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Photoluminescence studies of sintered diamond compacts

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Sintered diamond compacts have been examined by the technique of photoluminescence spectroscopy. The results suggest that the sintering process has produced considerable internal strain in the diamond grains, the amount of strain depending upon the grain size of the compacts; the smaller the grain size, the larger the amount of internal strain. Evidence is also presented for the formation of vacancies in the diamond grains during sintering, with the number of vacancies depending upon the grain size and the temperature of sintering. It is suggested that the vacancies are produced by the interaction of mobile dislocations during plastic deformation of the diamond grains when the compacts are being fabricated. A method is suggested for determining, under certain circumstances, the thermal gradients in a high pressure cell by examination of the luminescence spectra from diamond powders that have been compacted in different regions of the cell.

1. Introduction

Sintered diamond compacts are now commercially available for use in a wide variety of applications. Companies involved in their manufacture include De Beers, General Electric and Sumitomo; compacts are also being produced in the USSR.

The compacts are made by subjecting fine grain ($< 200\,\mu$m) diamond powders mixed with a small amount of metal ($< 20\%$ by volume) to high pressure and temperature. Temperatures of between 1300 and 1600° C and pressures of between 5 and 8 GPa are imposed to produce a tough agglomerate of partially bonded, randomly oriented diamond particles interspersed with metal. The metal is usually nickel, cobalt or iron.

Hall [1] and Stromberg and Stephens [2] established the conditions required for the sintering of diamond powders, and Katzman and Libby [3] investigated the sintering of diamond powders in the presence of a metal binder. Further work has been carried out on this sintering process [4–8] and it has been recognized that the formation of graphite on the surfaces of the particles and its subsequent reprecipitation as diamond via the metal solvent, is an important factor in the sintering process [7, 8]. There have been a number of reports [6, 9–11] that during fabrication of the compacts extensive plastic deformation occurs within the grains.

There is a considerable amount of information available on the optical properties of defects in both natural and synthetic diamonds (see review articles by Davies [12] and Walker [13]). Recently, Nachal'naya *et al.* [9] have used electron paramagnetic resonance and infrared absorption techniques to examine sintered diamonds. Luminescence techniques can, however, detect certain defects at concentrations orders of magnitude lower than the detection level with optical absorption techniques. Under certain circumstances luminescence techniques can detect optical defects at concentrations of between 10^{19} and $10^{21}\,\mathrm{m}^{-3}$. This can be compared with optical absorption measurements on diamond where the detection level is about $10^{24}\,\mathrm{m}^{-3}$. This paper describes how luminescence measurements were used to give information about the types of defect introduced into the diamond grains during sintering. The measurements were also useful as they suggested a method of determining thermal gradients experienced by compacts during their fabrication.

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2. Experimental procedure

The 488.0 nm or the 514.5 nm emission line of an argon ion laser was used to excite the luminescence of the diamond compacts. The laser was operated at a power of 0.2 W and focused to a spot of about 200 μm diameter. The depth of penetration was between 30 and 200 μm depending upon the grain size of the compact being examined. The reason for this variation in penetration was due to the absorption of the laser beam by the metal which was situated between the diamond particles. The resultant backscattered luminescence was measured with a SPEX1401 double beam spectrometer and cooled RCA.C31034 photomultiplier. A CBM Pet 4032 microcomputer was used for experimental control and data collection. An Oxford Instruments gas flow cryostat was incorporated into the apparatus when determining spectra of the compact at 77 K.

Initially the luminescence spectra of SYNDITE* compacts of different grain sizes were measured. The luminescence of the synthetic diamond powder used in the manufacture of these compacts was also measured. Then compacts of different grain sizes from other sources were examined and the intensity of luminescence of each specimen compared. When making quantitative comparisons between the intensity of luminescence for different compacts it was essential to allow for the variation in the depth of penetration of the laser beam from specimen to specimen. The method used was to measure the intensity of the first order Raman peak which is positioned 1332 cm^{-1} lower in wavenumber than that of the laser emission line being used to excite the luminescence. The intensity of this peak was linearly proportional to the power of the laser and the volume of diamond from which the luminescence was being excited. Thus the luminescence was normalized by dividing the luminescence intensity at specific wavelengths throughout the spectral range by the integrated intensity of the first order Raman peak. This procedure was followed in all the experiments.

