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# Linear Growth Rate and Sectorial Growth Dynamics of Diamond Crystals Grown by the Temperature-Gradient Techniques (Fe–Ni–C System)

**Y. V. Babich[a]*, B. N. Feigelson[b], and A. I. Chepurov[a]**

[a] *Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia*
[b] *Naval Research Laboratory, Washington DC, 20375, USA*
**e-mail: babich@igm.nsc.ru*

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**Abstract**—The paper reports data on the linear growth rates of synthetic diamond single crystals grown at high *P*–*T* parameters by the temperature-gradient technique in the Fe–Ni–C system. Techniques of stepwise temperature changes and generation of growth microzoning were applied to evaluate the growth rates of various octahedral and cubic growth sectors and variations in these rates with growth time. The maximum linear growth rates of the order of 100–300 μm/h were detected at the initial activation of crystal growth, after which the growth rates nonlinearly decreased throughout the whole growth time to 5–20 μm/h. The fact that the linear growth rates can broadly vary indicates that the inner structure and growth dynamics of single diamond crystals grown by the temperature-gradient technique should be taken into account when applied in mineral–geochemical studies (capture of inclusions, accommodation of admixture components, changes of the defective structure, etc.).

*Keywords:* synthetic diamond, temperature-gradient technique, linear growth rate

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## INTRODUCTION

Synthetic diamonds grown at high *P*–*T* parameters are conventionally utilized in various mineralogical and geochemical studies, for example, to elucidate the dependences of the morphology, defective structure, and physicochemical characteristics of diamonds on their crystallization parameters in nature. However, the possibility of obtaining experimental data on dependences of these properties on their growth conditions at high *P*–*T* parameters is largely limited by the fact that such growth systems are hard to monitor. For example, linear growth rates and their variations in the course of diamond growth under high pressures were studied only for growing diamonds in metal–graphite mixtures (Bezrukov et al., 1971; Litvin and Butuzov, 1972; Laptev and Khatelishvili, 1977; Samoilovich et al., 2000). Such a data pertaining to the temperature-gradient technique, which is also widely applied to grow diamond crystals for research and industrial needs (Wentorf, 1971), are still fragmentary or are time-integrated estimates averaged for the whole crystal (Vagarali et al., 1990; Burns et al., 1999; Sumiya et al., 2002; Babich et al., 2004). In view of this, we attempted to systematically study the linear growth rates and growth dynamics of various growth sectors of single diamond crystals synthesized by the technique of temperature gradient.

## EXPERIMENTAL SAMPLES

All of our diamond samples were synthesized by the temperature gradient technique in the Fe–Ni–C system at $p = 6.0$ GPa, $t = 1370–1550°C$ in a multianvil double-stage high-pressure apparatus of the split-sphere type (the Russian acronym is *BARS*). The samples were grown in a growth cell with a conventionally applied layout of carbon sources and seed crystal in a cylindrical growth volume (Wentorf, 1971; Vagarali, 1990; Chepurov, 1998; Pal'yanov, 1987; Burns, 1999), which is schematically represented in Fig. 1a. The carbon source was a graphite pellet, which was transformed into polycrystalline diamond during the first few minutes of the experiments at high temperature and pressure and then dissolved. The metal volume in the growth cell was approximately 500 mm$^3$, and the vertical temperature gradient was 40–50°C. The temperature and pressure were evaluated accurate to ±20–30°C and ±0.02 GPa, respectively. The temperature was varied accurate to 3–5°C. The studied crystals ranged from 0.6 to 1.2 carats, and the average mass growth rate varied thereby from 1 to 3 mg/h.

