

The effect of structure development in electron-irradiated type Ia diamond

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A type Ia diamond crystal with a nitrogen impurity in different forms was 3.5 MeV electron-irradiated with successively increasing doses 5×10^{16} , 2×10^{17} , 4×10^{17} , 2×10^{18} e/cm² and examined after each dose by positron annihilation, EPR and optical spectroscopy in visible and IR regions. After irradiation with highest dose a development of the defective structure of the crystal was revealed. A detail description of the phenomenon, data of EPR and optical measurements for different irradiation doses are given. The first results of cathodoluminescence studies of the as-developed structure are presented. Possible models of defects responsible for main lines in CL spectra are listed. © 1999 Kluwer Academic Publishers

1. Introduction

During irradiation of a solid crystal with energetic particles, lattice defects are known to form: vacancies, interstitials and/or other more complicated damages. An increased concentration of defects in the crystal structure causes changes in properties of materials. These changes are called the radiation effects. The studies of radiation effects in diamonds are the subject of many publications and some comprehensive reviews [1–3].

The majority of studies used the irradiation with electrons (at energies in the range from 0.5 to a few MeV) to create point defects, because even energetic electrons have rather small momenta and create only simple or primary defects—mono vacancies, interstitials or interstitial-vacancy pairs.

The investigations of radiation effects in diamond lead to new important understandings of properties of point defects, mainly vacancies in this crystal, their energy characteristics, symmetry, charge state, etc. However, as is rightly denoted in [4], “radiation effects in diamond, which were first systematically studied over thirty years ago, are still not fully understood”. Moreover, under certain conditions of intensive irradiation of type Ia diamond crystal with energetic particles, new phenomena may be revealed, as that described in this paper.

To produce vacancy defects, type Ia diamond crystal was irradiated with 3.5 MeV electrons successively increasing doses and after each dose the specimen was investigated using several methods, including positron annihilation (angular correlation of annihilation radiation, ACAR), electron paramagnetic resonance (EPR) and optical spectroscopy in the infrared (IR) and visible regions. In experiments the effect of the development of visible defective structure of the specimen has been revealed, which as far as we know was not observed before.

In the present paper the detail description of the phenomenon, data of EPR and optical measurements

depending of the irradiation dose as well as the first results of cathodoluminescence (CL) studies of the as-developed structure given. The measuring technique and the data positron annihilation in this specimen have been given in detail in [5] and in this paper are only mentioned.

2. Experimental

A specimen under study was a large natural diamond crystal ground almost parallel to the (111) plane into a hexagonal plate of about 10 mm in size and 2.1 mm thickness, colorless, of the clear water transparency.

Before irradiation the initial EPR, IR and ACAR spectra of the specimen were recorded. Then the diamond crystal was irradiated with 3.5 MeV electrons using a linear accelerator (the Institute of Physics of National Academy of Sciences of Ukraine, Kiev). The irradiation doses increased successively: 5×10^{16} , 2×10^{17} , 4×10^{17} and 2×10^{18} e/cm². The irradiation was performed by a pulsing electron beam having average current density of $5.3 \mu\text{A}/\text{cm}^2$, pulsation being $4 \mu\text{s}$ and the duty cycle 250 pulses/s. The temperature of irradiating with the first three doses did not exceed 60 °C, the irradiation with the latest dose occurred at cooling with liquid nitrogen (80–90 K). After each irradiation dose, the above mentioned as well as optical spectra in visible region were taken.

EPR and IR spectra were recorded at room temperature using a SE/X-2547 radiospectrometer produced by the “Radiopan” of Poland and German-produced UR-20 spectrophotometer; optical spectra in the visible region (400–800 nm) on a universal spectral calculational device. Transmission or absorption spectra were measured in a wholly white light of a tungsten incandescent lamp at 77 K using a nitrogen cryostat. The angular correlation of annihilation radiation was studied a spectrometer developed at the Institute of

Metal Physics of the National Academy of Sciences of Ukraine. ^{22}Na isotope with activity of 3.7×10^8 Bq was the source of positrons. Spectra were recorded at room temperature [5].

