Diamond Crystallization from a Sulfur−Carbon System at HPHT Conditions

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ABSTRACT: In this paper, we report on diamond synthesis in the sulfur−carbon (S−C) system at temperatures in the range of 1550−2000 °C and pressures of 6.3−7.5 GPa. It is established that crystallization of carbon phases (diamond and graphite), the degree of the graphite-to-diamond conversion, and diamond crystal morphology are primarily determined by the pressure−temperature (P−T) conditions. It is suggested that the most probable medium of diamond crystallization in the S−C system is the melting of carbon disulfide CS_2. Fourier transform infrared (FTIR) microspectroscopy revealed that synthesized diamond crystals contained nitrogen impurity in the form of A and C defects with a total nitrogen concentration up to 1500 ppm. For the crystals with high nitrogen content, hydrogen-related centers are typically observed. Addition of water to the S−C system results in a decrease in the diamond synthesis temperature and a change in diamond crystal morphology from cuboctahedron to octahedron.

Introduction

Among the nonmetallic-solvent catalysts used for diamond synthesis under high pressure−high temperature (HPHT) conditions, of particular interest are elemental substances, such as phosphorus and sulfur. An increased attention to these elements is to a greater extent stimulated by the fact that both phosphorus and sulfur are considered potential elements for diamond doping.[1−4] HPHT synthesis of diamonds in simple binary systems, like phosphorus−carbon (P−C) and sulfur−carbon (S−C), is also of interest for getting a better understanding of the mechanisms of diamond nucleation and growth from nonmetallic solvents. It has been established experimentally that melts of phosphorus and sulfur are able to dissolve carbon and provide diamond synthesis at high pressures and temperatures. Diamond crystallization in the P−C system has been studied in a number of works,[5−8] and it has been proved that phosphorus incorporates into the diamond structure under HPHT conditions. Studies devoted to diamond crystallization in the S−C system under HPHT conditions are scarce,[9,10] requiring further investigations. It should also be noted that experimental studies on diamond crystallization processes in the S−C system are of importance for understanding the conditions of natural diamond formation. For example, Haggerty,[11] considering models of diamond genesis, regarded sulfur as a possible catalyst reacting with hydrogen and carbon to produce different volatiles such as H_2S, COS, or CS_2. Sulfur is a relatively abundant element in the Earth's mantle,[12] forming mainly Fe and Ni sulfides, which are frequently observed as inclusions in natural diamonds[13,14] and may be involved in the diamond crystallization process.[11,15−17]

The present work is devoted to the study of diamond crystallization in the S−C system over a wide range of temperatures from 1550 to 2000 °C and pressures from 6 to 7.5 GPa and characterization of the synthesized diamond crystals.

Experimental Section

The starting materials were a graphite rod (99.99% purity), sulfur powder with purity not less than 99.99 %, and cuboctahedral synthetic

diamond crystals (500 μm) as the seed crystals. Experiments were carried out using an 8-6 type multianvil "split-sphere" apparatus with eight steel outer anvils, six tungsten carbide inner anvils and a 300 mm outer diameter of the sphere.[18] A high pressure cell had the shape of a tetragonal prism 19 × 19 × 22 mm with a graphite heater 9 mm in diameter and 15.8 mm in height. Temperature was measured in each experiment with a Pt−30% Rh/Pt−6% Rh thermocouple. Pressure was calibrated at room temperature by the change in resistance of standard substances and at high temperatures by the graphite−diamond equilibrium. Details of the calibration of the pressure−temperature (P−T) parameters have been presented elsewhere.[19] A graphite rod was machined into a capsule 7.2 mm in diameter and 7 mm high. Sulfur powder together with the seed crystals was pressed into a cylindrical sample and placed into the graphite capsule. Some experiments were performed with addition of Ti, as a getter, or H_2O. In the latter case, Pt capsules were utilized. The initial reagents (sulfur, distilled water, and graphite disk) were loaded into a Pt capsule and sealed by arc welding.[19] Phase composition of samples after experiments was examined using a powder X-ray diffractometer (XRD). Spontaneously nucleated diamonds and diamonds nucleated on seed crystals were studied by optical and scanning electron (SEM) microscopy. Crystallographic indices of faces of diamond crystals were determined using a two-circle goniometer GD-1. Spontaneous diamond crystals were characterized by infrared (IR) absorption spectroscopy to reveal their impurity content. IR spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer fitted with a Hyperion 2000 microscope. Inclusions in synthesized diamond crystals were studied by X-ray diffraction (XRD) using a Gandolfi camera and by Raman microspectroscopy. Raman spectra were measured using a Bruker Senterra dispersive Raman microscope.

