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Spatial distribution of "Amber" defects in diamond: results of IR mapping

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Abstract

Infra-red microspectroscopy was employed for investigation of spatial distribution of point defects in plates cut from natural diamonds. It is shown that distribution of "amber" defects does not correlate with that of the A-defects; moreover, they appear anticorrelated. Available data suggest that although formation of the "amber" defects is related to deformation processes, it also requires presence of exotic set of point defects.

Keywords: Diamond, infra-red spectroscopy, "amber" defects

Introduction

Infra-red spectra of plastically deformed brown diamonds, often with orange, gray, yellow, rose and green hues, sometimes contain set of absorption bands with maxima between 4000-4200 cm^{-1} (Massi et al., 2005). These defects were initially observed in yellow-brown diamonds with "amber" colour and thus were termed "amber". At present the amber defects (below AC) are found not only in brown diamonds with obvious slip planes ("graining"), but also in some rose-purple crystals with mechanical twinning (Titkov et al., 2008); in greenish-yellow and yellow diamonds where the dislocations are not confined to {111} planes (Titkov et al., 2015). Visible spectra of some of these samples lack absorption continuum responsible for the brown coloration.

At least four types of the "amber" centers are established (Massi et al., 2005). Few properties of the "amber" defects are reliably known: 1) in absolute majority of cases the ACs are observed in diamonds with significant nitrogen concentration in the A-form (note, however, that Samsonenko et al., 1974) reported similar absorption bands in deformed type II diamonds); 2) the amber defects are destroyed by heat treatment (Reinitz et al., 2000); 2) upon cooling fine structure of the IR absorption peaks becomes visible; moreover, at least some of the features show very strong temperature dependence (Massi, 2006). Up to present models of the amber centers (AC) remain unknown, albeit it was suggested that ACs are directly related to the nitrogen A-defects (N-N pair in diamond lattice) destroyed by dislocations. They might, therefore, be related with paramagnetic W7 center [N-C_2-C_2-N^+] (Massi et al., 2005)

With few exceptions, studies of IR bands of the amber centers were performed either on cut gem diamonds with related complications in spectra acquisition, or using large apertures. In the same time, it is well known that diamonds often possess complex internal structure and studies of bulk crystals may give biased results. In this Letter we present results of IR mapping of several natural diamonds containing amber defects with the aim to correlate its distribution with that of other IR-active defects.

Samples and methods

Spectral maps and linear profiles allowing investigation of spatial distribution of IR-active defects were acquired at room temperature using SpectrumOne (Perkin Elmer) FTIR spectrometer equipped with AutoImage IR microscope with corresponding software. Size of the studied regions was up to 6 mm^2. Square apertures with sizes between 50 and 100 microns were employed. At least 50 scans (in most cases 100 or more) with spectral resolution of 4 cm^{-1} were acquired in every point. All spectra were background-subtracted and normalized to the diamond lattice absorption at

2030 cm^{-1}. The contribution of the amber peak was calculated as an integral in the range 4153-4198. cm^{-1} (see Fig. 1). Due to large number of spectra we have not performed decomposition of one-phonon spectral region into the A- and B-nitrogen defects and only intensities at 1282 and 1175 cm^{-1} were taken into account. Albeit this process may introduce certain error, for purposes of the current largely qualitative investigation it is small enough due to predominance of the A-defects in most studied samples.

Polished plates laser-cut from several types of natural diamonds from placers of north-east part of Siberian platform were studied. Some of these crystals were previously studied using photoluminescence and optical spectroscopy (Zudina et al., 2013); EPR (Mineeva et al., 2013). Results of detailed spectroscopic and isotopic studies of samples 1P and 2P are given in (Titkov et al., 2015) and (Reutsky et al., 2017). In addition several natural and synthetic diamonds deformed in various conditions were studied. The current work presents data specifically related to the amber defects.

Results

Figure 1 shows several representative spectra of one of the studied diamonds. A small, but clearly observed unsymmetrical peak with maximum at 4166 cm^{-1} is due to the type I amber defect (AC1) in classification suggested by Massi et al., 2005. Broad shoulder towards high wavenumbers is due to transitions unresolved at room temperature.

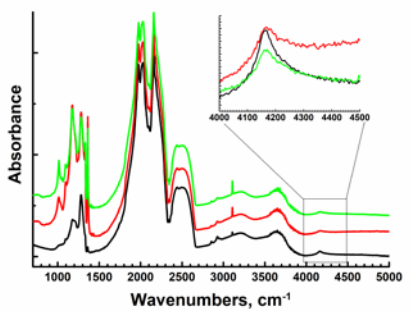

Fig. 1. Representative IR spectra of one of the studied diamond specimen; spectra of zones with variable content of nitrogen-related defects are shown. Inset shows range with bands due to the amber defect.

Top row of the Figure 2 shows distribution of the A- and amber defects in central part of the diamond specimen 1P (for details see Titkov et al., 2015). The central part of this crystal is almost pure IaA diamond with N content up to 465 at ppm; N content decreases considerably towards periphery. In the same time, the distribution of the AC1 defect does not follow obvious pattern and these defects tend to concentrate in a domain with relatively low content of A-defects.