Commercial compacts made from synthetic diamond powder were then heated to between 1300 and 1800° C with an imposed pressure of about 9.5 GPa. The temperature was measured with a tungsten–iridium thermocouple that had been corrected for pressure. The tetrahedral high pressure apparatus and the high temperature annealing procedures that were used have been described by Evans and Qi [14]. After annealing, the luminescence of the compacts was measured.

Owing to the small working volume in the high pressure cell it has not been possible to fabricate compacts with physical properties comparable to commercial compacts. Instead, model experiments were done in which 15 to 30 μm natural (MICRON SND*) diamond powders were packed into the tetrahedral high pressure cell and heated for 10 min at a temperature of 1300° C under an imposed pressure of about 9.5 GPa. This was repeated for a range of temperatures up to 1700° C. Since no metal binder was incorporated, the resultant agglomerates were very friable and differed somewhat from the commercial compacts but the grains had adhered sufficiently for handling and luminescence measurements to be done. The surface of the resultant cylindrical agglomerate was carefully removed until the cross-sectional plane containing the thermocouple junction was exposed. Subsequent luminescence measurements of the compacted diamond powder close to the thermocouple junction reduced any errors due to thermal gradients in the cell.

Finally, similar model experiments were repeated with 8 to 25 μm synthetic (MICRON MDA*) diamond powders. The synthetic diamonds were heated for 10 min at temperatures between 700 and 1800° C, under an imposed pressure of about 9.5 GPa. Once again, no metal binder was incorporated and all the luminescence spectra were recorded from a region adjacent to the thermocouple junction.

3. Results and discussion

3.1. Luminescence of commercial diamond compacts

The first specimens examined were 010 and 075 grade SYNDITE compacts. (Although these commercial compacts contain a range of diamond grain sizes they are usually graded according to an average grain size, which is quoted by the manufacturer, see Table II. Following this practice, all references to "grain size" should be taken hereafter as meaning the average grain size observed in the sample.) Synthetic MDA diamond powders similar to those with which Syndite was made [6] were also examined. The normalized luminescence spectra, measured with the specimens held at 77 K, are shown in Fig. 1. Curve c is the normalized luminescence of the MDA grains. The small peak

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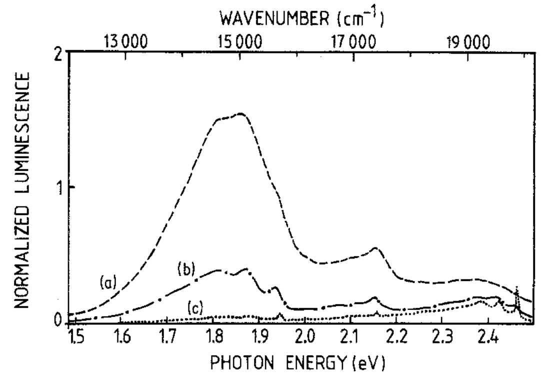

Figure 1 Normalized luminescence spectra of SYNDITE compacts held at 77 K. The spectra a and b are from SYNDITE compacts with an average grain size of 10 and 75 μm, respectively. Spectrum c is from synthetic MDA diamond powder.

at 1.945 eV is a zero phonon line and indicates the presence in the diamond grains of a low concentration of a defect consisting of a single substitutional nitrogen atom with an associated vacancy [15, 16]. The defect responsible for the peak at 2.15 eV is known as the 575 nm system [13]. Its structure has not been determined but it is suspected that single substitutional nitrogen atoms and vacancies are involved. The third zero phonon line at 2.464 eV is the H3 peak and is due to the presence of defects consisting of two nitrogen atoms and a vacancy in the configuration [N–V–N] and having Rhombic I symmetry [17] The wavelengths and wavenumbers of the three peaks are given in Table I.

Thus curve c shows that the diamond grains used in the fabrication of SYNDITE contained very low concentrations of at least three types of optical centre. The composition of one is unknown, the second is a single nitrogen atom and a vacancy and the third is composed of two nitrogen atoms and a vacancy (H3 centre). Luminescence is, however, only a qualitative indication of the presence of these defects. The intensity of the luminescence depends on a number of factors such as excitation efficiencies, for example. Hence it has not been possible to determine the actual concentration of the defects.