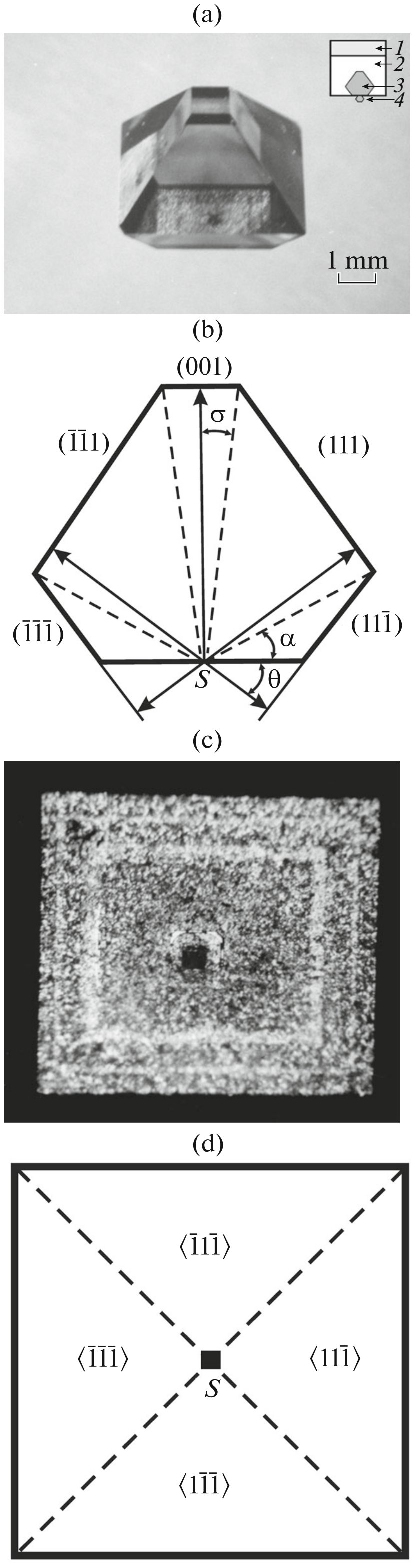

**Fig. 1.** Cuboctahedral single diamond crystal grown by the temperature-gradient technique with stepwise varied temperature. (a) Micrograph of the crystal. Note a number of rectangular growth zones in the base of the crystal, around the location of the seed crystal. The inset shows a generalized growth layout: *1*—carbon source (graphite pellet) *2*—solution–melt, *3*—crystal, *4*—seed crystal. (b) Schematized representation of the sectorial inner structure of the crystal, section parallel to the rhombododecahedron plane. (c) Base plane (reflected-light image) with clearly seen rectangular growth zones. (d) Schematic representation of growth sectors in the base plane. In the schematic representations of growth sectors: dashed lines mark the boundaries of the growth sectors, arrows are the growth vectors of the growth sectors, *S* is the locus of the seed crystal.

The crystals were grown on the cubic faces of seed crystals. To analyze the linear growth rates, the crystals were grown with generating temperature–time marks, a method commonly used to solve such problems (Vilke, 1977; Müller, 1988). Most of the crystals were grown according to conventional regimes, with various stepwise temperature variations that involved alternating isothermal phases, which lasted for 6 to 20 h, with the temperature differences up to 5% relative to the nominal experimental temperature. We also additionally studied a sample in which growth temperature microzoning was induced. The crystal had been grown previously and had been partly studied in the context of nitrogen aggregation (Babich et al., 2004). In this instance, the temperature was generally stabilized (within the range of 1470–1495°C), and growth microzoning was induced by current short-period (22.3 min) temperature variations within 3–5°C. Our detailed study of the linear growth rates allowed us to compare and analyze results obtained by different techniques. Crystals and platelets were examined under a Polam-L213 and Biolam-M optical microscopes, zoning in crystals was measured using a MOB-1-16x ocular micrometer. To enhance optical contrast, when analyzing microzoning in crystals we used an auxiliary lighting system that involved a source of reflected light in combination with a slit-shaped aperture.

## RESULTS AND DISCUSSION

All of the diamond crystals grown in temperature regimes with the generation of temperature–time marks show growth zoning of various scale, which can be seen mostly as variations in the color intensity (in yellowish brown shades) in the growth zones. The reason for the development of this zoning is an uneven distribution of structural admixtures, possibly, the substituting nitrogen and/or nickel. They are differently accommodated in the diamond structure depending on the growth conditions, particularly, growth temperature and growt rate (Kanda and Lawson, 1995; Babich and Feigelson, 2006). The examples of certain individual samples are employed below to illustrate different types of crystal zoning and their estimated growth rates.

