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High-pressure–high-temperature treatment of natural diamonds

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Abstract

The results are reported of high-pressure–high-temperature (HPHT) treatment experiments on natural diamonds of different origins and with different impurity contents. The diamonds are annealed in a temperature range up to 2000 °C at stabilizing pressures up to 7 GPa. The evolution is studied of different defects in the diamond crystal lattice. The influence of substitutional nitrogen atoms, plastic deformation and the combination of these is discussed. Diamonds are characterized at room and liquid nitrogen temperature using UV–visible spectrophotometry, Fourier transform infrared spectrophotometry and photoluminescence spectrometry. The economic implications of diamond HPHT treatments are discussed.

1. Introduction

A perfect diamond is absolutely colourless: photons from the visible range of the electromagnetic spectrum do not have sufficient energy to excite electrons from the very strong covalent bonds holding the diamond crystal together. Colour in diamond is produced by atomic scale impurities, the most common of which are substitutional nitrogen atoms [1]. These can be present in isolated form, or in aggregates of two, three, four and more atoms, very often in combination with vacancies. In general, nitrogen leads to yellow and orange–brown colours. According to the dominant nitrogen aggregate impurity, diamonds are classified as type IaA (containing predominantly A centres, i.e. nitrogen pairs), type IaB (containing predominantly B centres, i.e. groups of four nitrogen atoms, tetrahedrally surrounding a vacancy), type IaAB (containing both A and B centres) and type Ib (containing predominantly C centres, i.e. isolated substitutional nitrogen atoms). Very pure material, containing extremely small impurity concentrations, is called type IIa. Diamonds containing substitutional boron atoms

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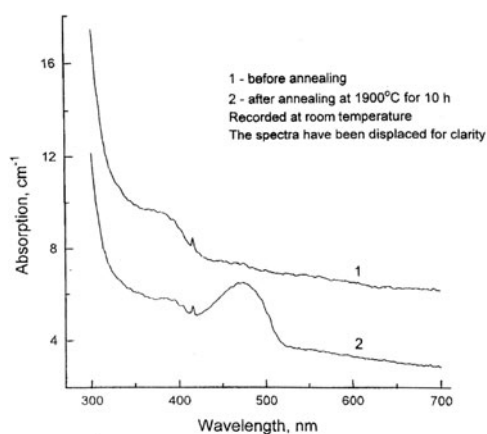


Figure 1. The optical absorption spectrum at room temperature for a type IaAB sample before and after HPHT treatment at 1900 °C for 10 h. The broad additional absorption band below 500 nm is due to H3 centres.

as the dominant impurity are classified as type IIb. In general their colour is blue to greyish blue. Colour in diamond can also be produced by more extended defects, such as those related to plastic deformation. In diamonds showing this phenomenon, slip planes along the (111) directions have been created by shearing stress at high temperature, deep below the surface of the Earth. Plastic deformation can easily be made visible using crossed polarization filters. In many cases, colour bands (mainly brown; in exceptional cases pink) can be seen to be associated with the slip traces. Coloration due to lattice distortion is quite common in natural type IIa diamonds. It can, however, also be observed in some material containing larger nitrogen concentrations. Typical examples are many stones from the Argyle mine in Western Australia.

Recent developments have stimulated considerable interest in defects related to plastic deformation [1, 2]. In 1999 a new commercial diamond colour enhancement method was announced in the USA by General Electric and Lazare Kaplan International. It was claimed that the technique allowed removal of the colour from a limited number of brown diamonds, making them (nearly) colourless. Subsequently it became clear that in this method, brownish type IIa material was subjected to high-pressure–high-temperature (HPHT) treatment, to remove the colour related to plastic deformation.

Later, a similar technique was announced by another US company, Novatek. Here, the main commercial application is the transformation of brownish type Ia material (showing plastic deformation) to yellow–green material using a HPHT treatment. Finally, it has become clear that similar techniques have existed for several years in Russia. The important economic implications surrounding these developments have caused researchers to focus more investigations on the nature of colour changes in diamond and to develop methods of detecting HPHT-treated stones. It is important to note that recently worldwide patent applications have been filed by General Electric, to protect the treatment methods and treatment detection techniques [3].

2. Experimental details and results

Natural diamonds of different types were HPHT treated using a ‘BARS’-type multi-anvil high-temperature press [4]. All samples were treated in the diamond stability region of the carbon phase diagram. Annealing experiments were performed on natural diamonds of type IIa, IaAB, IaB and mixed type Ib–IaA, in a temperature range up to 2000 °C at stabilizing pressures up to 7 GPa. The diamonds were characterized at room and liquid nitrogen temperature using UV–visible spectrophotometry, Fourier transform infrared (FTIR) spectrophotometry and photoluminescence spectrometry. Some typical examples are discussed here.

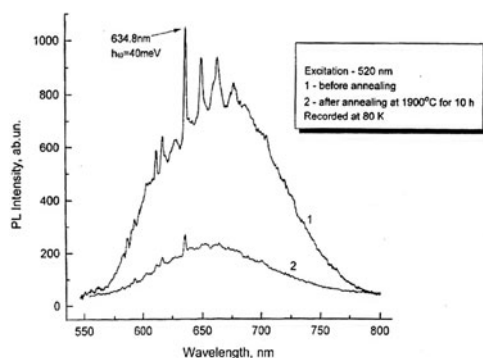


Figure 2. The photoluminescence spectrum at 80 K for a mixed type Ib–IaA sample before and after HPHT treatment at 1900 °C for 10 h.