TABLE I Equivalent units for the positions of the zero phonon lines of the three main defects observed in SYNDITE

Defect name [13]	Photon energy (eV)	Wavelength (nm)	Wavenumber (cm^{-1})
1.945 eV	1.945	637.7	15 681
575 nm	2.150	575.0	17 391
H3	2.464	503.2	19 873

Curve b shows the luminescence spectrum of the 075 compact. The zero phonon line at 1.945 eV is more intense and considerably broader than in curve c. The full width at half peak height is determined by two broadening mechanisms. The first is quadratic electron–phonon coupling at the defect [18]. The broadening due to this mechanism is temperature dependent and Davies [19] has shown that at temperatures below 80 K such broadening is negligible for colour centres in diamond. The second mechanism by which zero phonon lines can be broadened is by subjecting the colour centres to inhomogeneous lattice strains which perturb the energy levels associated with the colour centre. The spectra in Fig. 1 were recorded at 77 K and therefore, the broadening was due to inhomogeneous strain in the diamond lattice. Curve b shows the phonon side band of the 1.945 eV zero phonon line on the low energy side of this line. The side band arises from phonon-assisted transitions from the excited state to vibronic energy levels in the ground state. The structure on the phonon side band is related to the coupling of the defects to the diamond lattice. The two prominent peaks in the side band arise principally from coupling with 1 and 2 phonons each with an energy of 65 meV. These peaks were also broadened by inhomogeneous strain fields in the lattice. The zero phonon lines at 2.15 and 2.464 eV and their associated side bands also display strain broadening.

Curve a is the normalized luminescence spectrum of the SYNDITE compact with the smallest grain size, namely 10 μm. The intensity of the luminescence is considerably greater than in curve b. Also the strain broadening has increased such that the zero phonon 1.945 eV peak cannot be readily resolved and the phonon side band has lost its structure. In a similar way the 2.15 eV (575 nm) peak has increased in intensity and broadened, whilst the 2.464 eV (H3) peak cannot be resolved because of the strain broadening.

Comparison of the curves a and b with c shows that during the sintering process considerable strain was introduced into the diamond grains. The intensity of the luminescence also increased indicating an increase in the concentration of the luminescing defects. This has been interpreted as being due to the trapping of vacancies by nitrogen

TABLE II The commercial diamond compacts used in this work

Sample name	Grade	Average grain size (μm)
SYNDITE*	002	2
	010	10
	025	26
	075	75
STRATAPAX†	2830	8
	2530	100
GEOSET†	2102	60
COMPAX†	1620	3
	1330	8
	1520	28

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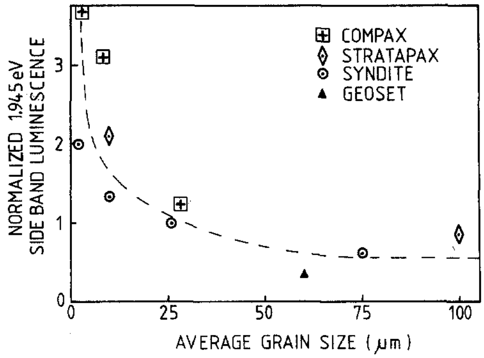

Figure 2 Normalized side band luminescence intensity of the 1.945 eV system for commercial compacts of different average grain sizes. (STRATAPAX, GEOSET and COMPAX are registered trademarks of General Electric.)

defects in the diamond grains. Isolated vacancies in diamond give rise to an optical absorption band that has a zero phonon line at 1.671 eV [20]. This system disappears at annealing temperatures in excess of 600° C [21]. This shows that at the temperatures used in the sintering process the vacancies were mobile and could be trapped by lattice imperfections. Curves a and b indicate that considerably more vacancies were produced in the 010 SYNDITE compact than in the 075 specimen. It has been stated previously that there is evidence that plastic deformation occurs in diamond grains during the sintering process and it is suggested that these vacancies were formed by the interaction of the mobile dislocations that produced the plastic deformation. The results thus suggest that more plastic deformation occurred and more internal strain was introduced into the finer grain compact (010) than the other (075). It would be expected that the number of mobile vacancies produced and the concentrations of the nitrogen defects would determine the intensity of luminescence. For these two SYNDITE compacts, made of synthetic diamonds, the single substitutional nitrogen atoms would be at a concentration of between 10^{24} and $5 \times 10^{25}\,\mathrm{m}^{-3}$. As the luminescence technique detects much lower concentrations of luminescence active centres, the intensity of the 1.945 eV peak and its side band (as with the other systems considered) would be determined only by the concentration of mobile vacancies which become trapped at nitrogen centres.

