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Electron paramagnetic resonance, cathodoluminescence and absorption spectroscopy of natural diamonds with CO 2 -I and 480 nm absorption bands

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Abstract

Behavior of oxygen impurity in diamond lattice remains poorly constrained. Collection of natural diamonds, both single crystals and impact-related nanopolycrystalline samples (yakutites), was characterized using Electron paramagnetic resonance (EPR), cathodoluminescence and absorption spectroscopy in order to address defects, tentatively ascribed to structural oxygen. The studied diamonds include samples with strong absorption by CO_2-I in infra-red spectra; the samples with O content determined using Secondary ions mass-spectrometry (SIMS) and those showing absorption band at 480 nm. In some single crystals paramagnetic OK1 and N3 defects, presumably comprising oxygen ions, are observed. In contrast, these defects are extremely rare or even absent in impact-related diamonds, even despite eventual presence of nanoinclusions of compressed CO_2 manifested in infra-red spectra. No correlation between these defects and O content determined by Secondary Ions Mass spectrometry is found. Comparison with previous Transmission Electron Microscopy investigation gives additional arguments supporting assignment of the 480 nm absorption band to oxygen impurity.

Introduction

Presence of oxygen impurity in diamond lattice was inferred long time ago from mass-spectrometry [Melton and Giardini 1981] and nuclear spectroscopy data [Mathez et al. 1993; Sellschop et al. 1980]. Both approaches showed absence of correlation between oxygen and nitrogen. However, these methods cannot discriminate between lattice impurity and occasional submicron inclusions, thus leading to ambiguities. Theoretical calculations of stability of several simple atomic configurations, such as complex of a substitutional oxygen with vacancy(ies) or with nitrogen (O-N), showed plausibility of oxygen incorporation into diamond lattice [Gali et al. 2001; Lowther 2003]. Experimentally, the presence of oxygen in diamond lattice is inferred from several spectroscopic techniques, although in most cases the assignment of the bands mentioned below is only tentative. An infra-red absorption band at ~ 1050 cm^{-1} is tentatively assigned to oxygen impurity [Malogolovets and Nikityuk 1981; Palyanov et al. 2016]. A prominent absorption band at 480 nm present in some natural diamonds might also be oxygen-related [Gali et al. 2001; Hainschwang et al. 2008, 2020]. Oxygen is possibly responsible for cathodoluminescence bands appearing after treatment of diamond by hot CrO_3 and hydrogen plasma at 800°C [Mori et al. 1992]. Photoluminescence lines in diamond films grown in presence of oxygen were interpreted as manifestation of oxygen-boron complexes [Ruan et al. 1993]. Ion implantation of ^{17}O and ^{16}O with subsequent annealing produces luminescing [Gippius 1993] and paramagnetic defects [Iakoubovskii and Stesmans 2002]; the latter plausibly corresponds to positively charged substitutional O_s^+ [Thiering and Gali 2016]. Oxygen-related paramagnetic and luminescing ST1 defect is encountered both in natural diamonds [Balasubramanian et al. 2019] and after ion implantation [Neugebauer et al. 2026]. In the latter study, it was shown that thermal annealing above 1500°C of diamond implanted with molecular oxygen produces complexes with two oxygen atoms.

Electron paramagnetic resonance (EPR) provides the least ambiguous evidence for involvement of the oxygen impurity in some of the paramagnetic defects. At least two defects encountered in natural diamonds, usually with low nitrogen aggregation state, are believed to comprise oxygen and nitrogen atoms: OK1 and N3, here notation accepted in EPR field is used [Newton and Baker 1989; van Wyk et al. 1992]. The exact model of these defects remain debatable, but most studies suggest involvement of substitutional oxygen, nitrogen and a vacancy. In some works [El-Kelany et al. 2020; Hill et al. 2001; Newton and Baker 1989; van Wyk et al. 1992] the OK1 center was interpreted as a C-N-C-O-C chain and the N3 as a C-N-O-C chain; both of them in < 110>. In another computational study the N3 defect is tentatively assigned to pair of neighboring substitutional atoms O_s-N_s, with less certain model for the OK1 [Etmimi et al. 2010]. Note that an alternative model of the OK1 and N3 defects assuming Ti-N defect was proposed [Nadolinny et al. 2009]. This model finds support in modelling using density functional theory [Czelej et al 2018], but other computational studies fail to provide convincing support of such structure [El-Kelany et al. 2020; Etmimi et al. 2010]. Several paramagnetic defects assigned to oxygen-vacancy complexes are reported for CVD diamonds [Breeze 2016; Cherati et al. 2023; Hartland 2014].

Infra-red (IR) spectra of some natural diamonds, so-called "CO_2-diamonds", both single crystals and nanopolycrystalline aggregates of impact origin, show absorption by compressed CO_2 [Chinn 1995; Koeberl et al. 1997]. Detailed studies using Infra-red microscopy [Barannik et al. 2021] and Transmission Electron microscopy [Shiryaev et al. 2023] of the CO_2-diamonds showed presence of numerous nanosized precipitates of CO_2 ice, likely formed during exsolution of oxygen impurity from diamond lattice. The later hypothesis implies possibility of preservation of oxygen traces in the lattice, which, potentially, could be detected spectroscopically.

