
MINERALS
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The Defect-Impurity Composition of Diamond Crystals with [100] Growth Pyramids from Placers of the Krasnovishersk District, the Northern Urals

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Abstract—The internal structure of cuboid diamonds and their spectroscopic features from recent alluvial placers of the Krasnovishersk District (the Northern Urals) have been investigated. Crystals were divided into four groups by their anatomy and spectroscopic features: cuboids of the II group (according to the Yu.L. Orlov classification): cuboids with a transparent core and peripheral zone saturated with inclusions; crystals with the joint growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids, and crystals with the sequential growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids. In all studied crystals, the regenerative formation of the [111] face steps together with the formation of tetragonal pits on the cuboid surface was the last stage of growth. Local photoluminescence investigations have been carried out for all cubic diamond crystals of the Urals for the first time. It was established that luminescence bands at 926 and 933 nm are related to growth pyramids of $\langle 100 \rangle$ and $\langle 111 \rangle$, respectively. Bands with peaks at 800, 820.5, 840, 860, and 869 nm were revealed in the luminescence systems of the cuboids of II group. We note that the cuboid diamonds from different regions of the world have similar internal structures and spectroscopic features.

Keywords: diamond, cuboid, the Urals, internal structure, FTIR, photoluminescence

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INTRODUCTION

Among diamonds in most of the primary diamond deposits, less than 1% are diamond crystals of the cubic habit. The proportion of cuboids in some deposits of Canada (Gurney et al., 2004) and Botswana (Schrauder and Navon, 1994) can reach 20%, but most of them are gray or black. A high proportion of cuboid crystals is characteristic of deposits in the Arkhangelsk region (Kriulina et al., 2012; 2019). The proportion of gem-quality cuboid diamonds in alluvial placers with an undetermined type of source (the Urals, Anabar–Olenek interfluvium, Kalimantan, and Sierra Leone) can reach up to 10% (Rossyp'..., 2007; Smith et al., 2009; Smit et al., 2018; Vasilev et al., 2018b). The predominance of dodecahedroids and a wide range of concentrations of nitrogen defects are characteristic features of such deposits (Kukharensko, 1955; Nefedov and Klepikov, 2018; Vasilev et al., 2013). Crystals of cubic habit may have a fibrous or cuboid internal structure. Fibrous crystals consist of slightly disoriented blocks that diverge from the central part of the crystal. As a rule, such crystals have chains of microinclusions in the $\langle 111 \rangle$ direction (Lang, 1974; Ragozin et al., 2017). The cuboid type of crystal growth is manifested in the form of curvilinear zoning in the $\langle 100 \rangle$ direction. An alternation of fibrous and

cuboid zones can be observed in the same crystal (Howell et al., 2012).

Yellow cuboids of the II group according to Yu.L. Orlov classification (1973) are of particular interest. Such crystals have a rare set of low-temperature centers in IR absorption and photoluminescence spectra (Titkov et al., 2015; Zedgenizov et al., 2016; Zudina et al., 2013). They often have a fancy color and, accordingly, a higher price. The presence of such crystals allows one to distinguish placers with an unknown type of primary source from known primary deposits.

Having studied collections of rounded diamonds from modern alluvial placers of the Krasnovishersk District (Vasilev et al., 2018b), the authors distinguished 12% of the crystals (cuboids, tetrahedroids, and dodecahedroids) with tetragonal pits on the cuboid surface. This feature of the relief is most often characteristic of growth pyramids $\langle 100 \rangle$, which makes it possible to distinguish crystals of the original cubic habit or mixed-habit growth among highly dissolved dodecahedroids. Cubic crystals contain many poorly studied systems in the photoluminescence (PL) spectra and are characterized by a complex internal structure. The set and distribution of PL centers in the volume of crystals and concentrations of active defects

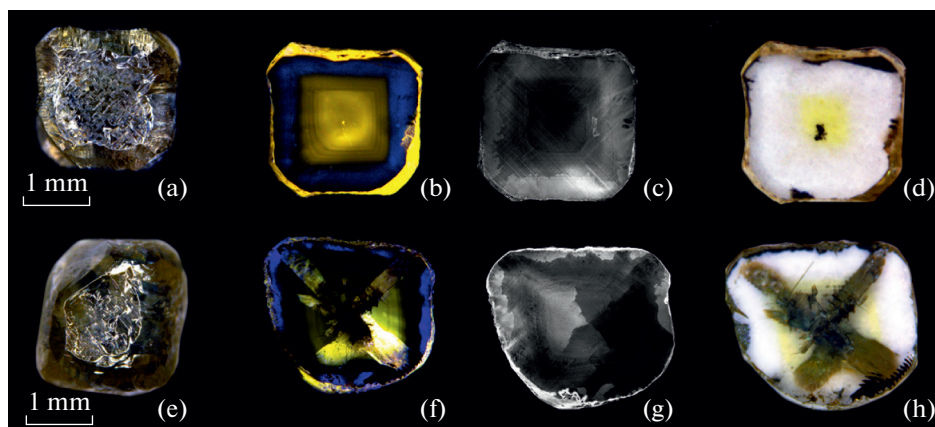


Fig. 1. The I-group cuboids of 600-66 (a–d) and 601-66 e–h): a, e, general view of crystals; images of polished plates: b, f, photoluminescence under 365 nm excitation; c, g, cathodoluminescence; d, h, transmitted light.

determined by IR absorption are important typomorphic features (Khachatryan, 2009). From this point of view, diamonds of the Urals and especially diamonds of a cubic habit have been fragmentarily and insufficiently studied. The objective of this study was to analyze the internal structure and defect-impurity composition of crystals with growth pyramids $\langle 100 \rangle$ from alluvial placers of the Krasnovishersk District.

