

Study of local concentration of single substitutional nitrogen atoms in microdiamonds from the Kokchetav massif

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Abstract: In this communication we present an estimation of the concentration of single substitutional nitrogen atoms (P1 centre) from EPR data in Kokchetav diamonds. We first performed an analysis of local P1 centre concentrations using van Wyk's treatment (van Wyk *et al.*, 1997) of the line width of the resolved EPR spectrum. Also by analysing the dependence of the line-width of the broad exchange line on the P1 concentration in range higher than 1000 ppm in synthetic diamonds, we obtained a calibration curve allowing the estimation of the local P1 centre concentration higher than 1000 ppm and the local volumes occupied by substitutional nitrogen atoms without taking measurements of microcrystalline volume. In addition to the development of a method for calculating high local nitrogen concentrations, the aggregation process in P,T-treated Kokchetav diamonds has been given considerable attention and it was shown that the rate of nitrogen aggregation in these diamonds is consistent with data given in Evans (Evans & Qi, 1982).

Key-words: microdiamond, Kokchetav massif, nitrogen aggregation state, EPR spectroscopy, high-temperature high-pressure treatment.

Introduction

The study of nitrogen impurity in diamond and its transformation to different aggregation states is of considerable value in reconstructing the conditions under which diamonds reside in the Earth's upper mantle. The IaA and IaB types where nitrogen atoms are in various aggregation states dominate natural diamonds, while the Ib type, where the main state of nitrogen impurity is a single substitutional nitrogen atom (P1 centre) is rare. In this respect metamorphic microdiamonds from the Kokchetav deposit are unique. Infrared (IR) data (De Corte *et al.*, 1998) indicated that the P1 centre concentration in them is at a level of a few thousand ppm. The EPR technique can provide important information about the growth conditions of these diamonds. The difficulties of studying these crystals are due not only to their small size but also to the high local content of paramagnetic centres resulting in the appearance of a broad EPR line due to exchange interaction, the line width being dependent on concentration. The tedious procedure of calculation of nitrogen impurity content is exacerbated by another problem associated with an inhomogeneous distribution of nitrogen centres throughout the crystal.

In natural diamonds of the eclogitic and peridotitic paragenesis most of the nitrogen impurities are in the form of complicated aggregations produced by diffusion under high temperature while the diamond resides in the upper mantle.

With the improvement in the technology and in the synthesis of diamond at high temperature and high pressure, Chrenko *et al.* (1977) and Evans & Qi (1982) were able to study the kinetics of solid state reactions in diamond containing nitrogen atoms. They have observed the transformation of nitrogen centres and proved that practically all of them, identified by IR and EPR techniques, were produced by aggregation of substitutional nitrogen atoms. These authors (Chrenko *et al.*, 1977; Evans & Qi, 1982) have studied the kinetics of the transformation of P1 centres to form A-centre pairs and of the latter to form B-centre defects, and have determined the constants and the activation energies for reactions of this type. Hereafter, many investigators used these data to reconstruct the residence conditions of diamonds in the mantle – the geological time and the temperature (Chrenko *et al.*, 1977; Evans & Qi, 1982; Taylor *et al.*, 1996).

Among natural diamonds, the samples of metamorphic origin from the Kokchetav deposit are a special case. This is due not only to the unusual type of deposit and the environments of the diamond growth, but also primarily to an excessively high content of single substitutional P1 nitrogen centres. Mass spectrometry data indicated the nitrogen concentration in some Kokchetav microdiamonds as 10000 ppm. Comparison with IR measurements shows that some fraction of the nitrogen may be assumed to occur as fluid inclusions. Physical classification assigns metamorphic dia-

monds to the Ib-IaA type. IR absorption spectra of the largest microcrystals (100 μm) show, along with the 1132 cm^{-1} line, an intense 1282 cm^{-1} system from A defects (De Corte *et al.*, 1998). In some microcrystals more than 50% of the single substitutional nitrogen atoms had been transformed into A centres. IR data are indicative of considerable variations both in nitrogen content and in the degree of nitrogen aggregation within individual single crystal. But such measurements were performed on individual examples of the largest microcrystals. As a whole, characterization of the most common small-sized portion of the microcrystals presents a real challenge. On the other hand, Kokchetav diamonds are unique among both natural and synthetic diamonds for such high P1 concentration and, to date, there are no essential data on the EPR and IR spectral features related to large nitrogen contents. In synthetic diamonds with a mean nitrogen concentration of 300 ppm, nitrogen pairs with $S = 1$ separated by two, four and five carbon atoms were observed (Nadolnny *et al.*, 1999). The presence of long-range sign-alternating indirect coupling interaction between two P1 centres through covalent C-C bonds suggests that a fraction of such nitrogen pairs are in a diamagnetic state. Also in synthetic diamonds, Bokii *et al.* (1986) have observed IR lines in the intermediate range 1132 to 1282 cm^{-1} assigned tentatively to nitrogen pairs separated by different distances.