Despite number of important studies, spectroscopic features of oxygen in diamond remain poorly understood. In this work, we present results of investigation of a collection of diamonds showing CO_2-related absorption using complementary spectroscopic methods: Electron paramagnetic resonance (EPR), cathodoluminescence, IR-vis absorption.

Samples and methods

Several sets of natural diamond single crystals were investigated. Two natural diamonds characterized by presence of compressed CO_2 in infra-red absorption spectra were earlier studied in detail in [Barannik et al. 2021]. Four type IaAB diamonds in which oxygen concentration was measured using Secondary Ions Mass-spectrometry [Shiryaev et al. 2010], although in a qualitative manner only, since no reference materials are available, make a second subset. Finally, two relatively large (~ 50 mg) type IAB natural diamonds from Sputnik kimberlite pipe (Yakutia) with absent O-related features were studied to check eventual misidentification of the paramagnetic O-related centers. In addition to the single crystals, six natural nano-polycrystalline diamonds of impact origin and showing CO_2-related infra-red absorption [Shiryaev et al. 2022], were analyzed. These diamonds, often termed "yakutites", were most likely produced by direct graphite-diamond transition during large scale Popigai impact event.

Electron paramagnetic resonance (EPR) spectra were acquired using Varian E-115 in X-range (~ 9.4 GHz) at modulation amplitude 0.1–0.01 mT, modulation frequency 100 kHz and microwave power of 0.2 mW. The scanning interval was 100 G. The [001] (L4) axis of single crystals was oriented parallel to the magnetic field vector (H || L4) to the ± 0.5° accuracy. The impact diamonds are closer to powdered material. Concentration of paramagnetic defects was calculated using ultradisperse nanodiamond reference material (VNIIFTRI, Russia); the total uncertainty is estimated as ± 25%, which is a conservative value.

Absorption spectra in visible range (380–760 nm) were recorded with a MSFU-K microspectrometer, with apertures matching mutually parallel faces in case of single crystals. Absorption of impact diamonds is generally too strong, thus reflection geometry was employed. Cathodoluminescence was excited using “cold cathode” (plasma); the spectra were collected at room temperature using MayaPro 2000 in the wavelength range 380–1100 nm.

Results

Electron paramagnetic resonance (EPR)

Typical EPR spectra of CO_2-diamonds are shown in Fig. 1. The spectra show rather strong set of lines, assigned to oxygen-nitrogen defects OK1 and N3 [Newton and Baker 1989; van Wyk et al. 1992]. The oxygen-related defects, especially the OK1, are also present in most other studied single crystals. Concentrations of the defects are shown in Table 1. Amount of other paramagnetic defects, such as single substitutional nitrogen, the P1 center in EPR notation, and of three nitrogens with a vacancy (P2) – is lower, often considerably, than that of the O-related centers. The quoted concentrations clearly represent volume-averaged values. Since some of the studied crystals show complex internal zoning (see “Cathodoluminescence” section), the oxygen content may vary considerable between the zones; such variations were earlier noted in SIMS measurements [Shiryaev et al. 2010].

Table 1
Paramagnetic defects (concentration in ppm) and SIMS and IR data for the studied single crystal diamonds.

Sample*	OK1	N3	P1	P2	N2**	W21	$^{16}O^{-}/^{13}C^{-}$ from SIMS [30]	Principal IR features; general peculiarities; inclusions[Barannik et al. 2021; Shiryaev et al. 2010]
FN 7112	2,5	1,4	0,1					CO_2. Graphite platelets
FN 7114	0,5		0,04					Zoned diamond. A + B+platelets+ 3107 cm^{-1} in a small zone. CO_2; carbonates and other inclusions.
2.41 (Nat1)			0,03	1,2	0,3		1.7E-3	no CO_2, zoned
2.60 (Nat2)	4,3						5.8E-3, 4.8E-3, 5.5E-3	A, 3107 cm^{-1}, no CO_2
2.63 (Nat3)	4,1						1.4E-3, 1.6E-3	B + A+3107 cm^{-1}, no CO_2
2.64 (Nat4)	0,1	0,2	0,06				5,2E-3	A + B+platelets+ 3107 cm^{-1}+CO_2
Sputnik pipe			0.06	0.3		0.13	6.11E − 4	
Ballas-like* **	-	-	-	-	-	-	6.19E − 4	Poor quality spectrum, numerous inclusions

* - in parentheses sample notation from [30].

** - Since no detailed structural model is available, the concentration is calculated assuming that the relevant signal is due to broken bonds at dislocations.

*** - polycrystalline sample.

Defects in EPR notation: P1 – single substitutional nitrogen (the C-defect in IR notation); P2 – three nitrogen and a vacancy (the N3 in absorption/luminescence spectroscopy); W21 – chain from three nitrogens; the unpaired electron is at the central one; OK1 – C-N-C-O-C chain in < 110> [Newton and Baker 1989]; N3 - C-N-O-C chain in < 110> [van Wyk et al. 1992].

Representative EPR spectrum of a natural nano-polycrystalline diamond (yakutite) is shown in Fig. 2; main properties of constituting components are provided in Table 2. With the exception of one of the

samples (2.81), no hints for the OK1 or N3 defects are found in yakutites. In the specimen 2.81 subtraction of the two Lorentzians from the experimental curve leaves a residue, which might be tentatively assigned to OK1 and N3 at few ppm levels. However, this assignment is very uncertain and is not discussed further.