RESEARCH METHODS AND SAMPLES

To study the features of the internal structure of 21 diamond crystals that weigh 0.10–1.39 carats from modern alluvial deposits of the Krasnovishersk District of the Northern Urals (VSEGEI collection, St. Petersburg), plane-parallel polished plates with a thickness of 0.45–0.8 mm and $\langle 100 \rangle$ orientation were made. Plates were cut through the central parts of the crystals and then polished on a diamond-charged wheel with 4–6 μm diamond powder.

The methods of studying the internal structure and spectroscopic studies have been described previously (Vasilev et al., 2018a, 2018b). Local measurements of nitrogen concentration in the form of A (N_A) and B1 (N_{B1}) defects and their total concentration (N_{tot}) were measured in the plates. As well, absorption coefficient and the position of the maximum of the B2 band (α_{B2} , ν_{B2}), the absorption coefficient of the 3107 cm^{-1} band (α_{3107}) corresponding to the $V_3\text{NH}$ defect (Goss et al., 2014), and the absorption coefficient of C defects (α_C) were determined.

RESEARCH RESULTS: INTERNAL STRUCTURE, IR SPECTROSCOPY, AND PHOTOLUMINESCENCE

The sample of the studied crystals is divided into several groups, which fundamentally differ in their growth and spectroscopic features.

(1) cuboids of the II group according to the Orlov classification (ten crystals).

(2) cuboids with transparent core and peripheral zone saturated with inclusions (three crystals).

(3) crystals with the joint growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids (six crystals).

(4) crystals with successive change of the growth mechanism (two crystals).

(1) Cuboids of the II group according to the orlov classification. Cuboids are united in a group with the slight dissolution of the edges (Fig. 1) and some dodecahedroids. Due to strong dissolution, dodecahedroids completely lost their original habit but preserved specific spectroscopic features. The complex habit of these crystals can be explained by laminar dissolution (Shafranovskii, 2001) or the dissolution of a crystal fragment. Some crystals are characterized by wavy zoning of the $\langle 100 \rangle$ pyramids. These are crystals of the IaA + Ib type, $N_{\text{tot}} = 20\text{--}300\text{ ppm}$. Systems of S1, S3, 635.1 and 636.8 nm are recorded in the PL spectra of such crystals (Zudina et al., 2013). Cuboids of the II group are similar to the cuboids of the Anabar–Olenek interfluvial (Zedgenizov et al., 2016). According to the ratio of nitrogen defects, such diamonds are ascribed to low-temperature ones.

A common feature of this group of studied crystals is the presence of a complex broad band centered at 635.1 and 636.8 nm with phonon repetitions and the maximum value of approximately 700 nm. These systems are confined to cores of crystals (Fig. 1) and are absent in their rims. When 785 nm was excited, 800, 820, 840, 869 nm lines and a doublet of 883.5/885 nm of a low-temperature Ni-containing center were recorded (Zaitsev, 2001) (Table 1). The core of the crystal has yellow luminescence and a yellow color due to C-centers. Towards the rim, it is replaced by a non-luminescent zone and then a zone with the blue luminescence of the N3 system. CL images of the 600-66 and 601-66 crystals (Figs. 1c, 1g) show that the nonluminescent zone has uneven, strongly curved boundaries.

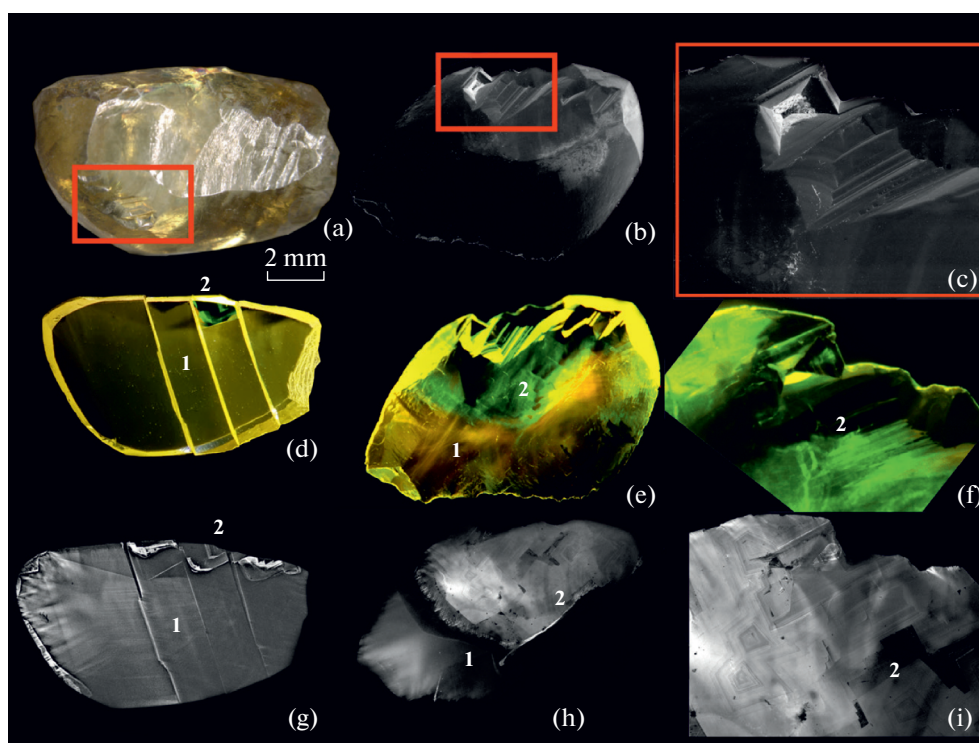


Fig. 2. An image of the strongly dissolved fragment of the I-group 126-76 crystal: (a) general view; (b, c) BSE images of the surface with rectangular pits; (d, e, f) photoluminescence under 405 nm excitation; (g, h, i) cathodoluminescence (1, cuboid zone, 2, octahedral zone); (d, g) polished plate, other, natural surface.

ies; this zone reaches to the surface over the several facets towards the $\langle 111 \rangle$ pyramid. Such a curved boundary appears to have a diffusion nature since it crosses the growth zoning. As well, some crystals have a very thin near-surface octahedral zoning in the $\langle 100 \rangle$ direction.