CL-studies were performed on a device developed on the basis of a “Camebax” scanning electron microscope [6] equipped with a MCD-1 monochromator (200–800 nm optical range). The device allows us to record CL spectra for regions of 1–7 μm in diameter on the surface of the specimen being studied, to define the integral (or in given spectral range) intensity of emission along the line of electron probe scanning and observe visually a two-dimensional pattern of distribution of integral intensity of the object luminescence, i.e. a CL-topogram. In the mode of recording CL spectra, the device resolution is about 0.5 nm between spectral lines. Accelerating voltage is between 10 and 30 kV, electron beam current from 3×10^{-6} to 3×10^{-9} A, temperature of measurements is 80 K.

3. Results and discussion

According to the initial IR spectrum, the specimen contains a considerable amount of nitrogen impurity in the form of A, B1 and B2 centers, which allows the diamond type to be defined [7] as Ia A/B (Table I). EPR measurements show that the specimen contains also nitrogen impurity in the form of paramagnetic centers: individual nitrogen atoms substituting for carbon and a complicated paramagnetic center P2 (defined as N3 in optics). Concentration of each paramagnetic center is $\leq 10^{17} \text{ cm}^{-3}$.

The specimen in the initial state was colorless and transparent. When irradiated with 3.5 MeV electrons, it changed the color from sky-blue at the dose of 5×10^{16} up to blue-green at $4 \times 10^{17} \text{ e/cm}^2$ remaining wholly transparent. After the irradiation with the dose of $2 \times 10^{18} \text{ e/cm}^2$ and an abrupt drop of temperature of irradiation, the specimen became opaque and a structure has developed that was visible by transillumination even to the unaided eye. A magnified photo of the crystal ($\times 8$) is given in Fig. 1. A dark background is attributed to the dark blue-green color of the diamond crystal.

This phenomenon has not been observed in irradiation with 1.5–2 MeV at a higher dose [8]. Such a phenomenon has not also been reported in [9], where a type Ia diamond crystal was irradiated with 3.5 MeV electrons at an integral dose of 10^{17} – 10^{18} e/cm^2 and in [10], where there was studied positron annihilation in 3.5 MeV electron-irradiated type Ia diamond crystals.

TABLE I Concentration of nitrogen impurity in different forms for type Ia diamond vs. the irradiation dose

N spectrum	Dose (e/cm^2)	N_A (cm^{-3})	N_{B1} (cm^{-3})	N_{B2} (cm^{-3})	ν_{B2}^{max} (cm^{-1})
1	0 (init)	1.21×10^{20}	8.75×10^{19}	4.43×10^{19}	1375
2	5×10^{16}	1.46×10^{20}	7.71×10^{19}	4.35×10^{19}	1365
3	2×10^{17}	1.40×10^{20}	8.64×10^{19}	4.69×10^{19}	1365
4	4×10^{17}	1.13×10^{20}	9.24×10^{19}	4.31×10^{19}	1367
5	2×10^{18}	1.13×10^{20}	1.12×10^{20}	5.02×10^{19}	1357

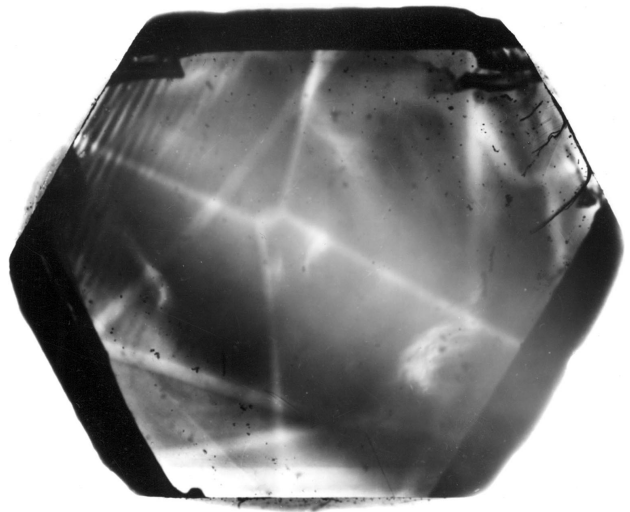


Figure 1 Photography of the type Ia diamond with as-developed structure.

To trace the dynamics of changes caused in the specimen by an intensive irradiation, let us consider dose dependences of EPR and optical measurements. Positron annihilation data [5] and optical spectra in visible region (400–800 nm) for different irradiation doses (Fig. 2) show that along with the increase in intensity of bands GR1 (741 nm) and ND1 (394 nm) associated, as is verified by direct positron annihilation, with an increase in concentrations of neutral and negatively charged vacancies, an intensive growth is observed of structureless absorption with the maximum at about 620 nm in the GR1 band, which is related probably also to B2 defects—platelets in the (100) plane [11]. In Laue diffraction patterns, these defects are shown by extra reflexes “spike” close to main reflexes of diamond. In the IR region, the B2 defect is found as an absorption band with a peak at 1370 cm^{-1} [12].

