	1.94
„31−1"	1.709	2.09
„24−2"	1.78	2.15

$3107\,\mathrm{cm}^{-1}$ of $N_3VH(a_{3107})$ center is equal to $8.1\,\mathrm{cm}^{-1}$. In „31−1" brown diamond : $[A(2N)] \sim 106\,\mathrm{ppm}$, $[B1(4NV)] \sim 170\,\mathrm{ppm}$, $[B2] = 2.1/1365\,\mathrm{cm}^{-1}$ and corresponds to type IaAB. However, „24−2" pink diamond contains nitrogen primarily in the form of *A* defects, $[A(2N)] \sim 44\,\mathrm{ppm}$, which corresponds to type IaA. IaAB type diamonds were subjected to more prolonged or high-temperature annealing in natural conditions then IaA type diamonds[3–10].

It is interesting that, despite similar color (pink), „24−2" and „8−1" diamonds differ considerably in nitrogen concentration (difference in defects in IR absorption) and, therefore, are of different types [1–5,6–11]. According to the type and concentration of nitrogen defects initially present in the diamond, position of the absorption band peak may be shifted and this defines pink or brown color of diamonds [4,5,7,12,13].

Figure 2 shows optical photos of the tested diamond surfaces. It may be noted that all diamonds have many plastic deformation regions caused by diamond growth in natural environment and appearing in the form of parallel hatching lines on the surface. Plastic deformation of crystals is implemented by two possible mechanisms such as twinning or dislocation slip in different temperature conditions [4,10,11–16].

Plastic deformations take a special place among diamond defects and require thorough investigation because their geometrical parameters (length and depth) considerably influence the diamond transmittance and PL spectra. During diamond growth, inclusions and inhomogeneities [5,6,8–12,15,17] aggregate around the crystal lattice defects throughout the crystal, which increases their local concentration by several times and, thus, PL intensity is considerably increased in such zones.

Figure 3 shows PL spectra taken on the diamond surface. Scanning was performed on $170\,\mu m$ long line (red arrowhead line in Figure 2). It can be seen that spectra obtained from the deformation region completely duplicate the typical view of the initial diamond spectrum, i.e. chemical composition of the diamond remains unchanged (without shift on PL wavelengths), however, due to higher concentration of nitrogen and related aggregates, PL signal from such zones becomes brighter.

Results and discussion

Detailed study of PL spectra allows to expand the considered spectral range and to define optical centers that contribute to the diamond color [18,19].

Figure 4 shows comparative spectra of plastic deformation zones (I_{max}) and diamond without plastic deformations (I_{min}). Scanning was performed using two devices having different settings, therefore the obtained spectra have different width (different diffraction gratings) and PL signal strength (different pump lasers). Ratio I_{max}/I_{min} characterizes nitrogen redistribution inside diamond and may indirectly indicate the degree of deformations occurring in the diamond. The curves show that the spectra of the studied diamonds differ a little. „8−1" diamond (Figure 4, *c*) has typical lines of 2NV defect (optical center H3 with zero-phonon line (ZPL) 503.2 nm) generated by single nitrogen atoms at high temperatures and being a permanent companion of crystal lattice defects [4,5,16]. „31−1" IaAB brown diamond spectrum (Figure 4, *b*) has 2NV (H3) and NV defects (optical center NV^0 with ZPL at 575 nm). In this case, in „24−2" IaA pink diamond (Figure 4, *a*) having, as IR spectroscopy shows (Figure 1), the lowest nitrogen concentration, such centers are not observed. Meanwhile, all diamonds have wide PL bands 450−550 nm and 650−800 nm. Occurrence of such bands may be caused by the presence of optical centers in the diamond that emit in a shorter spectral range (< 480 nm) beyond the detection limits of our equipment. Ratios I_{max}/I_{min} are shown in the table.

