Investigation of Nitrogen Aggregation in Diamond Using Long Duration Multi-Anvil Experiments and Optical and Small Angle X-Ray Scattering Analyses

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INTRODUCTION

Nitrogen is the principal elemental impurity in diamonds. It is believed that during high temperature annealing, single nitrogen atoms (C-defects) aggregate to form pairs (A-defects) and then to 4N around a vacancy (B-defects). Usually it is assumed that the defects are randomly dispersed in the diamond lattice (Davies, 1976; van Wyk and Woods, 1995). However measurements of hardness, thermoconductivity and X-ray diffuse scattering are consistent with a clustering of defects (Naletov et al., 1977; Ramanan et al., 1998).

We have recently reported the results of a Small-angle X-ray scattering (SAXS) investigation of a number of natural and synthetic diamonds in which only one type of defects is present (either A,B or C) (Shiryaev et al., 1999 and in press).

It was shown that diamonds with single substitutional N atoms (C defects, Ib type) as well as some stones with paired nitrogen (A defects, IaA type) do not scatter in the small angle region. Other IaA diamonds, however, contain isometric defects with a broad size distribution centred at ~500 Å (Figs. 1, 2a). Furthermore, diamonds with B-defects (IaB type) contain smaller isometric defects with diameters of ~80-100 Å which scatter approximately two orders of magnitude more strongly than clusters in IaA diamonds, (Figs. 1, 2b). These observations confirm previous work by Naletov et al. (1977) who demonstrated a correlation between the intensity of the diffuse scattering and IR absorption by nitrogen defects. It was further suggested that A and B defects are concentrated in clusters with bulk chemical compositions close to C_3N.

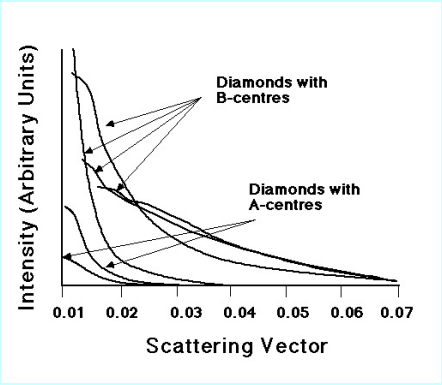

Fig. 1 Small angle scattering from natural Ia diamonds (Shiryaev et al., 1999) Scattering vector $s=4\pi\sin\alpha/\lambda$ ($Å^{-1}$).

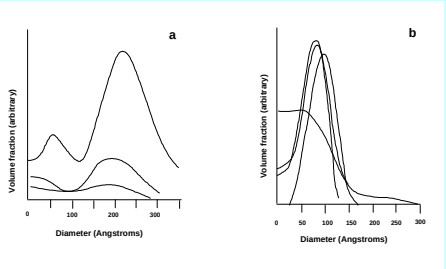

Fig. 2a Size distribution of scattering defects in diamonds with A centres.

Fig. 2b Size distribution of scattering defects in diamonds with B centres.

In order to investigate whether detected clusters were produced by nitrogen aggregation processes, we have subjected synthetic stones grown with Ni catalysts and originally containing only C-centres to high pressure and temperature for a range of durations and observed the resulting changes in spectra.

EXPERIMENTAL AND ANALYTICAL

High pressure experiments were carried out using the Walker-style 1000 ton multi-anvil press of the Lunar and Planetary Lab., University of Arizona at 7 GPa, ~1800°C for durations of up to forty days. Castable 14/8 assemblies with Re heaters were used and cubes were dressed with pyrophyllite gaskets backed with Teflon tape. Fragments of approximately 1 mm in maximum dimension from two synthetic diamonds were used, containing respectively 125 and 250 ppm atomic N. Samples were loaded into Pt capsules and packed with dry graphite. A strip of Re foil was located near the diamonds in some experiments in order to facilitate relocation of the stone within the capsule after the experiment. Pressures of 7 GPa were obtained at a ram force of 294 tons (U.S.) following calibration by Righter and Drake (2000) and are believed to approximate well to hydrostatic conditions. Temperatures were held at ~1595°C measured directly using WRe_{26}/WRe_5 thermocouples located on the outside of the heater with equivalent power being held constant for experiments where thermocouples failed. Measurements using a similar assembly with the thermocouple located at the hotspot confirm a temperature gradient of ~ 100°C/mm and so samples are concluded to have been subjected to temperatures of 1775 +/- 50°C.