IR spectra of our specimen are characterised by a strong absorption in the one-phonon region due to a high concentration of the nitrogen impurity. The assessment of the absorption rate in peaks of bands defined by centers A, B1 and B2 is difficult due to a considerable thickness of the specimen (transmission $< 10\%$). Therefore, absorption at 1100 and 1010 cm^{-1} was measured following the recommendations given in [13]. The absorption coefficient was calculated using the inner standard method. As the inner standard, a lattice absorption at the 2435 cm^{-1} was taken [14] and were measured before and after each dose. Nitrogen concentrations in A and B1 centers were calculated as shown in [13], while the concentration in B2 centers was assessed by the relation [15]: $N_{B2} = (3.5 \times 10^{18}) \alpha_{B2} \text{ cm}^{-3}$, where α_{B2} is the absorption coefficient in the peak of the 1370 cm^{-1} band. Calculation results from IR spectra are given in Table I.

The data of Table I show that in irradiation of type Ia diamond crystal at an increasing dose, the nitrogen concentrations do not change essentially and at the highest dose only some decrease in N_A and increase in N_{B1} and N_{B2} are observed. The last column of Table I shows variations in frequency (wavenumber)

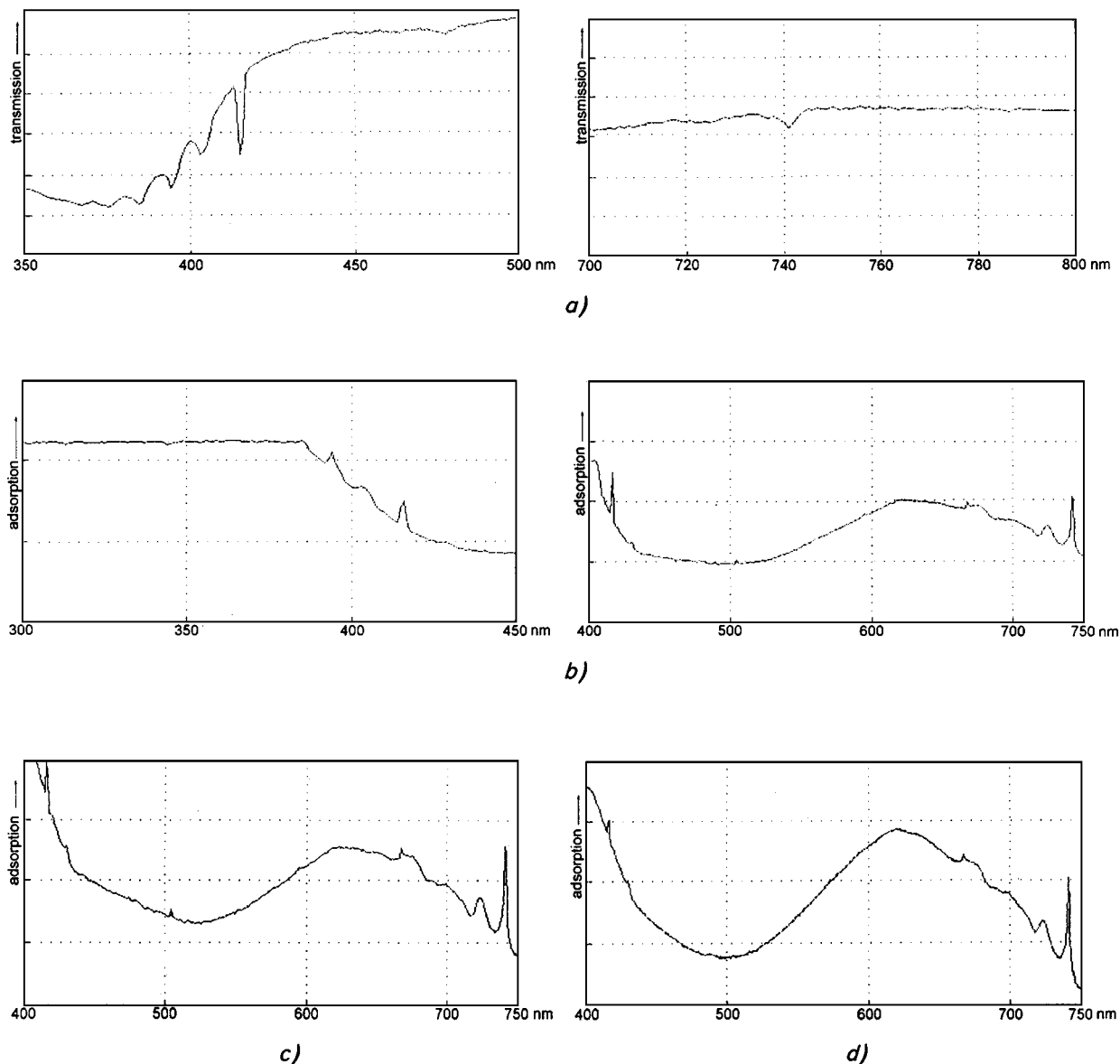


Figure 2 Absorption and transmission spectra in the visible region from a type Ia diamond crystal irradiated by 3.5 MeV electrons with the doses of: (a) 5×10^{16} , (b) 2×10^{17} , (c) 4×10^{17} and (d) 2×10^{18} e/cm².

of the absorption peak of the B2 band. The frequency decreases from 1375 cm^{-1} in the initial state down to 1357 cm^{-1} at the highest dose, which corresponds to an increase in platelet size from about 200 to 1500 \AA [15]. The observed change in $\nu_{\text{B2}}^{\text{max}}$ is not accompanied by any changes in intensity, halfwidth and symmetry of peak B2.