Across the sections of the 600-66 and 601-66 crystals, the N_{tot} , α_C , and α_{107} values decrease from the core to the rim; however, these parameters increase again in the subsurface zone of the 600-66 crystal (Table 1). The thickness of the octahedral zone in the 126-76 and 610-66 crystals is larger than in other samples (Fig. 2). These two radically different zones in these crystals are in sharp contrast in their spectroscopic features. The N_{tot} of the late octahedral zone in the 126-76 crystal is an order of magnitude greater than that in the dominant inner cubic zone of the crystal (40 and 400 ppm, respectively); the B2 defect is detected in the octahedral zone (Fig. 3a). A characteristic broad PL band with a maximum at approximately 700 nm (635.1 and 636.8 nm systems) is present only in the cubic zone of the crystal, whereas the intensive H3 system corresponds to the octahedral zoning (Fig. 3b). Both of these crystals have complex morphology and appear to be dissolved fragments. Sample 126-76 weighs 1.39 carats; the entire crystal was probably much larger.

Centers at 575 and 636.8 nm were recorded in five crystals. The presence of both systems at 635.1 and 636.8 nm was revealed in three samples (126-76, 610-66, and 158-76). These crystals are the most transparent; they have no zones saturated with microinclusions. Only the system of 635.1 nm was recognized in two samples; in two others it was only 636.8 nm. A wide band with a maximum at approximately 700 nm and the presence of a set of bands at 785-nm laser excitation (800, 820.5, 823, 840, 843, 847, 860, 869, 883.5/885, 890, and 912 nm) are present in all crystals of this group (Fig. 3c; Table 1). A unique feature of the first-group diamonds is “reverse” zoning: low-temperature defects C were recorded in the cores and high-temperature defects were recorded in the subsurface N3 zone. The nature of such zoning will be the subject of further research.

(2) Cuboids with a transparent core and an inclusion-bearing peripheral zone. These are crystals of the IaA type, $N_{\text{tot}} = 200\text{--}500$ ppm. The transparent cores of the crystals correspond to the joint growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids or only the $\langle 111 \rangle$ pyramid; the zone saturated with inclusions that dominates in the crystal corresponds to the growth of the $\langle 100 \rangle$ pyramids (Fig. 4). The yellow photoluminescence in these crystals is due only to the S1 luminescence system. There are distinct N3 and H3 systems and a weak 926 nm peak on the PL spectra.

Table 1. Spectroscopic features of studied crystals in different their growth zones

Crystal no.	Growth pyramids/zone	N _{tot} , ppm	N _{B1} , %	α_{B2} , cm ⁻¹	α_{3107} , cm ⁻¹	C	Features of photoluminescence, excitation at 350 and 488 nm	Features of photoluminescence, excitation at 785 nm
126-76	$\langle 100 \rangle$ /core	40	0	0.2	0.5	+	H3, S1, 531.5, 538.7, 540.5, 572.5, 575 , 576.7, 581.5, 586.7, 591.8, 595.5 , 635.1 + 636.8 , 700 sh* , 672.5, 681.5, 790.5	800 , 820.5 , 823, 840, 843, 847, 860, 869 , 883.5/885, 890, 912
223-76	$\langle 111 \rangle$ /rim	404	0	1.7	0	—	H3	—
	$\langle 100 \rangle$	52	0	0	2	—	H3 , 586.1, 612.5 , 700 sh , 681.3	820.5 , 840, 843, 847, 860, 869, 883.5/885 , 890, 904, 920, 926
601-66	$\langle 100 \rangle$ /core	237	0	0.1	5.7	+	H3, 575 , 590, 612.5, 636.8 , 700 sh , 926	820.5, 840, 883.5/885
600-66	$\langle 111 \rangle$ /rim	39	0	0	0.2	—	N3 , H3	—
	$\langle 100 \rangle$ /core	100	0	0.1	3.2	+	H3, 636.8 , 635.1, 700 sh	800 , 820.5 , 840 , 847 , 860, 869 , 883.5/885, 890, 912, 955, 986 (H2)
158-76	Rim	144	0	0	0.2	—	N3 , H3	—
	$\langle 100 \rangle$	105	0	0.1	1.7	—	H3, S1, 531.5, 538.7, 540.5, 572.5, 575, 576.7, 581.5, 586.7, 591.8, 595.5, 635.1 + 636.8 , 700 sh , 672.5, 682, 790.5	800 , 820.5, 840, 843, 847, 860, 869 , 883.5/885, 890, 912
605-66	$\langle 100 \rangle$	81	0	0.1	2.3	—	N3 , H3 , S1 , 575 , 612.5 , 635.1 , 700 sh , 682	800, 820.5, 840, 843, 847, 860, 869 , 883.5/885, 890, 912
610-66	$\langle 100 \rangle$ /core	20	0	0.2	0.6	+	524, 533.5, 542.5, 574.5 , 577.1, 578.7, 583.5, 588.7, 593.8, 597.5, 635.1 + 636.8 , 700 sh, 674.5, 683.5, 793	800 , 820.5 , 840 , 843, 847, 860, 869 , 880, 883.5/885, 890, 912, 930, 955, 964
685-66	$\langle 111 \rangle$ /rim	60	0	0	0.8	—	N3 , H3	—
	Core	235	0	0	3	—	N3 , H3 , S , 738, 926, 986 (H2)	926, 986 (H2)
602-66	Rim	230	0	0	2.8	—	—	—
	Core	396	0	0	5.2	—	N3 , H3 , S2	926
29-76	Rim	125	0	0	0.6	—	N3 , H3 , S2	—
	$\langle 111 \rangle$ /core	780	0	0.5	1.5	—		
123-76	$\langle 100 \rangle$ /core	740	0	0	12.7	—	H3, S , 603, 667, 693.7, 700.3, 787, 926	926
	$\langle 111 \rangle$ /rim	454	0	0	4.9	—	H3	
615-66	$\langle 111 \rangle$ /core	1485	66	34.4	5.4	—	N3 , S1 , 700.3, 787, 912 , 933	933
	$\langle 100 \rangle$ /core	1363	67	22.1	34.5	—	N3 , S1 , S2? , S3 , 603, 640 + 643, 700.3 , 787	
615-66	$\langle 111 \rangle$ /rim	860	67	20.4	1.1	—		
	$\langle 111 \rangle$ /core	520	<5	2	0	—	N3 , H3 , S?	926, 948
	$\langle 100 \rangle$ /core	260	0	0	4.4	—	H3, 603, 637 + 640, 667, 693.7, 700.3, 787, 926, 948	

