

Toward optically addressing single rare-earth ions in solid state

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Abstract—This work aimed at optically addressing a single photostable Eu^{2+} ion in calcium silicate (Ca_2SiO_4) nanocrystals. The sample was prepared by solid state reaction (SSR). The europium concentration of investigated samples are varied below 1000 ppm. Here we report red-shift in spectrum as the concentration of Eu^{2+} decrease. The fluorescence lifetime of Eu^{2+} in the 10 ppb sample had been determined.

I. INTRODUCTION

Interest in rare earth (RE) ions arose from several features such as long coherence time, which makes rare earth ion a candidate of quantum bits (qubits). However, to really deploy rare earth ion as quantum bits, one has to create single photon emitter, e.g. a single rare-earth ion in a crystal, instead of optically addressing the assemble. It had already been reported that detecting single rare earth ion [1] [2] by optical excitation and fluorescence detection is achievable. Here we aim to detect single europium divalent ion (Eu^{2+}) in di-calcium silicate crystal (Ca_2SiO_4). Notice that the host crystal is composed of elements that has most of its isotopes spin-free, meaning that the doped europium divalent ions is in a desirable environment for qubits.

In the host material of interest, the first excited state of Eu^{2+} is the lowest excited state $4f^65d$. The broad band emission of $4f^65d \ ^8S_{7/2} \rightarrow 4f^7$ transition peak is visible, where $4f^7$ is the ground state of Eu^{2+} . Currently, the absorption and emission spectra of $\text{Ca}_2\text{SiO}_4: \text{Eu}^{2+}$ of only high europium concentration (0.1 ~0.5 mol %) had been investigated due to interests in its application as phosphor. In this work, concentration quenching is likely to be a negligible factor[3]. Given the manufacture procedure we chose, the host crystal is likely to be composed of mainly $\beta\text{-Ca}_2\text{SiO}_4$ (monoclinic) [4]. It is expected that difference in crystal structures will produce distinct emission spectrum because the empty 5d state is not shielded from the crystal field, thus rendering the $f \rightarrow d$ transition strongly dependent on the host crystal.

II. EXPERIMENTAL SETUP

The setup used for finding the europium-doped nano particle is a confocal microscope, as shown schematically in Figure 1. The light beam for exciting Eu^{2+} is generated by a diode

pumped solid state laser. The tunable laser beam went through an optical fiber, reflected by a quartz plate (transmission 90%) and were focused on the sample by a $100\times$ oil objective (NA=1.3). The fluorescence emitted by the doped nanoparticles is collected by the same $100\times$ oil objective. A $10\ \mu\text{m}$ pinhole was used. The emitted photons arrive at either the photon-detector or the spectrometer, depending on whether the flip mirror is flipped or not. The photon detector is an avalanche photon detector (APD). A 625 nm short pass and a 450 nm long pass were placed in front of the APD so that the APD-detected photons primarily come from the broad band emission of Eu^{2+} . A 3D-piezo was used to scan over the sample.

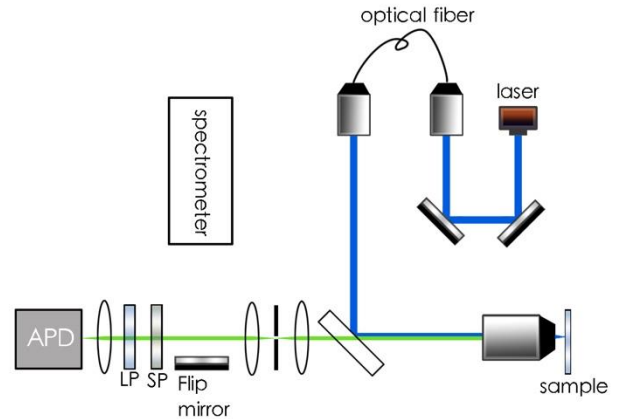


Figure 1 Layout of the confocal microscope.

III. METHODS

To prepare the Eu^{2+} -doped nanocrystal, CaCO_3 (99.99%), SiO_2 (99.99%) and $\text{Eu}(\text{NO}_3)_3$ (99.99%) powders of specific stoichiometric ratio, aiming at 1000 ppm, 120ppb, and 10 ppb, were mixed and finely grinded, and compressed into palates for pre-annealing, where an alumina boat is used. The pre-annealing process is based on the literature[5]. To reduce Eu^{3+} into Eu^{2+} ions, these palates were later fired in reduced atmosphere (5% H_2 , 95% N_2) at 1100, 1100 and 1200 $^\circ\text{C}$, respectively. The palates were cooled down to ambient temperature naturally

afterwards. The annealed palates were separately crushed down into nanoparticles. The 1000 ppm and 120 ppb particles were spin-coated on a glass slide out of isopropanol suspension, while for the 10 ppb sample was spin-coated on a quartz slide instead.