It is known that “giant” platelets of about $50 \mu\text{m}$ in size do not manifest themselves in IR spectra. Unirradiated diamond crystals with B2 defects show up as a wide structureless band in the 540–620 nm range [11]. Therefore, it can be suggested that the increase in absorption observed in spectra of the visible region at about 620 nm is caused by both irradiation-induced increase of platelets size observed in IR spectra and superposition the GR1 Band.

Fig. 3 illustrates variations of EPR spectrum vs. the irradiation dose (the spectrum taken at the irradiation dose of 2×10^{18} e/cm² is not given as it is similar to the one taken at 4×10^{17} e/cm²). In all cases spectra were recorded under the same conditions with the (111)

crystal axis being oriented parallel to the direction of external magnetic field \vec{H}_0 .

The analysis of spectra shows that the intensity of EPR lines from atomic nitrogen impurity decreases with each irradiation stage and after four irradiations it decreases by more than on the order of magnitude (in 20 times), while the intensity of lines from P2 center was virtually unchanged at all the irradiation stages (the same was observed for the N3 center at 415 nm in visible spectra). After irradiation at a dose of 2×10^{17} e/cm², in place of the abruptly decreasing central line of a nitrogen triplet (at $g \approx 2.0025$) appeared a new single EPR line, whose intensity increased with the irradiation dose. The line has not been identified up to now. It is possible that it indicates the appearance of a paramagnetic center, which is likely due to structural defect.

The results of direct CL studies of the as-developed structure are given in Figs 4 and 5 in the form of CL-topograms of various crystal regions and their respective CL spectra.