It is shown that in „8−1" diamond with the highest nitrogen concentration according to IR spectroscopy data, the difference in PL intensity between the zone with observed plastic deformations and the zone without such deformations is minimal. For „24−2" diamond, on the contrary, strong conversion takes place at low
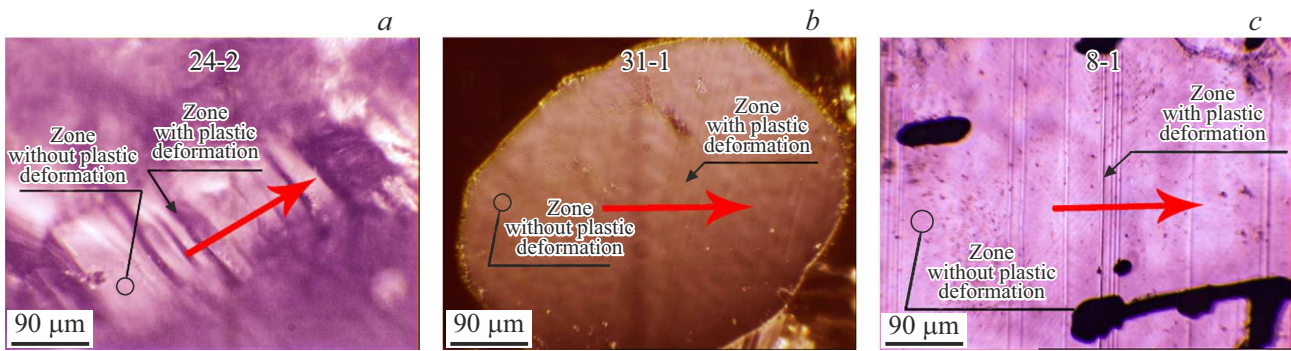
Figure 2. Optical photographs of diamond surfaces: pink IaA (*a*), brown IaAB (*b*), pink IaAB (*c*). Red arrowhead line shows scanning areas (arrow indicates scanning direction).
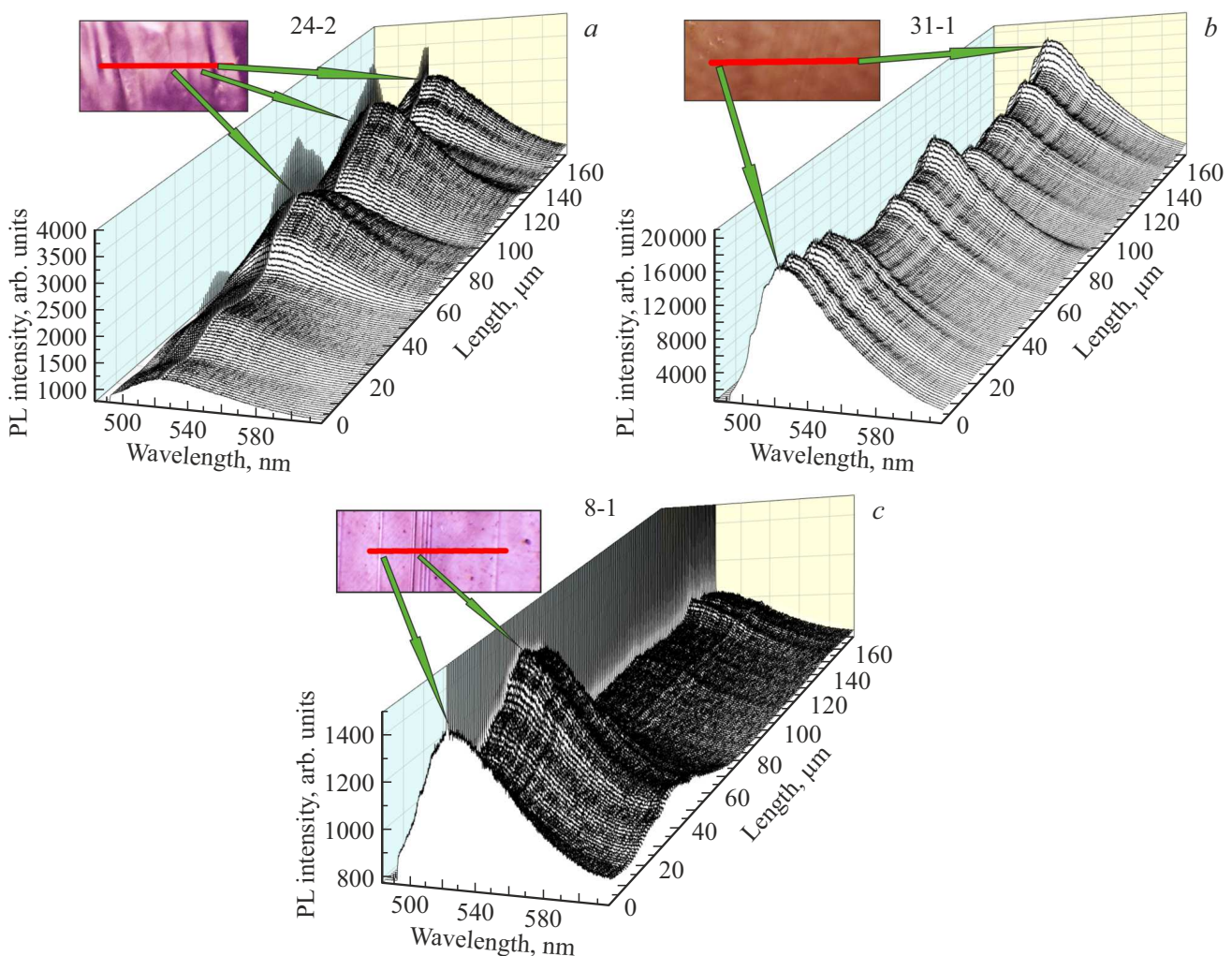