**Growth in stepwise varyed temperature regimes.** These diamond samples are characterized by clearly seen growth zones, which are often discernible even by the naked eye. Figure 1 shows one of these crystals, which was grown at an average temperature of 1470°C for 126 h, in a number of successive episodes 5–22 h long during which the temperature was varied from 60 to 100°C; the crystal is of cuboctahedral habit. The figure also shows diagrams explaining the sectorial zoning and the basal plane of the crystal (in which the seed crystal occurs) with growth zoning clearly seen in reflected light. The rectangular closed zones in the bottom part of the crystal (Fig. 1c) suggest that the growth rates of crystal sectors relative the vertical axis are roughly equal, which suggests that the crystallization environment was symmetric. However, the thicknesses of the zones significantly vary due to variations in the growth rates with time. Figure 2 shows micrographs of the bases of other two crystals, which were grown in slightly different temperature regimes and which are locally chipped and fractured. Such defects are fairly typical and were detected in some 30% of the samples grown in regimes of stepwise varied temperature. The character of these distortions and the presence of all growth zones even in fragments suggest that the crystals were fractured after they stopped growing. This, in turn, suggests that the crystals grown at significant temperature variations are more strongly internally stressed, and hence, the probability of their fracturing and chipping when cooled and/or depressurized after the experiments is higher.

Zoning on the basal planes of the samples makes it possible to conduct instant measurements to evaluate the growth rate without cutting the crystals. The growth rates were calculated from the measured zone sizes on crystal bases with regard for their symmetry and inner structures and for known time spans between temperature zones. The growth rate for the cubic sector ⟨001⟩ was evaluated from the growth rates of adjacent octahedral sectors and angle σ determined from the cubic face value (Fig. 1b). Although the temperature regimes and the character of the temperature–time zones were somewhat different, all of the crystals grown in stepwise varied temperature regimes show principally similar relationships between the growth rates of their sectors and the patterns of their variations during crystal growth. Figure 3 presents data on the growth rates illustrated by the example of the crystal whose base is shown in Fig. 2a. The growth sectors analyzed in the sample are subdivided into "upper" octahedral sectors, which grew at relatively high rates (Fig. 3a), "lower" octahedral sectors, whose growth rates were relatively low (Fig. 3b), and a cubic sector (Fig. 3c), whose growth rate was the highest. This distribution is explained by the morphologies of the crystals, which were grown on the cubic face of the seed crystal (Figs. 1a, 1b) as a consequence of, on the one hand, of the thermodynamic conditions of crystal growth (Sunagawa, 1984), and on the other, the orientation of the faces and their feeding specifics in the sector groups in the growth space (Babich et al., 2000). In the latter instance, the growth rates of crystal faces of certain sectors are always the higher, the closer to the carbon source they are (see Fig. 1a).