Data have been obtained from three experiments:

Experiment	No. of runs	Duration (hr)	Pressure	Sample temperature
1	6	10.65	7.2 GPa	1784 (+/- 50) °C
2	1	10.08	7.2 GPa	1770 (+/- 50) °C
3	1	960	7.0 GPa	1770 (+/- 50) °C

SAXS measurements were obtained in the angular region from 15′ to 1.2°. A Small-angle AMUR-K X-ray diffractometer with the Kratki-collimator and linear position-sensitive detector were used with a Ni-monochromated Cu-anode X-ray fine focus tube as the source of X-rays. Samples were attached to a lead mask and exposed for 4000 s. The experimental curves were normalised to primary beam intensity with corrections for sample absorption coefficients and holder scattering being applied. Calculation of the size distribution of scattering objects was performed using GNOM software. All distributions presented in this study are stable solutions against variations of a maximum size of scattering centres. The best agreement with the experimental data was achieved by approximation of scattering centres as a monodisperse system of hard spheres.

FTIR spectra were acquired with a Philips PU9800 FTIR spectrometer in the range 400 - 3500 cm^{-1} with 512 scans and at a resolution of 2 cm^{-1}. Deconvolution of spectra was achieved using software provided by David Fisher (D.T.C.) and based on work by Boyd et al. (1994, 1995).

RESULTS

Results are summarised in the following table:

Experiment	% A centres	B centres	SAXS results
1	42 %	None	weak, some >500 Å clusters
2	0	None	weak, some >500 Å clusters
3	16 %	None	pronounced 100-110 Å defects

FTIR spectra show that diamonds in all experiments contain C-centres with variable amounts of A centres (shown as % A in the table) and no B-centres (Fig. 3). Significantly more N was found to have aggregated to A centres in experiment 1 comprising of a number of short runs, compared to the single run of experiment 2 conducted for the same total duration. Almost two orders of magnitude increase in experimental duration (experiment 3) failed to achieve the same degree of aggregation as the multi-run experiment.

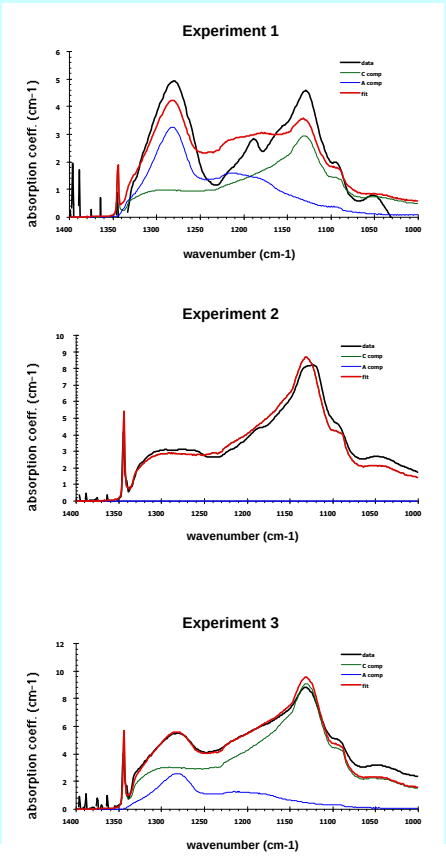

Fig. 3 Deconvoluted FTIR spectra of experiments 1 to 3.

The appearance of very pronounced scattering by defects of 100-110 Å in diameter in the long duration experiment (Fig. 4) shows strong similarities with natural IaB diamonds (Fig. 1; Shiryaev et al., 1999). The existence of small-angle scattering is a clear indication that inhomogeneous distribution of defects takes place, since randomly distributed point defects do not produce SAXS.