In this work we have focussed a detailed analysis of IR and EPR data on the concentration of P1 centres in Kokchetav diamonds. In order to perform the comparison between P1 centre contents in different local volumes of a crystal, we have used van Wyk's calculation (van Wyk *et al.*, 1997) of local P1 centre concentration based on an analysis of the line width in resolved EPR spectra. The evaluation of the local P1 centre concentration at levels higher than 1000 ppm and of the associated local volumes without resorting to measurement of microcrystal volume were performed using a calibration curve obtained for a synthetic diamond with the same level of nitrogen concentration. Along with the development of a calculation procedure for the case of high local concentrations, we have also investigated the process of nitrogen aggregation in Kokchetav diamonds upon annealing under high pressure.

Experimental data

Synthetic crystals of increased nitrogen content were produced to obtain the dependence of the linewidth of an exchange P1 EPR line on nitrogen concentration higher than 1000 ppm. Samples were grown at $T = 1400\text{ }^\circ\text{C}$ and $P = 5.5\text{--}6\text{ GPa}$ by the temperature-gradient techniques using a multi-anvil high-pressure apparatus of a split-sphere type. The Fe_3N compound, in amount of 1.3×10^{-4} bulk %, was added to the basic FeNiC system. Incorporated nitrogen forms and their concentrations were estimated from IR and EPR spectra. Three diamond crystals with local nitrogen concentration of 1600, 1900 and 2400 ppm were obtained. As a rule, as-grown crystals are characterized by inhomogeneous distribution of P1 centre concentration within a volume because of the peculiarities of nitrogen incorporation into dif-

ferent growth sectors. In the rim zone the P1 nitrogen form dominates while A defects in considerable concentration are observed within the crystal volume. Taking account of these details allowed us to calculate local concentrations in such crystals.

The microdiamonds studied here were selected from definite types of metamorphic rocks using available collections from the Kokchetav deposit, taking into consideration that the average size of Kokchetav diamonds is about 15 μm and that they are extremely non-uniformly distributed within the rocks. Initially, parallel plates were prepared from these rocks. Optical microscope examination of these plates allowed the selection of samples containing relatively large diamond crystals in quantity. Samples of garnet-pyroxene (samples 2-4) and pyroxene-carbonate (samples 92-99) rocks were selected for further examination. Thermochemical decomposition techniques were used to extract the microdiamonds. Final selection of the samples by size and habit was carried out using an optical microscope. The microdiamonds selected were subdivided into two groups based on their external crystal morphology: cuboids and aggregates consisting of small crystals of octahedral habit. Along with cuboids with convex planes cuboids with widely developed octahedral planes also occur. We interpreted the morphology of such cuboids as resulting from changing normal growth mechanisms layer by layer (Shatsky *et al.*, 1999).

EPR spectra were obtained at room temperature using a Varian E109 spectrometer operating at the X and Q bands. EPR spectra of diamond were recorded with 0.2 mW of microwave power to avoid microwave saturation. The saturation conditions were controlled by simultaneously recording the EPR spectrum from a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard. To calculate P1 concentration, a batch of microdiamonds was recorded at the same time as the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ reference. To estimate the P1 content in individual microdiamonds, the stones of approximately cuboid shape were selected and their sizes were measured under the microscope. Resolved hyperfine structure (HFS) of different line-width from nitrogen atoms representative of various P1 centre local concentrations was simulated using the program Simphonia. The local P1 centre concentration was obtained from the line width of the P1 EPR spectrum (van Wyk *et al.*, 1997). The ratio between integrated intensities defines the crystal volume containing one or other local concentration.

IR spectra both of Kokchetav and synthetic diamonds were measured using a Bruker F-IR spectrometer. The largest microcrystals of about 100 μm size were selected for this procedure. The comparison between IR and EPR data on P1 centre concentration were carried out using diamonds grown with nitrogen-containing admixtures and having local P1 centre concentration in different growth sectors ranging from 2400 to 500 ppm. To obtain an IR topographic map across the crystal section, a flat plate with different distribution of nitrogen centres was specially cut.

