Luminescence-lifetime mapping in diamond

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Abstract
This paper introduces a new technique to the study of diamonds: mapping the luminescence
lifetime of optical centres. The understanding of luminescence lifetimes in diamond is briefly
reviewed. Since lifetime mapping involves extended measuring times with focused laser
excitation, the stability of the H3 optical centre is investigated. We show that saturation of the
H3 luminescence requires excitation power densities in excess of 10 MW cm^{-2}. The
non-radiative energy transfer time from an H3 centre to an A aggregate is found to be equal to
that from N3 centres to A aggregates, at $\sim 3 \times 10^{-16} r^8$ s, where there are r bond lengths
between the H3 and A centres. Non-radiative energy transfer is shown to occur from the NV$^-$
band to the single substitutional nitrogen atoms: the single N atoms may quench luminescence
as well as the A aggregates of nitrogen. In contrast, a comparison of the decays from the very
similar H3 and H4 centres demonstrates that the B aggregate produces very weak quenching of
the visible luminescence from diamond.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In this paper we introduce a new technique to the study of diamonds: mapping the luminescence lifetime of colour centres. We discuss the possibilities and limitations of the technique, with examples.

Variations in the concentrations of impurities in different growth sectors of diamonds produced by high-pressure, high-temperature (HPHT) synthesis are very well known, and can lead to considerable differences in the properties of the diamond at different points. For example, when a sample is uniformly irradiated, the production of vacancies may differ by a factor of four in different growth sectors as a result of the different concentrations of nitrogen [1]. Significant spatial variations are known to occur at least down to the scale of micrometres. Given the current drive to using diamond in increasingly stringent technological applications, it is clearly necessary to understand more about the implications of spatial variations.

Luminescence is well known as a powerful technique for detecting impurities in semiconducting materials, and in favourable circumstances may detect impurities present at concentrations of 10^{-9}%, too low to detect by many of the other characterization tools. In diamond, many luminescent centres are known, and some have well defined atomic models [2]. However, simply imaging the intensity of luminescence gives an incomplete understanding of spatial variations in the sample: luminescence from part of the sample may be weak because there are few luminescent centres, or because the luminescence from the centres is quenched by other defects in that locality. Surface imperfections may refract the luminescence, to increase or decrease the intensity at the detector. These cases may be distinguished by mapping the decay time of the luminescence from the sample, giving data not only on the presence of particular optical centres but also on their relationship with other defects in the crystal.

Measurements on the lifetime of luminescence from the most common luminescing centres in diamond have been reported and have given valuable information on the centres, as discussed in section 2. However, to date, the lifetime measurements have been averaged over the bulk of the samples. Here we map the lifetime of the luminescence across

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a sample. In section 2 we review the information that can be derived from the lifetimes of luminescence. In section 3 we outline the methods that we have used in this work. In section 4 we discuss the possibilities of the technique, observing that it is necessary to use centres that are stable under the conditions of photo-excitation that are used, and in section 5 we demonstrate that the commonly observed H3 centre is amply stable. In section 6 we examine data from the H3, H4 and nitrogen–vacancy (NV$^-$) centres. We show that the transfer time from an H3 centre to an A aggregate is equal to that from an N3 centre to an A aggregate with the same separation; that the transfer time to a B aggregate is at least three orders of magnitude larger; and that in synthetic diamond the single, substitutional nitrogen atoms can quench luminescence.

2. Lifetimes in diamond

We will be concerned here with radiative centres that have intrinsic radiative decay times of the order of 10 ns. The centres discussed are, in the standard notation, 'N3', 'H3', 'H4' and NV$^-$. N3 is the smallest equilateral triangle of nitrogen atoms plus one vacancy, with trigonal symmetry [3]. H3 is known to be a nitrogen–vacancy–nitrogen chain [4] and is formed when a vacancy is trapped at the 'A' aggregate of nitrogen, while H4 is an analogous centre formed when the vacancy is trapped at the 'B' aggregate of nitrogen [5]. These nitrogen aggregates are respectively a pair of nearest-neighbour substitutional nitrogen atoms, and the smallest cluster of four nitrogen atoms, centred on a vacancy. If a vacancy is trapped at a single, substitutional, nitrogen atom, a nitrogen–vacancy centre is created [6], and here we use the centre in its negative charge state. All these centres produce luminescence in the visible part of the spectrum.

