SUPPORTING INFORMATION

Efficient quantum cutting hexagonal NaGdF₄:Eu³⁺ nanorods

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ESI-Figure 1. FTIR spectrum of the as prepared NaGdF₄:Eu³⁺ nanocrystals prepared using IL. The inset shows the FTIR spectra of pure C₂mimBr with absorption bands at 1571, 1627 and 1164 cm⁻¹ belonging to the imidazolium ring skeleton stretching vibrations; the bands at 3152 and 3099 cm⁻¹ are the stretching vibration of C(2)-H in the imidazole ring.¹ The absence of these bands in the NaGdF₄ nanocrystals confirms that nanocrystals are free of ionic liquid.



ESI-Figure 2. PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared at (A) 150°C using C₂mimBr, (B) 150°C without C₂mimBr and (C) 200°C without C₂mimBr. The reaction time is 5 hours and reactant ratio (Gd³⁺/F⁻ = 1:8) ["H" and "C" corresponds to hexagonal and cubic phase respectively.]



ESI-Scheme 1. Schematic crystal structure of hexagonal NaGdF₄.²



ESI-Figure 3. Energy dispersive X-ray analysis (EDAX) of pure, hexagonal NaGdF₄:Eu³⁺ nanocrystals.



ESI-Figure 4. SEM images of pure hexagonal NaGdF₄:Eu nanoparticle prepared solvothermally (a) without IL and (b) with IL.



ESI-Figure 5. Selected area electron diffraction pattern of NaGdF₄: Eu doped nanocrystals in the hexagonal phase synthesized at 200° C in the absence of IL. The marked spots are due to the (100) plane and coming from the bright spot of the dark field image mentioned in Fig. 1 (F). The dark field images related to the other spots are also taken and all confirm the hexagonal structure of NaGdF₄.



ESI-Figure 6. (A) Low magnification TEM and (B) HRTEM images of NaGdF₄:Eu³⁺ nanocrystals prepared at Gd³⁺/F ratio of 1:4. HRTEM image clearly shows the presence of both cubic and hexagonal lattice planes which matches with PXRD results and Rietveld analysis.



ESI-Figure 7. VUV excitation spectrum ($\lambda_{em} = 615 \text{ nm}$) of doped NaGdF₄:Eu³⁺ nanorods in the hexagonal phase. The spectrum was taken at the Beamline I (SUPERLUMI) at HASYLAB synchrotron facility.



ESI-Figure 8. Emission spectrum excited at 393 nm with a Xe lamp at room temperature of NaGdF₄:Eu doped sample prepared with a Gd^{3+}/F^{-} ratio 1:4. This sample contains cubic and hexagonal NaGdF₄:Eu.



ESI-Figure 9. Emission spectrum of hexagonal NaGdF₄:Eu excited at 272 nm with a Xe lamp at room temperature.



ESI-Figure 10. Emission spectra of hexagonal NaGdF₄ excited at 272 nm with a Xe lamp at room temperature (A) and liquid nitrogen (B). At low temperature the transitions from the higher levels such as ${}^{5}D_{3}$, ${}^{5}D_{2}$, and ${}^{5}D_{1}$ increase significantly (like under excitation with $\lambda_{ex} = 393$ nm, see main text Fig. 3B and 3D) compared to the measurement at room temperature.



ESI-Figure 11. Photoluminescence (PL) decays of 80°C dried pure, hexagonal NaGdF₄: Eu nanorods monitored (A) at the $({}^{5}D_{1}-{}^{7}F_{2})$ transition and the (B) ${}^{5}D_{0}-{}^{7}F_{2}$ transition of Eu³⁺ under 393 nm excitation. The decay curves in Fig S11A are fitted bi-exponentially. The average delay time is calculated by $t(\tau) = a_1 \tau_1 + a_2 \tau_{2,}$, where a_1 and a_2 are the contributions of the respective decay component. At room temperature a_1 , a_2 are 0.58 and 0.42 and τ_1 and τ_2 are 2.227 and 2.24 ms, respectively. For the sample measured at 77 K, a_1 , a_2 are 0.76 and 0.24 and τ_1 and τ_2 are 4.63 and 4.84 ms respectively. The decay curves in Fig S11B are fitted mono-exponentially.