Table 1. (Contd.)

Crystal no.	Growth pyramids/zone	N _{tot} , ppm	N _{B1} , %	α_{B2} , cm ⁻¹	α_{3107} , cm ⁻¹	C	Features of photoluminescence, excitation at 350 and 488 nm	Features of photoluminescence, excitation at 785 nm
612-66	$\langle 100 \rangle$ /core	1355	20	4.7	25.6	—	603, 640, 700.3, 787, 926, 948	926, 948
	Middle	958	15	3.2	12.5	—	N3, H3, 603, 612.5 , 637, 662, 680, 693.7, 700.3, 741, 926, 948	
122-76	$\langle 111 \rangle$ /rim	545	0.9	0	0.1	—	N3, H3	933
	$\langle 111 \rangle$ /core	878	50	17.7	1.4	—	912, 933	
	$\langle 100 \rangle$ /middle	860	48	8.6	12.9	—	603, 640 + 643, 700.3, 787, 926	
	$\langle 111 \rangle$ /rim	594	43	6.4	4.8	—	H3, GR1 , 552, 587, 636, 662	

* Middle band with a peak at 700 nm. Very strong systems are given in bold.

The crystals are either uniform in the distribution of nitrogen defects or close in their distribution to the first-group crystals. As an example, a uniform decrease in N_{tot} and α_{3107} from the core to the rim was noted in the 602-66 crystal (Fig. 4f) (Table 1). The difference from the first-group crystals is the uniform distribution of the intensity of the N3 system in volume; zones saturated with microinclusions have a yellow PL. The PL bands that are characteristic of the first-group crystals were not recorded. Carbonate bands are recorded on the IR absorption spectra in microinclusion-bearing zones.

(3) Crystals with joint growth of the $\langle 100 \rangle$ and $[111]$ pyramids. The joint occurrence of tetragonal and triangular etching pits is noted on the surface of the crystals. One characteristic feature of these crystals is the joint growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids (Fig. 5). N_{tot} = 600–1500 ppm, N_{B1} = 0–70% (Fig. 6), high α_{3107} , and there are many microinclusions in the cubic zones. The 933-nm luminescence band was recorded on the octahedron faces of the growth pyramids; bands at 787, 926, and 700.3 nm are localized in the cube pyramids (Vasilev et al., 2018a).

Rosette-like inclusions up to 5 μ m in size are located in the $\langle 100 \rangle$ pyramids of the 615-66 crystal. The CL image (Fig. 5f) shows that these inclusions are located in the central parts of 10–20 μ m domains with reduced CL intensity. As well, N_{tot} in the cubic domains of this crystal is two times less than that in the octahedral domains. An interesting feature of the crystals of this group is the completely different thermal history of their development. The 29-76 crystal contains only A defects; B2 defects are practically absent (α_{B2} = 0.5 cm⁻¹), while N_{B1} in 123–76 reaches 70% and α_{B2} in the octahedron sector reaches 35 cm⁻¹.

In all crystals, N_{tot} in the $\langle 100 \rangle$ domain is higher than in the synchronous $\langle 111 \rangle$ domain (Table 1).

(4) Crystals with a successive change of the growth mechanism. Such crystals show at least two successive stages of growth by different mechanism. For example, the core shows only octahedral zoning, which is changed by the concentric zoning of the $\langle 100 \rangle$ pyramids (Fig. 7b). Conversely, the core has the cuboid habit, and then it is replaced by the development of octahedral faces (Fig. 7, e). The crystal morphology may vary in dependence on the predominance of a particular pyramid at the last stage of growth. Both octahedroid- and tetrahedroid-type crystals and cuboid crystals can occur. Based on spectroscopic features, these crystals are generally similar to the previous group. The 933 nm band in the PL spectra is observed in the octahedral pyramids; the 787, 926, and 700.3 nm bands occur in the cuboid pyramids (Vasilev et al., 2018a).

The maximum N_{tot} and N_{B1} values were recorded in the central cuboid zone of the 612-66 crystal (Fig. 7d). Towards the periphery, their N_{tot} and N_{B1} decrease; a sharp drop in N_{tot} is noted in the peripheral octahedral zone. Along with the sequential change of the cuboid zone by the octahedral one, this crystal is characterized by a wide transition zone with alternation of dissolution and regeneration of the cuboid zone, as well as nucleation and dissolution of the octahedral steps with a transition to the octahedral faceting. This alternation is manifested in the variations of α_{B2} and α_{3107} . The octahedral zones are characterized by high α_{B2} and low α_{3107} values, while cubic ones have the opposite values.