Yakutites and their analogues of impact origin are sometimes termed lonsdaleite-containing diamonds; EPR spectra of such samples were described in [Shul'man et al. 1981]. The spectra recorded by us are qualitatively similar and were fitted with two Lorentzians, slightly displaced (0.1–0.7 G) from each other. A broad one is ascribed to point defects and the narrow component is ascribed to broken bonds in dislocation cores (in short "to dislocations"). For all the samples the ratio of intensities and widths of these bands are similar. The intensity ratio $S_{narrow}/(S_{narrow}+S_{broad})$ = 0.5–0.6; the width is ~ 2 G and 6–7 G, respectively. For one specimen (402) a third isotropic and angle-independent component is required, however, its unique assignment is yet unknown; it might be related to microinclusions of other minerals.

Table 2
Results of investigation of nano-polycrystalline diamonds (yakutites) using EPR. Concentration of dislocations-related paramagnetic defects and parameters of Lorentzian components used for spectra fitting.

Sample	N2, ppm	Io` Lorentz L1	Io` Lorentz L2	ΔH, Lorentz L1	ΔH, Lorentz L2	S1/(S1 + S2), %	Shift L1-L2, G
2.81	97	1155	220	1,65	6,7	56	0,15
401	277	1990	410	1,9	7	57	0,3
402	35	650	125	1,6	6	58	**0,95**
405	113	890	330	2,4	6,3	51	0,1
406	160	400	85	2	6,3	60	0,35
407	173	3470	470	1,8	6,3	68	0,7
408	123	485	105	2,1	6,3	61	0,5
409	155	615	135	2,1	6,1	61	0,3

Figure 3 shows correspondence between the total amount of oxygen in paramagnetic OK1 and N3 centers and $^{16}O^{-}/^{13}C^{-}$ ratio measured by SIMS [Shiryaev et al. 2010]. Recall that the later ratio is uncalibrated and serves as a very crude approximation only. Nevertheless, it is immediately clear that the SIMS and EPR data are not correlated. In fact, it is not surprising, since SIMS provides information about total concentration of an impurity in a thin layer, whereas EPR is sensitive exclusively to paramagnetic defects in the sample bulk. Moreover, high oxygen enrichment of the yakutite specimen analysed by SIMS is compatible with presence of microinclusions in these polycrystalline diamonds.

Absorption in visible range

Absorption spectra in visible range are shown in Fig. 4. For several single crystals, a weak band at ~ 480 nm is resolvable (Fig. 4a). The spectra of the CO_2-diamond FN7114, characterized by stark heterogeneity in color distribution ([Barannik et al. 2021] and Fig. 5), also differ from zone to zone. In the optically bright (transparent) zone characterised by stronger CO_2-I IR absorption, the 480 nm feature is present, whereas in the other, dark part, this band is not reliably distinguished (Fig. 4b). We note that complex patterns of color distribution such as bicolored specimen FN7114 and very irregular internal structure revealed by cathodoluminescence (Fig. 5a) are not unusual for natural diamonds with 480 nm absorption band [Lai 2025; Lai et al. 2024].

The absorption spectra of yakutites recalculated from measured reflection spectra are dominated by a broad band at 540–560 nm and the 480 nm feature is not identified (Fig. 4c). Such spectra are generally consistent with previous studies of impact ("lonsdaleite-containing") diamonds [Bochek et al. 1984; Yelisseyev et al. 2013, 2020].

Cathodoluminescence

Room temperature cathodoluminescence (CL) spectra of the studied samples and corresponding real color CL images are shown in Fig. 5. The spectra of single crystals are characterised by broad A-band with maximum between 450 and 550 nm. Implanted molecular oxygen might be responsible for appearance of a broad CL band centered at 460 nm [Neugebauer et al. 2026], but reliable confirmation of its presence in our samples is hindered by strong contribution of the A-band. Narrow lines are virtually absent for all samples except 2.41 and 2.63, where phonon replicas of luminescing N3 defect (ZPL at 415 nm) are present. In CVD diamond films grown in presence of oxygen the most prominent band tentatively ascribed to boron-oxygen complex is observed at 484 nm with several weaker lines between 455 and 483 nm [Ruan et al. 1993]. These lines are not pronounced in the studied samples.

Cathodoluminescence spectra of the yakutites markedly differ from single crystals and are dominated by two main bands peaking at ~ 440 and ~ 660 nm with overlapping weak narrower features at 692 and ~ 770 nm. The relative intensity of the main bands is sample dependent. Similar CL spectra were earlier reported from other impact diamonds [Pratesi et al. 2003]. Note that photoluminescence spectra of impact diamonds in general and of yakutites studied in this work are strongly dependent on excitation wavelength [Shiryaev et al. 2022; Yelisseyev et al. 2013, 2020] and also differ from the presented CL spectra. In particular, the PL spectra lack the shorter wavelength component. The assignment of these bands to specific defects is yet lacking, however, they are likely related to dislocations, eventually, ones decorated by impurities (see discussion in [Shiryaev et al. 2022]). Very heterogeneous distribution of CL intensity and, presumably, of relative intensities of the contributing bands, imply highly non-uniform distribution of related defects on micron-scale. This, in turn, may explain the observation that PL (and, likely, CL) spectra recorded at different spots on a single yakutite specimen vary considerably [Shiryaev et al. 2022].