Results and Discussion

The results of experiments performed in the S−C system at 6.3, 7.0, and 7.5 GPa and temperatures ranging from 1550 to 2000 °C are summarized in Table 1. Duration of the experiments was from 3 to 40 h. Long run times were applied to minimize the kinetic effects and yield reliable information on the formation of carbon phases in the experiments. At 6.3 GPa, the results differed considerably depending on temperature. At 1550 °C (S-1), neither spontaneous diamond nucleation nor diamond growth on the seed crystals was established. Small amounts of regrown metastable graphite was found on the capsule walls and seed crystals. After the seed crystals were cleaned from the graphite, traces of corrosion were observed on their surfaces. In run S-2 (1650 °C), metastable graphite and slight diamond

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Table 1. Experimental Results^a

run N	P, GPa	T, °C	time, h	diamond growth on seeds	diamond nucleation	mechanism Gr → Dm transformation	α, % Gr → Dm transformation	diamond morphology	metastable graphite
S-1	6.3	1550	12	−	−				+
S-2	6.3	1650	20	+	−				+
S-3	6.3	1750	9	+	+	TGG	<1	{111} > {100}	+^{b}
S-4	7	1550	20	+	−				+
S-5	7	1600	40	+	−				+
S-6	7	1700	40	+	+	FG, TGG	50	{100}, {111}	+
S-7	7	1750	7	+	+	FG, TGG	30	{100}, {111}	−
S-8	7	1800	7	+	+	FG, TGG	40	{111}, {100}	−
S-9	7	1900	3	+	+	FG, TGG	60	{111}, {100}	−
S-10	7	2000	17	+	+	FG	<1	{111}	+^{b}
S-11	7.5	1600	40	+	−				+
S-12	7.5	1700	18	+	+	FG, TGG	20	{100} ≫ {111}	−

^{a} FG, film growth; TGG, temperature gradient growth; α, degree of the graphite-to-diamond transformation ($\alpha = M_{Dm}/(M_{Dm} + M_{Gr})100$, where M_{Dm} is the mass of the obtained diamond and M_{Gr} is the mass of residual graphite). ^{b} In these runs, newly formed graphite is a stable carbon phase.
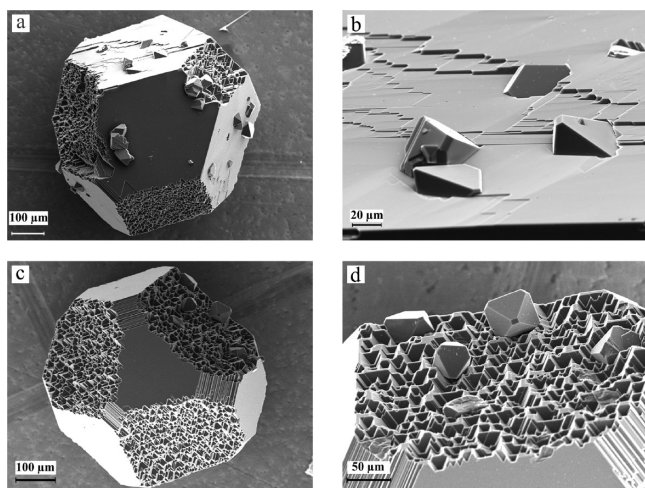

Figure 1. SEM micrographs of diamond seed crystals from run S-3: (a) overall view, (b) growth layers and spontaneous crystals on the (111), (c) seed crystal, and (d) surface morphology of diamond layers on the (100) and (110) surfaces.

growth on the {100} and {111} faces of the seed crystals were detected, but no spontaneous diamond nucleation was established. At 1750 °C (S-3) spontaneously nucleated diamond crystals were found in the bottom part of the capsule. The crystals were up to 50 μm in size and showed dominant {111} and minor {100} faces. Hence, the stable growth form under these conditions is octahedron. Diamond growth layers were detected on the seed crystals. Surface morphology of the growth layers was different depending on the surface indices. The {111} faces showed flat growth layers, whereas pyramidal relief and striation were observed on the {100} and {110} faces, respectively (Figure 1). Specific morphology of the {100} and {110} surfaces resulted from the regeneration by the schemes {100}-to-{111} and {110}-to-{111}, respectively. This means that the seed crystals (cuboctahedrons) transform to a form stable at the experimental conditions (octahedron). In the upper part of the capsule, crystals of metastable graphite with sizes of about 100 μm grown on the initial capsule graphite were found.