Both parameters are at their minimum in the peripheral octahedral zone (Table 1). Bands at 603, 637 + 640, 700.3, 787, 926, and 948 nm were recorded in the PL spectra of the central zone of this crystal, while systems of N3 and H3 and bands at 612.5, 662, 680, and 693.7 nm appear in the intermediate zone.

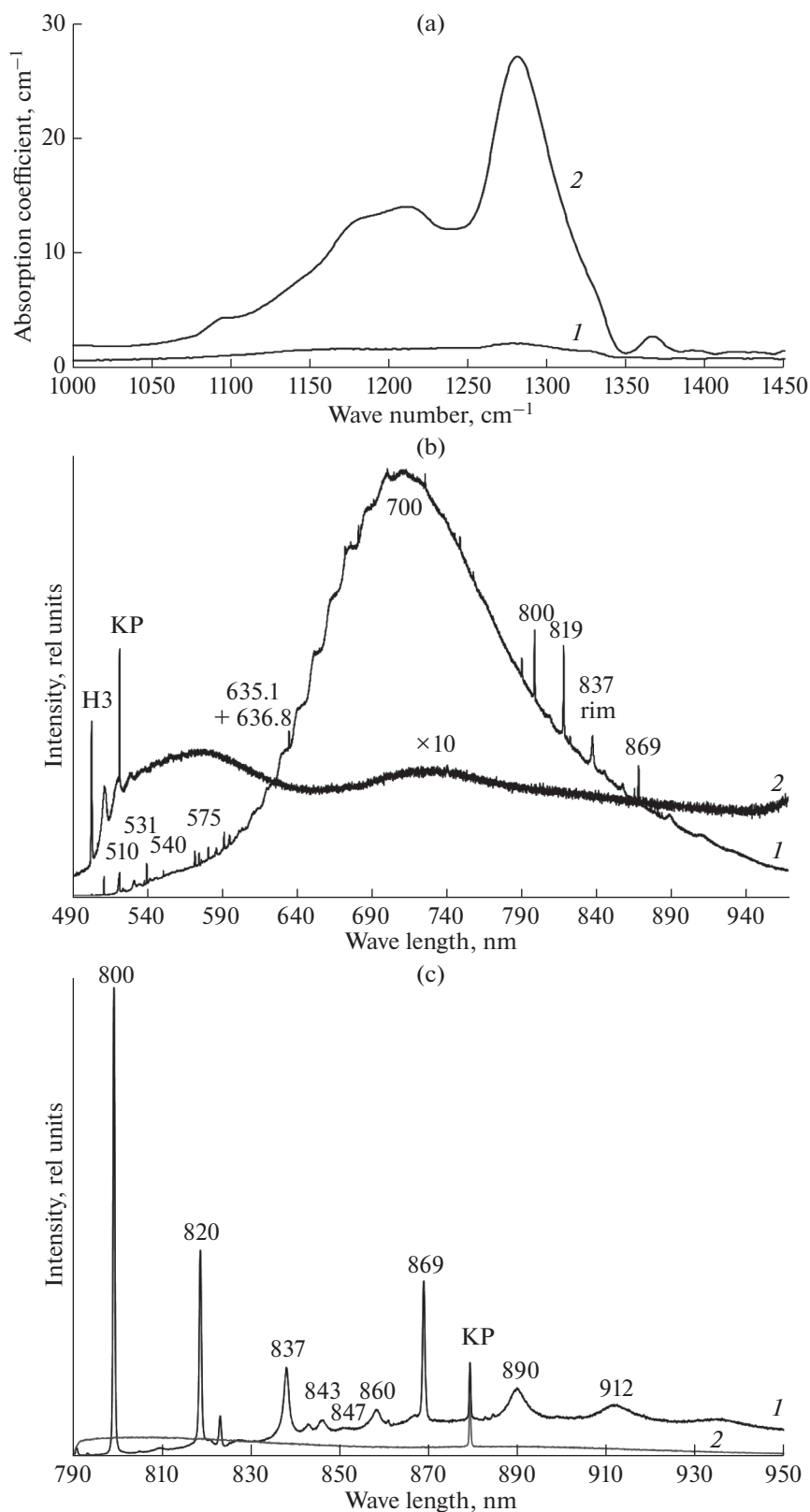


Fig. 3. The spectra of the 126-76 diamond recorded in different growth zones (1, homogeneous cubic zone; 2, octahedral zone): (a) FTIR absorption; (b) photoluminescence at 488 nm excitation; (c) photoluminescence at 785 nm excitation, at 77 K.

