

Inclusions of Metal Solvent and Color of Boron-Bearing Monocrystals of Synthetic Diamond

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Abstract—Cuboctahedral diamond monocrystals of physical classification type IIb weighing from 0.1 to 2 carats and with minor faces {110}, {311}, and {511} have been synthesized. The crystals are characterized by various hues of blue and dark blue depending on the amount of B in the system. A characteristic feature of these diamonds is a sectorial structure expressed in a nonuniform color distribution. The following types of metallic inclusions in the crystals have been recognized: faceted isometric, lamellar, and extended inclusions; unfaceted irregular and drop-shaped inclusions; and microinclusions. These inclusions are related to the chemical composition of the metal solvent.

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INTRODUCTION

Natural blue boron-bearing diamonds (physical classification type IIb) are extremely rare. In fact, they occur exclusively in the Premier and Swarttruggens kimberlite pipes in South Africa and are not found in placers or primary deposits in Russia (Vecherin et al., 1997). Some features, largely the light carbon isotopic composition, allow the supposition that their origin is related to subduction of the Earth's crust during the Proterozoic (Afanas'ev et al., 2002). Hence, boron incorporated into the crystal structure was derived from the crust.

At the same time, the studied diamond crystals are low-nitrogen. The unique physical properties of type IIb diamonds, the high demand for them, and their extreme rarity in nature make the synthesis of such crystals combined with study of their properties of great interest. Synthesis is also necessary for interpretation of the origin of natural diamond.

EXPERIMENTAL

Type IIb boron-bearing diamonds were synthesized with a high-pressure multianvil apparatus of the split sphere type (Chepurov et al., 1997) in Fe (30 wt %)-Ni (70)-C and Fe (30 wt %)-Co (70)-C systems at 5.5–6.0 GPa and 1350–1450°C during 80–120 h. The growth rate of crystals ranged from 0.2 to 5 mg/h depending on the thermal gradient in the operating cell. Titanium was used as an absorbent of nitrogen. Fixed amounts of B₂O₃ were added to the charge for doping of low-nitrogen crystals with boron.

The synthesized diamond crystals were treated with acids and studied under an optical microscope as 1- to 3-mm-thick polished plates parallel to {100} and with IR, UV, and Raman spectroscopy and X-ray imaging. Damaged diamonds of 2–3 mm in size containing numerous inclusions were used for X-ray imaging. XRD patterns were obtained using a URS-55 diffractometer equipped with a Gondolfi camera with Cu radiation and an exposure interval of 10 h.

RESULTS AND DISCUSSION

Cuboctahedral diamond monocrystals weighing from 0.1 to 2 carats (maximum size 7 mm) with minor faces {110}, {311}, and {511} were synthesized. A nonuniform color distribution with blue and colorless growth sectors is characteristic (Figs. 1a, 1b). Blue color is caused by incorporation of boron into the diamond structure, with octahedral and rhombododecahedral growth sectors being colored areas (*The Properties...*, 1979). The color contrast increases with an increase in the concentration of boron oxide in the charge. Colorless zones are not changed, whereas colored areas become deeper in color (from light blue through blue to practically opaque areas (Table 1)). Sectors in synthetic boron-bearing diamonds were previously reported by Rooney (1992), Burns et al. (1999), and Novikov et al. (2003).

Crystals of synthetic boron-bearing diamond with *p*-type conductivity demonstrate characteristic bands in the IR spectrum (Fig. 2) related to electron transitions in the boron impurity atom (*The Properties...*, 1979). Continuous absorption beginning at 2985 cm⁻¹ is attributed to photoionization of the boron atoms. Absorption decreases in the UV region, resulting in a blue color of diamonds. A broad band at 1290 cm⁻¹ with an accom-