To investigate optical properties, near-UV light of 405 nm was used to pump the europium ions into the first excited state. Suitable nanoparticles were found under the confocal microscope. The 1000 ppm sample was scanned with continuous APD data acquisition, and laser was in cw mode, while for scanning the sample of 120 ppb and 10 ppb, data acquisition was gated, and laser was pulsed. For verifying that the fluorescence is indeed from Eu^{2+} ions, the photoluminescence (PL) spectrum was taken by the spectrometer, and compared with the reported spectrum of 0.1 mol % concentration $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$. The fluorescence lifetime were also taken. According to literature, the excitation wavelength in this experiment has a comparatively low excitation efficiency.

IV. RESULTS AND DISCUSSION

A. Ion stabilization

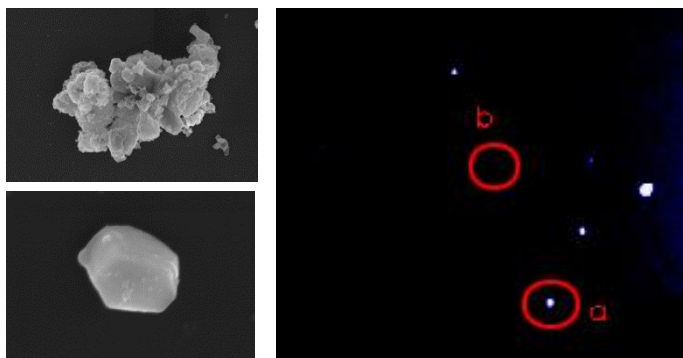


Figure 2 (a) A poorly formed crystal and (b) a well-formed crystal were imaged using SEM. (a) and (b) are both of 1000 ppm concentration. The total volume of (a) is approximated to be at least 3 times larger than (b). (c) is the scanned confocal image.

Although we can easily find photostable nanoparticles in the 1000 ppm sample, relatively few were found in the 120 ppb sample. Under the confocal microscope, nanoparticles of intermediate europium concentration mostly photobleached and did not show the expected lifetime of Eu^{2+} . From the images obtained by scanning electron microscopy (SEM), it is shown that photo-stable nanoparticles had better formation and resembles well-cut crystals more. It is then deduced that most of the europium ions failed to end up in the properly formed crystal. To address the problem of poor crystal formation, the 10 ppb sample was annealed under 1200 °C. Indeed, the 10 ppb sample gave a greater proportion of photostable $\text{Eu}:\text{Ca}_2\text{SiO}_4$ nanocrystals. While we already verified that the employed procedure has a very low yield of crystals that emit stably, we also suspect the proportion of stabilized is low. This suspicion has not been tested.

B. Spectrum

The spectrometer emission spectrum has a wavelength resolution of 0.213 nm. The multiband emission, as shown below in Figure 3, peaked at around 510 nm. The overall spectrum is a combination of two distinct emissions; the shorter wavelength and the longer wavelength emission are attributed to Eu^{2+} that occupies Ca(1) site and Ca(2) site, respectively. Both emission are purported to result from the lower energy level, in crystal field splitting. The general emission peaks all peaked at longer wavelengths than the reported 502 nm in investigation of ~0.1 mol % concentration $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$.

