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Abstract

Full Text

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PHYSICS

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INFRARED ABSORPTION SPECTRA OF DIAMONDS WITH DIFFERENT PHYSICAL PROPERTIES

(Presented by Academician A. V. Shubnikov, 28 IV 1965)

Despite the numerous works devoted to the study of diamond absorption spectra in the IR region, the nature of individual absorption bands (especially in the region around 8 μ) is still unclear. Some authors believe that the 8 μ absorption is due to the structural features of diamonds of the so-called type I ([1]) or to defects in the lattice structure ([2], [3]), while others hold that the absorption of diamonds in this region is caused by the presence of impurities ([4], [5]).

Fig. 1. Characteristic absorption spectrum of type I diamonds (sample No. 35)

In a number of works a correlation was noted between the intensity of diamond absorption in the region around 8 μ and their other properties ([1], [2]). Therefore, further study of the IR absorption spectra of diamonds differing in luminescence, absorption in the UV part of the spectrum, color, and other properties is of interest.

Figure 1 gives a characteristic spectrum of a type I diamond (sample No. 35), and Table 1 gives the positions of the absorption-band maxima of the samples studied. It should be noted that differences in the sizes and thicknesses of the samples, as well as in the resolving power of the instruments used, may account for some discrepancy in the positions of the absorption maxima. For these reasons it was difficult to make a quantitative estimate of the intensities of the absorption bands.

From the data given in Table 1 it is seen that, in the interval 4-6 μ, in the region of lattice absorption of diamonds, the absorption spectra of different samples are almost identical, and the main differences lie in the absorption in the region 7-9 μ. Samples Nos. 655, 1610, 70M, and 9012 are transparent in the region 7-

9 μ. Their transparency edge in the UV region of the spectrum lies, for samples Nos. 655 and 70M, near 2250 Å, for No. 9012 near 2300 Å, and for 1610 near 2500 Å; in the Laue photographs obtained from these samples,

there are no secondary extra-reflections characteristic of type I diamonds (ˆ6). Diamonds Nos. 655 and 1610 have a blue glow under photoexcitation; diamonds Nos. 70M and 9012 do not luminesce. Diamonds Nos. 70M, 9012, and 136, under the action of mixed reactor radiation (integral dose 10^{17} neutrons/cm^2), acquired a dark-green color. Sample No. 136 was then subjected to heat treatment (annealing for 30 h at 600°), after which the green color changed to ruby-red. However, the absorption of these diamonds in the IR region of the spectrum did not

Table 1

Positions of the maxima of diamond absorption bands in the IR region of the spectrum

Sample No.	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
35	1097		1190	1236		1368	1967		2017	2154
655			Transparent				1975*			2160
1610			Transparent				1980*		2020	2170
70M**			Transparent					2003	2041	2160
9012			Transparent					2003	2044	2170
40A	1095		1188	1236		1368		2003	2044	2164
136***	1093	1116*	Intense band	Intense band	1315*	1378		2004	2004	2164
1668***	1100		1202	1290			1975		2025	2170
228		Transparent		1288				2004	2004	2164
202		Transparent		1232				2003	2004	2160
10	1096		1176	1238		1377			2041	2173
47	1100		1176	1238		1377			2041	2172
14	1100		1176		1324	1377			2041	2073
107	Very intense band	Very intense band	1176		1333				2041	2124
6745	1100		1182	1230	1315	1368	1990	2015		2170
13420	1100		1182	1294		1376		1955		2170
2457	Very intense band	Very intense band	Very intense band	Very intense band	1342*	1384			2036	2173
26A	1097		1190	1236			1967		2017	2155

* Approximate position of the band edges.
** Spectra identical before and after irradiation.
*** Spectra identical before and after irradiation and heat treatment.

change. This permits the assumption that the crystal-lattice defects formed in diamonds under the action of radiation (and subsequent heat treatment) do not alter the transparency of diamonds in the region around $8\,\mu$ in transparent samples (Nos. 70M, 9012) and do not affect the intensity or the position of the absorption maxima in diamonds that absorb light in this region (Nos. 136, 1668).