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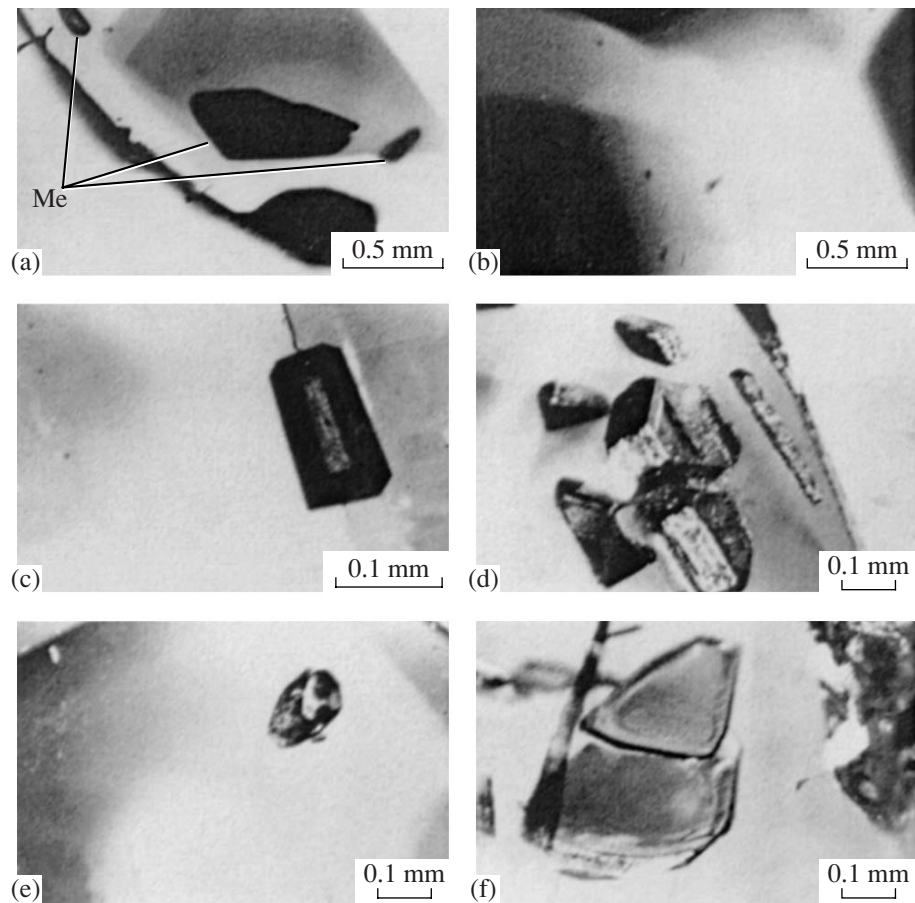


Fig. 1. Structure of synthetic diamond crystals: (a, b) sectorial structure; (c–f) metallic inclusions.

panying band at 1332 cm^{-1} is attributed to chemically bonded B–N atoms. The absence of differences between the spectral characteristics of natural and synthetic diamonds of type IIb should be emphasized (Smith and Bosshart, 1999).

Inclusions of metal solvent are the main defects of synthesized diamonds (Figs. 1c, 1d). The results of X-ray imaging are listed in Table 2. Diamond lines in the XRD pattern are not indicated in this table. The X-ray results obtained are consistent with the reference data for Fe,Ni alloy with an Fe content of 46 wt % (Fig. 3), which is higher than the Fe concentration

(30 wt %) in the initial metallic charge. However, it should be kept in mind that the solubility of the dissolved carbon contained in the metallic alloy after the run is about 10 at % (2 wt %) under experimental conditions (Chepurov et al., 1997). The solubility of such an amount of carbon leads to an increase in the unit cell parameters of metallic nickel by 1% (Strong, 1965), i.e., by 0.034 Å . This effect results in a higher unit cell parameter of the Fe,Ni alloy in diamond-hosted inclusions (3.58 Å) as compared with pure Fe (30%)–Ni (70%) alloy (3.56 Å).

Table 1. Color of synthetic diamond monocrystals versus amount of B_2O_3 in the initial system

Weight of B_2O_3 , mg	Color of diamond crystals	Weight of source (graphite), mg	Composition of metal catalyst, g	Run number
0.26	Light blue	816	Ni(1.0)Fe(3.9)	2-36-03
0.5	Blue	822	Ni(1.0)Fe(3.9)	2-33-03
0.7	"	934	Co(1.3)Fe(2.8)	2-05-04
0.75	"	918	Co(1.3)Fe(2.8)	2-04-04
0.8	"	708	Ni(0.5)Fe(3.6)	2-50-03
1.5	Dark blue	708	Ni(2.7)Fe(2.7)	2-42-03

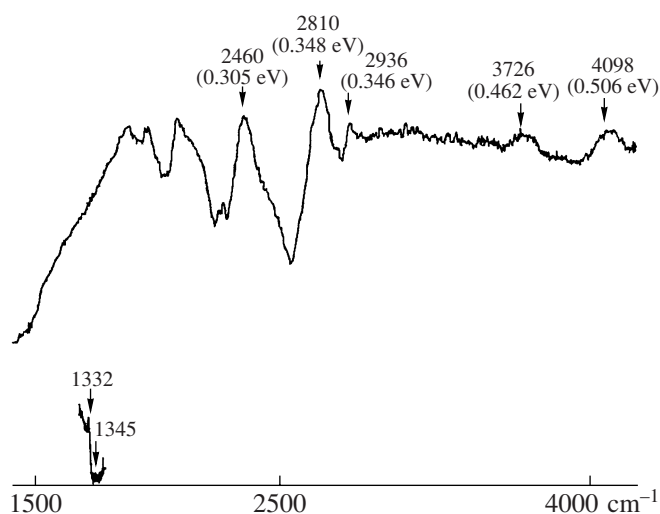


Fig. 2. IR absorption spectrum of synthetic boron-bearing diamond crystal.