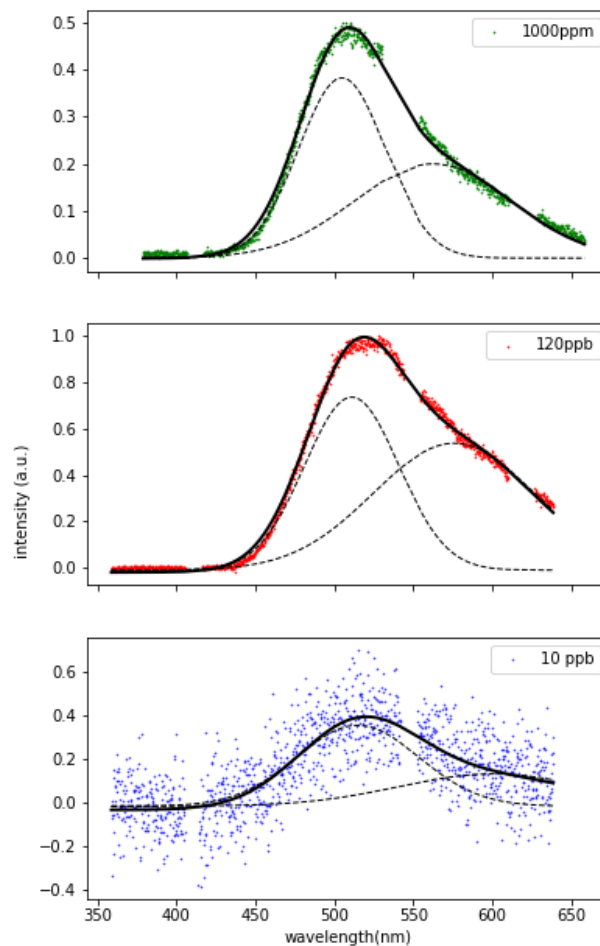


Figure 3 The broad band peaked at (top) 505.26(3)nm, (middle) 527.86(1) nm, and (bottom) 515.14(3) nm. Data taken at certain wavelength is removed because of the scattered “junk” laser light and the light from monitors.

As the concentration of europium decrease, the position of the emission peaks of Eu^{2+} occupying both Ca(1) and Ca(2) sites red-shifted, which is tentatively attributed to that Eu^{2+} ions experiencing a stronger crystal field splitting in host crystals. The increasing strength of crystal field is due to that Ca^{2+} ions has a smaller radius compared to that of Eu^{2+} , which can be

described by: $D_q \propto R^{-5}$, where D_q is the crystal field strength, and R is the bond length between the central ion and ligand ions.[6]

Nevertheless, it is surprising to see a red-shift of such magnitude at ppm and ppb levels.

	Ca(1)	Ca(2)
1000 ppm	504.76(7)	562.28(0)
120 ppb	510.96(0)	575.75(6)
10 ppb	514.76(0)	595.92(4)

Table 1 shows the tentative wavelength emission peak of divalent europium ions in nano-particles. The unit of the measured wavelength is nanometer.

C. Lifetime

For the 10 ppb sample, the fluorescence lifetime of Eu under 298K and ambient pressure is 0.62(1) μ s. Photons allowed to pass the two filters were all collected and counted during the fluorescence lifetime measurement. This is longer than the reported fluorescence lifetime of the 510 nm emission in literature [7]. It has been established theoretically that, at lower rare earth concentration, quenching caused by interactions between neighbours is less probable, thus has longer fluorescence lifetime. [8]

As shown in Figure 4, an unknown photon source of ultra-short lifetime exists. This unknown photon source also appears in poorly-formed crystals, which does not give the target spectrum. This is the reason why, as mentioned previously, the data acquisition had to be gated during the scan.

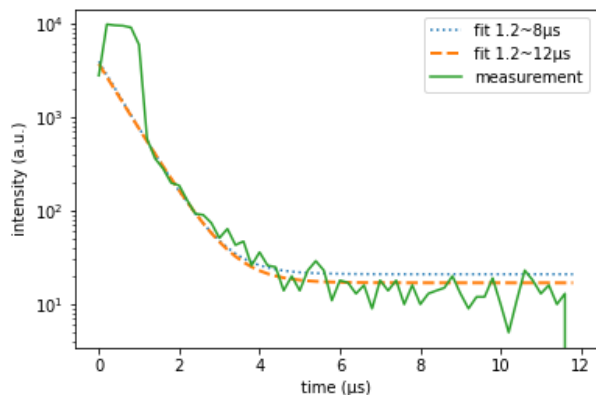


Figure 4 The fluorescence lifetime of 10 ppb nano-particle. Data of the first 1.2 μ s is not included in the data for the exponential fitting.

D. Future Work

Since the aim of this work is to find photostable single europium ion in spin-free host crystal, the primary future work is to verify the existence of single ions in crystal by performing the anti-bunching experiment in the Hanbury Brown-Twiss setup. However, before doing so, the sample manufacture procedure should be optimized so as not to suffer from the poor yield of photostable nanoparticles.

Besides reaching single ion, low europium concentration (\sim ppb) crystals would be also interesting in that optical detecting magnetic resonance (ODMR) under cryogenic temperature can be performed.

V. CONCLUSION

In conclusion, Eu^{2+} in Ca_2SiO_4 show two emission bands. From the spectrum taken, red-shift exists despite that the samples investigated in this work are of concentrations at ppm or ppb level. The reason for the shifting emission bands is tentatively attributed to a changing crystal field. The lifetime of Eu^{2+} in the 10 ppb nanocrystal is 0.62(1) μ s,

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