In experiments performed at 7.0 GPa and relatively low temperatures, 1550 °C (S-4) and 1600 °C (S-5), regrown metastable graphite and diamond growth layers on the seed crystal were found. Spontaneous nucleation of diamond was not established even in a 40 h run (S-5). Increasing the temperature to 1700 °C (S-6) resulted in intense diamond crystallization. The degree of the graphite-to-diamond conversion in this run was approximately 50%. Synthesized diamond
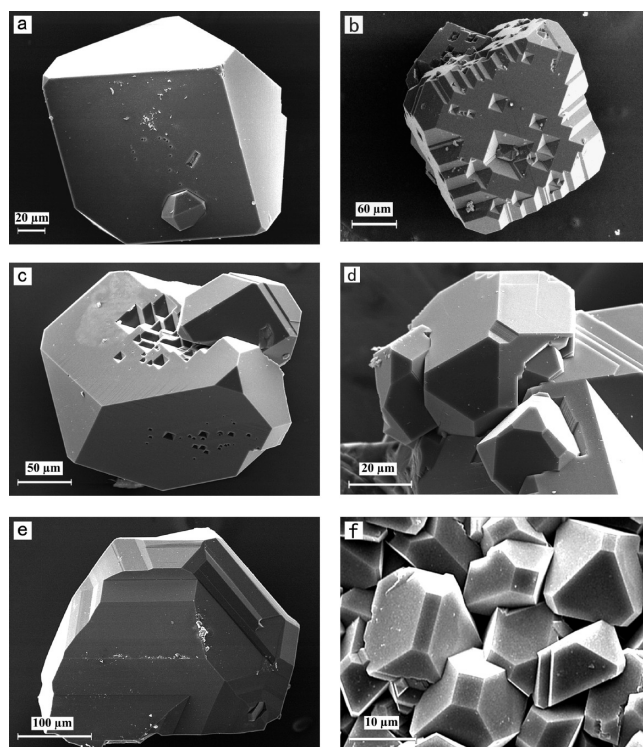

Figure 2. SEM micrographs of diamond crystals synthesized in the sulfur-graphite system: (a, b) crystals with dominating {100} faces from run S-6, (c, d) cuboctahedral crystals from run S-7, (e) diamond twin with octahedron, cube, and trapezohedron faces from run S-8, and (f) octahedral crystals with minor (100) faces from run S-9.

crystals were up to 500−700 μm in size, and sizes of the crystals resulting from growth on seeds reached up to 1 mm. Two types of diamond crystals, formed via FG (film growth) and TGG (temperature gradient growth), respectively, were clearly identified. Previously, diamond crystallization by these methods was described for growth systems of various compositions.[20−23] Small amounts of metastable graphite were found only in the upper part of the capsule. At higher temperatures, 1750 °C (S-7), 1800 °C (S-8), and 1900 °C (S-9), spontaneous nucleation of diamond and diamond growth on seeds were established, but no metastable graphite was detected. Note that as the temperature increased (runs S6−S9), the role of the {111} faces in the crystal habit increased relatively to the {100} faces (Figure 2). In some cases, cuboctahedral crystals showed extra faces (Figure 2e). Goniometric measurements revealed that these faces corresponded to a trapezohedron with crystallographic indexes {411} and {944}, as found previously.[10] At a still higher
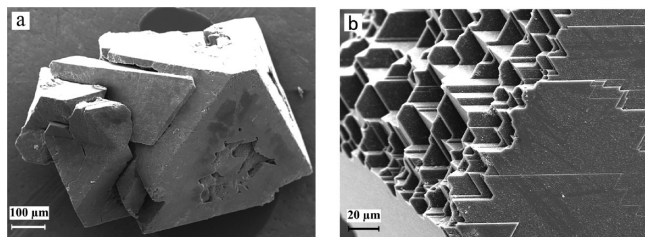
Figure 3. SEM micrographs of diamonds from run S-10: (a) octahedral crystals and (b) regeneration growth patterns on the (100) face and growth layers on the (111) face of seed crystal.

temperature, 2000 °C (S-10), large, up to 400 μm, crystals of metastable graphite, a few black octahedral diamond crystals (Figure 3a), and diamond growth layers on the seed crystals were found. The {100} faces of the seed crystals regenerated by the {100}-to-{111} scheme (Figure 3b).