Discussion

Cathodoluminescence spectra of the studied diamonds do not show lines, tentatively ascribed to oxygen impurity. This might be explained by broadening due to room temperature, or, more likely, by their absence in the studied diamonds. Indeed, these lines were observed only in CVD films, either grown in presence of boron or treated in conditions, hardly applicable to natural single crystals. Therefore, the CL spectra are not discussed below; however, the CL imaging is useful for assessment of samples' heterogeneity, which is difficult to observe by other methods.

Although many possible configurations of oxygen impurity in diamond are possible [Gali et al. 2001; El-Kelany et al., 2020; Etmimi et al. 2010; Lowther 2001; Thiering and Gali, 2016], two O-related paramagnetic defects encountered in natural diamonds involve both oxygen and nitrogen. In diamond production of some geological provinces, such defects are relatively common. For example, in Anabar river placers (Yakutia, Russia) up to 13% of crystals contain the OK1 defect [Vyatkin et al. 2023]; in Karpinsky-1 pipe of Zolotitsky kimberlite field (Arkhangelsk region, Russia) up to 15% of diamonds contain this defect [Garanin et al. 2021]. The OK1 and, less frequently, the N3 defect, were found in more than 50% of cubooctahedral diamonds from an eclogitic xenolith from Udachnaya pipe (Yakutia, Russia) [Nadolinny et al. 2009]. The OK1 and N3 defects are usually found in crystals with low nitrogen content. However, natural type Ib diamonds often possess complex internal structure and one-phonon region of their IR spectra may contain contribution of other defects (e.g., the Y-center) [Hainschwang 2014], thus making evaluation of the N content for whole (i.e. non-sectioned) crystals somewhat ambiguous. In most reported cases, the concentration of the OK1 defects does not exceed 0.5 ppm, whereas the P1 centers (single substitutional nitrogen) are considerably (at least an order of magnitude) more abundant. In contrast, in diamonds studied in this work, the OK1 concentration is higher than that of the P1 centers and in some cases, the P1 is absent at the limits of the sensitivity of the employed setup.

According to Table 1, the concentration of paramagnetic O-related defects in the studied crystals may reach ~ 4–5 ppm, which is in line with previous estimates [Nadolinny et al. 2009]. Absence of a correlation between the EPR results and semi-quantitative SIMS measurements is not surprising, given marked differences between these analytical methods: the former gives concentration of specific paramagnetic defects, whereas the latter provides of total O content, including EPR-silent defects and eventual microinclusions. The presence of O-containing microinclusions in the CO_2-diamonds and in yakutites was inferred both from IR spectroscopy and from analysis of N-O correlations [Shiryaev et al. 2010].

Let us first consider the single crystals. For the most of the studied crystals, qualitative correlation between the 480 nm and the presence of the O-related EPR defects may be proposed (see Fig. 4a and Table 1). However, the concentration of the OK + N3 defects is not directly related to strength of the 480 nm band. An interesting correlation between TEM results [Shiryaev et al. 2023] and optical absorption spectra is noted for the bicolored CO_2-diamond FN7114. The spectra of the bright (transparent) zone show weak, but obvious band at ~ 480 nm (Fig. 4b). The dark zone is characterized by stronger overall

absorption and the 480 nm band is not pronounced. Within each zone, the spectra are rather similar, which is in line with IR profiles reported in [Barannik et al. 2021]. The TEM images of foils extracted from the bright and dark zones show presence of platelet-like and quasi-isometric CO_2-I precipitates, respectively [Shiryaev et al. 2023]. Comparison with behavior of SiO_x precipitates in Si implies that the platelets correspond to lower annealing temperatures and high supersaturation of O impurity in silicon lattice, whereas the octahedral defects form at higher T and low supersaturation [Fujimori 1997]. Taking this into account and the fact that the size distribution of the precipitates in our study indicates that the impurity segregation process is incomplete, we come to the conclusion that the 480 nm absorption band may indeed be oxygen-related: it is pronounced in the zone with higher oxygen supersaturation in the diamond lattice. The diamond FN7112 with less pronounced 480 nm may also fit this model, despite domination of the isometric precipitates. First, its overall absorption is weaker, allowing better discrimination of the broad bands. Second, the process of oxygen segregation in this specimen was complicated by formation of graphitic platelets, some of them showing oxygen enrichment on graphite-diamond interface. Presumably, a noticeable fraction of the impurity is still retained in the lattice.

Although several plausible static configurations of the oxygen impurity in diamond lattice are known, we are not aware of studies of oxygen diffusion in diamond. Thus, discussion of possible relation between the CO_2-I precipitates and O-related defects (including paramagnetic ones) is necessarily speculative. Crystallographic similarity of diamond and silicon may be useful for understanding oxygen behavior in diamond. However, in silicon oxygen is initially present as substitutional impurity, whereas in diamond various configurations of substitutional atoms are discussed. Thus, direct extrapolation from silicon to diamond is clearly ambiguous. Despite all uncertainties, we may suppose that behavior of oxygen impurity in diamond generally follows that in silicon. Oxygen behavior in silicon is strongly influenced by other lattice impurities (e.g., carbon) and by thermal history of the particular specimen (see extensive review [Borghesi et al. 1995]). Relative fraction of oxygen dissolved in silicon lattice and segregated as SiO_x precipitates varies widely depending on the treatment temperature and duration; morphology, crystallinity and exact composition of the precipitates is also determined by the treatment and presence of impurities. Whereas paramagnetic O-related lattice defects may be relatively common in natural diamonds [Garanin et al. 2021; Pratesi et al. 2003; Vyatkin et al. 2023], the CO_2-I precipitates are formed only in peculiar conditions.