The normalized luminescence spectra of a number of commercial compacts with different grain sizes were measured. These compacts, which were all made with synthetic diamonds, are listed in Table II.

The results are shown in Fig. 2 which gives the normalized luminescence of the phonon side band of the 1.945 eV system for the different compacts. Despite the probable differences in the manufacturing conditions, the luminescence intensity tends to decrease for compacts of increasing grain size. This result suggests that the amount of plastic deformation, and hence the mobile vacancy concentration, depended upon the grain size; the smaller the grain size (for the range available in this work) the larger the amount of plastic deformation. This suggestion will be tested by examining the grains using transmission electron microscopy.

All the luminescence spectra of these compacts showed considerable broadening of the zero phonon peaks. To study this effect in more detail, high resolution scans of the zero phonon line at 1.945 eV were performed for SYNDITE compacts with grain sizes of 2, 10, 26 and 75 μm. This was a laborious process and entailed about 5 h of machine time for some of the scans. Allowance was made for the background intensity. The results are shown in Fig. 3, which gives the full width at half height of the 1.945 eV zero phonon line for the different compacts. With decreasing grain size the amount of broadening increased. Davies [22] estimated that the internal stress, S, was related to the half width, W, of the 1.945 eV zero phonon line, measured at 77 K by

$$S = \frac{W}{10} \qquad (1)$$

where S is in GPa and W is in meV. Application of this relationship to the results in Fig. 3 shows that the diamond grains in the SYNDITE compacts con-

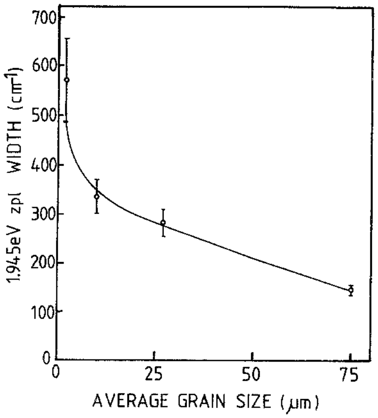

Figure 3 Variation of the full width at half height of the 1.945 eV zero phonon line (zpl) for SYNDITE compacts of different average grain size. The measurements were done at 77 K.

tained considerable internal stress varying from about 2 GPa for the 75 μm compact to about 6.5 Gpa for the 2 μm specimen.

These stresses are of the same magnitude as the external pressure imposed during the fabrication of the compacts and indicates that on removal of the pressure, the close packed, partially bonded grains were unable to relax elastically owing to irreversible changes produced by the sintering process. The presence of high stress in these crystals was confirmed by performing high resolution scans of the first order Raman peak. Fig. 4 shows the full width at half peak height of the first order Raman peak for the SYNDITE samples. Parsons [23] has investigated the effects of hydrostatic pressure on the position of the Raman line relative to that of the exciting laser emission line. He reported a shift rate of 3.6 cm^{-1} GPa^{-1} and also that the widths of Raman line increased from 2 cm^{-1}, for a limited region of a diamond, to 4.5 cm^{-1} when a large region was examined, due presumably to inhomogeneous internal strain.

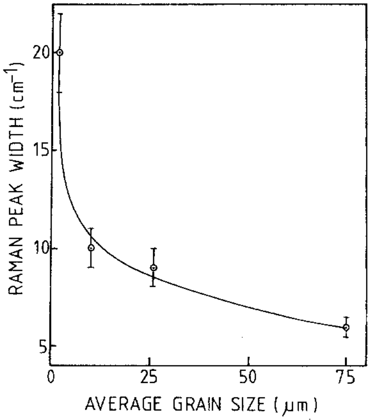

Figure 4 Variation of the full width at half height of the first order Raman peak for SYNDITE compacts of different average grain size. The measurements were carried out at room temperature.

We interpret the broadening of the first order Raman peak shown in Fig. 4 as due to regions of high strain in the diamond grains. It should be noted that the relationship of the width of the first order Raman peak with grain size follows closely that of the 1.945 eV zero phonon line shown in Fig. 3.

3.2. Heating of commercial diamond compacts

In an attempt to obtain further information about some of the processes involved in the sintering of diamond, a commercial compact, SYNDITE 010 was heated for 30 min at 1300° C with an imposed pressure of about 9.5 GPa. The process was repeated on a second specimen, heating for the same time at 1800° C with the same pressure imposed. The normalized luminescence spectra are shown in Fig. 5. Curve a is that of the SYNDITE compact prior to heat treatment. The prominent feature is the phonon side band associated with the 1.945 eV system. Curve b is the spectrum of the compact which had been heated at 1300° C. The side band associated with the 1.945 eV system has been reduced in intensity and that associated with the 2.464 eV (H3) system has intensified due to the heat treatment.