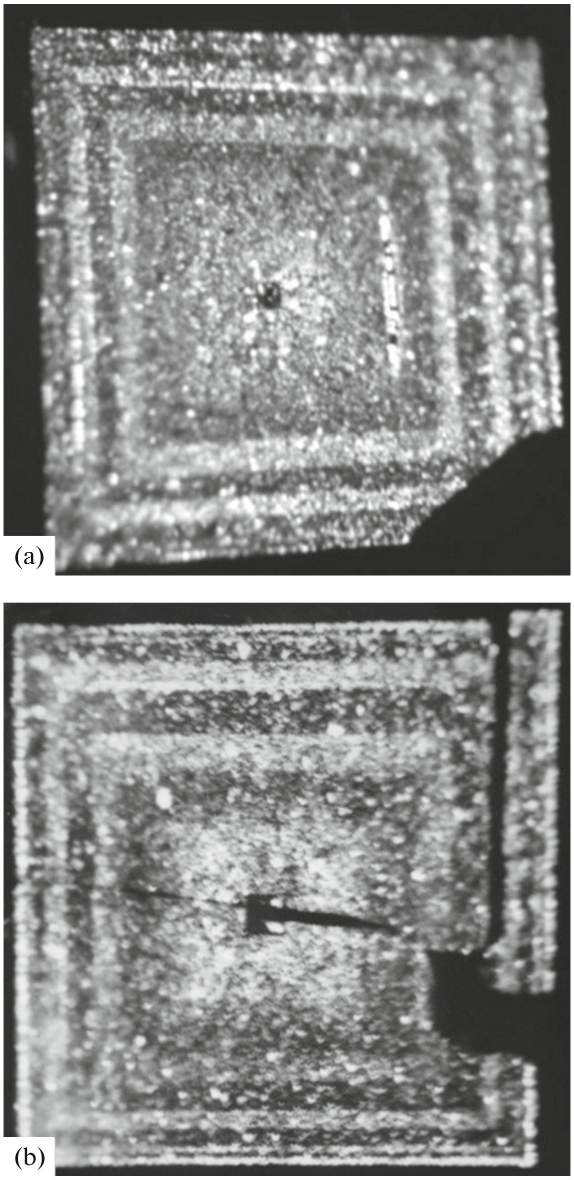

**Fig. 2.** Reflected-light micrographs of the basal planes of diamond crystals grown by the temperature-gradient technique in different regimes of stepwise temperature variations. The average growth temperature was 1460°C. Total growth time: (a) 125 h (the temperature between zone was varied from 100 to 120°C, the growth time of each zone was 8–20 h); (b) 120 h (the temperature between zone was varied from 90 to 100°C, the growth time of each zone was 6–20 h). Both crystals were (a) chipped and (b) fractured after their growth.

The growth dynamics of all sectors also shows certain systematic variations with time. First, the linear growth rates in all sectors are much higher during the early growth of the crystal and are 5–19 times higher than during its late growth. Thereby the absolute

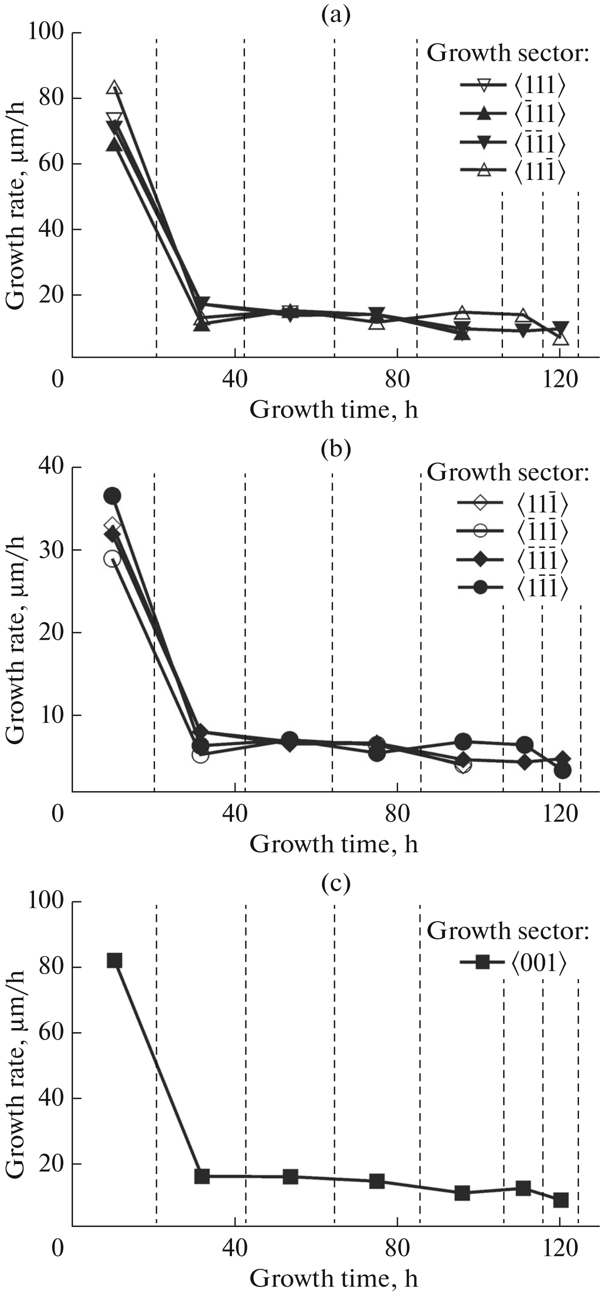

**Fig. 3.** Variations in the growth rates of various growth sectors in a single crystal (shown in Fig. 2a) with time. (a) In the "upper" octahedral growth sectors; (b) in the "lower" octahedral growth sectors; (c) in the ⟨001⟩ cubic growth sector. Dashed lines show the time boundaries of zones in which the linear growth rates were determined.

