THE EFFECT OF HEATING AND PRESSURE ON SOME PHYSICAL PROPERTIES OF DIAMONDS

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1968

SovietRxiv

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UDC 548.4

CRYSTALLOGRAPHY

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THE EFFECT OF HEATING AND PRESSURE ON SOME PHYSICAL PROPERTIES OF DIAMONDS

(Presented by Academician N. V. Belov, 31 I 1968)

The study of the effect of heating under pressure on the properties of diamonds is of interest in connection with those changes that occur in crystals as a result of various diffusion phenomena. In paper (^{1}), a possible similarity was indicated between disturbances of the crystal lattice of diamond caused by neutron bombardment and by the action of high temperatures and pressures. Dyer (^{2}) proposed that, under natural conditions, type Ib diamonds were transformed into type Ia diamonds through migration of dispersed nitrogen and its condensation into platelets. The study of such transformations is of practical importance, since diamonds with an increased concentration of platelets possess great

Table 1

Principal features of the crystals studied

Specimen	Origin, habit, and weight in carats	Color of crystals before treatment	Color of crystals after treatment	Intensity of the EPR signal of dispersed nitrogen, in relative units, before treatment	Intensity of the EPR signal of dispersed nitrogen, in relative units, after treatment	Changes in the visible and IR absorption spectra after treatment	Changes after treatment in the absorption spectra in the visible and UV regions
A-1	Natural, irregular form, 1.2 ct	Yellow	Green	70	125	–	–
A-2	Natural flattened octahedron, 0.83 ct	Almost colorless with a yellowish tint	Colorless	20	24	No	Increase in absorption in the region from 3500 Å to the absorption edge
A-3	Natural flattened octahedron, 0.58 ct	Same	Same	9	13	No	Same

Specimen	Origin, habit, and weight in carats	Color of crystals before treatment	Color of crystals after treatment	Intensity of the EPR signal of dispersed nitrogen, in relative units, before treatment	Intensity of the EPR signal of dispersed nitrogen, in relative units, after treatment	Changes in the visible and IR absorption spectra after treatment	Changes after treatment in the absorption spectra in the visible and UV regions
A-4	Natural flattened octahedron, 0.7 ct	Almost colorless with a bluish tint	Did not change	0	0	No	No
A-5	Natural flattened octahedron, 0.7 ct	Almost colorless with a greenish tint	Same	0	0	No	No
A-6	Synthetic diamonds of cuboctahedral habit, total weight 0.1 ct	Yellow-green with predominance of yellow color	Yellow-green with predominance of green color	17	25	–	–

Specimen	Origin, habit, and weight in carats	Color of crystals before treatment	Color of crystals after treatment	Intensity of the EPR signal of dispersed nitrogen, in relative units, before treatment	Intensity of the EPR signal of dispersed nitrogen, in relative units, after treatment	Changes in the visible and IR absorption spectra after treatment	Changes after treatment in the absorption spectra in the visible and UV regions
A-7	Synthetic diamonds with boron impurity, of cuboctahedral habit, total weight 0.1 ct	Black	Black	3	8	–	–
A-8	Synthetic diamonds of cuboctahedral habit, total weight 0.1 ct	Green	Green	112	146	–	–

strength (^{3}). In work (^{4}) the possibility was reported of experimentally studying the migration of nitrogen atoms in diamond. In contrast to the process of nitrogen condensation, which, according to Dyer’ s suggestion, is characteristic

Fig. 1

Figure 1: Fig. 1

of diamonds under natural conditions, heating under pressure of both synthetic and natural crystals leads to an increase in the content of nitrogen in disperse form. In the present work some results of a further study of this phenomenon are presented.

The objects of detailed investigation were 5 natural Yakut diamonds and several varieties of artificial ones, synthesized by a known technology (5–7).

Fig. 1. Characteristic absorption curves of natural diamonds in the ultraviolet and visible regions of the spectrum.
1—before treatment, 2—after treatment

The main features of the crystals studied before and after their treatment are given in Table 1. The treatment consisted in holding the samples for several hours at temperatures of the order of 1000-1200° and pressures of about 55 kbar in a graphite medium.

