

Infrared spectroscopy of natural *Type Ib* diamond: Insights into the formation of *Y*-centers and the early aggregation of nitrogen

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ABSTRACT

The growing interest in the spectroscopic properties of *Type Ib* diamonds has revealed several complexities associated with nitrogen (N)-related defects that have yet to be identified. One defect in particular, the *Y*-center, produces a characteristic spectrum in the N-region ($\sim 1000\text{--}1400\text{ cm}^{-1}$) that is extremely common in the IR spectra of diamonds with a dominant *Type Ib* component. In this study, a suite of 178 *Type Ib* + *IaA* diamonds with variable N-aggregation states (%IaA) and N contents was examined to evaluate the effect of *Y*-center absorbance on the results obtained from standard deconvolution of the N-region. To achieve this, a new deconvolution routine was developed that incorporates the *Y*-center spectrum (obtained by decomposition of *Type Ib* spectra), and an updated spreadsheet (*Caxbd_Inherit_2024-Ib*, Online Materials¹) for processing the IR spectra of *Type Ib* diamonds is provided here. It is shown that neglecting *Y*-center absorption during least-squares fitting of the IR spectra of *Type Ib* + *IaA* diamonds results in poor-quality fits of the N-region that may result in erroneous *C*- and *A*-center contents. The identity of the *Y*-center, and the relevant absorption coefficient, have not been constrained. However, several studies have shown that *Y*-centers are structurally related to single-substitutional N (called N_S^0 or *C*-centers); thus, the *Y*-center contents were calculated using the *C*-center absorption coefficient. Using the new deconvolution method, it is shown that neglecting *Y*-centers may result in N-aggregation states that vary by $\pm 10\%$ IaA and total N contents (N_{tot}) that may be overestimated by >100 at. ppm. The samples studied here have an average N_{tot} of ~ 100 at. ppm, and errors in %IaA and N_{tot} may be much larger for diamonds with higher N_{tot} . Such errors translate to potentially significant discrepancies in the calculated mantle residence times on the order of hundreds of millions of years. Comparisons of the normalized *Y*-center content and %IaA show that *Y*-centers are an intermediate defect that is produced from 0 to 40 %IaA at the expense of *C*-centers and then consumed from 40–100 %IaA to produce *A*-centers. A strong linear correlation with some IR peaks between 1400 and 1350 cm^{-1} (e.g., 1358 cm^{-1}) is observed. Evidence supporting the assignment of such peaks to defects containing interstitial carbon and nitrogen (C_i and N_i) is described, suggesting that the formation of *Y*-centers is driven by interstitial-assisted aggregation. Moreover, the *Y*-center itself may be an intermediate form of N_S^0 linked to C_i or N_i or larger interstitial complexes that become unstable with increasing N-aggregation (mantle residence time/temperature). Evidence for alternative hypotheses for the identity of the *Y*-center involving O- and Ni-related defects and *X*-centers is also discussed.

Keywords: Diamond, *Type Ib* diamond, FTIR spectroscopy, defects, N-aggregation, substitutional nitrogen, *Y*-centers, Spectroscopy in geology: a decade of breakthroughs