Curve c is the spectrum of the compact which had been heated at 1800° C. In this case the side

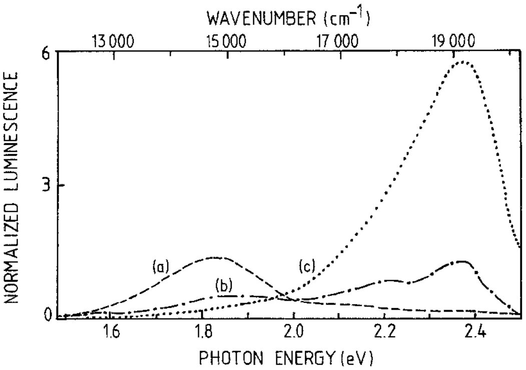

Figure 5 Normalized luminescence spectra of 0 1 0 SYNDITE compacts after heat treatments under pressure. Spectrum a is from a compact prior to heat treatment; spectrum b is for a compact after heating for 30 minutes at 1300° C and spectrum c is for another compact after it had been heated for 30 min at 1800° C.

band of the 1.945 eV system has virtually disappeared and the side band of the H3 system has increased considerably. In the previous section it was suggested that plastic deformation during the sintering process produced mobile vacancies that attached themselves to the nitrogen defects. The trapping of the vacancies by single nitrogen atoms produced the predominant feature in curve a. Curve b shows that during the heat treatment at 1300° C, some of the single nitrogen atoms have migrated and H3 centres have been formed. This is the first stage of nitrogen aggregation in diamond [14, 24]. Some of the vacancies produced during the heat treatment have been trapped by single nitrogen atoms to form the 1.945 eV system and others have been associated with two nitrogen atoms as indicated by the presence of the H3 system. It appears that the vacancies become trapped efficiently than at A centres (two nitrogen atoms). But there is a difference between his experiments and the ones reported here. In Collins' work the A centres and single nitrogen atoms existed in the samples initially, whereas in the present experiments H3 centres were being formed by the migration and aggregation of single nitrogen atoms via a vacancy mechanism. It may be that in the experiment of Collins when a vacancy was trapped by an already existing A centre an internal rearrangement was necessary ([N–N–V] → [N–V–N]) to form a stable H3 centre. In the present experiments such a rearrangement was unnecessary as the migrating single nitrogen atom would have a vacancy associated with it when it met another single nitrogen atom and formed a stable H3 centre ([N–V] + N → [N–V–N]). This could account for the difference in the relative trapping efficiencies of vacancies reported by Collins and in the work described in this paper.

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The heat treatment at 1300° C would result in a far higher concentration of single nitrogen atoms than of A centres (two nitrogen atoms). This would be so even if enhanced vacancy diffusion of the nitrogen atoms occurred because of the presence of the introduced mobile vacancies [25, 26]. Despite the predominance in number of the single nitrogen atoms, the 1.945 eV side band was reduced by the heat treatment at 1300° C and the H3 side band increased. This suggests that the vacancies have been preferentially associated with two nitrogen atoms rather than with the single nitrogen atoms. This process has gone to completion during the heat treatment at 1800° C. The large increase in the H3 side band shown in curve c was due both to aggregation of single nitrogen atoms at 1800° C and also to an increase in the number of vacancies formed as a result of increased plastic deformation (to be expected at this high temperature [27]).

3.3. Luminescence of natural diamond agglomerates

The increase in vacancy concentration as the temperature of annealing was raised has been confirmed using the agglomerates made with natural diamond grains, as described in Section 2. The normalized luminescence spectra are shown in Fig. 6. The curves show that, as the sintering temperature was increased, the H3 system progressively increased in intensity. In natural diamonds, in the context of this work, the highest concentration of defects involving nitrogen are the A centres (two nitrogen atoms) with a very low concentration of single substitutional nitrogen atoms. A typical concentration of A centres would be 10^{26} m^{-3} with a single nitrogen concentration of 10^{20} to 10^{22} m^{-3}. This suggests that the grains contained a distribution of A centres that were about 2.2 nm apart on average providing a high concentration of traps for the vacancies produced in the annealing experi-