Figure 1 shows the EPR spectrum in the sample grown in the presence of increased nitrogen content. As one can see, the EPR spectrum from donor nitrogen comprises the known P1 spectrum and, superimposed on it, a broad line with $g = 2.0025$. The line width of each individual P1 line is

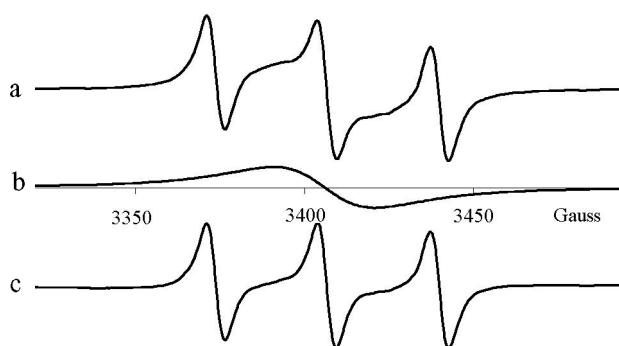


Fig. 1. EPR spectrum of synthetic diamond (a) and results of its deconvolution (b and c). b – EPR spectrum is due to 1900 ppm of P1 centre, c – EPR spectrum is due to 470 ppm of P1 centre.

5.2 G and that of the broad single line is 20.1 G. The average content of nitrogen donor atoms, C_{av} , was equal to 810 ppm whereas analysis of the line width of the resolved P1 spectrum gives a local concentration $C_1 = 470$ ppm. To calculate the local P1 centre concentration, C_2 , corresponding to the broad single EPR line we used the $CuSO_4 \cdot 5H_2O$ standard and the following expressions:

$$C_{av}(V_1 + V_2) = C_1V_1 + C_2V_2 \quad (1)$$

The value obtained was equal to 1900 ppm. The volume (V_1) containing nitrogen at a level of 470 ppm forms 79% of the whole crystal volume while the nitrogen concentration of 1900 ppm is in the remaining 21% of the volume (V_2).

IR measurements of the content of nitrogen in different forms at various analytical sites show values close to the mean values of P1 centre concentration. Typically A defects occur in the vicinity of a seed because these crystalline zones were exposed to P,T treatment throughout the growth period. What do the IR data obtained show? In all cases they present a mean value along the [111] direction from a seed to the crystal surface. The EPR features observed above are due to the presence of high P1 centre content in the crystal rim, which had been only slightly P,T-treated, and to the internal zones where a portion of nitrogen atoms had been transformed to the A form. Note that the diamond rim zones were grown over a large temperature gradient during the gradual cooling process that results in capturing dispersed nitrogen atoms.

Two other synthetic crystals grown with the addition of Fe_3N have local regions with P1 centre concentrations of 1600 and 2400 ppm. The line widths of the broad line due to exchange interaction appropriate to such P1 centre concentrations are of 22.3 and 15 G (Fig. 2), respectively.

These data allowed us to build a correlation showing the dependence of the width of this broad line on the nitrogen concentration. This dependence is shown on Fig. 3.

Microdiamonds from dolomitic marbles fall within the 10 to 30 μm size region. The EPR spectrum from a batch of such microcrystals shows the well-defined triplet of lines, the width of the central line being 3 G (Fig. 4). The spectrum was readily simulated for a line-width of 3 G. According to van Wyk *et al.* (1997), such a line width corresponds to a P1 centre concentration of 275 ppm. A value close to 275 ppm

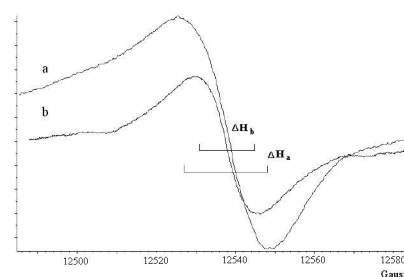


Fig. 2. EPR spectra of synthetic diamonds with high content of nitrogen. a – content of P1 centres is 1600 ppm, $\Delta H_a = 22.5$ Gauss ; b – content of P1 centres is 2400 ppm, $\Delta H_b = 15.0$ Gauss.