Whereas oxygen in the studied single crystal diamonds was most likely trapped during growth in relatively stable conditions, the impact-related yakutite samples represent another extreme case. The IR bands corresponding to CO_2 ice compressed to several GPa are fairly common in impact diamonds related to Popigai crater [Koeberl et al. 1997; Shiryaev et al. 2022] or in nanopolycrystalline compacts synthesized at very high static PT conditions [Shiryaev et al. 2006]. These bands originate from micro- or nanoinclusions of CO_2, eventually with impurities such as water, nitrogen etc. Such inclusions are difficult to visualise using TEM due to extremely complicated internal structure of impact diamonds, consisting of randomly oriented nanocrystallites leading to appearance of moiré patterns precluding simple interpretation. These gas-fluid inclusions were clearly trapped during rapid, perhaps, quasi-

instantaneous, conversion of sp^2-C to diamond phase. Thus, they are clearly distinct from the O-containing precipitates in single crystals discussed above, which are formed as a result of decomposition of supersaturated solid solution. Consequently, one may suggest that formation of known paramagnetic defects comprising both O and N atoms does not occur at noticeable extent.

Conclusions

Collection of natural diamonds comprising single crystals and nanopolycrystalline impact samples was characterized by spectroscopic complementary methods with the aim to detect oxygen-related defects. These results are compared with previous studies of the same samples using infra-red (IR) spectroscopy, Secondary Ions Mass spectrometry (SIMS) and Transmission Electron Microscopy (TEM). We show that paramagnetic OK1 and N3 defects, tentatively comprising oxygen, are relatively common in single crystals; most often, their concentration does not exceed 4–5 at. ppm. These defects are present both in diamonds showing IR absorption by CO_2-I and in samples lacking such features. The OK1 and N3 defects are not common in the impact diamonds. The discrepancy between the single crystals and impact diamonds in this respect is explained by markedly different mode of formation of the CO_2-I phase: precipitation of structural O impurity in the former case and entrapment of growth medium in the later. There is no correlation between O concentrations measured by SIMS and Electron paramagnetic resonance (EPR), which is explained by sensitivity of the later to paramagnetic defects only. Analysis of absorption spectra combined with previous TEM results suggests that the 480 nm absorption band may be indeed oxygen-related.

Declarations

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Author Contribution

AAS – conceptualization, methodology, investigation, supervision, writing; SVS – investigation, writing; ADP - methodology, investigation, TH - methodology, investigation. All authors have read the manuscript and agree with its content.