At 7.5 GPa and 1600 °C (S-11), an aggregate of metastable graphite crystals, located on the capsule cap, and slight diamond growth on seeds were established. Despite a run rime as long as 40 h, no spontaneously nucleated diamonds were found. At 1700 °C (S-12), metastable graphite did not crystallize and both diamond spontaneous nucleation and diamond growth on the seed crystals took place. Morphology of the synthesized crystals varied from cuboctahedron to cube with negligible {111} faces. Diamond crystals produced in all the experiments had yellow color of different intensities from light yellow to greenish yellow. At 7.5 GPa and 1700 °C, an additional experiment (S-13) was performed, where Ti was added to the S−C system as the getter. Diamond crystals produced in this run, like in S-12, showed mainly cubic habit but were colorless or gray. Experiment S-14 was performed at 7.0 GPa and 1600 °C for 19 h in the S−H$_2$O−C system. It was found that during the experiment the Pt capsule lost its hermiticity due to the reaction of Pt with S and formation of PtS sulfide. Nevertheless, almost all initial graphite transformed to diamond. The produced diamond crystals had a light-yellow color and showed an exclusively octahedral habit. Note that at the same $P-T$ conditions and considerably higher run time (S-5), no spontaneous nucleation of diamond was observed in the S−C system. Consequently, addition of H$_2$O to the S−C system leads to a decrease in $P-T$ conditions of diamond synthesis.

The results of experiments on crystallization of carbon phases in the S−C system, including data from previous studies, are summarized in a $P-T$ diagram shown in Figure 4. First of all, note that the $P-T$ conditions of diamond synthesis in the S−C system, determined in this study, are considerably lower than those established previously.[9] This can be accounted for by much longer run times in our study (from 3 to 40 h) than in the work of Sato and Katsura,[9] where experiments were within 1 h long. This demonstrates that kinetic effects play an important role in the diamond nucleation processes. In addition, our results reveal a systematic change in the crystallization of carbon phases as the temperature increases: metastable graphite → metastable graphite, diamond growth on seeds → metastable graphite, and spontaneous nucleation of diamond → spontaneous nucleation of diamond only. A similar tendency was previously found for other nonmetallic systems, e.g., carbonate−silicate[24] and carbonate−chloride.[23] Figure 4 also demonstrates a systematic change of diamond morphology from cube to octahedron depending on $P-T$ conditions. Similar dependence has been established previously for metal−carbon systems.[25,26]

In the preceding studies[9,10] it has been suggested that diamond crystallization in the S−C system takes place from carbon
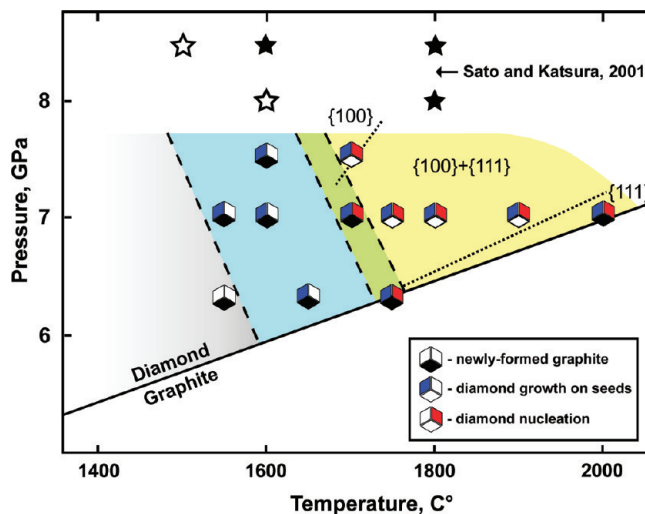