Figure 3. Surface luminescence spectra in natural diamonds when pumped by 488 nm laser: pink IaA (*a*), brown IaAB (*b*), pink IaAB (*c*); red line — 170 μm long line, on which scanning was performed. Green arrowhead line shows plastic deformation area on the diamond surface and its PL spectrum in the same area (plastic deformation zones are highlighted in Figure 2).

nitrogen concentration in the diamond. This is probably attributed to the „saturation" of dislocations with moving nitrogen atoms and impossibility of further absorption [5–12].

Figure 5 shows distribution of the intensity of RS signal in the depth of the diamond. It may be noted that plastic deformation zones on the surface continue also inside the diamond. Moreover, their
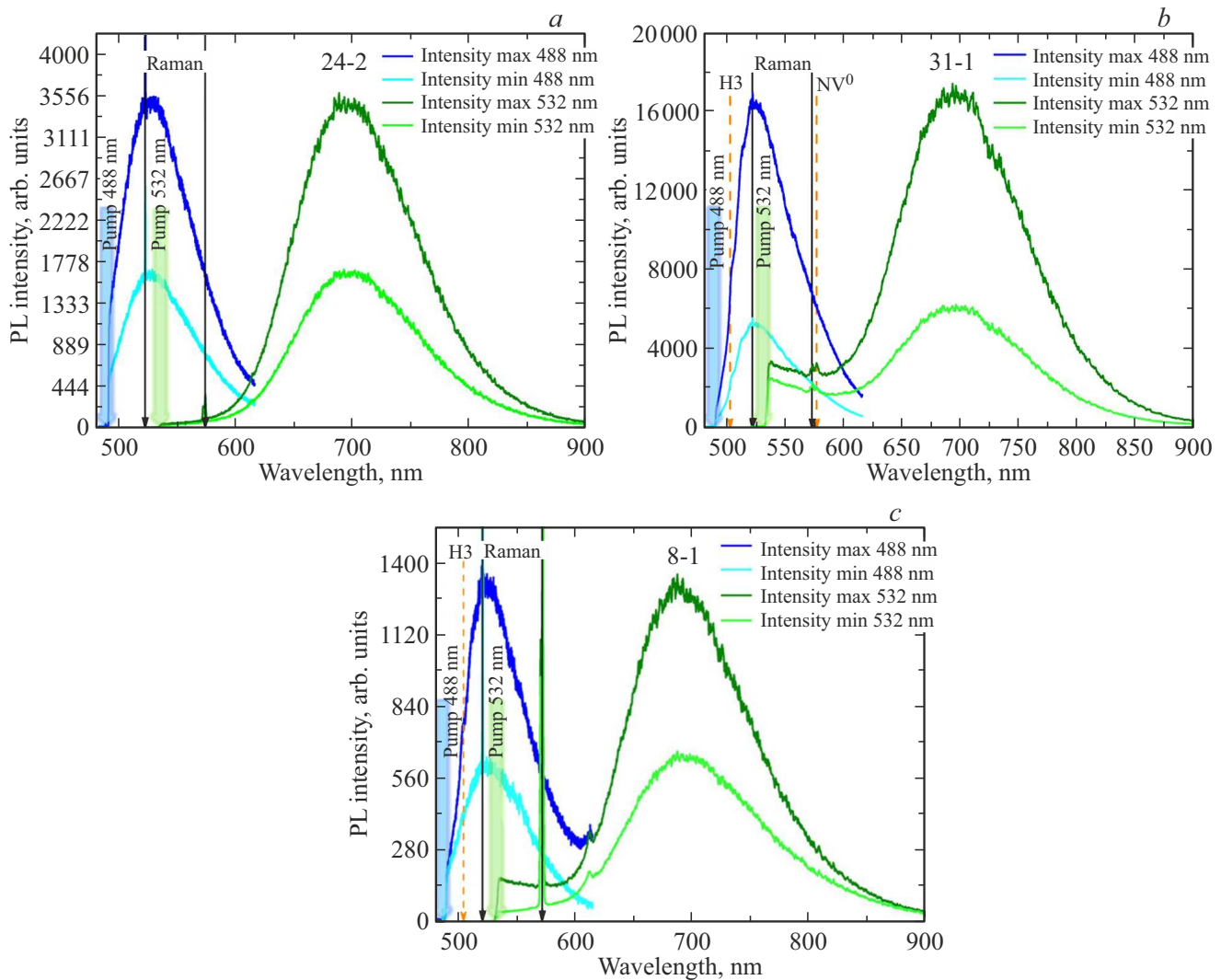
Figure 4. PL spectra in natural diamonds when pumped by 488 nm and 532 nm laser: pink IaA (*a*), brown IaAB (*b*), pink IaAB (*c*).

period remains unchanged and angle to the surface depends on the diamond growth conditions and performed cutting. Therefore, regular nitrogen-vacancy transformation chains in the plastic deformation zone are intensified, which is of great interest for diamond defect detection and identification of growth conditions [4,5,7,17].

Conclusion

Division of diamonds into two groups allowed to establish connection between the morphological features and their color, nitrogen defects concentration and PL properties. The study of layout and composition of plastic deformation regions has shown that occurrence of complex nitrogen defects defining the diamond properties in natural colored diamonds is more preferable in the disturbed crystal lattice structure regions and

the view of and concentration of the defect depend on growth temperature conditions of the whole crystal.

Conflict of interest

The authors declare that they have no conflict of interest.