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Data Availability

The raw data will be available on reasonable request

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Figures

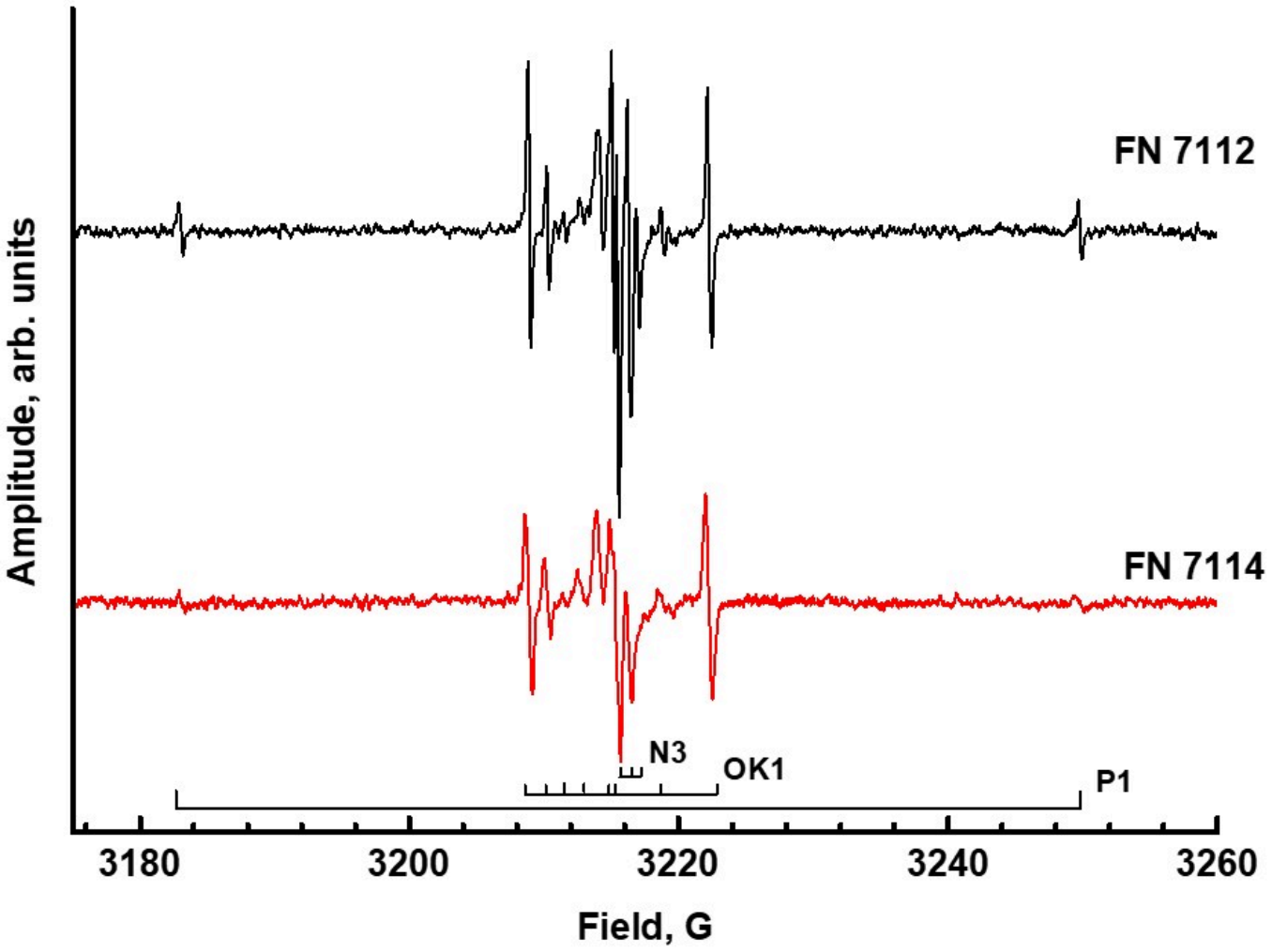


Figure 1

EPR spectra of FN 7112 and FN 7114 diamonds. The FN7114 spectrum is shifted vertically for clarity.

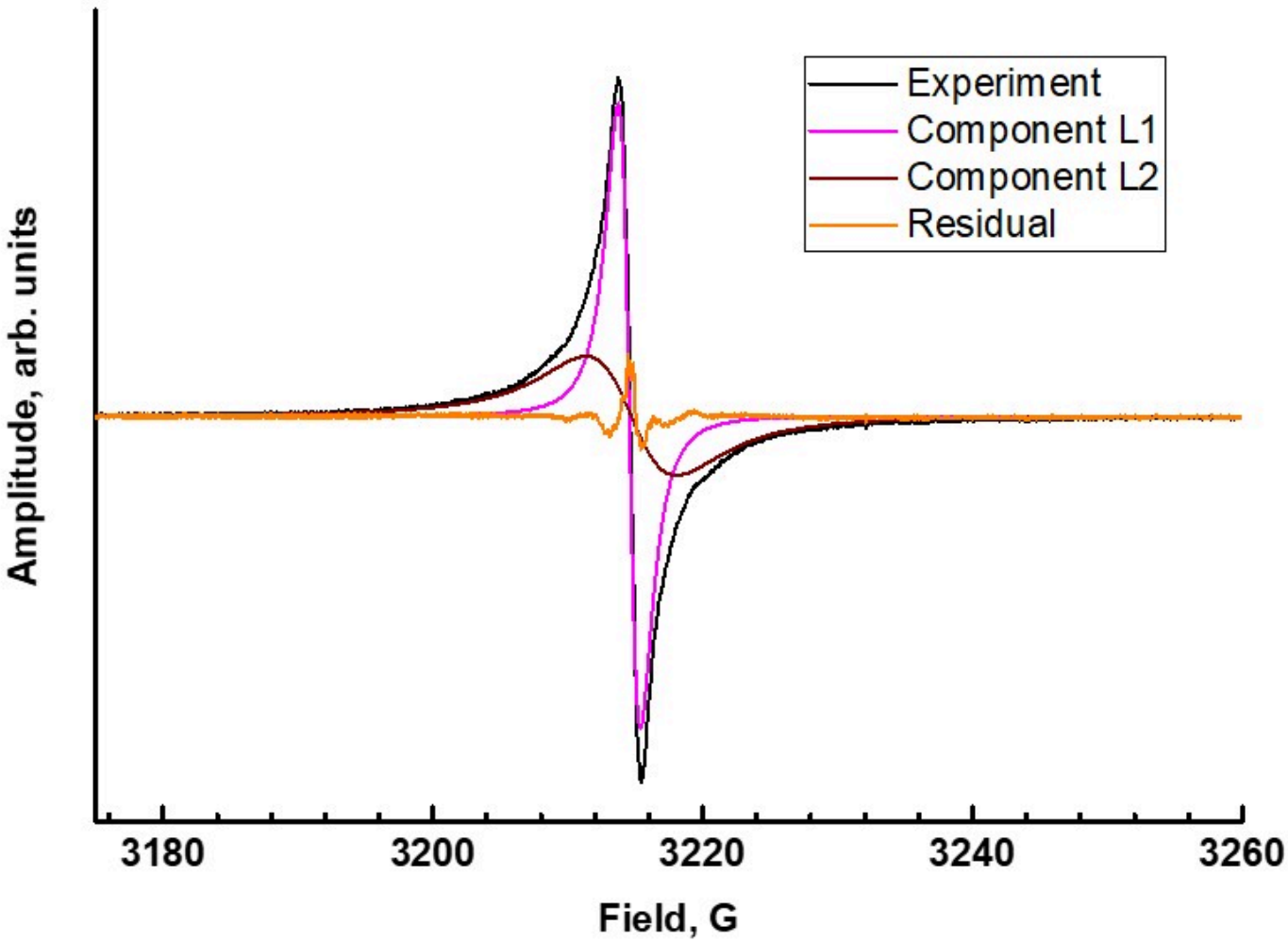


Figure 2

EPR spectra of yakutite diamond.