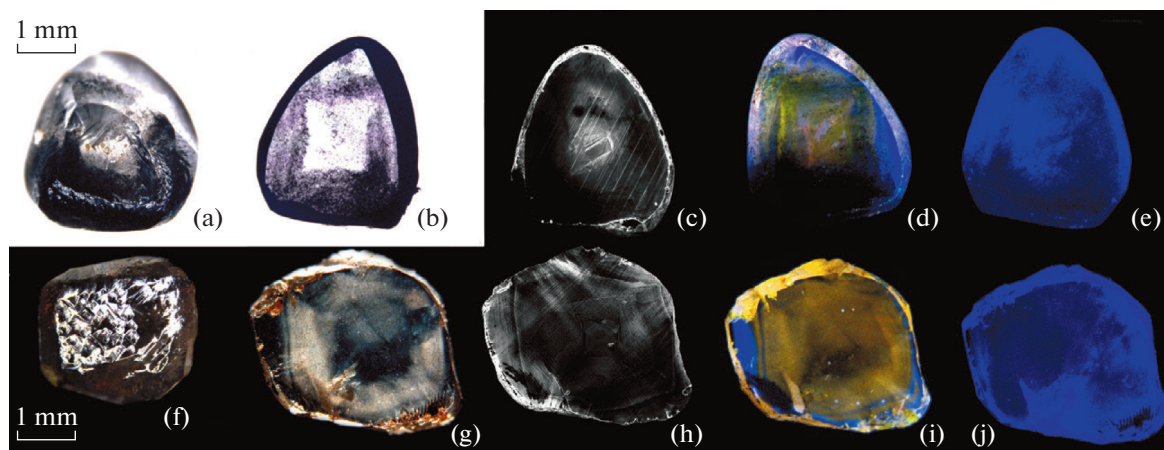


Fig. 4. The 685-66 and 602-66 II-group diamond cuboids: (a, f) general view. Images of plates: (b, g) transmitted light; (c, h) cathodoluminescence; (d, i) photoluminescence under 405 nm excitation; (e, j) distribution of the N3 photoluminescence intensity under 405 nm excitation, through light filters of the edge 450 nm and blue SS4.

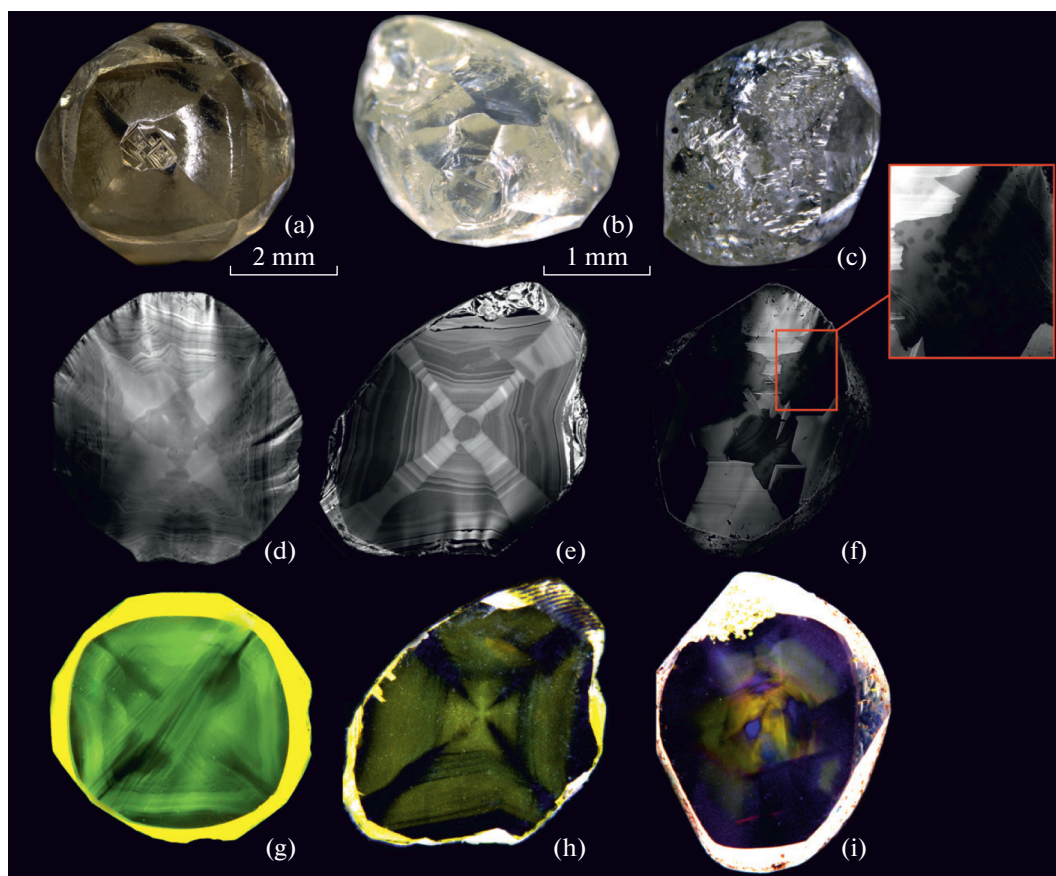


Fig. 5. The III-group diamonds with simultaneous growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids; general view: (a) 123-76, (b) 29-76, (c) 615-66. Plates: (d, e, f) cathodoluminescence; (g, h, i) photoluminescence under excitation 365 nm (i) and 405 nm (g, h) through the 450 nm edge light filter. Insert: the fragment with spots of the locally decreased CL intensity, containing rosette-shaped inclusions in their cores.