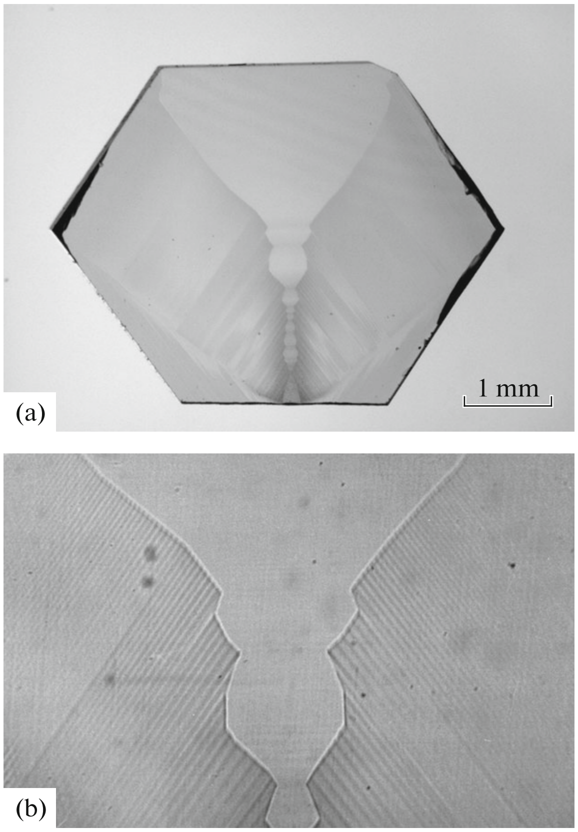

**Fig. 4.** Photograph of the platelet cut off parallel to the rhombododecahedron plane of a single diamond crystal that was grown using the induced-zoning method. (a) Micrograph of the platelet with discernible growth sectors; (b) microzoning in octahedral growth sectors (central part of the platelet).

growth rates vary from 50–80 to 3–9 μm/h in the more developed octahedral growth sectors, from 22–37 to 2–5 μm/h in less developed octahedral sectors, and from 75–100 to 6–12 μm/h in the cubic growth sectors ⟨001⟩. Note that the cubic growth sector is characterized by the maximum growth rate, and this is consistent with that fact that the proportion of cubic faces in the crystals is at a minimum (it is known that face forms whose growth rates are maximal tend to taper out). Second, the linear growth rates vary within the ranges specified above fairly unevenly: the greatest decrease occurs within the first 20–40 h of crystal growth, which then continues at relatively low rates, close to the final ones.

**Growth associated with the development of microzoning.** These samples do not display zoning visible to the naked eye, and hence, we conducted all measurements under a microscope equipped with an ocular micrometer or by using platelets that are usually cut off parallel to the rhombododecahedron plane (Fig. 4a). Our microscopic studies indicate that the growth microzoning of the platelet is most clearly pronounced in octahedron sectors (Fig. 4b). When measuring this zoning, we recorded the sequential numbers of the zones, their thicknesses, current size of the cubic face, and certain parameters of the inner structure of the crystal. As an illustration of the measured parameters, Fig. 5a shows data on the thickness of the zone depending on the growth vector in the more developed "upper" octahedral growth sectors of faces (1 1 1) and

