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Multiple growth events in diamonds with cloudy microinclusions from the Mir kimberlite pipe: evidence from the systematics of optically active defects

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Abstract

We present new data on the main and additional optically active defects in diamonds with cloudy microinclusions from the Mir kimberlite pipe. It has been found that reshaping might have occurred either in a closed system with nitrogen and hydrogen depletion or owing to new portions of a diamond-forming fluid/melt. The internal structure and the distribution of optically active defects suggest both continuous growth of such diamonds and a multistage scenario with a series of postcrystallizational transformations, including resorption, high-temperature annealing, and degradation of nickel–nitrogen complexes.

Keywords: diamond; nitrogen; hydrogen; FTIR spectroscopy; photoluminescence

Introduction

The wide range of impurity defects known for natural diamonds is related mainly to the substitution of carbon atoms by nitrogen, boron, titanium, etc. The nitrogen content of the present-day upper mantle is calculated at 2.5×10^{19} mol (0.24 ppm) based on the bulk and isotopic compositions of gases in MORB glasses at an average C/N ratio of 500. It is controlled by the recycling of volatiles as a result of mantle degassing and the subduction of crustal rocks (Bebout, 1995; Javoy et al., 1986; Marty, 1995; Marty and Dauphas, 2003; Zhang and Zindler, 1993). According to Cartigny et al. (2001a), the initial C/N ratio in the diamond-forming medium varies from 200 to 500, whereas nitrogen content is calculated at 2 to 400 ppm based on the incompatible and, vice versa, compatible behavior of this impurity with respect to growing diamond (Cartigny et al., 2001a). On the other hand, the nitrogen content of diamonds of different origins can be >1 at.% but is usually no more than 3500 at. ppm (e.g., (Cartigny et al., 2001a,b)).

Infrared-spectroscopy studies of diamonds, which have become conventional, permit detecting nitrogen centers of several types, including single paramagnetic C- (Dyer et al., 1965), A- (pairs of substituting nitrogen atoms in neighboring positions) (Sobolev and Lisoivan, 1978), B1- (four substituting nitrogen atoms forming a tetrahedron around a vacancy) (Jones et al., 1992), and B2-defects (planar interstitial defects in the planes {100}, "platelets") (Woods, 1986). However, note that most of existing models for "platelets," observed from the absorption band of vibration of the C–C bond at 1360–1400 cm^{-1}, presuppose the presence of interstitial carbon atoms (Berger and Pennycook, 1982; Cowley et al., 1984; Davies, 1970; Lang, 1964, 1979). For the aggregation of C-centers into A-type defects and then into B1-type defects, the dependence on the time and temperature of diamond residence under mantle conditions was studied experimentally (Taylor et al., 1996). Along with nitrogen impurity centers, both natural and synthetic diamonds are characterized by absorption related to optically active hydrogen (Woods and Collins, 1983). Information about some additional optical defects, including those containing atoms of transition metals,

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can be obtained mainly using EPR- and photoluminescence spectroscopy (Bokii et al., 1986; Evans et al., 1984; Nadolinny et al., 1997, 2003; Walker, 1979; Yelisseyev et al., 1996; and others). For example, experimental studies revealed a whole range of defects in the form of nickel–nitrogen complexes in diamonds (see detailed description in (Lang et al., 2004; Yelisseyev and Kanda, 2007)), but no relationship was observed between these defects and the growth of the principal habits of natural diamond, except single diamonds with a sectorial structure (Lang et al., 2004, 2007; Plotnikova et al., 1980; Welbourn et al., 1989).

The content of impurities in the crystallization medium is one of the most important factors used to explain the morphology and internal structure of growing diamond (Kamiya and Lang, 1965; Palyanov et al., 2013a,b), along with oversaturation (Sunagawa, 1990), phase state of the medium, and the rate of diffusion of carbon atoms toward the growth front (Chernov, 1980). On the other hand, it is presumed that the nitrogen content of diamonds, according to different authors, can be controlled by nitrogen content and the C/N ratio in the diamond-forming fluid/melt (Cartigny et al., 2001a,b; Deines et al., 1987; Smart et al., 2011; Stachel et al., 2009), the conditions of diamond residence in the mantle (Boyd et al., 1994; Chrenko et al., 1977; Evans and Qi, 1982; Taylor et al., 1996), and growth rate (Khachatryan and Kaminsky, 2003; Palyanov et al., 1997). The pattern of nitrogen distribution between diamond and melt/fluid also remains disputable (Cartigny et al., 2001a; Stachel et al., 2009).