　　When an optical centre is excited from its ground electronic state to an excited electronic state, the centre is energetically unstable and will decay back to the ground state, emitting a photon, at a rate $1/\tau_r$, where τ_r is the intrinsic radiative lifetime of the transition. If there are no competing de-excitation channels, the intensity $I(t)$ of the luminescence measured at a time t after an instantaneous excitation is simply $I(t) = I(0)\exp(-t/\tau_r)$. At low temperature, the radiative decay time of the N3 centre is $\tau_r = 41 \pm 1$ ns, for H3 it is $\tau_r = 16.7 \pm 0.5$ ns, for H4 $\tau_r = 19 \pm 1$ ns (for 488 nm excitation) [7–9]. For the NV$^-$ centre, the radiative decay time has been reported as $\tau_r = 13 \pm 0.5$ to 12 ns [10, 11]. Recent work has established that the decay time depends on the spin state, but the relevant transition here involves the $m_s = 0$ spin state [11]. For each band, the decay time is essentially the same at low temperature and at room temperature, allowing measurements here to be made at the more convenient room temperature. The only complication in the intrinsic radiative lifetimes is that for the H4 centre; the decay time increases approximately linearly as the wavelength of the photo-excitation decreases, becoming 23 ns at 300 nm excitation, as the photo-excitation is absorbed into higher excited states of the H4 centre [9].

　　The intrinsic lifetime τ_r is very significant in that it measures the 'strength' of the optical transition. For example,
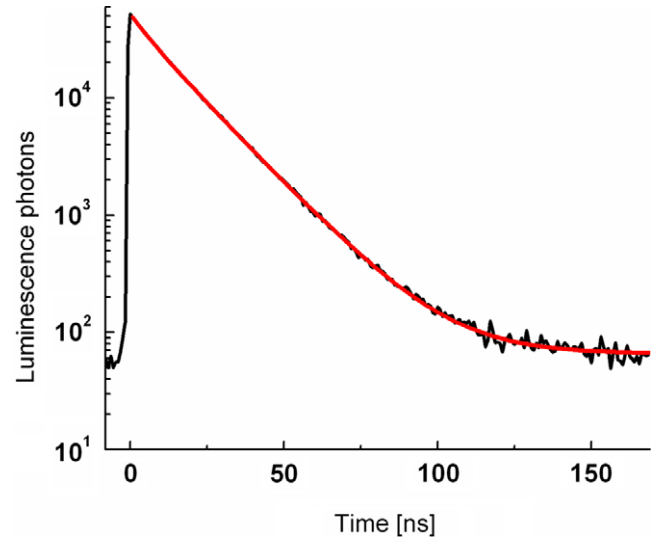

Figure 1. Decay of the H4 luminescence from a type IaB diamond with 560 atomic-ppm B nitrogen and less than 5 atomic-ppm A nitrogen. The sample has been irradiated with 10^{18} cm^{-2} 2 MeV electrons and then annealed at 800 °C to generate H4 centres. The room-temperature decay of the H4 luminescence is mono-exponential through three orders of magnitude down to the background level of 60 units, as shown by the line through the data. The decay time is 15 ns.

detailed balance arguments show that the absorption coefficient μ integrated over all the photon energies E spanning the total absorption band of the centre (including its vibronic sidebands) is related to the decay rate by

$$\int \mu(E)\,\mathrm{d}E = \frac{1}{\tau_r}\frac{g_g}{g_e}\frac{\pi^2}{9}\frac{\hbar^3 c^2}{E^2}\frac{(n_r^2+2)^2}{n_r^2}N. \quad (1)$$

Here, N is the concentration of the optical centres, g_g, g_e are the degeneracies of the ground and excited electronic states, and n_r is the refractive index of diamond. SI units have been used and the Lorentz correction for the effective electric field has been assumed. Equation (1) has the importance of linking the intrinsic radiative lifetime τ_r to the concentration N of the centres. It appears to be correct within an order of magnitude for the very compact electronic transitions found for the lowest excitations of many centres in diamond [12]. At present, even when they are determined directly from experimental data, the calibration factors for optical centres in diamond (excluding the basic forms of nitrogen) are generally uncertain to within a factor of about two [13].

