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Oxygen distribution and speciation in bulk of monocrystalline diamonds and its correlations with other impurities

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Oxygen in diamond lattice remains elusive impurity. Mass-spectrometry and nuclear probes show presence of oxygen in all diamonds in concentrations ranging from <100 to 1000 at.ppm. Detailed studies [1] have shown that in virtually every diamond there exists "inclusion-independent" oxygen which is believed to be present as a structural impurity. Recent studies of natural diamonds showing strong absorption by CO2 in IR spectra [2] suggest that these monocrystalline diamonds contain oxygen as a lattice impurity. However, up until now evidence for incorporation of O during diamond growth is scarce and little is known about related defects.

The aim of the current study is to show conclusively whether or not O can exist as a growth-related structural impurity in diamond. Several types of monocrystalline diamonds with and without CO2 IR absorption were analysed by techniques sensitive to chemical composition (SIMS) and to structure (Small-Angle X-ray Scattering (SAXS) and X-ray topography) [3].

For the SIMS investigation high ion current of 100 nA Cs+ ions in conjunction with an 8 μm field-of-view were employed. Due to prolonged storage of the sample mount in high vacuum conditions the O background signal was very low. Both spot analyses and mapping of O lateral and depth distributions were performed. In some CO2-rich diamonds oxygen is distributed heterogeneously at the micron-scale, suggesting its presence in submicron inclusions, which, in turn, are irregularly distributed throughout the sample. Such inclusions could correspond to heterogeneities with sizes of 100-200 nm revealed by SAXS. However, in some of these diamonds O is distributed homogeneously, suggesting that it might be present as a lattice impurity. The most important proof of structural position of oxygen impurity comes from simultaneous measurements of N and O concentrations. Plots of N vs O concentrations show clear correlations, obeyed as for several analyses spots on individual diamonds as well as for sets of diamonds. Notably, the slopes of the N-O correlations differ between diamonds showing CO2 absorption in IR and for “normal” diamonds. As expected, O contents are higher in the former group, suggesting that in CO2-rich diamonds oxygen is present both the lattice and in microscopic inclusions. This study is the first work showing correlation of structural nitrogen impurity with oxygen content of diamonds, thus providing strong analytical support for earlier hypothesis [2] that O may be present as a lattice impurity in natural diamonds.

Theoretical calculations of relative stabilities of oxygen in diamond show a very strong dependence on the position of the Fermi level in the crystal [4, 5]. According to these results oxygen behaviour in diamond and, in particular, its diffusivity strongly depends on the nitrogen concentration and speciation. Though the O–N pair appears to be a stable defect at low temperatures, mutual repulsion of positively charged N and O ions creates a vacancy-like state in between them [5]. Since most impurities in diamond diffuse by a vacancy-assisted mechanism, such a configuration may be destroyed by annealing. The calculated strength of the C–O bond in diamond is lower than the C–C bond and preferential breaking of the C–O bond seems plausible. Therefore, despite its relatively common presence, oxygen is not always detected by spectroscopic methods if no annealing has been performed. Apparently, the presence of O hinders IR-activity of N-related defects.

From the geochemical point of view the existence of oxygen as a lattice impurity in diamond is of considerable interest. First of all, it adds another important isotopic system in addition to C and N. Second, it emphasises the importance of the O partition coefficients in measurements of intrinsic oxygen fugacity of diamonds.

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