Figure 4. $P-T$ parameters of diamond and graphite crystallization in the S−C system. Dashed lines demarcate fields of crystallization of carbon phases. Dotted lines demarcate fields of crystallization of diamond crystals with a cubic, cuboctahedral, and octahedral habit. Stars refer to experiments of Sato and Katsura[9] (open and solid symbols indicate whether diamond synthesis was found or not, respectively).
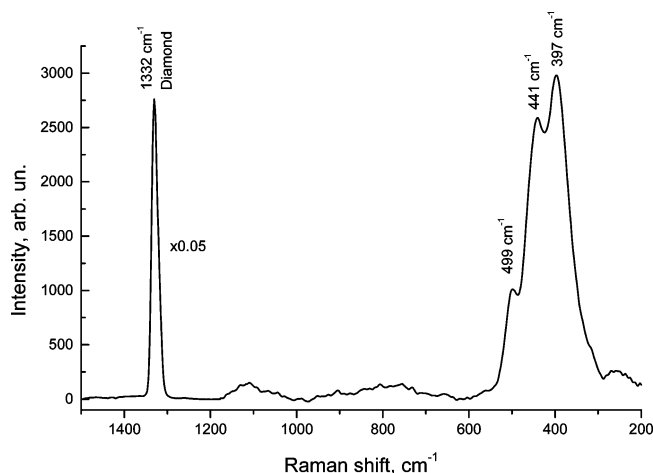

Figure 5. Micro-Raman spectrum recorded from the red inclusions. A peak at 1332 cm^{-1} is due to a diamond.

solution in sulfur melt. This conclusion was made on the basis of the fact that the XRD patterns of the run products showed dominant reflection corresponding to orthorhombic sulfur (α-S) and diamond. Note, however, that some minor reflections, which could be assigned to sulfur oxide graphite (CSO$_3$), were also observed.[10] In the present study, we found that synthesized diamonds contained two types of inclusions: dark-red and black. Diamond crystals with the red and black inclusions were studied by X-ray diffraction using a Gandolfi camera. The XRD patterns of the substance constituting red inclusions showed reflections (d/n) at 2.11, 4.09, and 2.88 Å, in the intensity decreasing order. Analysis of the black inclusions showed that they are composed of another phase(s) with the main reflections (d/n) at 4.13, 3.73, and 1.64 Å. It is clear that neither red nor black inclusions correspond to α-S. Furthermore, using available XRD databases, we were unable to identify these substances. Figure 5 shows a Raman spectrum recorded for the red inclusions. It consists of at least three relatively broad overlapping peaks at 397, 441, and 499 cm^{-1}. This spectrum differs from those known for sulfur at high pressures[27] or solid CS$_2$, measured at high pressures
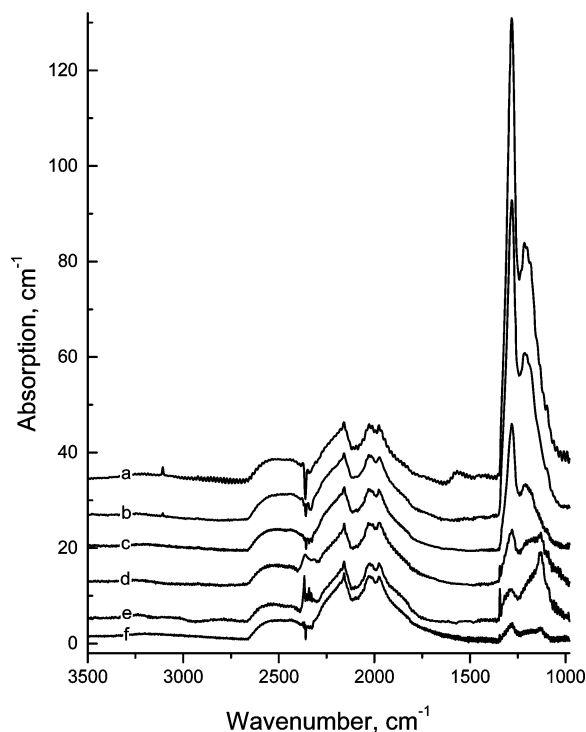
Figure 6. Typical FTIR spectra recorded for diamond crystals synthesized in the S−C system: (a, b) run S8, (c, f) run S6, and (d, e) run S7. Spectra have been displaced vertically for clarity.

using diamond anvils.[28] According to the phase diagram of CS_2, constructed for pressures up to 20 GPa and temperatures up to 600 °C,[28] it is supposed that at high pressures and elevated temperatures the most likely phase is the black polymeric form of CS_2.[28,29] Taking into account the results of preceding studies, we may suppose that the most likely medium of diamond crystallization is the melt of carbon disulfide CS_2, which decomposes upon quenching, producing α-S, detected by XRD in the run products. However, being entrapped as inclusions in diamond, this substance was preserved and after experiments formed "red" and "black" phases.

