Spectroscopic studies on carbonado diamond

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Carbonado is a natural polycrystalline diamond found in alluvial deposits in the Central African Republic and Brazil. This diamond looks black and is highly porous. Unlike other natural polycrystalline diamonds, carbonado has no mantle-derived inclusions and its carbon isotope value is very low (delta13C = -23 to -30permillage). Additionally, carbonado exhibits strong luminescence (photoluminescence and cathodoluminescence) induced by nitrogen and by vacancies existing in the crystal lattice. The origin of carbonado is controversial, but several hypotheses have been proposed:

1. Direct conversion of organic carbon under high-pressure conditions (the Earth's interior)
2. Shock metamorphism induced by meteoritic impact at the Earth's surface
3. Radiation-induced diamond formation by spontaneous fission of uranium and thorium

For clarifying the origin of carbonado, optical properties(photoluminescence, Raman, and infrared) were investigated in this study. The photoluminescence images and spectra of carbonado were collected using confocal laser microscope (spatial resolution: ˜1 um) and Scanning Near-field Optical Microscopy (SNOM; spatial resolution: ˜300 nm) for studying the heterogeneity of photoluminescence. Raman spectra of carbonado were measured using confocal laser microscope. The Raman shift of diamond is known as pressure scale [1] and the residual stress in carbonado was studied. For photoluminescence and Raman experiments, the studied sample is from Central African Republic (CAR) and was polished to optical grade. Infrared spectra of carbonado were examined for investigating the aggregation state of nitrogen in diamond, because the aggregation state of nitrogen changes with temperature and residence time. For infrared experiments, carbonado was crushed and washed with HF, HClO4, and HNO3.

Mapping of the photoluminescence intensity of carbonado using confocal laser microscope and SNOM showed that the emission intensity was lower at the grain boundaries, indicating that the degree of crystallinity is low at those regions. Photoluminescence spectra of carbonado observed using confocal laser microscope and SNOM comprised three sharp bands at 504, 575 and 638 nm with their side bands and the color of photoluminescence changed according to its location. The results of Raman spectra revealed that the residual stress locally exists underneath the sample surface and the maximum stress value observed in this study was 0.72 GPa. These results supports that carbonado had been at a high-pressure condition. The Raman band width revealed normal width (6.2 cm-1) in full width at half maximum (FWHM), however, in a halo that width increased up to 9.6 cm-1, indicating the crystallinity is low in a halo region. Infrared spectra of carbonado showed the two nitrogen-induced absorption, 1344 and 1282 cm-1. This result indicates that the aggregation state of nitrogen is between Type Ib and Type IaA, and this state is relatively initial stage. This result implies a young age of crystallization, or unusually cool conditions of mantle storage, or both.

[1] H. Boppart, J. van Straaten, I.F. Silvera, Phys. Rev., B 32 (1985) 1423.