　　Figure 1 shows the decay of the H4 emission measured in this work, when there are negligible non-radiative decay channels. (The details are described in section 6.2.) The intensity dies exponentially with time over three orders of magnitude in the decay, down to the background level. In contrast, figure 2 shows the decay of the H3 luminescence from a natural octahedral diamond with a mean concentration of 550 atomic-ppm of nitrogen in the A aggregated form (substitutional pairs). The decay is faster than the intrinsic radiative lifetime of $\tau_r = 16.7$ ns, and it is clearly non-exponential. It has been established that the A aggregate
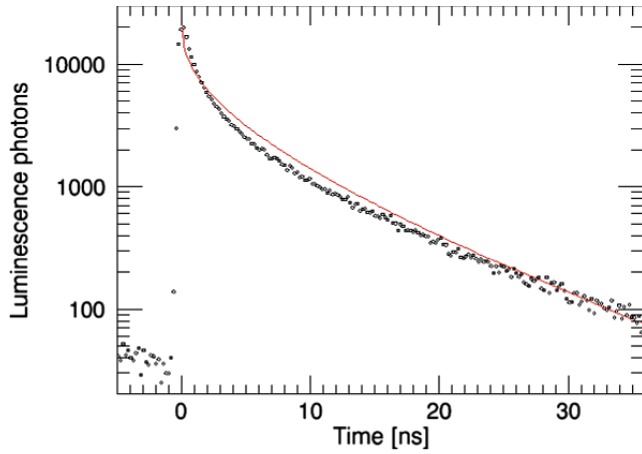
Figure 2. Decay of the H3 luminescence from a type IaA diamond with 550 atomic-ppm of nitrogen in the A aggregated form. The sample has been irradiated with 10^{18} cm^{-2} 2 MeV electrons and then annealed at 800 °C to generate H3 centres. The room-temperature decay of the H3 luminescence is shown through three orders of magnitude down to the background level 20 units. The decay is non-exponential, and is closely fitted with equation (3), as shown by the line. ($\tau_r = 16.7$ ns, $I(0) = 23\,800$, $k = 2.7$.)

quenches luminescence from the H3 centres [8] and from the N3 centres [7]. The A aggregate has no detectable absorption in the visible spectrum, even though it may be present at concentrations in excess of 1000 atomic-ppm. Consequently, we may exclude the possibility that the A aggregate has electric–dipole transitions in the visible spectrum. (It does have strong electric dipole transitions to higher energy [14].) However, it is possible that higher-order optical transitions may be allowed in the visible spectrum. Data for the specimen dependence of the H3 and especially for N3 establish that energy transfer may take place from the luminescent centre to the A aggregate by the 'dipole–quadrupole' mechanism [7, 8]. The mathematics of the process may be pictured in terms of the electric dipole of the luminescent centre emitting a 'virtual' photon, which is absorbed in an electric quadrupole transition by the A aggregate [15]. The rate of transfer of the energy decreases as the eighth power of the separation r of the luminescing centre and the A aggregate. Despite the rapid decrease with increasing r, the mechanism results in considerable loss of luminescence, as implied by the reduced decay time in figure 2. The lifetime for the luminescence from one particular optical centre is then τ, where

$$1/\tau = 1/\tau_r + 1/\tau_n. \tag{2}$$

The statistical variation in the local concentration of A aggregates results in different centres having different non-radiative transfer rates τ_n, and the decay with time becomes non-exponential, figure 2.

　For the N3 centre, the intrinsic radiative decay time is $\tau_r = 41 \pm 1$ ns, but interactions with the A aggregates reduce the decay time [7]. Assuming that the optical centres and the A aggregates are randomly distributed in the crystal, and that the energy transfer occurs through the dipole–quadrupole

mechanism, the intensity measured from the bulk crystal at a time t after excitation is predicted to be [16]

$$I(t) = I(0) \exp[-t/\tau_r - k(t/\tau_r)^{3/8}], \tag{3}$$

where the power 3/8 is specific to dipole–quadrupole coupling. The parameter k determines the non-radiative quenching. It depends, first, on the strength of the interaction between the luminescent centre and the A aggregate. It is convenient to introduce a time τ_t so that $1/\tau_t$ is defined, formally, as the rate of energy transfer that would occur from the optical centre to one A aggregate placed one bond length (0.154 nm) from the centre. The parameter k also depends on the mean concentration of the A aggregates, which may be measured from the infrared absorption μ_A (in cm^{-1}) produced by the A aggregates at the standard calibration wavelength of 1282 cm^{-1}. Finally, k depends on geometrical factors. Combining these,

$$k = 1.0 \times 10^{-4} (\tau_r/\tau_t)^{3/8} \mu_A. \tag{4}$$

This theory has been applied to the luminescence quenching of the N3 centre [7]. k was found to be proportional to μ_A, as expected from equation (4), in samples for which the average decay time varied by over a factor of two. The resulting value for the N3 centre, with μ_A in cm^{-1}, was