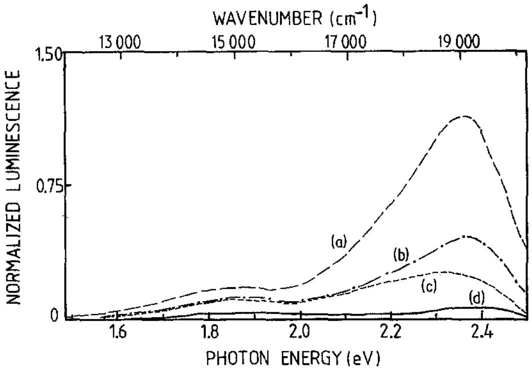

Figure 6 Normalized luminescence spectra of agglomerates made from natural diamonds after different heat treatments under pressure. Spectra a, b and c are from compacts that have each been heated for 10 min at 1700, 1500 and 1300° C, respectively. Spectrum d is from natural (MICRON SND) diamond powder.

ments. The increase in the intensity of the H3 side band shows that more vacancies were produced and trapped at A centres as annealing temperatures were increased. This suggests, as before, that more plastic deformation occurred in the grains as the temperature was raised. There is a possibility that the increase in the vacancy concentration as the annealing temperature was raised could be accounted for by the thermal production of vacancies so as to attain thermodynamic equilibrium concentrations appropriate to the different temperatures. This possibility was tested by the following experiment. The infrared absorption spectra of two natural diamonds were measured and these showed that in both specimens the nitrogen was present predominantly as A centres (two nitrogen atoms) at a concentration of 0.12 at %. Photoluminescence measurements could not detect the presence of any H3 centres. The sensitivity of the measurements was sufficient to place an upper limit on the normalized H3 luminescence intensity of 10^{-3}. The diamonds were heated at 1800° C in an inert atmosphere at atmospheric pressure for 30 min. The luminescence spectra were again measured. No detectable change in the luminescence spectra as a result of the heat treatments was observed. Therefore, it is concluded that, even at the highest annealing temperatures used in the present studies, the number of vacancies generated thermally was not sufficient to account for the observed increase in the luminescence intensity of the H3 system in the diamond compacts. In Fig. 6 the increase in the intensity of the 1.945 eV side band as the annealing temperature was raised, was probably due to single nitrogen atoms which had been produced by the dissociation of a small proportion of A centres. Such a dissociation is necessary in order to maintain thermodynamic equilibrium between the A centre concentration and that of the single nitrogen atoms [28]. Since the single nitrogen concentration would be far lower than that of the A centres (even at 1700° C) the increase in the intensity of the 1.945 eV side band with temperature shown in Fig 6 indicates that in these experiments with compacts made of natural diamonds, the vacancies were trapped more efficiently at single nitrogen atoms rather than at A centres. This is in accordance with the results of Collins [25] and the opposite of the effects observed with commercial compacts made of synthetic diamonds (Fig. 5).

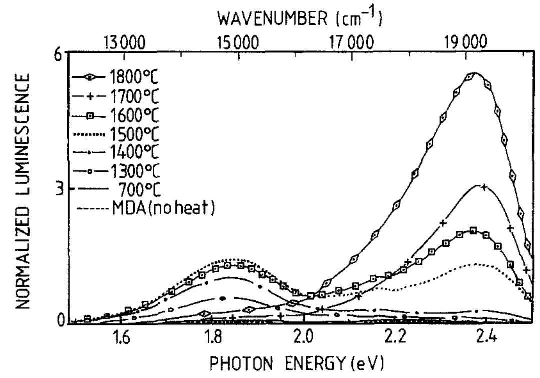

Figure 7 Normalized luminescence spectra of synthetic diamond agglomerates that have been formed by compaction for 10 min at temperatures from 700 to 1800° C under pressure. For purposes of comparison, the spectrum for untreated synthetic (MICRON MDA) diamond powder is also shown.