References

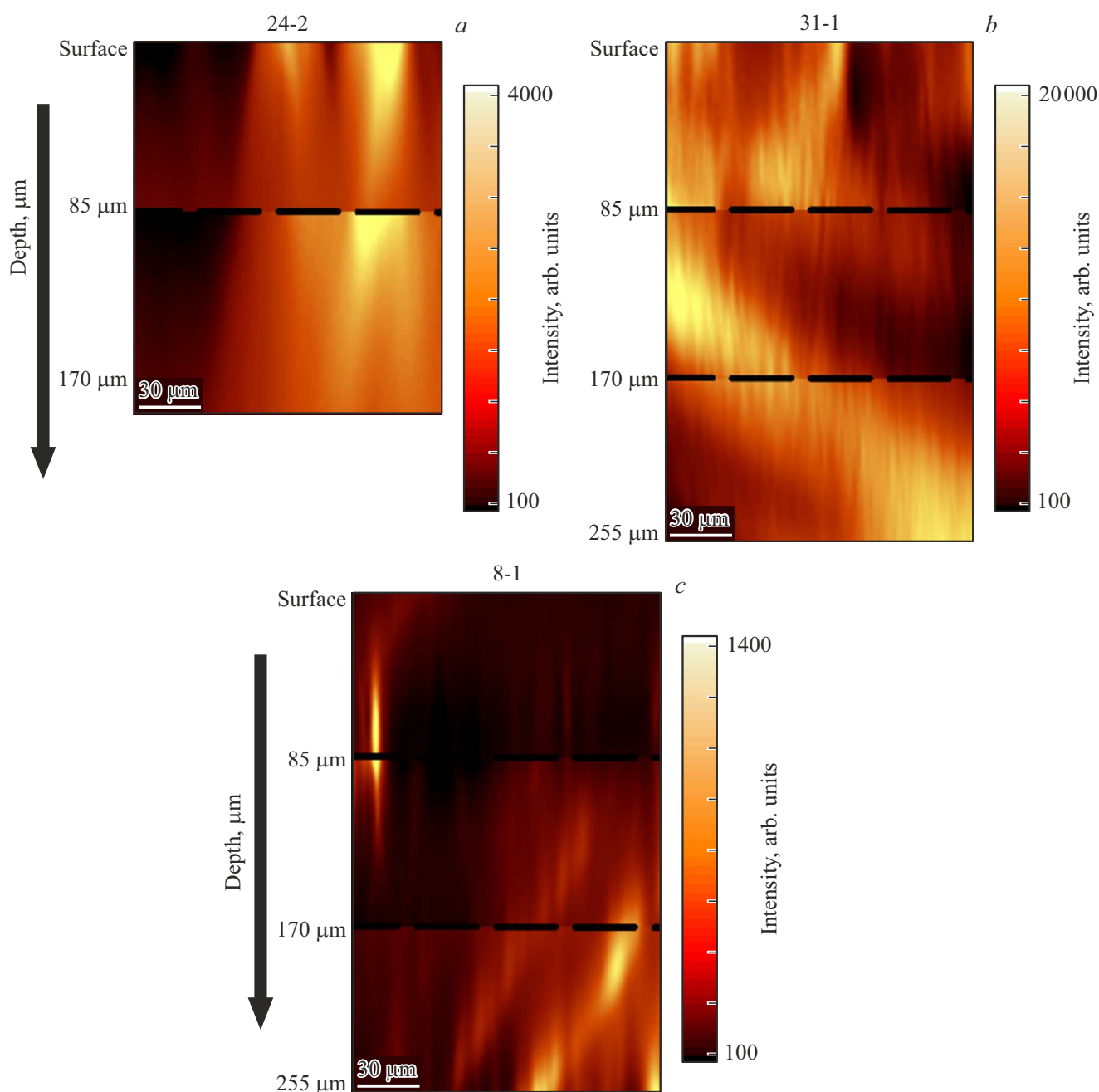[1] Y.C. Chen, P.S. Salter, S. Knauer et al. Nature Photonics, **11** (2), 77–80 (2017). DOI: 10.1038/nphoton.2016.234

Figure 5. RS signal intensity distribution inside natural diamonds: pink IaA (*a*), brown IaAB (*b*), pink IaAB (*c*).