(−1 −1 1). The linear measurements were carried out accurate to ±1 to 2 μm, which is smaller than the symbols in the figure. As can be seen in the diagram, the thicknesses of zones in the sectors systematically decrease from 60–70 to 4–5 μm away from the seed crystal. toward peripheral zones as a consequence of a decrease in the growth rate of the crystal with time. To illustrate this tendency, data obtained on the major growth sectors were represented as dependences of the linear growth rates on time. The linear growth rate was determined from the ratio of the thickness of a zone to the known time of its growth, and the current time of crystal growth was determined by directly counting the number of the zones overgrowing the seed crystal (Fig. 5b). The figure presents results on the linear growth rates of all growth sectors in the left-hand part of the platelet (data on the right-hand part practically exactly coincide with them). Compared to the data obtained by the technique described above, these are better consistent with the aforementioned local growth rates of the growth sector groups (Fig. 3) and show more details of their variations. For example, it became clear that the local linear growth rates are somewhat higher during the early growth of the crystal and reach 100–110 μm/h in less developed octahedral sectors, 170–180 μm/h in more developed octahedral sectors, and 300 μm/h in the cubic growth sector. It was also confirmed that the early growth of the crystal is the most dynamic, and the growth rate is at a maximum within the first 20 h and then two to six times diminishes relative to these initial values. The further decrease is more even: starting at 20–25 h, the growth rates of all sector lie within the range of 15–20 μm/h and amount to 5–25 μm/h during late growth. The decrease in the local growth rates detected using this technique significantly varies from sector to sector and is generally 10- to 25-fold (Fig. 5b).

This technique also allowed us to discover a somewhat greater variability of the growth rate in the cubic sector, as is well seen in comparison with the quite even variations in the growth rates in octahedral sectors (Fig. 5b). This effect is seen in Fig. 4c, in which the variations in the size of the cubic growth sector can be compared with the even variations of visible zoning (and hence, also the growth rate) in octahedral sectors. Note that the cubic and octahedral growth sectors occur in a single crystal and, hence, grew at the same *P*–*T* parameters in a closed growth system. These contrasting variations in the growth rates of the sectors led us, with regard for the relations between the morphology of synthetic diamond and its *P*–*T* growth parameters (Sunagawa, 1984), to the only possible conclusion that the growth rates of cubic sectors are much more susceptible to *P*–*T* parameters than the growth rates in octahedral sectors (and hence, also to current inaccuracies in their maintaining). This conclusion illustrates the possibility of utilizing data on variations in the sizes of cubic growth sectors, for example, as a tool to additionally control the accuracy of maintaining the *P*–*T* growth parameters of crystals.

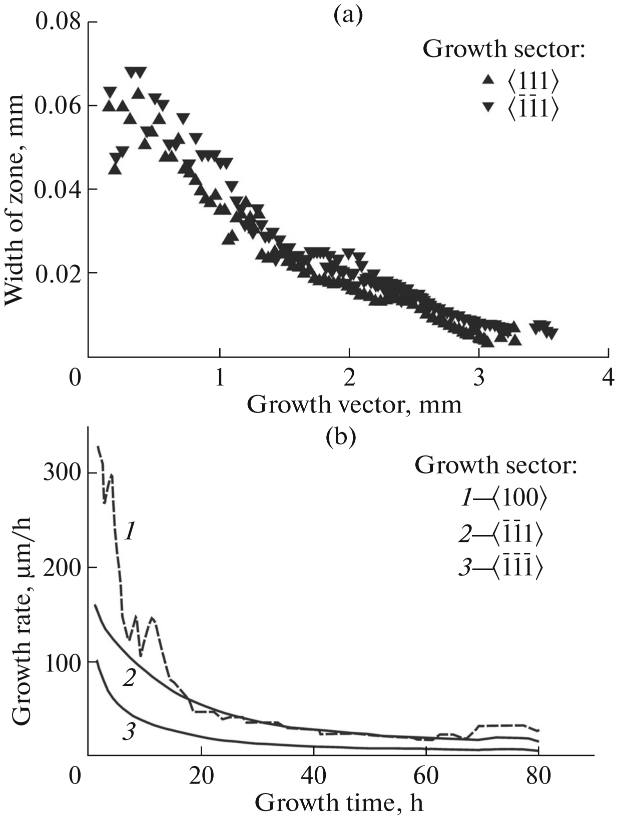

**Fig. 5.** Data on microzoning and growth rates of a single diamond crystal determined in the platelet shown in Fig. 4a. (a) Measured widths of the zones along the growth vectors in the "upper" octahedral growth sectors; (b) variations in the linear growth rates with time in various growth sectors in the left-hand part of the platelet.