$$k(\text{N3}) = (0.11 \pm 0.01)\mu_A. \tag{5}$$

This value corresponds to the non-radiative transfer time between an N3 centre and an A aggregate, separated by r bond lengths, of

$$\tau_t(\text{N3}) \sim 3 \times 10^{-16} r^8 \text{ s}. \tag{6}$$

To place the figure in context, the transfer time would be equal to the intrinsic radiative decay time for the N3 centre when one A aggregate was 10 bond lengths (1.5 nm) from the N3 centre. If we think of the A aggregates as occupying a regular cubic array in the diamond, with one N3 centre at the centre of a cube and 10 bond lengths from a corner, the concentration of nitrogen in the A aggregates would be ∼200 atomic-ppm. This value is found in many natural diamonds. Clearly, dipole–quadrupole quenching is a significant process in many diamonds, even though the energy transfer process is only effective over a few nanometres (for centres with $\tau_r \sim 10$ ns).

3. Techniques employed

Luminescence lifetime mapping images of 256 pixels × 256 pixels were obtained using a Leica TCS SP2 inverted scanning confocal microscope coupled with a Becker & Hickl time-correlated single photon counting (TCSPC) card SPC830 in a 3 GHz, Pentium IV, 1 GB RAM computer running Windows XP. A 467 nm pulsed diode laser (PLP-10 470, Hamamatsu) with a pulse duration of 90 ps was used as the excitation source. The repetition rate was 5–20 MHz, depending on the decay rate of the luminescence. Excitation was focused through a 10 or 40× air objective, with a numerical aperture (NA) of 0.75, to a size of ∼1.5 μm by ∼1.5 μm. Emission with a wavelength longer than 525 nm was collected through a band pass filter

on to a cooled PMC 100-01 detector (Becker & Hickl, based on a Hamamatsu H5772P-01 photomultiplier). The acquisition time was typically 2000 s for each image, and for the results presented here, a line scanning speed of 400 Hz was used.

Measurements of the intensity as a function of excitation power were made using a Leica TCS SP 4Pi microscope equipped with 1.2 NA glycerol immersion objectives. Excitation was by 488, 476 or 453 nm lasers, focused to an estimated area of 250 nm square. The sample was at room temperature.

Infrared absorption measurements were made using a Perkin-Elmer GX FTIR spectrometer, at room temperature.

4. Temporal and spatial limitations

The accuracy of the decay time is determined by several factors, including the statistics of the measurements, the stability of the equipment and the stability of the sample, discussed in section 5. In our measurements, instrumental uncertainties arise from the pulse length $\Delta t_p = 90$ ps of the excitation laser, the transit time spread of $\Delta t_t \sim 200$ ps of the carriers in the detector, and electronic jitter, $\Delta t_j \sim 1$ ps. These independent sources sum to give an instrumental uncertainty Δt_i of

$$\Delta t_i^2 = \Delta t_p^2 + \Delta t_t^2 + \Delta t_j^2. \tag{7}$$

Evaluating gives $\Delta t_i \sim 0.25$ ns for our equipment.

A more significant cause of uncertainty in our measurements is the random noise in the photon counting. The data at each pixel are gathered by counting the number of photons $n(t)$ emitted in the measurement window at different times, t. Ideally, that number would be given by $n(t) = n(0) \exp(-t/\tau)$, where $n(0)$ is a well-defined initial value. In practice, the number measured is expected to have a noise level so that the actual measurement will be randomly distributed about the ideal value, with a standard deviation of $\sqrt{n(t)}$. As a result of the noise on the decay plot, the measured decay time at each pixel will be different, even if the equipment is totally stable and the decay times are in fact identical. The standard deviation in the decay times is then proportional to $\sqrt{n(0)}$, and the measured decay times from different pixels lie on a normal distribution, as we will see later in figure 6. Consequently, the precision in the decay time improves in proportion to the square of the acquisition time, if all other parameters are fixed. An alternative way of improving the accuracy in the decay time is to amalgamate the counts at one point plus its immediate neighbours, giving a factor of 9 increase in intensities, and so an improvement by a factor of 3 in the accuracy of the decay time, but at a loss of spatial resolution. These expectations have been observed in our equipment.