Diamonds Nos. 35, 136, 40A, and 1663 are flattened spinel twins of octahedra (i.e., triangular plates); Nos. 35, 136, and 1668 are transparent and colorless (Nos. 136 and 1668 before irradiation), while diamond No. 40A is slightly smoky in color; all of them do not luminesce under photoexcitation. Their transparency edge in the UV is located at about 2900–3000 Å, where there are absorption lines near 3020, 3036, 3064, 3088, 3110, 3154, 3178, 3200, and 3300 Å. The position of the maxima of the absorption bands of these diamonds in the region around $8\,\mu$ is the same (see Table 1) and does not change after their irradiation (Nos. 136, 1668) with ionizing or mixed radiation and subsequent heat treatment. Diamond No. 1668 was irradiated in a cyclotron with protons of energy 14.5 MeV. The irradiated area of the diamond surface turned dark brown. After heat treatment (20 h of annealing at 700–800°) the color in this thin near-surface layer did not change, but it acquired the ability to luminesce (a yellow-green glow consisting of a narrow line at 5033 Å and a group of adjacent bands) under photoexcitation. An analogous natural

color, luminescence, and absorption in the ultraviolet region of the spectrum is diamond No. 228.

On the basis of electron paramagnetic resonance (EPR) data, it may be assumed that the centers responsible for such coloration and luminescence include displaced carbon atoms (^7). However, the absorption of these diamonds in the region around $8\ \mu$ is different: specimen No. 228 is transparent up to 1288 cm^−1 ($7.8\ \mu$); in the spectra of diamond No. 1668 there are absorption bands near 1100, 1202, and 1290 cm^−1 (9.09; 8.46; $7.8\ \mu$) both before and after irradiation. These data confirm the assumption that such lattice defects as displaced carbon atoms do not affect the absorption of diamonds in the region around $8\ \mu$. In addition, this also indicates that there is probably no direct dependence between the centers of yellow-green luminescence (i.e., centers at λ 503 mμ) and the centers responsible for absorption near $8\ \mu$.

The transparency edge and absorption in the ultraviolet part of the spectrum of the rounded smoky diamond No. 202 are the same as in diamonds Nos. 35, 136, 1668, 228, and others. In the luminescence spectrum of this diamond, in addition to the blue and yellow-green components, a group of lines near 6000 Å is observed ([8,]9). According to EPR data (^7), it may be assumed that they contain a boron impurity. However, the absorption of smoky diamonds in the infrared region is analogous to the absorption of brown specimens and differs by greater transparency (the maxima at 9.09 and 8.46 μ are absent) from colorless diamonds, diamonds colored by irradiation, and other specimens (except Nos. 1610, 70M, 655, and 9012). Thus, with respect to absorption in the 8 μ region, brown and smoky diamonds occupy an intermediate position between type I and type II diamonds according to (⁀6).

Diamonds Nos. 10, 14, 47, 107 are round-stepped crystals of octahedral habit, formed by rather thick growth layers, clean, colorless, transparent (⁀9). Their luminescence spectra have the same structure and contain the 4152 Å line, a group of adjoining bands, and a yellow-green component, in which the most intense lines are located near λ 4891 and 5234 Å. The difference in the energies of these lines is ~0.165 eV (~7.5 μ), which corresponds to the region of one-phonon absorption of diamonds.

In the ultraviolet part of the spectrum, the transparency edge of diamonds of this type differs for different specimens. Thus, specimens Nos. 10 and 47 are transparent up to 2900 Å; in their absorption spectra, lines are observed in the 3020–3300 Å region; the transparency edges of diamonds Nos. 14 and 107 lie near 2600 and 2300 Å, respectively, and in their absorption spectra there are no lines in the 3020–3300 Å region. In the literature it has been suggested (1,6) that between the transparency edge of diamonds in the ultraviolet part of the spectrum and in the infrared region around 8 μ there is a reliable correlation: diamonds whose transparency edge lies in the 2200–2800 Å region are also transparent in the region around 8 μ; diamonds in which continuous absorption begins near 2800–3000 Å also absorb in the region around 8 μ. This correlation is also observed in the specimens (with the exception of Nos. 14 and 107) studied in the present work.