Summarizing the experimental data obtained using both techniques, we conclude the following. All data on the linear growth rates are mutually consistent, and regardless of the methods, the trends and ranges of their variations are closely similar for all samples. Our experimental results also demonstrate that the sectors belonging to a single crystal form can yield significantly different linear growth rates, which are at a maximum during the early growth of the crystal and then decrease as multiple steps. In principle, such growth sectors can be regarded as separate crystalline individuals, which grew at different rates. Considering that the technique of temperature gradient is implemented at high *P*–*T* parameters in closed growth systems, it can be generally concluded that the experimentally determined variation tendencies in the linear growth rates are typical of this variant of the technique. Note that the detected variation patterns with time are similar to those detected using another technique of diamond synthesis under high pressures: diamond synthesis from a metal–graphite mixture, when the highest growth rates were also detected early in the process of diamond growth and then decreased (Litvin and Butuzov, 1974; Samoilovich et al., 2000). At the same time, the overall order of the growth rate in our experiments was two to three orders of magnitude lower, and this highlights significant differences between the growth mechanisms in these techniques. This is likely explained by the fact that, in contrast to the method of diamond synthesis, in which the main role is played by diffusion (Fedorov and Chepurov, 1984; Osugi et al., 1984), in the temperature-gradient technique, carbon is transported with the participation of convection (Kirdyashkin et al., 1986; Pal'yanov, 1997; Demina et al., 2009).

From the methodical viewpoint and with reference to the dynamics of diamond growth, it is worth mentioning that the method of generating growth microzoning is the most informative and does not necessarily involve damaging the samples. At the same time, the method of stepwise temperature variations is the simplest and most rapid, and this technique is highly suitable for estimating general tendencies in the variations of growth rates without cutting the samples. It is also worth mentioning that the perfectness of the crystals testifies that single diamond crystals devoid of visible inclusions and flaws can be grown at a rate as high as 0.3 mm/h by the solution–melt method. Thereby high local growth rates and their broad variations in synthetic diamonds offer further possibilities of accurate comparative studies of a single crystals within a broad range of its growth rate at exactly the same growth parameters (temperature, pressure, composition of the growth medium, occurrence of minor admixtures, etc.)

In conclusion it should be mentioned that the experimental data presented above for broad enough variations in the local linear growth rates indicate that the inner structure and growth dynamics of single crystals grown by the temperature-gradient technique should be taken into consideration when used to study the mineralogy, capture of inclusions, and defect structure of diamonds and diamond-forming processes.

## PRINCIPAL RESULTS AND CONCLUSIONS

Summarizing analysis of experimental data on the growth dynamics of diamond crystals grown by the temperature-gradient technique shows that, along with differences in the growth rates of various crystal faces related to the specifics of their feeding, the growth rates also significantly vary with time when a crystal grows. For example, the maximum ratio of current growth rates of various faces is approximately 1 : 3, while the maximum ratio of the final to initial growth rates reaches 1 : 25. The maximum growth rate (which is 100–300 μm/h for our samples) was reached during the very early growth of the crystals and then gradually decreased to the lowest values of some 5–20 μm/h. The growth rates of cubic growth sectors are much more susceptible to growth conditions than the growth rates of octahedral sectors.

Data obtained by different techniques are highly consistent with one another and led us to conclude that the variations detected in the linear growth rates are typical of diamond crystals grown by the temperature-gradient technique at high *P–T* parameters. The fact that the local linear growth rates can significantly vary indicates that the inner structure and growth dynamics of single crystals grown by the temperature-gradient method should be taken into account when these crystals are used in mineralogical–geochemical studies (capture of inclusions, accommodation of admixtures, variations in the defect structure, etc.)

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## REFERENCES

Y. V. Babich and B. N. Feigelson, “Distribution of nitrogen-related defects in diamond single crystals grown under nonisothermal conditions,” Inorg. Mater. **42** (9), 971–976 (2006).

Y. V. Babich, B. N. Feigelson, D. Fisher, A. P. Yelisseyev, V. A. Nadolinny, and J. M. Baker,”The growth rate effect on the nitrogen aggregation in HTHP growth synthetic diamonds,” Diamond Relat. Mater. **9**, 893–896 (2000).