The spatial resolution in these measurements has been limited to the pixel size, which was typically 1.5 μm × 1.5 μm here. Since there is direct photo-excitation of the optical centres, the excitation energy is deposited directly into the optical centres, and into the excited state of the luminescence transition. (The only exception is possibly the H4 centre, where excitation may be into higher excited states, but still at the same centre [9].) This excitation process is in contrast to measurements using above-band-gap excitation (or cathodoluminescence), where the bulk diamond is excited and the energy must then be transferred to the optical centre. In the photo-excitation measurements used here, there is no loss in spatial resolution as a result of indirect excitation.

5. Photo-stability

A lifetime image of adequate signal to noise ratio requires several tens of minutes of integration time. It is essential that the sample remains unchanged during this time. Under optical illumination, the concentration of active luminescence may change. For example, charge transfer affects optical centres [17] and is readily enhanced by suitable photo-excitation. Recently, stimulated emission has been used to locate nitrogen–vacancy centres in a diamond with near-bond-length precision [18]. The centres were photo-excited by one pulsed light source. A second, powerful, and carefully shaped, pulse of light stimulated emission to rapidly kill the luminescence from most of the NV$^-$ centres, leaving only some visible in the field of view. The power density in this stimulated emission depletion (STED) beam had to be over 20 MW cm^{-2} [18].

In the present experiments, only one excitation beam is used, but charge transfer can still occur. Our lifetime mapping has used an excitation at 476 nm, 2.65 eV. This energy is greater than the ionization energy of 1.7 eV of the single nitrogen atom, but in most natural diamonds the concentration of single nitrogen atoms is negligible compared to the concentrations of the optical centres (typically 10^{17} cm^{-3} here). More significantly, the A aggregates have no electric dipole transitions in the visible spectrum, but have been assumed to have quadrupole transitions. We know nothing about the absorption into those centres and how it may affect the luminescent centres. Even if there are no charge transfer processes, absorption of the excitation beam by the luminescent centre depletes its ground state, reducing the number of optical centres available for excitation, so resulting in saturation of the luminescence.

To investigate the photo-stability in samples of interest here, we have excited H3 centres, present at concentrations of $\sim 10^{17}$ cm^{-3} in a natural diamond with 550 atomic-ppm of nitrogen in the A aggregates, and with no other forms of nitrogen detectable by infrared absorption. Figure 3 shows the luminescence intensity from the H3 band as a function of excitation power at three excitation wavelengths, 488 nm (2.54 eV), 476 nm (2.60 eV) and 453 nm (2.74 eV), focused to a nominal 250 nm square. The excitation used for figure 3 corresponds to a nominal maximum power density of 1.3 MW cm^{-2}. We define μ as the absorption coefficient produced by the optical centre at the excitation wavelength, in a conventional absorption experiment, that is, in the limit of low power. The absorption is then $\mu = KN$, where N is the concentration of the optical centres and K a calibration constant. When a high intensity beam travels through the sample, the change in intensity in a thickness Δx is $\Delta I = -I\mu n_g \Delta x / N$, where n_g / N is the fraction of the centres in the ground state. The number of excitations per unit area of the beam, per unit time, is then $-\Delta I / h\nu$, where $h\nu$ is the photon
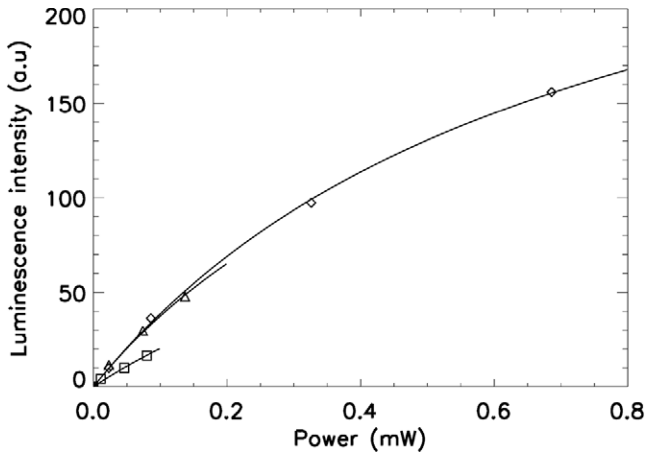
Figure 3. Luminescence intensity from the H3 centre in a type IaA sample with 550 atomic-ppm of nitrogen. The lasers were focused on a size approximately 250 nm square. Diamonds are for 488 nm excitations, triangles for 476 nm and squares for 453 nm. The lines are calculated as discussed in section 6.

energy. In a steady state, this excitation rate is equal to the de-excitation rate n_e/τ of from the excited state. The intensity of the luminescence is proportional to n_e, and

$$n_e = \frac{N}{[1 + (h\nu/\tau K I)]}. \qquad (8)$$

The luminescence intensity is linear in the excitation as long as $I \ll h\nu/\tau K$. For the H3 centre, $K \sim 7 \times 10^{-22}$ m^2 at the wavelengths of interest, from the calibration data of [12]. With $h\nu \sim 2.6$ eV, and a dominant lifetime of $\tau \sim 6$ ns in the sample used for figure 3, saturation is expected to be significant at a power density of $h\nu/\tau K \sim 10$ MW cm^{-2}.

