

Ultra short luminescence lifetime of ruby nanocrystal inclusions in Ib diamond

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Abstract: We report the observation of abnormal luminescence behaviour of ruby nanocrystals embedded in diamonds. The work has been carried out using high spatial resolution confocal microscopy at 300 K in a synthetic Ib diamond. Spectral analysis shows slight red shifts of ~ 0.1 meV due to the mechanical pressure induced by diamond lattice. More surprisingly, the photoluminescence decay measurements show very short lifetimes, typically 80 μ s, compared with the usual value of about 3 ms in bulk crystal.

1. Introduction

Recently a very sharp photoluminescence (PL) line at 1.789 eV with lifetime of 7 ms at room temperature has been reported for a set of HPHT diamonds [1]. This defect center awakened great interest because of its unique linewidth at room temperature, which can be as small as 1 meV. Due to the fact that all those samples were grown in a Fe containing chamber and had some similarities in luminescence characteristics with Ni- and Co-related centers, an interstitial Fe-related point defect was suggested as a possible atomic model. On the other hand, remarkable analogies between the luminescence features of this defect center and the ruby crystal ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) have been found.

We investigated this defect center using PL based measurements at room temperature, which analyze the spatial, spectral and time dependent characteristics of the luminescence. Most remarkably we found a dramatic reduction of the lifetime.

2. Experimental details

The investigated diamond sample was a commercially available HPHT synthetic Ib diamond from Drukker International, (0.5 x 0.5 x 0.25) in size.

In contrast to other conventional and well-established techniques for diamond defect research, a high resolution scanning confocal microscope was employed, which had been once developed for detection of single $[\text{N-V}]^-$ centers in diamonds [2]. This system provides a spatial resolution of 500 nm (FWHM) in lateral direction and 1-2 μ m in the optical axis. Luminescence excitation is provided by a cw Nd:YVO₄ laser operating at 532 nm, with the option of fast switching for lifetime measurements. Energy dependent measurements have been carried out with a home-built grating spectrometer with maximal spectral resolution of 0.7 meV.

To avoid errors in estimation of the overall detection efficiency the results are calibrated with data of the well known single $[\text{N-V}]^-$ centers measured by the same setup.

3. Measurements and results

Before its final identification this investigated defect center will be termed the “1.79 eV center”. All the observed 1.79 eV centers appeared as points (Fig.1 (a)). They were photostable even under high excitation power over weeks of measurement. The luminosity profile in one transversal direction of the 1.79 eV center (Fig.1 (a))

is compared with that of a $[\text{N-V}]^-$ center (Fig.1 (b)). The FWHM of the two profiles agree within the errors of the Gaussian fit of the data. In the two dimensional scans the 1.79 eV centers differed from the single $[\text{N-V}]^-$ centers only in the luminous brightness. A rough estimation of the overall emission rates at saturation I_∞ yields $I_\infty(1.79 \text{ eV})/I_\infty([\text{N-V}]^-) \approx 70$. Note, this value varies for different 1.79 eV centers from 40 to 100.

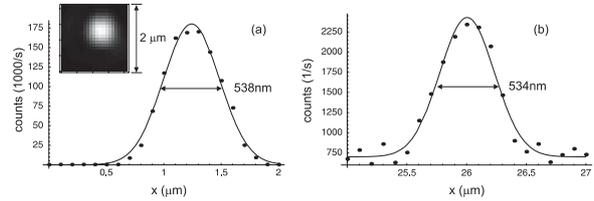


Fig.1. (a) Luminescence of a 1.79 eV center on a two dimensional scan and its intensity profile in x-direction. (b) Intensity profile in x-direction of a single $[\text{N-V}]^-$ center.

As opposed to the case of most point defects in diamonds, a dominant fraction of the luminescence of the 1.79 eV center is concentrated in a sharp zero-phonon line near 1.789 eV even at room temperature. Fig.2 (a) shows the two peaks of the ZPL. A fitting with a double-Lorentzian model delivers a line at 1.7852(3) eV with linewidth of 1.23 ± 0.01 meV and another at 1.7888(8) eV with linewidth of 0.88 ± 0.014 meV. To eliminate the errors in calibration of our simple grating spectrometer, a spectrum of Cr^{3+} ions in a sapphire window was measured, which is displayed too. This spectrum consists of the two well-known lines of ruby crystal, one at 1.7853(4) eV with linewidth of 0.83 ± 0.019 meV and the other at 1.7890(3) eV with linewidth of 0.65 ± 0.024 meV.

To measure the lifetime of PL decay the excitation laser was chopped and the laser pulse form is seen in Fig.2 (b). Instead of the expected lifetime on a scale of milliseconds, the luminescence intensity decays much faster. Another surprising result is that the decay can be much better described by a two-component exponential model than by a single-component one. For a 1.79 eV center, a fitting with two exponential functions yields a value of 15.3 ± 0.4 μ s for τ_1 and 86.7 ± 1.42 μ s for τ_2 . To verify that the luminescence of the two lines do not decay with different time constants, the measurement was repeated through the spectrometer for each of the

lines separately. Within errors the measurements delivered the same results for the two lines. The lifetime shows variation from center to center.