Photoluminescence investigation of samples in the initial state showed negligible concentrations of vacancy-related centres (low ppb level). Annealed diamonds, however, showed that up to 0.1 ppm of vacancies were generated during high pressure and temperature treatment and survived quenching.

DISCUSSION

FTIR spectra show that long continuous annealing induces much slower nitrogen aggregation rates than a number of short annealing cycles with the same integrated time. Previous workers using a number of short duration runs observe almost complete aggregation from C to A-centres under the same conditions. This observation suggests that run *quenching* introduces a significant effect on the rate of aggregation.

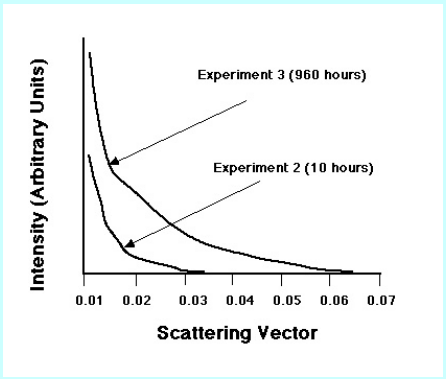

Fig. 4 Small angle scattering curves for Experiment 2 and 3

Heating and/or deformation of diamonds generates considerable numbers of vacancies. Once created, vacancies actively participate in nitrogen diffusion. Before being trapped one vacancy can assist in the migration of as many as 50 N atoms (Collins 1982; Mainwood, 1994). Once trapped they either annihilate with interstitials or form stable complexes with lattice atoms. We suggest that in a sequence of short anneals new sinks are generated (during PT-changes) and defects are released from already present traps. The sink saturation, therefore, is not reached. In the case of continuous runs at stable conditions no more vacancies are generated and after their formation the nitrogen migration rate decreases considerably. Our SAXS measurements suggest that such continuous runs produce a new type of defects existing as clusters of ~100 Å diameter. The extent of clusterisation could serve as a measure of maturity of diamonds.

At present the composition of these clusters is unknown and cannot therefore be assumed to be nitrogen-related. From X-ray diffuse studies Ramanan et al. (1998) suggest that clusters consist of vacancies and interstitials. As the difference in electronic density of our clusters and the diamond matrix is large it is more likely, that clusters are either vacancy-rich or contain impurity atoms such as N. To verify whether the clusters are nitrogen-related we are performing annealing studies on nitrogen-free (IIA) diamond.

Our observation of suppressed aggregation rate and the formation of clusters may have a bearing on some discrepancies observed in the results of classical kinetic modelling of nitrogen aggregation. A second order kinetics model ($kt = 1/c_t - 1/c_0$, where c_t and c_0 are the concentrations of single nitrogen atoms before and after annealing, t is the duration of annealing and k is a rate constant) is widely used and found to produce sensible ages for diamonds in many cases. However, for a considerable number of natural diamonds, mantle residence times calculated from the degree of N aggregation exceed the age of the Earth. A possible explanation for the occasional failure of classical models is supported by Mainwood (1995) who showed theoretically that nitrogen migration in octahedral growth sectors is vacancy-assisted, whilst in cubic sectors, direct interchange of C with N atoms of a higher energetic barrier takes place. In order to attempt to calculate residence times from kinetic models, vacancy-revealing PL studies should therefore be performed. Once data for additional experimental durations is obtained we expect that the rate of diffusion thus calculated will be more relevant to interpretation of a significant proportion of natural samples.

SUMMARY

♦ Aggregation rates in single long duration experiments are significantly slower than cumulative experiments using a number of quench events. Rate equations based on single long duration experiments will likely be more relevant to natural systems, particularly those involving significant octahedral growth.

♦ Sufficiently long annealing leads to the formation of impurity and/or vacancy-rich clusters of a well determined size.

♦ During continuous annealing vacancy concentrations quickly reach saturation, which slow down diffusion and in some cases may alter the principal diffusion mechanism.

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