Microscopic study of the crystals revealed faceted (isometric, lamellar, and extended) inclusions of metal solvent and unfaceted irregular or drop-shaped inclusions. These inclusions appear opaque with a strong metallic luster even in thin diamond plates (less than 0.01 mm). They occur separately or as groups in host diamond crystals. In relatively pure crystals, the inclusions are mainly located adjacent to the seed. In damaged crystals, inclusions occur in the crystal volume as well as in the apex and edge areas. Separate microinclusions and groups of them scattered in the crystal volume also occur. Location of inclusions within blue octahedral growth sectors is noted.

The morphology of faceted inclusions corresponds to the morphology of the host diamond; i.e., they have the same crystallographic forms: {111} and {100} and less frequently {110} and {311}. The “facets” of inclusions are parallel to the respective facets of the diamond. The habit of faceted inclusions depends on their location in the diamond crystal. Lamellar inclusions

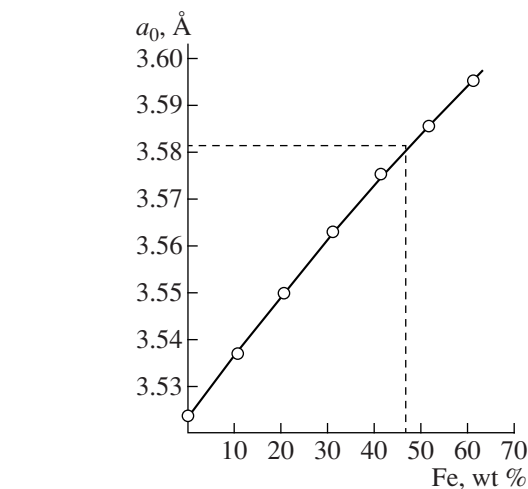


Fig. 3. Unit cell parameter of Fe,Ni alloy versus iron content (ASTM, card no. 23-297).

occur near diamond facets, while extended ones are confined to edge areas.

Inclusions of the growth medium (metal solvent) in synthetic boron-bearing diamonds are the main difference from natural blue diamonds, where inclusions do not usually occur except cloudlike microinclusions of unknown composition (Smith and Bosshart, 1999). However, the amount of inclusions is related directly to the growth rate of diamonds. They appear at a growth rate of more than 1 mg/h, and at a rate of 4–5 mg/h their amount reaches approximately 10 vol % or higher. Therefore, the absence of growth medium inclusions indicates a low growth rate of diamonds.

The second distinctive feature of synthetic and natural diamonds of type IIb is irregular coloration of the former (Shigley et al., 1995; Smith and Bosshart, 1999). As was mentioned above, this difference is related to the trapping of boron atoms mainly by octahedral growth sectors, whereas octahedrons and cubes are the main faces of synthetic diamonds. Natural diamonds show zoning by octahedrons, while zoning by

Table 2. Results of X-ray imaging of metallic inclusions in diamond

<i>hkl</i>	(Fe, Ni) alloy with an Fe content of 60.84 wt % (reference data: ASTM, card no. 23-297)			Metallic inclusions in diamond		
	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>a</i> ₀ (Å)
111	2.08	2.076	10	2.066	10	3.578
200	1.80	1.798	8	1.793	8	3.586
220	1.270	1.271	5	1.265	5	3.578
311	1.083	1.084	8	1.081	6	3.585
222	1.037	1.038	5	1.033	5	3.578
400	0.900	0.899	3	—	—	—
<i>a</i> ₀ = 3.5956 Å				<i>a</i> ₀ (mean) = 3.581 Å		

cubes is absent (Shigley et al., 1995). An inner sculpture of the "tatami" type is present in some diamonds (Smith and Bosshart, 1999). The origin of this sculpture is not clear. It is suggested that this sculpture is superimposed, i.e., was formed during annealing of natural diamonds as a result of ductile deformation of crystals in the mantle (Orlov, 1973).

Despite the above differences between natural and synthetic diamonds of type IIb, their properties are controlled by specific growth conditions. The convergence of growth conditions is possible based on an understanding of blue diamond formation and further development of experimental techniques.

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