Several light yellowish-brown type IIa diamonds, showing signs of plastic deformation, were treated for up to 12 h at $T = 1500\text{--}1900\text{ }^{\circ}\text{C}$ and $P = 7\text{ GPa}$. A decrease in the brownish coloration was observed after the treatment at 1900 °C.

A typical Argyle type IaAB yellowish-brown diamond of 0.20 ct, showing signs of plastic deformation, was treated for 10 h at $T = 1900\text{ }^{\circ}\text{C}$ and $P = 7\text{ GPa}$. After annealing, the sample showed a yellow–green colour, mainly due to optical absorption by and fluorescence of H3 optical centres (a combination of two nitrogen atoms and a vacancy, N–V–N, with a zero-phonon line at 503 nm). Absorption spectra before and after treatment are shown in figure 1. Before treatment the sample showed blue fluorescence due to N3 centres (three nitrogen atoms and a vacancy, with a zero-phonon line at 415 nm). This fluorescence was strongly inhomogeneous. A large part of the sample was inert under UV excitation. After annealing, a strong greenish luminescence was observed, due to H3 centres. This luminescence too was inhomogeneous. It dominated in areas which were inert before annealing. In the infrared spectrum, the ‘amber centre’ (a series of broad absorption bands near 4150 cm^{-1}) disappeared completely upon treatment.

A number of mixed type Ib–IaA natural diamonds of African origin were HPHT treated at $T = 1900\text{ }^{\circ}\text{C}$ and $P = 7\text{ GPa}$ for 10 h. The results of the annealing were most obvious in the photoluminescence spectra. A large number of different features were observed, obviously due to the variation of the defects present in the natural stones [5]. An interesting example is shown in figure 2, for a 0.12 ct sample. A photoluminescence band with the zero-phonon line at 634.8 nm and replicas due to phonons with energy of 40 meV are observed.

As could be expected, aggregation from isolated nitrogen to A centres was observed in the infrared spectra. This is illustrated in figure 3 for a 0.19 ct sample.

In the infrared spectra, the amber centre disappeared from all stones in which it was observed before treatment. In two of the samples, the carbon–hydrogen stretch vibration line at 3107 cm^{-1} was increased by an order of magnitude. This is not a general rule, however. For other stones it was essentially unchanged after treatment.

A light yellowish-brown type IaB diamond showing plastic deformation and containing a very low concentration of nitrogen impurities (estimated to be approximately 20 ppm) was HPHT treated for 12 h at $T = 1850\text{ }^{\circ}\text{C}$ and $P = 7\text{ GPa}$. Before annealing the stone showed a continuously rising ‘brownish’ absorption spectrum and peaks of the N9 centre (236 and 230 nm). As a result of the treatment the N3 absorption band appeared, indicating the formation of these centres during annealing (figure 4).

Before annealing, the sample showed a weak whitish-blue fluorescence. Due to the treatment this fluorescence increased considerably, mainly because the strength of the N3 band was augmented by about an order of magnitude.

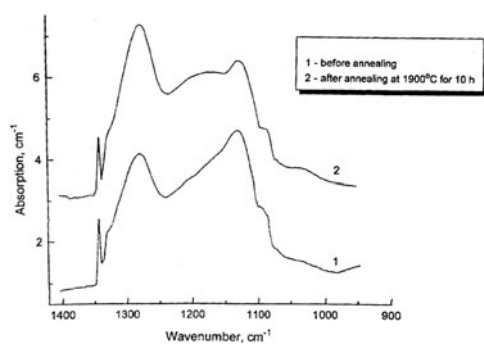


Figure 3. The infrared absorption spectrum at room temperature for a mixed type Ib-IaA sample before and after HPHT treatment at 1900 °C for 10 h. After treatment, increased absorption by A centres (1280 cm^{-1}) relative to C centres (1134 cm^{-1}) can be observed.

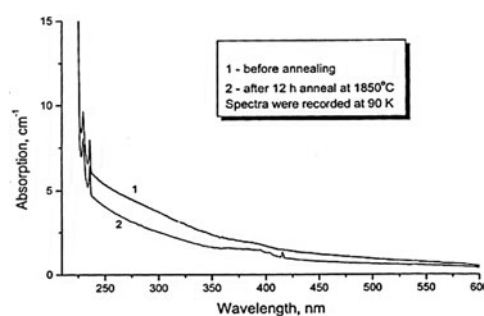


Figure 4. The optical absorption spectrum at 90 K for a type IaB sample before and after HPHT treatment at 1850 °C for 12 h. After treatment the N3 band can be observed.

Finally, it should be noted that the 490.7 nm luminescence line, which is related to plastic deformation, could be observed for this stone before treatment. After treatment it had decreased considerably, in line with claims that this feature can be used for the detection of treated stones [1, 3].

3. Conclusions

Different commercial applications of diamond HPHT treatment are emerging: producing colourless and fancy colour diamonds. These results could have an important influence on the value of the stones. For commercial reasons it is important to develop methods for identifying treated diamonds. HPHT treatment experiments on natural diamonds have shown a wide variety of results, depending on the initial characteristics of the stones. Some of the treatment results are understood, and some are not. It is clear that more research is necessary before the physical processes taking place during treatment can be fully understood.

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