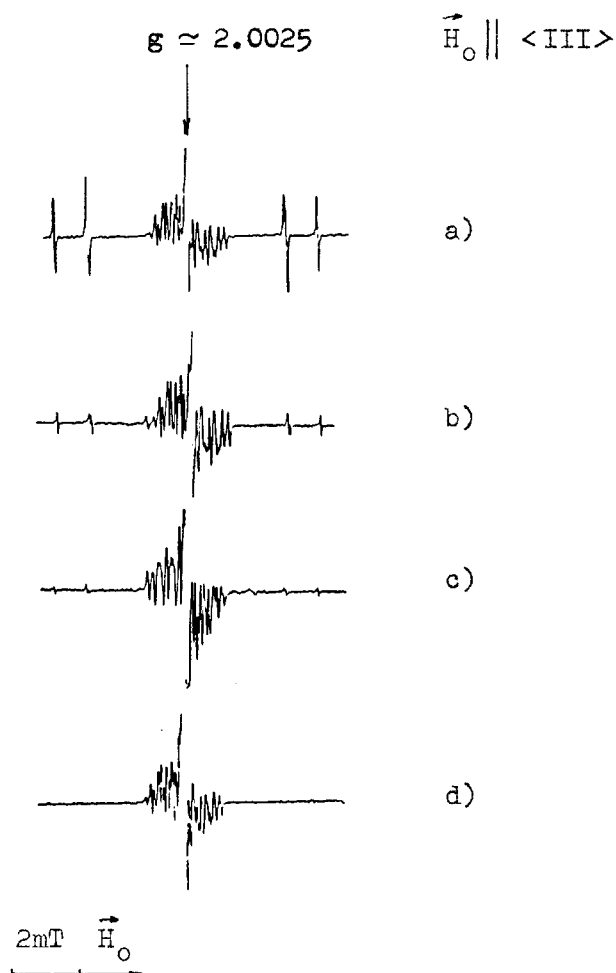


Figure 3 EPR spectra from type Ia diamond: (a) before irradiation, and after irradiation 3.5 MeV electrons with doses: (b) 5×10^{16} , (c) 2×10^{17} and (d) 4×10^{17} e/cm².

Three characteristic zones of CL-emission have been revealed. Zone 1 with an emission mainly in the region of about 600 nm (orange-red luminescence) contains formations in the form of protruding and located one over the other hexagon-planes. Their protruding parts are seen in Fig. 4a and b and different angles between sides of individual hexagons in Fig. 4c. Zone 2 is adjacent to zone 1 sweeping it. Under an electron beam, zone 2 develops a bluish color and a luminescence in the green-blue region of the spectrum. The zone contains elongated planar formations of almost rectangular form (Fig. 4a and b). The mutual arrangement of planes is seen in Fig. 4b. Zone 3 representing the main part of the crystal is transparent by eye with the luminescence in the blue region of the spectrum at about 400 nm (Fig. 4d). In all the photos of Fig. 4, the scale is: 1 cm–70 μ m.

CL spectra of zones 1 and 2 exhibit the main lines at 575, 490.7, 484.5 and 389 nm, while zone 3 is characterised by a set of lines: at 511.5, 490.7, 484.5, 439, 430 and 415 nm (Fig. 5). The 389 nm system taken at a longer recording time is shown separately.

In CL spectra of zones 1 and 2, the system 575 nm is the most intensive. The papers reviewing centers of defects in diamond [11, 16, 17] indicate that this system usually manifests itself after either an irradiation and

annealing above 500 °C or activation by an electron beam as is in our case. It is stated in [16] that the center at 575 nm incorporates a single atom of nitrogen and a vacancy. However, based on the center behavior in ion-implanted diamond crystals and on available literature data, the authors of [18] have concluded that the 575 nm system represents a vacancy bonded with the nearest single nitrogen atom in a tetrahedral interstitial in the $\langle 100 \rangle$ direction.

As a result of irradiation, the 389 nm center manifests in all type diamonds but there is no unambiguous interpretation of its model. For example, according to [16] this center contains interstitial carbon and a single atom of nitrogen, and the following possible variants of the model are given in [17]:

1. an interstitial atom of nitrogen;
2. a substituting atom of nitrogen bonded with interstitial atoms of carbon;
3. a substituting atom of nitrogen shifted along the $\langle 111 \rangle$ axis to form a carbon-nitrogen elongated pseudomolecule.

It has been clearly brought out in [19] that the 490.7 nm system is associated with plastically deformed regions of a diamond crystal and is often observed inside crystal growth bands.

Though it remains transparent, the main part of crystal (zone 3) has the highest quantity of defect centers. The center at 511.5 nm is assigned to intrinsic interstitials [20], and at 439 nm to the effect of a vacancy-nitrogen defect [18], at 430 nm to neutral vacancies [20] and the center at 415 nm is a well-known N3 center, i.e. three substituting atoms of nitrogen in the $\langle 111 \rangle$ plane bonded with a common vacancy [11, 16, 17, 20].

It follows from the above that the main lines (excluding the 490.7 nm system) in CL spectra from all zones are attributable to the interstitial carbon, nitrogen in a substituting or interstitial positions, vacancies and/or combinations of these defects.