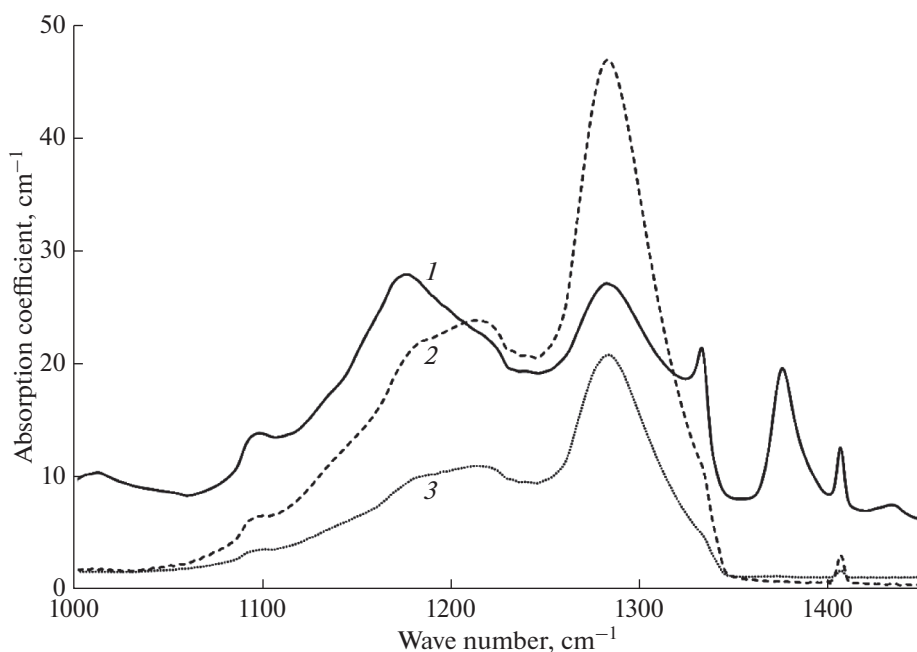


Fig. 6. FTIR absorption spectra of crystals with simultaneous growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids: (1) 123-76; (2) 29-76; (3) 615-66.

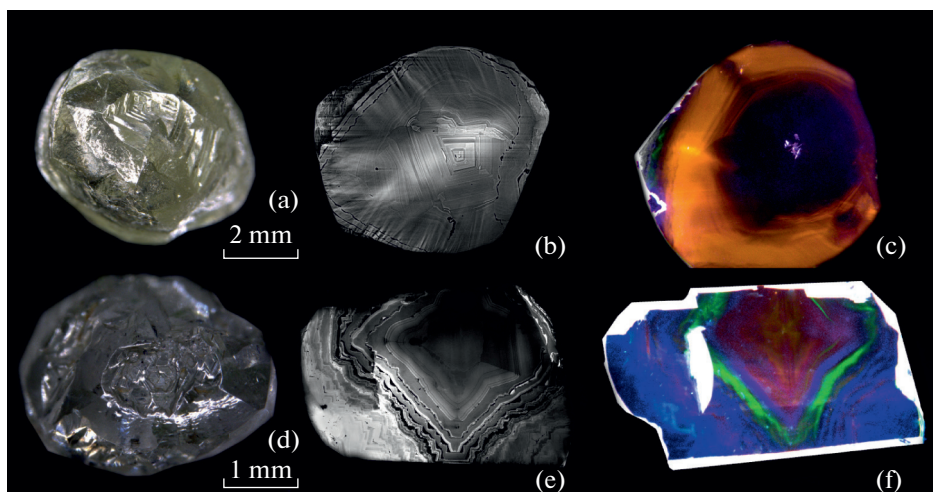


Fig. 7. The IV group-crystals with the consequent change of their growth mechanism. A general view: (a) 122-76, (d) 612-66. Plates: (b, e) cathodoluminescence; (c, f) photoluminescence under excitation 405 nm through the 450 nm edge light filter.

Only the N3 and H3 systems were recorded in the spectra of the peripheral zone.

DISCUSSION

Our investigations have shown that there are several groups of crystals with $\langle 100 \rangle$ growth pyramids that cover almost the entire natural variety of diamond crystals of cubic habit in placer deposits of the Krasnovishersk district of the Northern Ural. The diagnostics of cuboids is complicated by the strong dissolution of

the vast majority of crystals. Among all groups are crystals whose peripheral zone is characterized by the development of regeneration steps of the octahedral faces following the general direction of growth of the cuboid faces. The octahedral steps begin to grow on the already formed cuboid. The tangential regeneration growth rate is much higher than the growth rate limited by two-dimensional nucleation. Zones with polycentric growth of the regeneration surface in the $\langle 100 \rangle$ direction are an indicator of a complex internal crystal structure.

Table 2. The general features of crystals of four different groups with [100] pyramids.

Group	Internal structure	IR spectroscopy	ФЛ-системы
The II-group cuboids (after Yu.L. Orlov classification)	$\langle 100 \rangle$. Thin peripheral zone $\langle 111 \rangle$	$N_{\text{tot}} = 20\text{--}300$ ppm, C-center. N_{tot} in the peripheral zone $\langle 111 \rangle$ is by an order of magnitude greater	575, 635.1, 636.8, 700 sh, 800, 820, 840, 860, 869, 882.5 nm, etc. Peripheral zone $\langle 111 \rangle$: N3 H3
Cuboids with transparent core and peripheral zone saturated with inclusions	$\langle 100 \rangle$ and $\langle 111 \rangle$ or only $\langle 111 \rangle$; zone with inclusions, $\langle 100 \rangle$	IaA-type crystals, $N_{\text{tot}} = 200\text{--}500$ ppm. Predominantly homogenous	N3, H3 N3, H3, S1, S2, S3, 926
Crystals with joint growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids	$\langle 100 \rangle$ and $\langle 111 \rangle$. Thin peripheral zone $\langle 111 \rangle$	$N_{\text{tot}} = 600\text{--}1500$ ppm, $N_{\text{B1}} = 0\text{--}70\%$, α_{3107} to 35 cm^{-1} . N_{tot} in the peripheral zone $\langle 111 \rangle$ is by an order of magnitude less	N3, H3, S1, S2, S3. 933 nm in $\langle 111 \rangle$ pyramids; 787, 926, 700.3 nm in $\langle 100 \rangle$ pyramids
Crystals with successive change of growth mechanism	$\langle 100 \rangle \rightarrow \langle 111 \rangle \rightarrow \langle 100 \rangle \rightarrow \langle 111 \rangle$. Stages of dissolution and regeneration. Thin peripheral zone $\langle 111 \rangle$	$N_{\text{tot}} = 500\text{--}1400$ ppm, $N_{\text{B1}} = 20\text{--}50\%$, α_{3107} to 26 cm^{-1} . Contrast zoning	N3, H3, S1, S2, S3. 933 nm in $\langle 111 \rangle$ pyramids; 787, 926, 700.3 nm in $\langle 100 \rangle$ pyramids

The studied crystals are divided into four groups based on growth patterns and spectroscopic features. The first two groups can be attributed to low-temperature cuboids that were under the mantle conditions for a short time. They differ in the presence and distribution of PL systems at excitations of 488 and 785 nm. The other two groups include higher-temperature and multistage crystals that are more complex in their internal structure and thermal history (Table 2).