[2] V. Bharadwaj et al. J. Phys. Photonics, **1**, 022001 (2019). DOI: 10.1088/2515-7647/ab0c4e

[3] Yu.L. Orlov. *Mineralogiya almaza* (Nauka, M., 1984), 264 p. (in Russian)

[4] E.A. Vasilev. J. Appl. Spectrosc., **86**, 512–515 (2019). DOI: 10.1007/s10812-019-00850-0

[5] A.M. Zaitsev. *Optical properties of diamond: a data handbook* (Springer Science & Business Media, 2013), 502 p. DOI: 10.1007/978-3-662-04548-0

[6] R.A. Khmelnitsky. *Vvedenie v gemmologiyu almaza* (M., 2021) (in Russian).

[7] V. Garanin, K. Garanin, G. Kriulina, G. Samosorov. *Diamonds from the Arkhangelsk Province, NW Russia* (Springer, Cham, Switzerland, 2021), 265 p.

[8] G.B. Bokiy, G.N. Bezrukov, Yu.A. Kluev, A.M. Naletov, V.I. Nepesha. *Prirodnye sinteticheskie almazy* (Nauka, M., 1986), 220 p (in Russian).

[9] J.E. Field (ed.). *The Properties of Natural and Synthetic Diamond* (Academic Press, London, 1992). DOI: 10.1002/crat.2170280504

[10] B. Dishler. *Handbook of spectral lines in diamond* (Springer, Berlin, Germany, 2012), 468 p. DOI: 10.1007/978-3-642-22215-3

[11] S.I. Kudryashov, P.A. Danilov, N.A. Smirnov, A.O. Levchenko, M.S. Kovalev, Y.S. Gulina, O.E. Kovalchuk, A.A. Ionin. Opt. Mater. Express, **11** (8), 2505 (2021). DOI: 10.1364/OME.427788

[12] I.A. Dobrinets, V.G. Vins, A.M. Zaitsev. *HPHT-Treated Diamond* (Springer, Berlin/Heidelberg, Germany, 2013), 257 p. DOI: 10.1007/978-3-642-37490-6

[13] E. Gaillou, J.E. Post, N. Bassim, M. Fries, T. Rose, R. Stroud, J.E. Butler. Diam. Relat. Mater., **19** (10), 1207–1220 (2010). DOI: 10.1016/j.diamond.2010.06.015

[14] A.T. Collins. Diam. Relat. Mater., **1**, 457 (1992). DOI: 10.1016/0925-9635(92)90146-F

[15] G. Kriulina, E. Vasilev, V. Garanin. Dokl. Earth Sci., **2**, 627 (2019).

[16] O.P. Yuryeva, M.I. Rakhmanova, D.A. Zedgenizov, V.V. Kalinina. Phys. Chem. Mineral., **47**, 20 (2020). DOI: 10.1007/s00269-020-01088-5

[17] D. Howell, D. Fisher, S. Piazolo, W.L. Griffin, S.J. Sibley. Am. Mineral., **100**, 1518 (2015). DOI: 10.2138/am-2015-5044

[18] S.I. Kudryashov, V.G. Vins, P.A. Danilov, E.V. Kuzmin, A.V. Muratov, G.Y. Kriulina, J. Chen, A.N. Kirichenko, Y.S. Gulina, S.A. Ostrikov et al. Carbon, **201**, 399 (2023). DOI: 10.1016/j.carbon.2022.09.040

[19] S.I. Kudryashov, R.A. Khmelnitskii, P.A. Danilov, N.A. Smirnov, A.O. Levchenko, O.E. Kovalchuk, M.V. Uspenskaya, E.A. Oleynichuk, M.S. Kovalev. Opt. Lett., **46** (6), 1438 (2021). DOI: 10.1364/OL.414583

Translated by E.Ilyinskaya