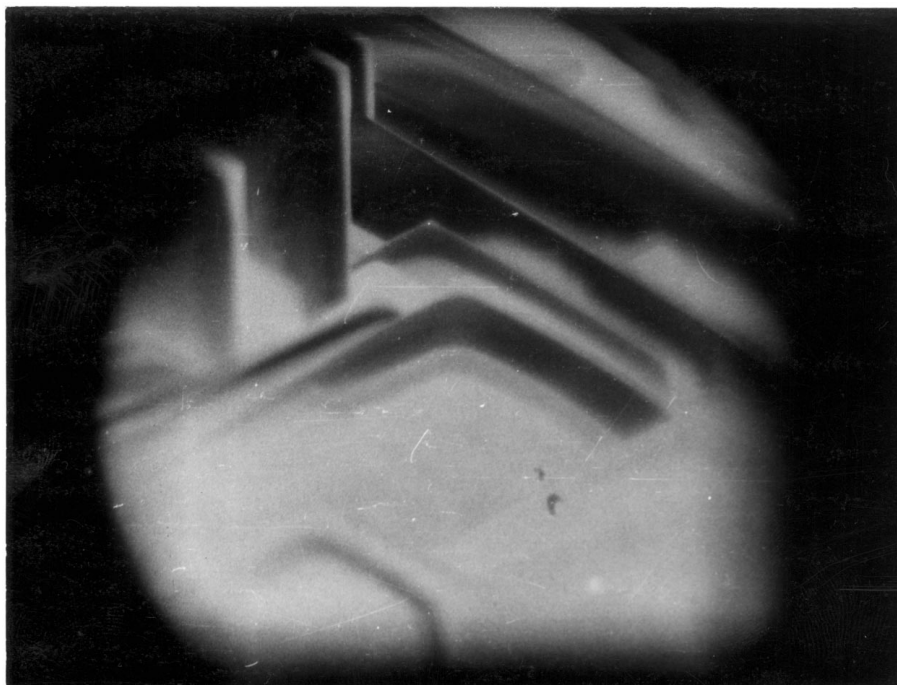
It has been shown [21] that directly during the irradiation of the type IIa diamond with 300 kV electrons at 16 and 87 K, there occur a formation and growth of clusters of defects due to the mobility of interstitial carbon. In our case, during an intensive irradiation of the diamond crystal having a sufficiently high concentration of impurity nitrogen with higher-energy electrons at higher temperature, interstitial-impurity complexes, probably, form. Evidently, CL spectra of zones exhibit this fact in main lines.

Considering planar formations (Fig. 4) as a final result of irradiation with electrons, some additional irradiation with positrons and excitation with analytical light, one may assume that these formations have grown up to visible sizes. Mobile carbon interstitial that binds with nitrogen seems most likely to be a basic building material for these planar defects.

It is interesting to note that patterns of zones 1 and 2 in CL topograms are very similar to the models of planar defects described by Sobolev [22]. However, the size of hexagons we revealed exceeds that of even "giant" platelets. The occurrence of a plastic



(a)



(b)

Figure 4 CL-topograms for zones of type Ia diamond: (a), (b), (c) zones 1 and 2, (d) zones 3. Scale is: 1 cm-70 μm . (Continued.)

deformation (490.7 nm) supports the assumption that hexagons originated as growth defects of a crystal.

4. Conclusions

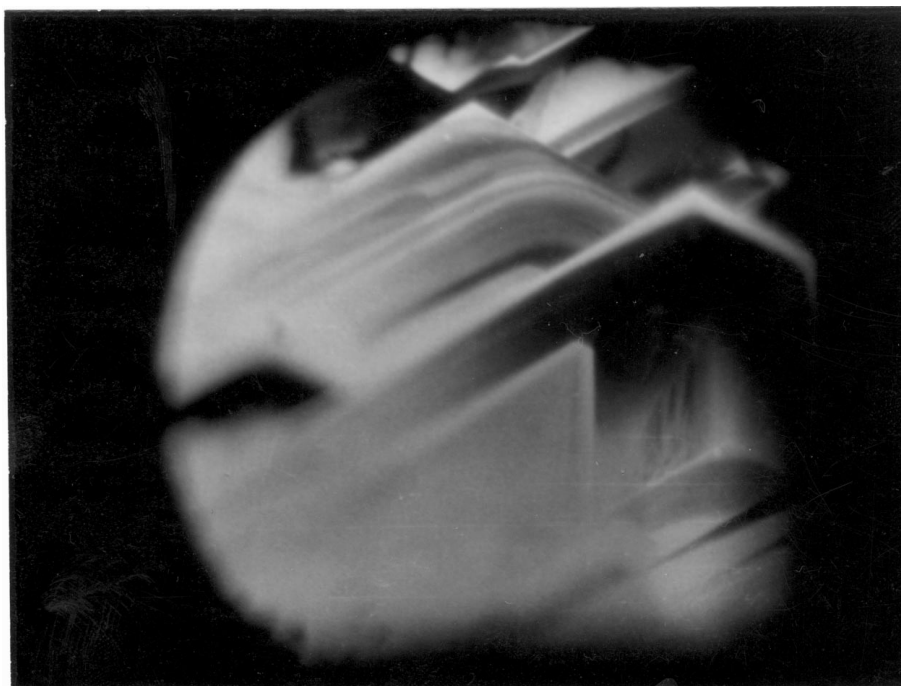
As a result of intensive irradiation influence on type Ia diamond crystal having nitrogen impurity in different forms, an effect of the development of the visible defective structure of this crystal has been revealed.

