

CL AND FTIR MAPPING OF NITROGEN CONTENT AND HYDROGEN DISTRIBUTION IN A DIAMOND FROM THE MIR PIPE - CONSTRAINTS ON GROWTH HISTORY

Griffin¹, Brendon J., Bulanova², Galina P. and Taylor³, Wayne R.

¹Centre for Microscopy and Microanalysis, University of Western Australia, Nedlands, Australia 6907

²YIGS, Russian Academy of Sciences, 39 Lenin Av., Yakutsk 677007, Sakha, Russia

³Department of Geological Sciences, University College London, Gower St, London WC1E6BT, U.K.

Introduction

Cathodoluminescence (CL) and more recently Fourier Transform infrared microspectrometry (FTIR) allow examination of internal structure of diamond and provide information on nitrogen content, hydrogen content and the thermal history of the diamond (Milledge and Mendelssohn, 1988; Meyer et al., 1994) however only few correlative data have been published between the techniques (Taylor et al., 1995). To address this and the more general question of diamond growth, the internal morphology of a polished plate [(110) section] of an octahedral macrodiamond of unknown paragenesis from the Mir Pipe, Yakutia, has been examined in detail through comparison of panchromatic or conventional cathodoluminescence (panCL), monochromatic cathodoluminescence (monoCL) and Fourier Transform infrared microspectroscopy (FTIR) data. This plate has been previously studied by Beskrovanov (1992).

Analytical techniques

The diamond plate was initially examined by conventional CL techniques. The CL from both sides of the plate was compared. The images are similar, indicating that the features observed in CL are essentially orthogonal to the plate surfaces and coherent through the plate. FTIR measurements were then collected on a 200 μm spaced 22 x 22 point grid over the plate. These data have been reduced to yield nitrogen concentration and hydrogen peak area (at 3107 cm^{-1}) data following the methods described by Taylor et al. (1990). PanCL images have been recorded at temperatures from 300 K to 80 K using a liquid helium stage in a scanning electron microscope. A range of monoCL spectra have been recorded at 80 K from the regions of the plate exhibiting variations in panCL and FTIR characteristics.

Results

Three main regions are defined by the panCL and FTIR data (figure 1). Within these regions additional fine zones or complex structures can be identified. The central region, ~300 μm across, is crystallographically complex. It consists of a zonally sectorial structure comprised of octahedral zones of blue luminescence and cubic sectors (lobes) of blue-green luminescence, the latter visible as a skeletal central cross. This complex structure would appear to represent an initial cubo-octahedral growth form. In the growth centre of the diamond is a small black inclusion, possibly graphite. The central region is overgrown by a 300 μm thick region which shows a very low panCL intensity. The outermost region of 800 μm thickness is composed of 50-100 μm wide octahedral layers, which exhibit alternating high and low panCL intensity.

The FTIR data matches closely the pattern of panCL intensity variation. The central region is uniformly high in nitrogen (~600 atomic ppm) and is fully aggregated (pure type IaB diamond). The lobes of the central cross have a lower nitrogen content (~400 atomic ppm) relative to the surrounding octahedral zones. Generally platelets are absent or are low in concentration and restricted to the lobes. The small zone surrounding the growth centre has the highest nitrogen content at ~900 atomic ppm. Nitrogen aggregation is uniformly complete (type IaB) across all sectorial structures in the central region. The intermediate region contains low nitrogen levels

(<100 atomic ppm), is variably aggregated, and may consist of a fine intergrowth type I and type II diamond. The rim contains moderate nitrogen concentrations (~200 atomic ppm) and is predominantly unaggregated (type IaA).

Hydrogen distribution follows the general pattern of nitrogen concentration, being highest in the central region of the diamond and lowest in the rim region. In detail, however, it exhibits a bimodal relationship with the concentration of nitrogen present in the type B defect site. One group of hydrogen data, within the normalised range 1.5 to 2.25, is insensitive to nitrogen variation over a range of 200-700 atomic ppm. These data all lie within the outer zone of the central region of the diamond and are insensitive to the sectorial nature. The remaining hydrogen data is linearly correlated with the 'B' nitrogen concentration and the data points lie with the central core and the outer regions of the diamond. These relationships define three zones within the plate which correlate with the CL and nitrogen distribution data.

The fine structure resolved by panCL, however, is not resolved by FTIR. FTIR cannot resolve structures finer than ~240 nm laterally in contrast to the panCL emission which may resolve structures as fine as 1.5 nm (for a 10 keV electron beam energy). This is evident in a plot of absorbance values at 1313 cm⁻¹ and 1282 cm⁻¹, the mixed FTIR data lying between the 1:1 and 1:2 correlation lines. PanCL intensity does not correlate with nitrogen concentration at room temperature. With cooling to 80 K the CL image contrast changes significantly and a broad peak appears at ~575 nm in the CL spectra. Preliminary spectral data show a direct correlation of this ~575 nm peak intensity with the measured nitrogen concentration

Discussion

The CL and FTIR data are consistent although the contrast mechanisms involved in CL are complex and not simply related to nitrogen and hydrogen abundance or state of aggregation. The higher spatial resolution of the CL provides finer scale structural detail which should be considered in conjunction with the FTIR data. FTIR data from uncut stones must be treated with caution but can be internally checked for coherence.

The aggregation states, hydrogen and nitrogen data across the plate indicate that the diamond grew in at least three distinct episodes. The fully aggregated central region represents the first stage of growth, this was followed by a period of mantle residence at >1200° C in which all A nitrogen was converted to the B form. At a later time the middle and rim regions overgrew the core (second and the third growth stages respectively). During growth, the diamond habit evolved as follows: Cubo-octahedron (zonally-sectorial) -- cubo-octahedron (zonal) -- octahedron. The panCL images show the distinctive transition from a normal (continuous) mechanism of growth in cubic sectors to a mixed and then finally to a tangential (layer by layer) mechanism of growth.

The nitrogen concentration data exhibit variations that reflect both growth events and crystallographic influence. Aggregation state and hydrogen abundance appear insensitive to crystallography and reflect growth and residence histories. This diamond grew initially under conditions of relatively high nitrogen and hydrogen abundances which progressively changed, through either partitioning effects in a closed system or environmental changes in an open system, to a lower level. A subsequent and discrete growth stage produced the variable, low nitrogen overgrowth.

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Figure 1: Panchromatic CL image by SEM of plate 1137. Scale bar is 1 mm. The sectorial lobes of the central cubo-octahedral growth are distinct. Fine layering is evident in the outer octahedral zone