The lines in figure 3 are fits of equation (8) in the form that the luminescence intensity L is $L = a/(1 + b/p)$, where a and b are fitting constants, and p is the excitation power. The specific values for 488, 476 and 453 nm excitation are respectively $b = 0.73$, 0.57 and 0.65 mW. If we assume that the area excited in the confocal microscope is a square of 250 nm edge, the values of b correspond respectively to $\sim$12, 9 and 10 MW cm^{-2}. We noted that b is proportional to the absorption coefficient at the excitation wavelength. The sequence of values is understandable: the absorption in the H3 band is larger at 476 nm than 488 nm, consistent with the lower value of b. At 453 nm, there is competition for absorbing the excitation light from the absorption continuum that underlies the H3 band, decreasing the intensity absorbed by the H3 centre and so tending to increase the value of b.

These results indicate that the saturation of the H3 luminescence with increasing power is simply the result of de-population of the ground state. There is no evidence for hysteresis in the luminescence, implying no long-term charge transfer effects even at these powers. Evidently the weak quadrupole absorption by the A aggregates does not result in charge transfer.

6. Specific luminescence bands

6.1. The H3 band

We have seen in section 5 that the H3 luminescence band in natural type IaA diamond is highly photo-stable. We take it as a first example. Figure 2 shows data amalgamated across a type IaA sample with 550 atomic-ppm of nitrogen in A aggregates. The line is a fit of equation (3), using the intrinsic radiative decay time of 16.7 ns. We recall that equation (3) is based on the assumption that the H3 centres and the A aggregates are randomly distributed, which will not be obeyed exactly. However, its use involves a minimum of parametrization. Fitting equation (3) requires

$$k(\text{H3}) = (0.08 \pm 0.02)\mu_A. \qquad (9)$$

Given $\tau_r = 16.7$ ns, the transfer time to an A aggregate placed r bond lengths from the H3 centre is

$$\tau_t(\text{H3}) \sim 3 \times 10^{-16} r^8 \text{ s}, \qquad (10)$$

effectively in agreement with the value for the N3 centre, equation (6). The N3 centre luminesces in the range 2.5–3 eV, and the H3 centre in the range 2–2.5 eV, implying that luminescence through the visible spectrum may be quenched by the A aggregates.

Figure 4 shows the luminescence map of the same sample. On the left is an image of the intensity of the H3 luminescence. On the right is a luminescence map, taken at 1.5 μm pixel size. The false colours indicate the decay time, with red long (6 ns) and blue short (2 ns). There is a close correlation between the intensity and the decay time. Since an H3 centre is created from an A aggregate plus a vacancy, spatial correlations are likely between the H3 centres and the A aggregates; the interesting point is that on the micron scale, averaging has taken place across most of the sample.