Y. V. Babich, B. Feigelson, and A. Yelisseyev, “Nitrogen aggregation and linear growth rate in HPHT synthetic diamonds,” Diamond Relat. Mater. **13**(10), 1802–1806 (2004).

G. N. Bezrukov, V. P. Butuzov, and V. A. Laptev, “Kinetics of growth of synthetic diamond crystals of different habit, Dokl. Akad. Nauk SSSR **200** (5), 1088–1091 (1971).

R. C. Burns, J. O. Hansen, R. A. Spits, M. Sibanda, C. M. Welbourn, and D. L. Welch, “Growth of high purity large synthetic diamond crystals,” Diamond Relat. Mater. **8** (8–9), 1433–1437 (1999).

A. I. Chepurov, I. I. Fedorov, and V. M. Sonin, “Experimental study of diamond formation at high *P–T* parameters (application to model of natural diamond formation,” Geol. Geofiz. **39** (2), 234–244 (1998).

S. E. Demina, V. V. Kalaev, V. V. Lysakovskyi, M. A. Serga, T. V. Kovalenko, and S. A. Ivahnenko, “Computer modeling of diamond single crystal growth by the temperature gradient method in carbon-solvent system,” J. Cryst. Growth **311**, 680–683 (2009).

I. I. Fedorov and A. I. Chepurov, “Mass transfer of carbon and specifics of diamond crystallization in metallic systems,” Sverkhtverd. Mater. **5**, 6–11 (1984).

H. Kanda and S. C. Lawson, “Growth temperature effects on impurities in HP/HT diamonds,” Ind. Diamond Rev. **55** (565), 56–61 (1995).

A. G. Kirdyashkin, I. I. Fedorov, A. I. Chepurov, and Yu. M. Borozdov, "Mass transfer of carbon during diamond recrystallization," Sverkhtverd. Mater., No. 3, 23–29 (1986).

V. A. Laptev and G. V. Khatelishvili, "Change in the shape of single diamond crystals during their growth," in *Crystal Growth* (Nauka, Moscow, 1977), Vol. 12, pp. 172–176 [in Russian].

Yu. A. Litvin and V. N. Butuzov, "Kinetics of diamond growth from solution in metal melt," in *Crystal Growth* (Nauka, Moscow, 1977), Vol. 9, pp. 65–75 [in Russian].

G. Müller, *Convection and Ingomogeneities in Crystal Growth from the Melt* (Springer, Berlin, 1988).

J. Osugi, T. Arase, K. Hara, and F. Amita, "Diamond formation in molten nickel (research note)," High Temperature–High Pressure **16**, 191–195 (1984).

Yu. N. Pal'yanov, A. F. Khokhryakov, Yu. M. Borzdov, A. G. Sokol, V. A. Gusev, G. M. Rylov, and N. V. Sobolev, "Conditions of growth and true structure of the synthetic diamond crystals," Geol. Geofiz. **38** (5), 882–906 (1997).

M. I. Samoilovich, N. G. Sanzharlinskii, and B. I. Zadneprovskii, "Method of assessment of growth rates of synthetic diamond crystals," in *Mineral Synthesis,* Ed. by B. A. Dorogovin (VNIISIMS, Moscow, 2000), Vol. 3, pp. 71—74 [in Russian].

H. Sumiya, N. Toda, and S. Satoh, "Growth rate of high-quality large diamond crystal," J. Crystal Growth **237–239**, 1281–1285 (2002).

I. Sunagawa, "Morphology of natural and synthetic diamond crystals," in *Materials Science of the Earth's Interior,* Ed. by I. Sunagawa (TERRA PUB., Tokyo, 1984), pp. 303–330.

S. Vagarali, M. Lee, and R. C. DeVries, "Progress of large diamond growth technology and future prospects," J. Hard Mater. (UK) **1** (4), 233–245 (1990).

R. H. Wentorf, "Some studies of diamond growth rates," J. Phys. Chem. **75** (12), 1833–1837 (1971).

K. T. Wilke, *Kristall-Zuchtung* (VEB Deutscher Verlagd. Weissenschaften, Berlin, 1973)

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