Differences in the structural, impurity, and isotope characteristics of octahedral and cubic diamonds indicate different conditions of their formation (Bokii et al., 1986; Orlov, 1984). The inconsistency of the previous model for the evolution of diamond morphology from high-temperature octahedra to low-temperature cuboids was shown by finds of natural diamonds with signs of a cuboid–octahedron transformation in kimberlites and ultrahigh-pressure metamorphic rocks (Izraeli et al., 2004; Logvinova et al., 2008; Rondeau et al., 2007; Shatskii et al., 1998; Skuzovatov et al., 2011; Zedgenizov et al., 2006). The present paper is aimed at the reconstruction of the conditions of crystal genesis by the consideration of the impurity characteristics of natural diamonds with cloudy microinclusions from the Mir kimberlite pipe (Yakutian diamond-bearing province), whose U–Pb age was previously estimated at 361 (Devis et al., 1980) and 353 Ma (Spetsius et al., 2002).

Methods

Eight diamond crystals with clouded cores containing abundant microinclusions were plane-polished to plates 0.3–0.5 mm thick, parallel to one of the planes of a rhombic dodecahedron to study their internal structure and impurity compositions. The diamonds were cleansed in HCl and distilled water, dried, and then placed in In foil (for IR spectroscopy) and epoxy (for cathodoluminescence imaging). For the cathodoluminescence studies, the diamond plates were covered with a graphite coating.

A preliminary analysis of the crystal morphology was performed using a Zeiss Stemi SV-6 stereoscopic microscope and a Hitachi TM-1000 SEM. The CL images were obtained using a LEO 1430VP electron microscope at 10 nA and 20 kV.

Infrared-absorption spectra in different growth zones of diamonds were obtained using a Bruker Vertex 70 spectrometer with a HYPERION 2000 IR microscope, with an aperture of 50×50 μm at 7500–750 cm^{-1} and with a spectral resolution of 2–4 cm^{-1}. The self-absorption of the diamond lattice in a two-phonon spectral region (12.8 cm^{-1} by 2030 cm^{-1}) was used as an internal standard (Zaitsev, 2001).

The distribution of luminescence in diamonds was studied by confocal luminescence microscopy with a temporal resolution using a MicroTime 200 luminescence microscope at the Irkutsk Branch of the Institute of Laser Physics. The patterns of distribution of luminescence over the sample were obtained during excitation from lasers with wavelengths of 405, 450, and 532 nm. Luminescence spectra in different crystal zones were measured at 77 K during excitation from a picosecond pulse laser with a 375-nm wavelength.

Results

Morphology and internal structure of the diamond crystals. The studied diamond crystals, ~1 mm in size, are of octahedral habit with flat (sometimes, stepwise) octahedron faces and hummocky cuboid faces (term in accordance with (Moore and Lang, 1972), with a parallel or sheaflike striation on the combination surfaces of the rhombic dodecahedron (Fig. 1). Both the octahedron and cube faces have etch figures (polygonal holes). Sometimes the edges and vertices of the diamond crystals also have features of dissolution. Studies in transmitted light showed that the microinclusion-bearing crystal cores are of cubic or irregular shape and differ considerably in size: from few tens of microns to 60–70% of the whole crystal volume (Fig. 2). This situation becomes more evident from the study of plane-parallel crystal plates (Fig. 3). Unlike the micrographs, the cathodoluminescence images clearly show the curvilinear and cuboid shape of the cores with abundant microinclusions (Fig. 4). The growth of the cubic core in the studied crystals is followed by gradual reshaping and the formation of a cube–octahedral transition zone and the final octahedral shape with no evidence for dissolution.

However, a clear boundary without a transition zone is observed for some samples between cubic core and octahedral rim (Fig. 4*c*, *d*); note that in samples MS-2, MS-7, and MS-9, the cubic core has smoothed outlines, which suggests dissolution.

Description of the IR absorption of the diamonds. Infrared spectra of the cubic core and octahedral rim of diamond MS-1 with contrasting characteristics are shown in Fig. 5. Data on the major impurity characteristics of the studied diamonds are presented in Table 1. The spectrum of