6.2. The H4 band

In section 6.1 we proposed that the A aggregate quenches luminescence in the visible spectrum from different optical centres at similar rates. We would certainly expect that the very similar luminescence from the H3 and H4 bands would be quenched by A aggregates at the same rate. The decay data for the H4 band in figure 1 were obtained from a sample with negligible A aggregates (less than 5 ppm A-nitrogen), but with 560 atomic-ppm of nitrogen in the B aggregates—the same concentration of nitrogen as produces strong quenching of the H3 band, figure 2. Each B aggregate contains four nitrogen atoms, compared to two in the A aggregates, so there are half the B aggregates relative to A aggregates, but if the transfer time to each B aggregate were the same as to an A aggregate, significant quenching would be observed. The mono-exponential form of the data for the H4 band in figure 1 implies that the transfer time from an H4 centre to a B aggregate placed fictitiously one bond length away would be $\tau_t > 4 \times 10^{-13}$ s, and we have no evidence that the B aggregate quenches the luminescence at all.
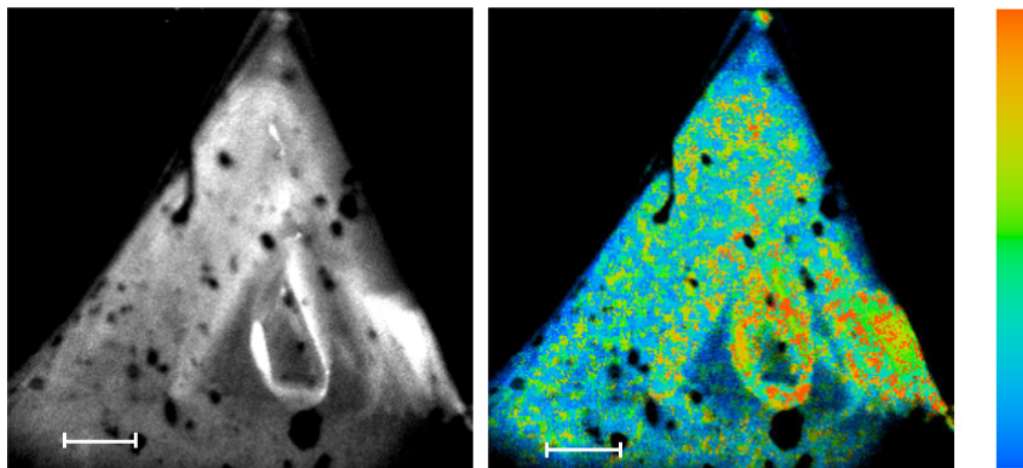
Figure 4. Left, image of the intensity of H3 emission from a natural octahedral diamond with 550 atomic-ppm nitrogen in the A aggregate. The sample is 1.5 mm across, and the image pixel size is 1.5 μm. Right, coloured on-line, is a lifetime map in false colours, with red indicating 6 ns and blue 2 ns. In monochrome, the longer decay times have the lighter shading, shorter decay times have darker shading, and there is no luminescence from black areas. The scale marker shows a 50 μm length.
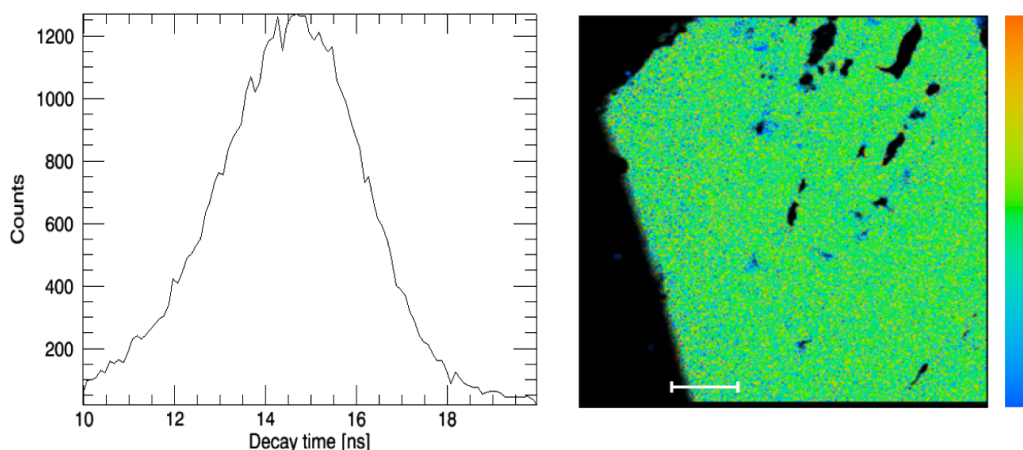

Figure 5. Right, luminescence decay time map for the NV$^-$ band in a synthetic diamond with nitrogen undetectable by infrared absorption. The scale marker shows a 50 μm length. The false colours (on-line) indicate short times by blue (10 ns) and long times by red (18 ns), but these are only statistical fluctuations about the mean, shown by the normal distribution of measured decay times on the left. In monochrome, the statistical distribution of decay times produces the speckling, with longer decay times having lighter shading.

6.3. The NV$^-$ band

The negatively charged nitrogen–vacancy band has been studied intensively to exploit its novel properties [19]. It is readily produced in HPHT synthetic diamond by radiation damage followed by annealing, so that the vacancies are trapped at the single substitutional nitrogen atoms in the samples. There have been no investigations into whether the single nitrogen atom quenches luminescence from optical centres. The NV$^-$ band has an intrinsic radiative decay time for the $m_s = 0$ spin states of 12–13 ns, section 2. In a sample with no nitrogen detectable by infrared absorption, we measure the decay time to be 14.5 ± 0.5 ns. Luminescence lifetime mapping establishes that the sample is uniform, on the scale of micrometres, figure 5.