3.4. Luminescence of synthetic diamond agglomerates

The normalized luminescence spectra of synthetic diamond agglomerates (fabricated as described in Section 2) together with untreated MDA powder are shown in Fig. 7. The variation in the luminescence intensity for the side bands of the 1.945, 2.15 (575 nm) and 2.454 eV (H3) systems compared with temperature of compaction is shown in Fig. 8. The intensity of the 1.945 and 2.15 eV (575 nm) bands increased with temperature to

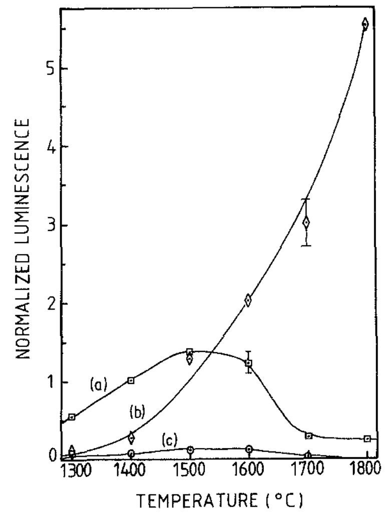

Figure 8 The variation of the normalized side band luminescence of the three main defects observed in synthetic diamond agglomerates at different temperatures of compaction. Curves a, b and c represent the 1.945, 2.464 (H3) and 2.15 eV (575 nm) systems, respectively.

about 1500°C and then decreased as the H3 system increased. This trend continued until 1800°C when the spectrum consisted entirely of the H3 system with the other two having virtually disappeared. These results can be explained by two factors which varied as the temperature of the compaction was increased; the first factor being the increase in the mobile vacancy concentration and the second the onset of nitrogen aggregation at about 1300°C. The spectra in Fig. 7 indicate that, at 700°C, although vacancies would have been mobile, very few were being produced owing to the limited amount of plastic deformation occurring at this low temperature.

As the temperature was increased more vacancies were produced as a result of increasing amounts of plastic deformation. At 1300°C the single nitrogen atoms began to migrate through the lattice via a vacancy mechanism. When a nitrogen atom encountered another one, an H3 centre was formed (two nitrogen atoms plus a vacancy in the [N–V–N] configuration). The vacancy may have broken away from the H3 centre leaving an A centre or the H3 centre may have remained as a stable defect. In common with the results obtained from the heating of commercial compacts, the luminescence intensity of the H3 system increased as the temepratuer of compaction was raised and that of the 1.945 eV system decreased. This supports our suggestion that a vacancy was bound more strongly at a H3 centre than at a 1.945 eV centre.

4. Application

When high temperatures are used in conjunction with high pressures in a process, it is very difficult to measure the thermal gradients present in the pressure cell. The presence of thermal gradients could have an effect on the uniformity of a product such as a sintered diamond compact. The results from Section 3.4 provide a means by which thermal gradients in a pressure cell could be determined in some limited circumstances. As described in Section 2, synthetic diamond powders were compacted at different temperatures for 10 min. The behaviour of the luminescence of the agglomerate so produced is summarized in Fig. 8. Fig. 9 shows the ratio, R, where

$$R = \frac{\text{intensity of the 2.464 eV side band}}{\text{intensity of the 1.945 eV side band}} \quad (2)$$

as a function of the measured temperature of compaction. If during compaction the time of heating was reduced, the curve would be shifted to higher temperatures and if times of greater than 10 min were used, the curve would be shifted to lower temperatures. The effective range of temperature measurement lies between 1300 and 1800°C. An agglomerate was made by subjecting synthetic diamond powder to a measured temperature of 1600°C for 10 min at a pressure of about 9.5 GPa. The resultant agglomerate was in the shape of a cylinder. The laser beam was focused to a 200 μm diameter circular spot and the ratio R was determined at points across a circular face of the agglomerate. Having measured R, the temperature experienced by each point was calculated using Fig. 9. By removing appropriate amounts of the surface to expose the inner regions, the temperatures experienced at points throughout the agglomerate were similarly calculated. Having determined a matrix of temperature points within the agglomerate, it was possible by means of interpolation to estimate the isotherms in the cell, as is shown in Fig. 10.

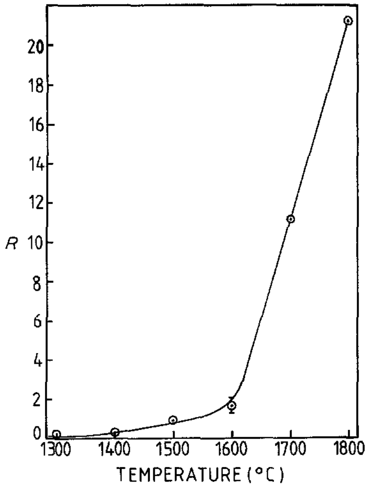

Figure 9 The variation of the ratio R (as defined by Equation 2) with different temperatures of compaction.