For the infrared absorption measurements, a number of spontaneous diamond crystals of suitable sizes and quality were selected. Typical IR spectra recorded for diamonds crystallized in the S−C system are presented in Figure 6. All of the samples showed absorption in the defect-induced one-phonon region ($1400-800$ cm^{-1}) caused by nitrogen impurity. In most cases, the A-form of nitrogen (pairs of nearest neighboring substitutional nitrogen atoms) prevailed, but some samples also showed absorption due to the C-form of nitrogen (single substitutional nitrogen atoms). The strength of the nitrogen related absorption varied significantly between the samples even from the same growth run. The nitrogen content in the form of A and C defects was determined by decomposing the IR spectra into A and C components and using the conversion factors of 25 atomic ppm cm^{-1} of absorption at 1130 cm^{-1} for the C defects and 16.5 atomic ppm cm^{-1} of absorption at 1282 for the A defects.[30] The calculations gave values of nitrogen concentrations ranging from less than 50 ppm to approximately 1500 ppm. As a rule, samples with higher nitrogen concentrations contained nitrogen impurity mainly in the form of the A defects. This partly can be accounted for by the fact that the rate of nitrogen aggregation (conversion of C-form nitrogen to A-form) increases with increasing initial nitrogen content. In addition, since this process is a kinetic phenomenon, diamonds crystallized in the same run

but at different points of time would show different degrees of nitrogen aggregation. Samples with high concentrations of A defects also exhibited a weak absorption peak at 3107 cm^{-1}, which is related to hydrogen-related point defects. Diamond crystals synthesized in the S−H_2O−C system (S-14) contained both A and C defects with concentrations of approximately 250 and $150-180$ ppm, respectively. Diamonds produced in run S-13 (S−C+Ti) showed no detectable defect-induced absorption, indicating that Ti acted as the nitrogen getter.

Summary

The minimal $P-T$ conditions of spontaneous nucleation of diamond in the S−C system are determined by both temperature and pressure and are equal to 1750 °C at 6.3 GPa, 1700 °C at 7 and 7.5 GPa and, taking into account the data of Sato and Katsura,[9] between 1500 and 1600 °C at 8.5 GPa. At pressures in the range of $6-7.5$ GPa and temperatures $1550-1600$ °C, spontaneous crystallization of metastable graphite and slight diamond growth on the seed crystals take place.

In the S−C system with an increase in crystallization temperature in the range of $1700-2000$ °C at $6.3-7.5$ GPa, the morphology of diamond crystals changes gradually from cubic habit to octahedral habit. Diamond cuboctahedrons exhibit sometimes the {411} and {944} faces. The degree of the graphite-to-diamond conversion considerably increases with temperature.

The most probable medium of diamond crystallization in the S−C system is melt of carbon disulfide CS_2, rather then sulfur melt, as supposed previously.

FTIR microspectroscopy revealed that the diamond crystals contained nitrogen impurity in the form of A and C centers. In experiments with a long duration, strong variations in both total nitrogen content from ≤10 to 1500 ppm and nitrogen aggregation degree from <10 to 90% were found. This probably is due to formation in long experiments of diamonds of different generations. For crystals with high nitrogen content, hydrogen-related centers are typically observed.

Addition of water to the S−C system leads to a decrease in the diamond synthesis temperature and a drastic change of diamond morphology from cuboctahedron to octahedron. The diamond crystallization environment in this case is a C−O−H−S fluid. Spectroscopic analysis of synthesized crystals revealed nitrogen impurity in the form of A and C centers with a total concentration of about $400-500$ ppm. Addition of Ti to the S−C system results in crystallization of nitrogen-free type IIa diamonds.

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