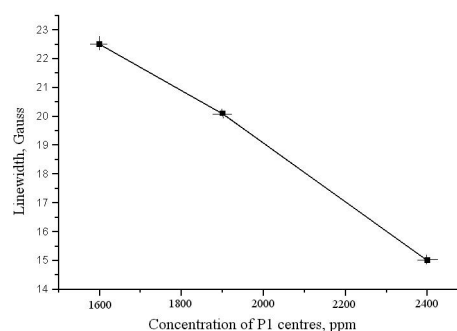


Fig. 3. Dependence of exchange EPR line width on the concentration of P1 centres.

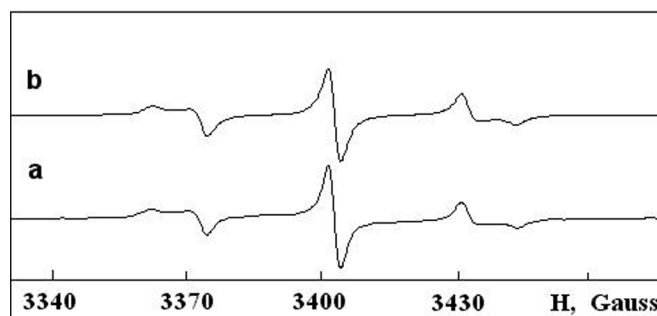


Fig. 4. Experimental (a) and theoretical (b) EPR spectra of P1 centers in Kokchetav microdiamonds from carbonate.

was calculated for a batch of Kokchetav diamonds using the standard of concentration.

To study diamonds from garnet-pyroxene rocks, stones of pure cubic habit with linear sizes of 60, 90 and 120 μm were selected under the microscope. The crystals selected give identical EPR spectra consisting of the intense broad line and a system of narrow lines from P1 centres (Fig. 5). The width of the single line varies from 20.3 to 20.1 G. The line width of the resolved P1 EPR spectrum varies from 3.25 to 4.0 G with a decreasing linear size of the crystal. This means that in the diamonds under study the local P1 centre concentration in some regions may be as great as 1900 ppm and there are also observed regions where the P1 centre local concentration ranges from 300 to 365 ppm, depending on the cube size. Using the ratio between integrated intensities of the resolved spectrum and the exchange-narrowed line, we calculated for these three sizes (120, 90 and 60 μm)

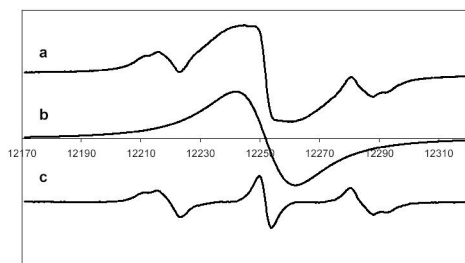


Fig. 5. Experimental EPR spectrum of P1 centers in Kokchetav microdiamonds from garnet – pyroxene rock (a) and results of its deconvolution (b, c).

the ratio between local volumes in crystals with high (1900 ppm) and low (300 to 365 ppm) P1 centre concentrations. It varies in the range 2 to 1.4 as crystal size decreases from 120 to 60 μm .

The influence on the nitrogen aggregation process due to high-pressure annealing has been studied in microdiamonds from garnet-pyroxene rocks. Prior to the experiment the crystals were yellow in colour. Analysis of microdiamonds EPR spectra before annealing shows the existence of two local concentrations of P1 centres – 1900 and 350 ppm. The crystals were annealed at 1700 °C and 7 GPa for 12 hours, after which they appear considerably bleached. Their EPR examination shows the single broad line to have disappeared, and only the resolved P1 EPR spectrum is observed. Simulation indicates that the spectra obtained may be due to P1 centres resulting in lines with a width of 3.8 and 1.3 G. This suggests that in annealed microdiamonds regions with local concentrations of 350 and 110 ppm were present. Solving the kinetic equation of the second order for aggregation of nitrogen impurity to form A-centres

$$Kt = 1/C - 1/C_0 \quad (2),$$

we found the constant for such a solid-state reaction, $K = 3.0 \cdot 10^{-6} \text{ min}^{-1} \text{ ppm}^{-1}$ for $T = 1700 \text{ °C}$, which is consistent with data given in Evans & Qi (1982) for the case of a hopping diffusion mechanism in natural diamonds. A similar value was obtained by analyzing the nitrogen transformation in local regions with low concentrations.