EPR and optical spectroscopy data permit some changes in appropriate spectra with increasing dose of

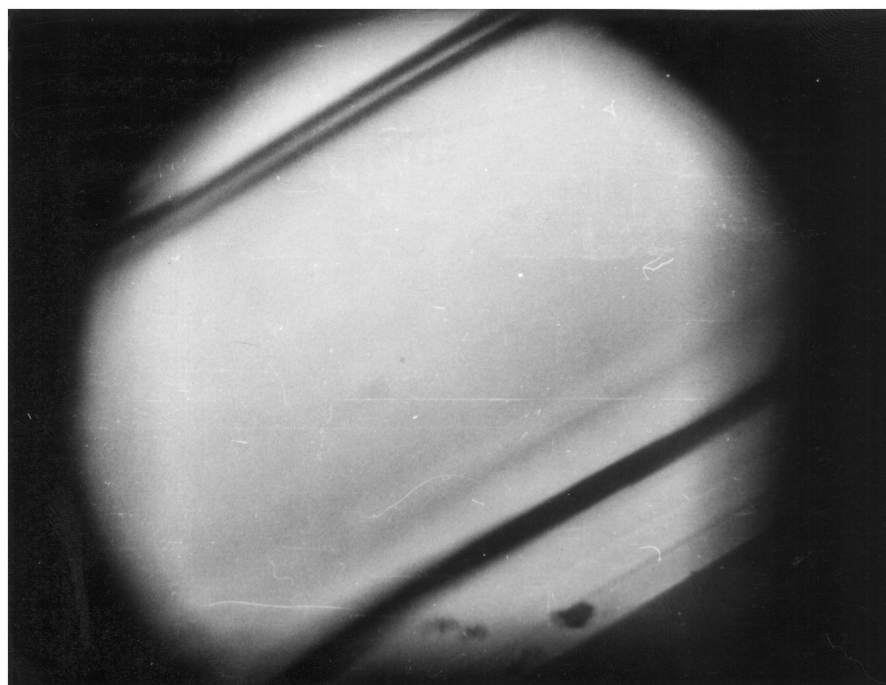
irradiation to be observed and correlated. The following results should be noted:

1. Along with the increase in intensity of bands GR1 (V°) and ND1 (V^{-}), the intensive growth with dose irradiation is observed of structureless absorption with a maximum at about 620 nm in visible region;

2. The change of ν_{B2}^{max} in IR spectra from 1375 cm^{-1} in initial to 1357 cm^{-1} after maximal dose;



(c)



(d)

Figure 4 (Continued.)

3. EPR spectra show the appearance of a single EPR-line, whose intensity increases with the irradiation dose, in place of the abruptly decreasing central line of a nitrogen triplet (at $g \approx 2.0025$).

In CL-topograms of zones with a visible defective structure, formations in the form of protruding and located one over the other large hexagon-planes were revealed. In CL spectra of these zones the main lines are at 575, 490.7 and 389 nm. It is suggested that the major building material for the growth of these planar defects is most likely mobile interstitial carbon that binds with nitrogen. However, within the hexagons the most inten-

sive is the system at 575 nm, whose model is a vacancy bound with a single nitrogen atom in tetrahedral interstitial. The line at 490.7 nm attests the presence of plastic deformation.

Based only on first results of study of the developed defective structure, one cannot unambiguously determine its origin and give a comprehensive answer to the question about structure of planar defects. This problem calls for further detailed investigations of this diamond specimen.