Figure 2 c-d shows similar maps for a region in the specimen 2P. Again, no correlation between distribution patterns of the A- and AC1 defects are observed.

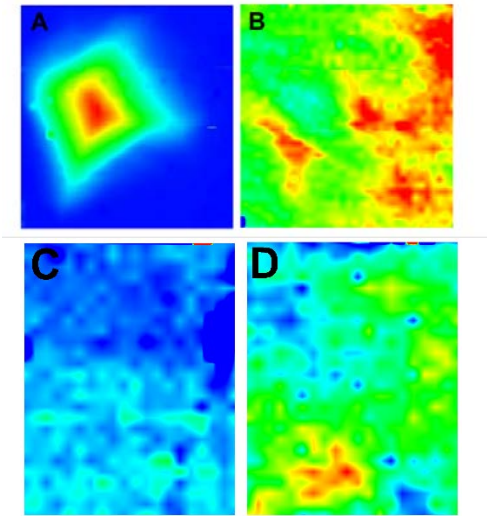

Fig. 2. Maps of the A-defect (A, C) and type I amber defect (B, D) distributions. Top row – sample 1P (horizontal size 3.4 mm), bottom row – 2P (horizontal size 1.8 mm) (Titkov et al., 2015). Red indicates stronger absorption. The relative intensity of the colors differ between the images and is selected to improve perception. Methods of the maps' production is described in corresponding part of the paper.

A Figure 3 shows a representative map of spatial distribution of the amber defects and of A nitrogen-related center in a strongly deformed natural diamond. The figure clearly shows that the type I amber defects are most abundant in the elongated zone characterised by low content of total nitrogen and of the A-defects in particular. This zone is adjacent to a region enriched with microinclusions (most likely mica), which lies closer to a growth center of the crystal and tentatively one might suggest that the amber defects populate a new growth zone. We note that somewhat similar situation was earlier noted for the Amber defect type III, which is distributed as a narrow band (~1 mm) in peripherial part of a diamond specimen 1P (Titkov et al., 2015).

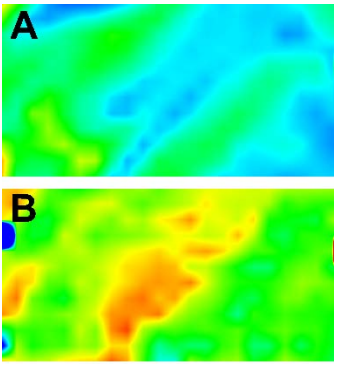

Fig. 3. Maps of the A-defect (A) and type I amber defect (B) distribution in strongly deformed natural diamond. Horizontal size 1.2 mm.

Re-examination of IR spectra of synthetic diamonds intentionally heavily deformed at HPHT conditions (Shiryaev et al., 2007) show weak features with maxima around 4068 cm^{-1} which might represent the amber defect type 4, thus supporting the deformation origin of these centers.

Discussion and conclusions

Literature data on the amber defects suggest that these defects are intimately related to diamond deformation. Observation of the amber defects only in diamonds where the A-defects are present lead to hypothesis (Massi et al., 2005) that the ACs are similar to paramagnetic centers W7, which can be regarded as an A-defect destroyed by a dislocation, i.e. $[N\text{-}C_2\text{-}C_2\text{-}N^+]$ (Shcherbakova et al., 1975). However, direct correlation between the amber defects and the W7 centers was questioned by (Mineeva et al. 2013) based on investigation of large collection. However, question of relative sensitivity of EPR and IR towards respective defects remains unknown, especially in view of possible heterogeneous spatial distribution. We note that (Samsonenko et al., 1974) reported bands resembling the amber defects in natural brown type II diamonds.

In spatially-resolved study with a 50 μm aperture Massi (2006) showed that absorption by the amber defect is observed only at the deformation band, albeit only few points were acquired. However, in our own investigation of a plate prepared from a natural violet diamond (see Konstantinova et al., 2006 for detailed description of this sample) the amber defect type I (maximum at 4168 cm^{-1}) is present, but its association with optically visible deformation bands is uncertain.

The IR mapping shows that the amber defects are not directly related to the A-defects, rather anti-correlation is observed. One might suggest that the anticorrelation reflects destruction of significant fraction of the A-defects, but such explanation is unlikely. For example, Reinitz et al. 2000, showed that the amber defects are readily destroyed by HPHT treatment in conditions where major N-related defects remain unchanged. Whereas in some diamonds the Amber defects seem to be distributed as spots, in other they form bands with shapes resembling growth zonation. The only plausible mechanism of formation of a narrow deformed zone following growth morphology of a diamond is to propose that at least in some cases nitrogen point defects may strongly influence mechanical properties of diamond (Naletov et al., 1979), resulting in differences in deformation behavior of zones with different types and concentration of point defects.

Therefore, albeit this work does not provide a model of amber defects, it shows that their formation requires both deformation and rather peculiar combination of growth-related point defects.

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