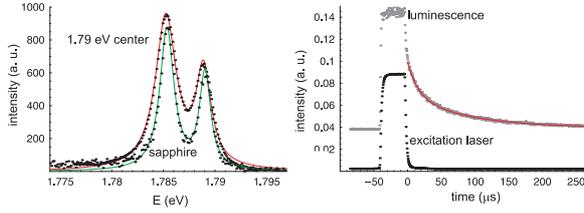


Fig.2. (a) Experimental data and fits of the spectra of the 1.79 eV center (red line) and the Cr^{3+} in sapphire window (green line). (b) Experimental data of the luminescence decay measurement. The red line represents a two-component exponential fit.

For comparison, the same measurement has been performed on the sapphire window and again, two time constants were observed with $\tau_1=3.16\pm 0.11 \mu\text{s}$ and $\tau_2=509\pm 330 \mu\text{s}$. In order to resolve the fast decay, the detection time interval was restricted to $500 \mu\text{s}$, therefore the longer time constant could only be determined with a large error.

4. Conclusions and discussion

Because the apparent size of 1.79 eV centers in confocal microscope does not differ from that of a single [N-V] center, which is limited by diffraction, the real size of the luminous region must be below 300 nm.

The emission rate at saturation I_∞ of a group of two-level systems can be calculated by

$$I_\infty = \gamma N / \tau \quad (1)$$

where γ is the overall detection efficiency, N is the number of two-level systems and τ is the lifetime of the excited level. Based on the data of a single [N-V] center, the number of light emitters within a luminous region can be derived from its luminosity at saturation and the lifetime. It is estimated to be 2.8×10^5 . The inclusion of nanocrystals is the only reasonable explanation for concentration of so many light emitters within such a small region. According to the spectrum it should be ruby nanocrystals.

If we assume that the ruby nanocrystals are cubes with usual Cr^{3+} density of 1.58×10^9 ions/cm³, with the very short decay time we obtain a size of 260 nm, which is consistent with the observation in two dimensional scans of our confocal microscope. Notice, that a ruby nanocrystal with regular decay time would be larger by a factor of more than 3, which must be visible with the optical resolution.

To explain the two-component exponential decay of the luminescence, we must look into the dynamics of the luminescence of a Cr^{3+} ion in ruby crystal. Fig.3 (a) illustrates relevant energy levels. Due to the small size we can ignore the stimulated emission. After the excitation laser is turned off, the rate equations for the

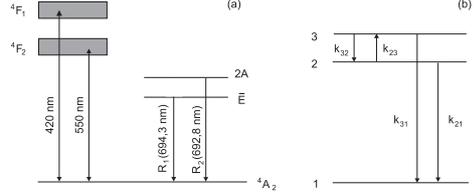


Fig.3. Energy levels of Cr^{3+} ion in ruby crystal.

three-level system in Fig.3 (b) can be easily solved. The k_{ij} in Fig.3 (b) are coupling coefficients. The solutions for population numbers $n_2(t)$ and $n_3(t)$ are both sum of two exponential decays with

$$\frac{1}{\tau_{1,2}} = \frac{k_{21} + k_{23} + k_{31} + k_{32} \pm \sqrt{\Delta}}{2}$$

$$\Delta = (k_{21} + k_{23} + k_{31} + k_{32})^2 - 4(k_{21}k_{31} + k_{23}k_{31} + k_{32}k_{21})$$

If the coupling between excited and ground level is weak, that is $k_{23}, k_{32} \gg k_{21}, k_{31}$, we get a very fast and a very slow decay as we measured for Cr^{3+} in sapphire window. In Contrast, if the four coupling coefficients are comparable, the two time constants have similar magnitudes as observed in the investigated nanocrystals.

The red shifts in the spectrum indicate that the ruby nanocrystals are under mechanical pressure. The measured red shift of 0.043 nm means a pressure of 1.18 kbar [3]. Because of the small size of the nanocrystals, Cr^{3+} ions are probably under different pressures, which can cause a homogenous broadening of the spectral lines. On the other hand pressure can enhance the lifetime of PL decay [4]. Fortunately 1.18 kbar show only negligible influence on the lifetime.

One possible reason for the ultra short lifetime is that the Cr^{3+} ions are subjected to another refraction index than that in normal ruby crystals, because the size of the nanocrystals is much smaller than the luminous wavelength. But this QED effect only results in a factor of $n_{\text{diamond}}/n_{\text{ruby}}$. Another interesting issue to explore is the influence of diamond phonons, which, however, is beyond the scope of the present work.

In summary, The 1.70 eV center in Ib diamonds was identified to be inclusion of ruby nanocrystal. However, the Cr^{3+} ions of the ruby nanocrystal inclusions show a much faster luminescence decay time than that in bulk crystals.

5. References

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