We believe that the revealed phenomenon of the developed defective structure in type Ia diamond under intensive irradiation opens new possibilities for

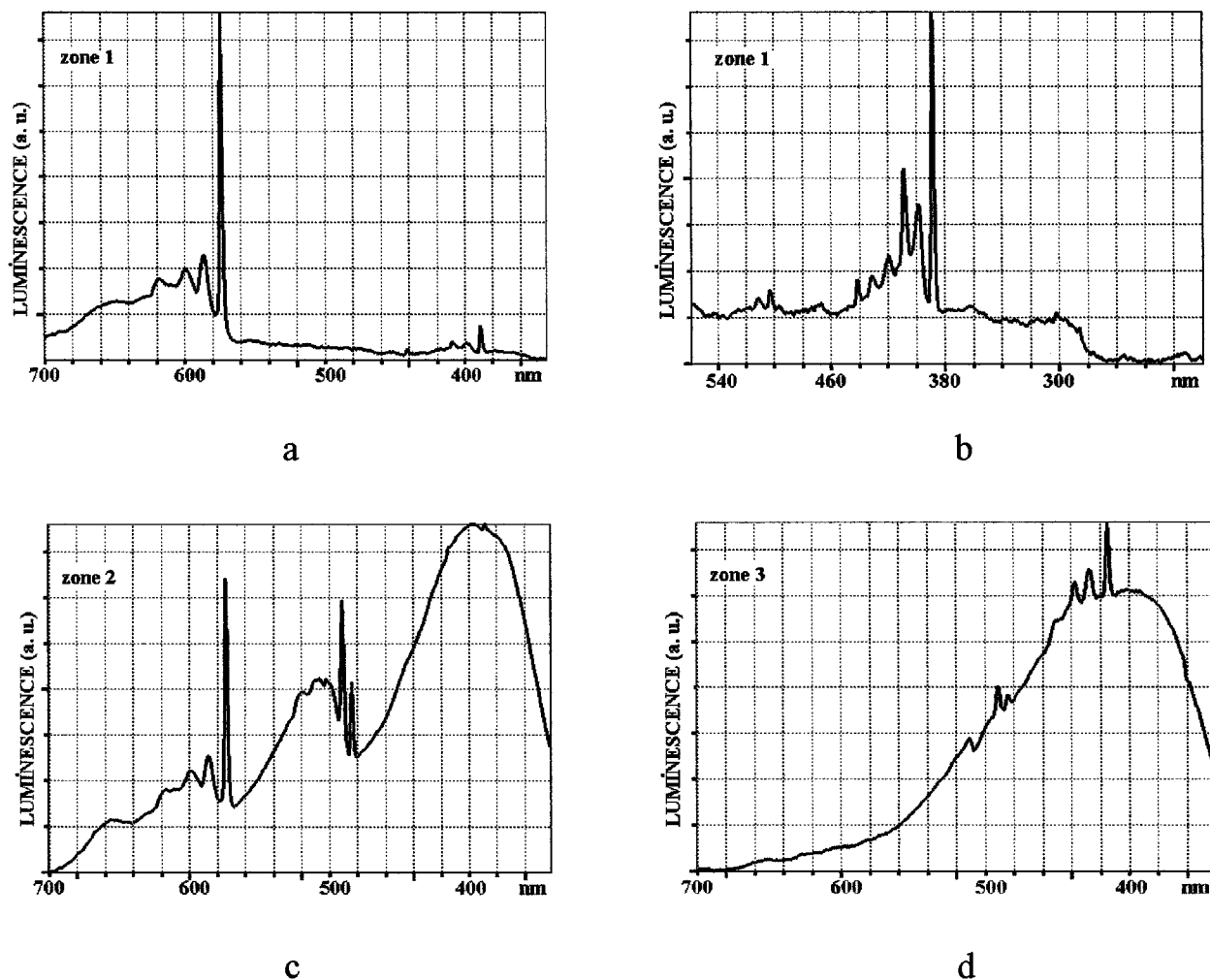


Figure 5 CL spectra from zones in type Ia diamond: (a) zone 1, (b) zone 1 (the system 389 nm taken at a longer recording time), (c) zone 2 and (d) zone 3.

experimental studies of the formation and structure of nitrogen defects in diamond as well as the role of intrinsic point defects in their formation.

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