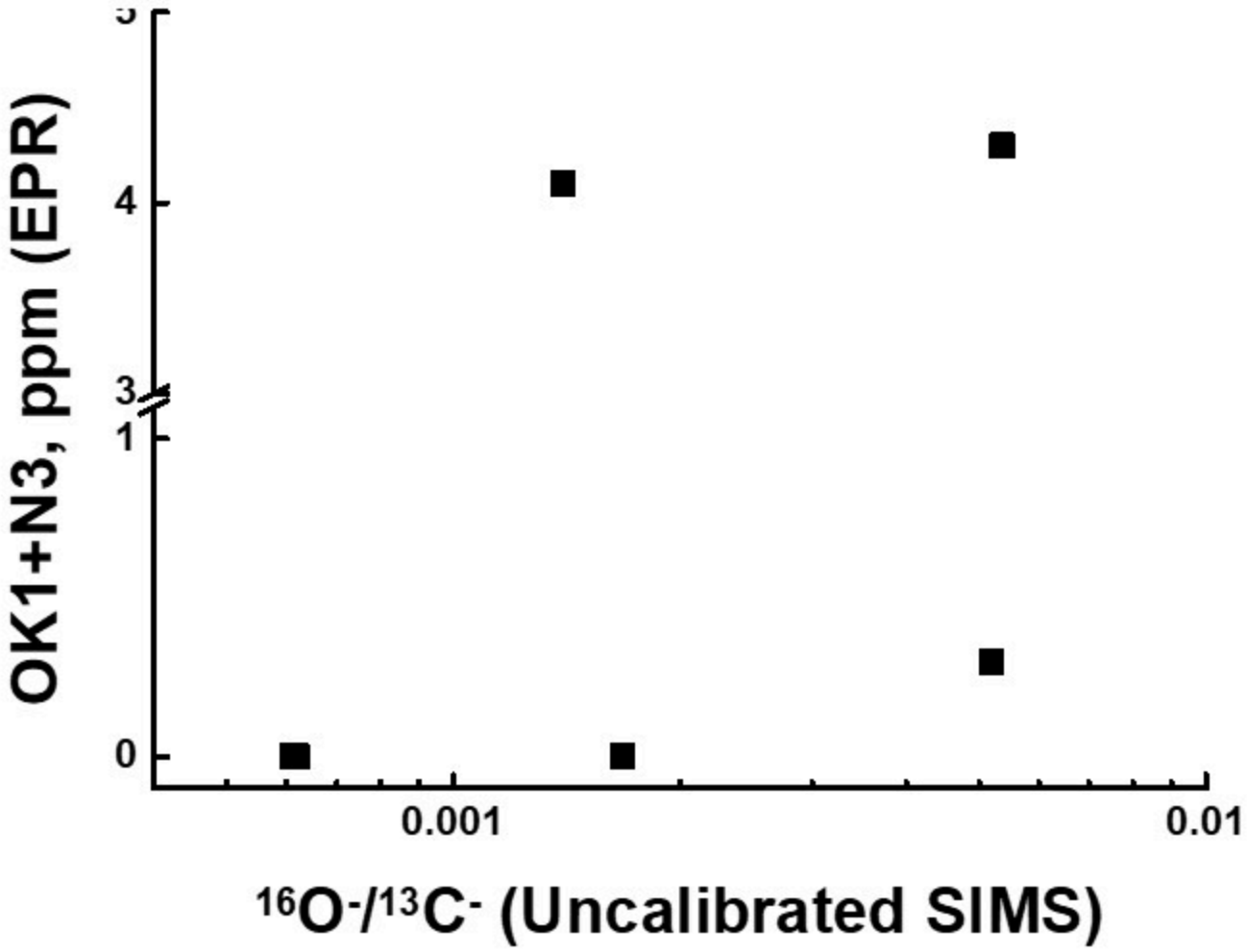


Figure 3

Comparison of concentration of O-related paramagnetic defects OK1 and N3 with $^{16}O^-/^{13}C^-$ ratio measured using Secondary Ions mass spectrometry [Shiryaev et al. 2010].