Annealing microdiamond from garnet-pyroxene rocks at 1850 °C, 7 GPa during 2 hours transformed the P1 centre initial local concentrations of 1900 and 350 ppm to 550 and 130 ppm respectively. The aggregation rate of nitrogen at this temperature is described by expression (2), is equal to $1.07 \cdot 10^{-5} \text{ min}^{-1} \text{ ppm}^{-1}$ and is also consistent with the data of Evans & Qi (1982) for 1850 °C.

Discussion

Our investigations performed on synthetic diamonds grown with the addition of nitrogen-bearing compounds provided a basis for constructing the dependence of the line width of the broad exchange line in the nitrogen P1 centre concentration range of 1600 to 2400 ppm. This allows us to analyze the P1 local content in microdiamonds from the Kokchetav massif. The results obtained here on measuring local con-

centrations of the P1 centres lead to the following conclusions.

The P1 centre concentration (1900 ppm) in diamonds from the garnet-pyroxene rocks considerably exceeds that (275 ppm) for stones from the carbonate rocks. The latter diamonds were also characterized by a uniform distribution of P1 centres. On the contrary, diamonds of garnet-pyroxene rocks had two regions showing marked distinctions in the distributions of P1 content. This was attributable to different total nitrogen concentrations in various diamond zones or to a different degree of nitrogen aggregation, or both. The IR data are of decisive importance in resolving this question. Indeed, the study of cuboids from the garnet-pyroxene rocks has shown wide variations both in the degree of nitrogen aggregation and nitrogen content within a single crystal, when the depth of focus is varied (De Corte *et al.*, 1998). The data obtained estimated the P1 centre content ranging 50 to 30 percent whereas the nitrogen concentration was variable by more than a factor of 2. No correlation between the nitrogen content and the proportion of P1 centres was observable. Based on this evidence we suggest that a difference in the P1 concentration is mostly due to the variations in the total nitrogen content over the whole crystalline volume. Now it is hard to tell which crystal regions contain increased or reduced nitrogen concentrations. X-ray topography revealed a central core in diamonds from the garnet-pyroxene rocks (De Corte *et al.*, 1998), but the ratio between core and rim volumes in the crystals differs by several times from the ratio between volumes with low and high P1 centre concentration. Thus, there is no strict correlation between the nitrogen distribution and internal crystalline structure revealed by X-ray topography.

The diamonds from dolomite marble display a uniform nitrogen distribution and low P1 centre concentration. This suggests diverse fluid sources for the two types of diamond-bearing rocks. Mass-spectrometry analysis for nitrogen content and its isotopic composition has provided additional evidence (Cartigny *et al.*, 2001). According to these data diamonds from the garnet-pyroxene rocks contain several times as much non-structural nitrogen as the diamonds from dolomite marble. IR measurements suggest that non-structural nitrogen may be present in fluid inclusions. The two-stage crystallization of diamonds in the garnet-pyroxene rocks, exhibited by their internal structure and nitrogen distribution, can be explained by a change in the composition of the fluid in the first and second stages of the growth. However an external source of the fluid is unlikely. The difference between fluid composition in dolomite marbles and garnet-pyroxene rocks indicates rather an internal source of fluid. Low mobility of the fluid during the diamond crystallization process is suggested by such facts as contrast in diamond-content of the same type of rocks, different nitrogen content in the diamonds from interbedded carbonate rocks and biotite gneisses. It follows from isotopic-geochemical studies that the garnet-pyroxene rocks are restites (Shatsky *et al.*, 1999). The experimental results (Palyanov *et al.*, 2001) are evidence in favour of these observations. As known during metamorphic evolution the nitrogen present in organic matter could be located in potassium minerals by replacement of potassium by ammonium (NH_4^+). One of

these minerals occurring widely in the high-pressure metamorphic rocks is phengite, considered as a possible transporter of water and incompatible elements into the mantle (Hermann *et al.*, 2001). At present phengite is not observable in garnet–pyroxene rocks but the diamonds housed in garnets frequently occur together with phengite. Based on these facts the changes in fluid composition are assumed to be due to melting, phengite resulting in a sharply increased nitrogen content in the system.

High-temperature annealing of microdiamonds at high pressure confirms Evans's values (Evans & Qi., 1982) for the rate of the nitrogen aggregation to form A-centre. According to IR data, more than 50% of the nitrogen in microdiamonds from the garnet–pyroxene rocks is in form of A defects (De Corte *et al.*, 1998). Considering that the peak temperature of metamorphism in these rocks is near 1000 °C, their residence time at these parameters could not be more than 0.5 million years.

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