Absorption spectra were recorded for the natural crystals investigated (both before and after treatment) in the infrared (400-4000 cm^{-1}), visible, and ultraviolet (2200-8000 Å) regions of the spectrum. In addition, changes in the intensities of lines in the EPR spectrum associated with the nitrogen impurity in disperse paramagnetic form were recorded (8,9). Thermoluminescence curves were also recorded for all the samples studied in the temperature range 20-400° (the heating rate during luminescence was 1°/sec). Before luminescence the samples were excited by X-ray radiation (tube with a tungsten anode, current 18 mA, voltage 45 kV). Typical absorption spectra in the ultraviolet and visible regions of the spectrum, as well as the most characteristic luminescence curves, are presented respectively in Figs. 1 and 2. The infrared absorption spectra did not differ from the usual absorption spectra of type I diamonds (10,11) and therefore are not given.

The thermoluminescence curves shown in Fig. 2 indicate a decrease after treatment in the intensities of the luminescence peaks of artificial diamonds in the region 100-115°. As was shown earlier (12), this peak is associated with the presence in the crystals of centers of the $N9$ type (13,14), i.e., donor-acceptor aluminum-nitrogen (or boron-nitrogen) pairs. Thus, it may be considered that under the action of high temperatures and pressures destruction of $N9$ centers can occur.

The change in color of diamond A-1 (see the table) from yellow to green deserves attention. As is known, coloration of diamond crystals green occurs under the action of ionizing radiation (γ, neutron, or electron) (15,16). It is assumed that this coloration is due to centers formed on interstitial carbon and carbon vacancies. Upon annealing, radiation-colored green diamonds change their color

Fig. 2. Characteristic thermoluminescence curves of the initial (a) and pressure-treated (b) diamonds. The curves are designated by the numbers of the corresponding specimens (see Table 1).

Figure 2: Fig. 2. Characteristic thermoluminescence curves of the initial (a) and pressure-treated (b) diamonds. The curves are designated by the numbers of the corresponding specimens (see Table 1).

to golden brown (15,16). A similar coloration is possessed by diamonds with a boron impurity synthesized in a nitrogen medium. Diamonds without a boron impurity, under the same growth conditions, acquire a dark-green color (diamonds A-8).

Paramagnetic centers arising upon irradiation as a result of the capture of electrons by carbon vacancies have been identified by the EPR method; moreover, the intensity of the corresponding lines decreases as the color changes from green to yellow (15).

Depending on the type of diamond, the arising bands of optical absorption are classified as ND-I (interstitial carbon near nitrogen platelets) in type Ia diamonds and ND-II (interstitial carbon near single nitrogen atoms) in type Ib diamonds (16). Bands of the ND type lie in the region 3.2–3.8 eV, in contrast to the GR-I and GR-II bands lying in the region of 2 eV, which are attributed, respectively, to vacancies near nitrogen platelets or single nitrogen atoms (16).

The experimental data presented make it possible to suppose that the effect of heating under pressure is reduced, in our case, to the following:

1. An increase occurs in the nitrogen content in paramagnetic dispersed form owing to the destruction of centers of type $N9$ and the dissociation of platelets or, possibly, molecular nitrogen (N_2), which is present in diamonds and diamond-like crystals (17,18).
2. The number of vacancies and interstitial carbon atoms increases, which is manifested in a change in color and in an increase in absorption in the UV region of the spectrum.
3. Heating under pressure of diamonds not containing nitrogen does not change their color. This indicates that the formation of defects of the vacancy and interstitial-carbon type in crystals containing a nitrogen impurity requires substantially smaller energies in comparison with the energies of formation of analogous defects in nitrogen-free diamonds.

Fig. 2. Characteristic thermoluminescence curves of the initial (a) and pressure-treated (b) diamonds. The curves are designated by the numbers of the corresponding specimens (see Table 1).

All-Union Scientific-Research Institute
for the Synthesis of Mineral Raw Materials

Received
24 I 1968

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Note: Figure translations are in progress. See original paper for figures.