The yellow diamond crystals with PL systems at 575, 635.1, and 636.8 nm and a wide band with a maximum at approximately 700 nm corresponds to low-temperature cuboids with C-centers. A similar photoluminescence pattern is characteristic of the second-group cuboids from placers of the Anabar–Olenek interfluvial (Zedgenizov et al., 2016; Zudina et al., 2013). A wide band with a maximum at approximately 700 nm has been described in diamonds with yellow luminescence (Collins and Mohammed, 1982). Upon excitation of 785 nm, intense lines at 800, 820.5, 840, 860, and 869 nm and a doublet 883.5/885 of the low-temperature Ni-containing center were recorded in the PL spectra of such cuboids (Table 1). The transition to the tangential mechanism of growth is accompanied by the development of the N3 and H3 systems and the disappearance of systems at 575, 635.1, and 636.8 nm, as well as a wide 700 nm band. The second group of cuboids is characterized by higher N_{tot} values, the absence of the C-center, PL systems of 575, 635.1, and 636.8 nm, and a broad 700 nm band. It is probably a higher-temperature group.

The 933 nm band in the $\langle 111 \rangle$ pyramids is observed in the PL spectra of crystals with joint and sequential growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids; bands at 787, 926, and 700.3 nm are observed in the $\langle 100 \rangle$ pyramids. Sometimes, a weak peak at 637 nm is present in the $\langle 100 \rangle$ pyramids.

The N_{tot} values in peripheral octahedral regeneration zones in the II-group cuboids are several times higher than those in the cubic zone of the same crystals. Conversely, the N_{tot} in the peripheral octahedral zone of regeneration growth in crystals with the joint and sequential growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids is several times lower than that in the other diamond crystals. The I-group crystals have a heterogeneous distribution of the blue luminescence of the N3 system. It is characteristic of only the peripheral zone of the crystals, while blue luminescence in crystals of the other three groups is observed over the entire section.

Comparison of the studied crystals with the diamonds from the nearest known primary Arkhangelsk placer deposits (Kriulina et al., 2012; 2019) led to the following conclusions.

(a) The second-group cuboids, as well as crystals with joint and sequential growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids, were found in the Arkhangelsk and Ural placers. The dissolved cuboids and tetrahexahedroids were found both in the Arkhangelsk and the Ural sources, but the degree of dissolution in the Ural crystals is much higher;

(b) Bands that were not detected in the absorption spectra of Ural diamonds were recorded in the infra-

red absorption spectra of Arkhangelsk crystals with $\langle 100 \rangle$ pyramids (Kriulina et al., 2019). All the II-group crystals from the Ural placer deposit show the 883/885 nm luminescence in the low-temperature Ni-bearing center. The latter is recorded much less frequently in diamond crystals from the Arkhangelsk placer deposits;

(c) Most crystals among crystals with $\langle 100 \rangle$ pyramids from the Arkhangelsk placer deposits do not have the regeneration zone of octahedral growth. Many skeletal cuboids are in these deposits, which are absent among the Ural diamonds. The stage of the skeletal cuboid growth is noted only in the central parts of the Ural crystals and is always replaced by the regeneration zone of octahedral growth.

Thus, crystals with the $\langle 100 \rangle$ growth pyramids include an entire set of nitrogen defects based on the degree of transformation: crystals with single C-centers, with A centers, and with a high nitrogen concentration and a fraction of defects B1 amounting to 70%. Based on these results, one can assume that part of the cubic crystals formed at the first stages of diamond formation followed by regenerative overgrowing by the octahedral zone, as shown by Beskrovanov (1992). Some crystals are common low-temperature cuboids with carbonate inclusions, corresponding to the last stage of diamond formation. Large crystals of jewelry quality were formed at all stages.

CONCLUSIONS

Based on internal structure and spectroscopic features, diamond crystals with growth pyramids $\langle 100 \rangle$ from alluvial placers of the Krasnovishersk district of the Northern Urals were divided into four groups. Crystals of the I group include zonal cuboids with C defects, which are similar to “amber” crystals from the Anabar–Olenek interfluvium, Kalimantan placer deposit (Indonesia), and Zimmi placer deposits (Sierra Leone). Intense PL was recorded in the near-infrared interval with peaks at 800, 820.5, 840, 860, and 869 nm, and a doublet of the low-temperature Ni-bearing core of 883.5/885 nm in all crystals of this group. The II group of crystals includes cuboids with transparent cores and rims saturated with inclusions. Transparent cores of the II-group crystals correspond to the joint growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids or only the $\langle 111 \rangle$ pyramid. The inclusion-bearing zone, which composes most of a crystal, is formed by pyramids. The III group consists of crystals with the joint growth of the $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids. These individuals are characterized by different thermal evolution and a high concentration of nitrogen.

A similar group of crystals was selected from the Marange placers, Botswana (Smit et al., 2016) and studied. The IV group consists of crystals with subsequent growth of $\langle 100 \rangle$ and $\langle 111 \rangle$ pyramids. The last stage of growth of all studied crystals was regeneration development of facet steps $\langle 111 \rangle$.

The studied crystals with $\langle 100 \rangle$ pyramids are quite rare. However, they were found in many regions with placer diamond potential, whose sources are still unknown. The subsequent investigation of such crystals and determination of formation conditions are necessary to reveal the features of primary diamond sources.

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