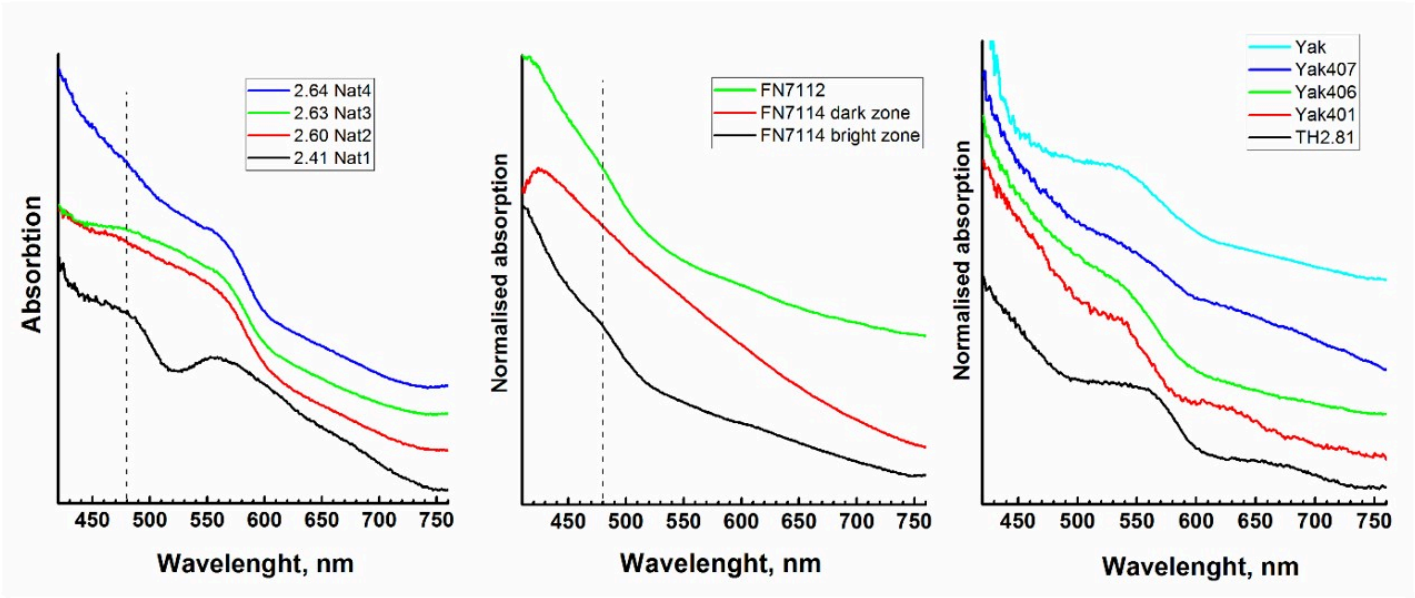


Figure 4

Absorption spectra of the studied diamonds in visible range. Vertical dash line is at 480 nm.

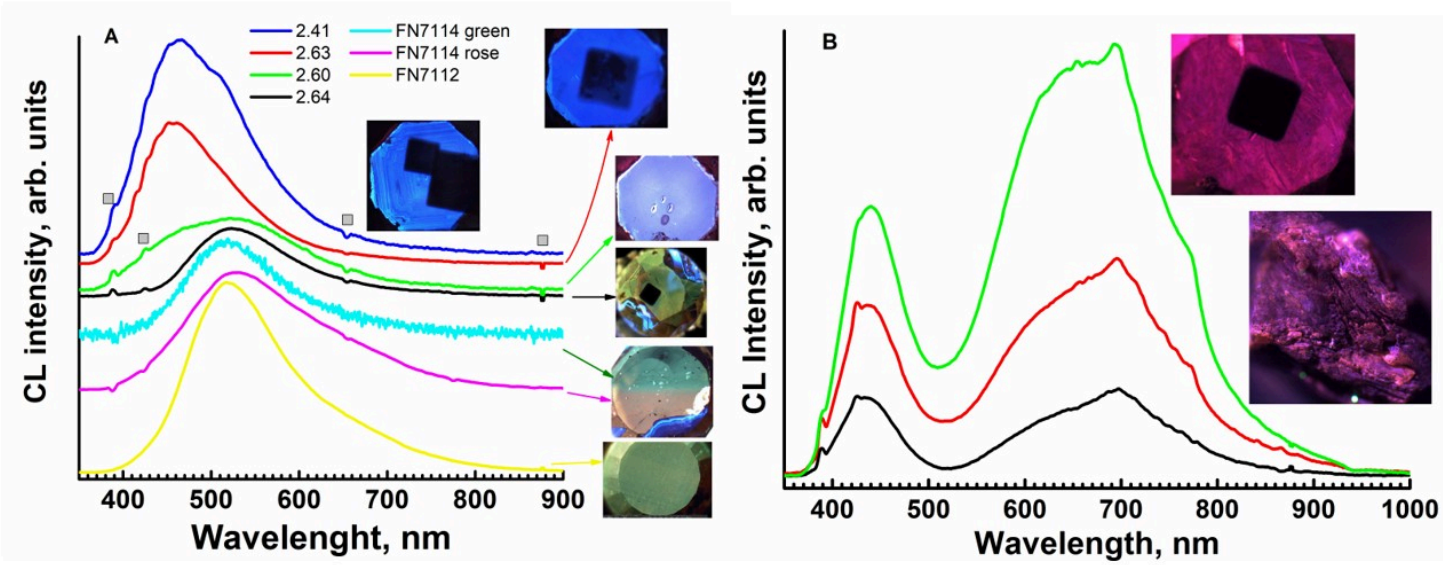


Figure 5

Cathodoluminescence spectra and real color images of the samples. Gray squares show features due to background plasma. The spectra are displaced vertically for clarity, but intensities are unchanged. Black squares and elliptical features on the images are caused by SIMS damage (see text). In (b) one of the images show polished sample, the second – a larger whole yakutite specimen.