The isotherms clearly indicate that the thermocouple was acting as a heatsink and was the main cause of the thermal gradients within the cell. This is one of the disadvantages of using a thermocouple. Once a calibration curve similar to Fig. 9 has been produced, however, the thermocouple could be removed from the high pressure cell and the temperature within the cell determined from the luminescence exhibited by the compact.

This "remote" technique may be particularly

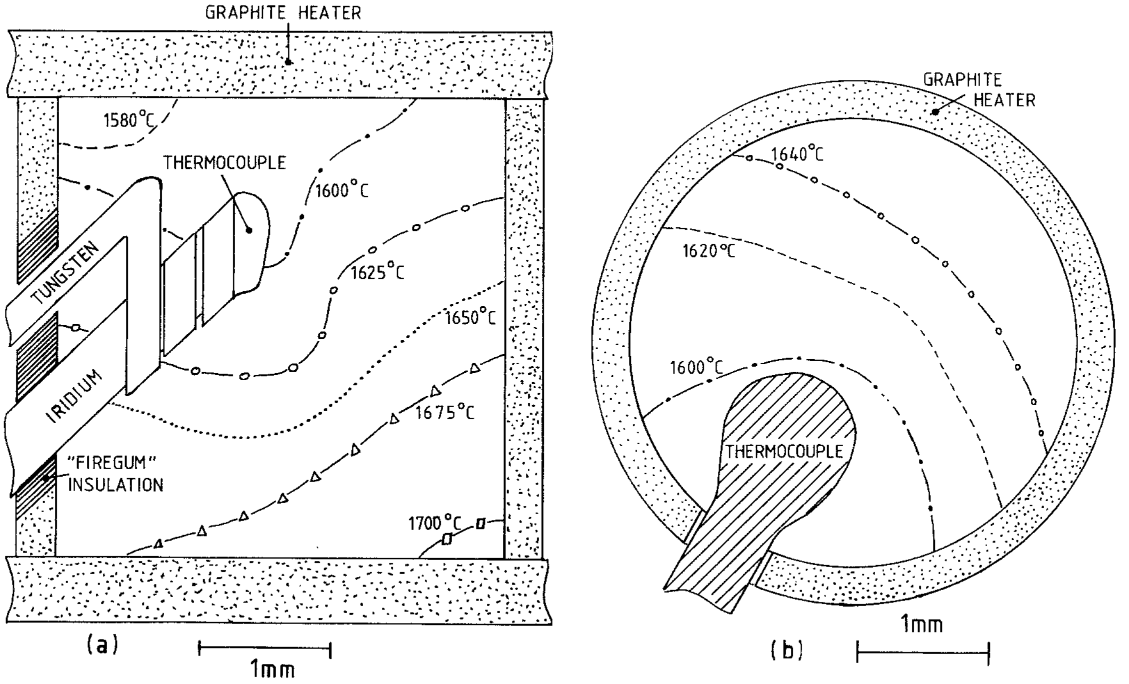

Figure 10 Estimates of the temperature gradients experienced by central sections of a synthetic diamond agglomerate while it was being compacted in the high pressure cell. (a) A vertical section; (b) a circular cross-section. In this example the temperature, as measured by the thermocouple, was held at 1600° C for 10 min.

useful in the type of high pressure apparatus which is employed in diamond synthesis [29], as it is often difficult to insert thermocouples into the reaction volume. Furthermore, diagrams such as those shown in Fig. 10 may provide valuable information for the design of such high pressure apparatus.

5. Conclusions

1. A survey of the luminescence spectra of commercial compacts made with synthetic diamonds shows that the diamond grains are under considerable internal strain. The amount of strain depends upon the grain size of the compacts; the smaller the grain size, the larger the internal strain.

2. The intensity of luminescence is greater for compacts of smaller grain size. It is suggested that the luminescence intensity is determined by the number of mobile vacancies produced by plastic deformation during the sintering process. These vacancies are trapped by nitrogen defects to form luminescence centres. The results indicate that the amount of plastic deformation is larger for compacts of smaller grain size.

3. Heat treatment of commercial compacts under pressure produces a larger amount of plastic deformation as the temperature of treatment is increased. Examination of changes in the luminescence spectra for the annealed compacts also suggests that aggregation of the single nitrogen atoms occurs at temperatures of 1300° C and above to produce H3 centres.

4. A method is described in which luminescence measurements can be used, under certain circumstances, to determine the thermal gradients present in a high pressure cell.

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