However, the single nitrogen atoms produce a continuum of absorption, starting at $\sim$1.9 eV. This continuum overlaps the luminescence from the NV$^-$ band, which is in the range 1.4–2 eV. Energy transfer may occur through the dipole–dipole coupling mechanism [15]. This process couples the electric dipole of the luminescing centre, which is established experimentally [6], to an assumed electric dipole at the single nitrogen centres which produces the strong absorption continuum. In dipole–dipole coupling, the rate of energy transfer decreases as the separation to the sixth power. We have only examined one sample of synthetic diamond, with a relatively high average nitrogen concentration of 130 atomic-ppm. Figure 6 shows the distribution of decay times from the NV$^-$ band and an image of the luminescence, taken at micrometre spatial resolution, across the growth faces of the sample. The decay time is predominantly 7 ns, with a small area of 12 ns at an interface. The sample had been irradiated with a typical dose of $\sim 2 \times 10^{18}$ cm^{-2} 2 MeV electrons, creating only of the order of 10^{18} cm^{-3} radiation defects. In type Ia samples, such a radiation dose has no effect on the decay times. It appears that the reduced decay time is the result of the nitrogen *in the single, substitutional form*. To investigate this further, and establish if the dipole–dipole
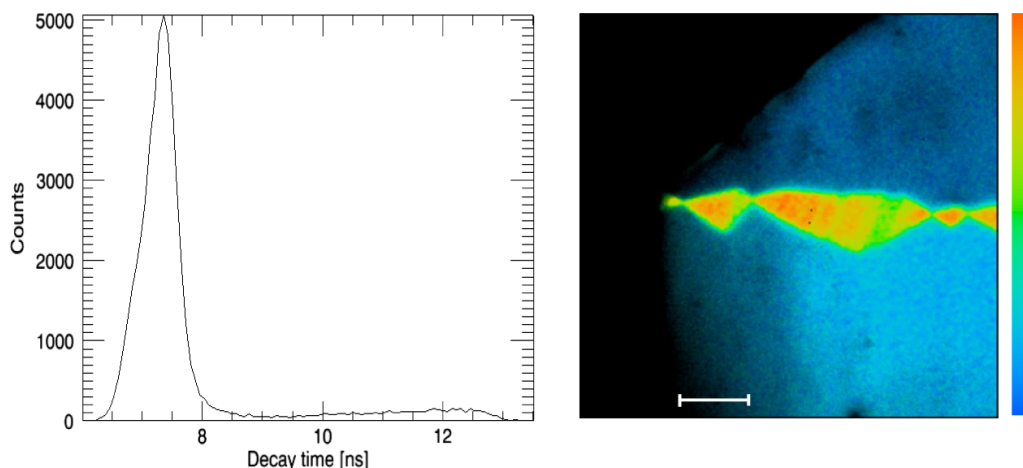
Figure 6. Right, luminescence decay time for the NV$^-$ band in a synthetic diamond, with an average nitrogen concentration of 130 atomic-ppm in the single, substitutional form, mapped over two major faces and their edge. The scale marker shows a 50 μm length. The faces show the short decay times of 7.3 ns in the plot at left, with decay times in the junction of 12.5 ns. The false colours (on-line) range from blue (2 ns) to red (12 ns). In monochrome, the longer decay times have the lighter shading, shorter decay times have darker shading, and there is no luminescence from black areas.

energy transfer mechanism is appropriate, requires study of synthetic diamonds with different nitrogen contents.

7. Summary

Taking the H3 centre as a working example, we have shown that it is stable under intense optical excitation, up to power densities of ~10 MW cm^{-2}. In the absence of charge transfer processes, this result is likely to be the same for all dipole-allowed luminescing centres in diamond. We have shown that both the H3 and N3 centres, which luminescence in the visible spectrum, can transfer energy to the A aggregates of nitrogen at the same rate, corresponding to a timescale of ~$3 \times 10^{-16} r^8$ s, where there are r bond lengths between the H3 and A centres. The short-range transfer process allows small volumes of A aggregates of nitrogen to be detected. Previously, only the A aggregates have been identified as quenching luminescence, but we have shown that the decay time of the important NV$^-$ centre can be reduced in synthetic diamond by a high content of nitrogen in the single, substitutional form. In contrast, quenching by the B aggregate has not been detected, and the transfer time from an optical centre to a B aggregate is at least three orders of magnitude longer than to an A aggregate at the same distance.

Acknowledgments

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