It seems possible to us to explain the presence of absorption bands near 8 μ in specimens Nos. 14 and 107, which are transparent up to 2600–2300 Å, on the basis of the features of their luminescence spectra. The distance between the two narrowest and most intense luminescence lines is approximately 0.165 eV. This makes it possible to assume the presence in these diamonds of levels, transitions between which may give rise to absorption near 8 μ, independently of the transparency edge of such diamonds in the ultraviolet region and of the presence in them of the usual centers responsible for absorption near 3000 Å and absorption in the region around 8 μ, found in the remaining diamonds.

The transparency edge of diamonds Nos. 6745, 13420, 2457, and 26A in the ultraviolet region of the spectrum is located near 3000 Å. These specimens differ from one another

from one another in their luminescence spectra, color, and impurities. Diamond No. 6745 is colorless, No. 13420 is a yellow-green one, No. 2457 is a golden-yellow octahedron, and No. 26A is a yellow cube. In the study of diamonds by EPR methods it was established (7) that colorless pure crystals give no signal in the EPR spectrum. The EPR spectra of differently colored diamonds proved to be highly individual and complex. Only in the simplest cases was it possible to decipher them for certain groups of diamonds: brown diamonds (Nos. 1668 and 128) contain displaced carbon atoms, smoky ones (No. 202) contain boron, and yellow cubes and octahedra (No. 26A) contain nitrogen. The EPR spectra of diamonds Nos. 13420 and 2457 proved to be very complex, and it was not possible to decipher them. The absorption of diamonds Nos. 6745, 13420, 2457, and 26A in the region around 8μ does not differ substantially from the absorption spectra of colorless and pure diamonds (Nos. 35, 136, 1668, etc.).

Sutherland, Blackwell, and Simeral (2) divided all infrared absorption bands of diamonds in the region of 8μ into group A—1093, 1203, 1282 cm^{-1} (9.1, 8.3, 7.8 μ) and group B—780, 1003, 1171, 1332, 1426 cm^{-1} (12.9, 10.0, 8.5, 7.5, 7.3, and 7.0 μ). Later Kaiser and Bond (5) concluded that the presence of group-A bands is due to a nitrogen impurity. In the specimens studied in the present work, we were unable to obtain either the parallelism, noted by the authors (2), in the appearance of separate groups of bands, or a parallelism between their intensity and absorption near 3154 or 4152 Å, or to relate them to a nitrogen impurity.

Thus, from an analysis of the results obtained it follows that:

1. Between the absorption of diamonds in the infrared region around 8μ and in the ultraviolet region of the spectrum there is a sufficiently clear correlation: diamonds transparent in the ultraviolet down to 2250-2700 Å are also transparent in the infrared region around 8μ. Diamonds transparent down to 2800-3100 Å (in whose absorption spectra a group of bands is observed in the interval 3020-3300 Å) also absorb in the region around 8μ. Apparently, the centers responsible for absorption around 3000 Å also determine the absorption around 8μ.

2. These centers are not formed after irradiation of diamonds with protons or neutrons, nor after irradiation followed by thermal treatment. Thus, they are not defects of the diamond crystal lattice that can be formed in diamonds as a result of such action.

3. It may be assumed that these centers are due to the presence of impurities in diamonds. However, within the limits of the sensitivity attained, we were unable to identify the type of impurity with the impurities previously determined in diamonds (7,10).

4. The conclusions made above do not apply to diamonds of the type Nos. 10, 14, 47, 107, which have a special structure of the yellow-green component of the luminescence spectra. In these diamonds, absorption around 8μ may be due to transitions between levels responsible for the luminescence lines 4890 and 5203 Å, and is not connected with absorption in the ultraviolet region of the spectrum.

5. No correlation was found between absorption around 8μ and the intensity of the blue and yellow-green (centers 415 and 503 mμ) luminescence of

diamonds.

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