Judd-Ofelt parameter calculation

Judd-Ofelt parameters are calculated to get more insight into the structural changes surrounding the Eu³⁺ ion due to change of crystal phases.³ The Judd-Ofelt parameter (Ω_2) gives information on the intensities or nature of the hypersensitive transitions of the Eu³⁺ ion. The experimental intensity parameters (Ω_2) were determined from the emission spectra for Eu³⁺ ion based on the ⁵D₀ \rightarrow ⁷F₂ electric-dipole transition and the ⁵D₀ \rightarrow ⁷F₁ magnetic dipole transitions as the reference and they are estimated according to the equation

$$A = \frac{4e^2\omega^3}{3\eta c^3} \frac{1}{2J+1} \chi \sum \Omega_2 \langle {}^5D_0 \| U^{(2)} \| {}^7F_2 \rangle^2$$
(1)

Where $A_{0\lambda}$ is the coefficient of spontaneous emission, e is the electronic charge, ω is the angular frequency of the transition, h is Plank's constant, c is the velocity of light, χ is the Lorentz local field correction and is expressed as $\chi = \eta(\eta^2 + 2)^2 / 9$ where η is the refractive index of the sample which is experimentally determined, $\langle {}^5D_0 || U^{(2)} ||^7 F_2 \rangle^2$ is the squared reduced matrix elements whose value is independent of the chemical environment of the ion and it is 0.0039 for J=2. Since the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ transition is relatively insensitive to the chemical environment around the Eu³⁺ ion, therefore, it can be considered as a reference for the whole spectrum and the coefficient of spontaneous emission is calculated according to the relation

$$A_{0J} = A_{01} (I_{0J} / I_{01}) (\gamma_{01} / \gamma_{0J})$$
(2)

where γ_{01} and γ_{0J} are the energy baricenters of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions, respectively. A_{01} is the Einstein's coefficient between ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ levels and it is calculated using $A_{01} = \eta^{3}(A_{0-1})_{vac}$; where η is the refractive index of the sample and $(A_{0-1})_{vac}$ are 14.65 sec⁻¹. J-O parameters (Ω_{2}) for the sodium gadolinium fluoride sample is calculated by the above explained method. The value of J-O parameter (Ω_{2}) is $13.94 \times 10^{-20} \text{ cm}^{2}$ for pure hexagonal phase (prepared at Gd³⁺/F ratio 1:8) under excitation at 394 nm and room temperature but for the mixed phase of cubic and hexagonal (prepared at Gd³⁺/F ratio 1:4) the value is much less ($5.8 \times 10^{-20} \text{ cm}^{2}$). Higher Ω_{2} value for hexagonal sample suggests that Eu³⁺ ion resides at more asymmetric environment in pure hexagonal phase.



ESI-Figure 12. Energy level diagram of $Gd^{3+}-Eu^{3+}$ system depicting transitions and energy transfers.

Quantum yield calculation

Quantum yield for the NaGdF₄:Eu³⁺ ion is calculated by the method of Wegh et al.⁴ First the intensity ratio of ${}^{5}D_{0} / {}^{5}D_{1, 2, 3}$ was calculated both for the ${}^{6}G_{J}$ and ${}^{6}P_{J}$ levels excitation and these values are 16.67 and 8.44 respectively. Now from these intensity ratios, the efficiency of the cross relaxation step can be determined according to



and it is seen that the ratio $P_{CR}/P_{CR}+P_{DT}$ (P_{CR} is the probability of the cross relaxation and P_{DT} is the probability of direct energy transfer from Gd^{3+} to Eu^{3+}) is 0.87; which means that 8.7 of 10 Gd^{3+} ion in the ${}^{6}G_{J}$ excited levels relax through a two step energy transfer to Eu^{3+} , resulting in two visible photons whereas 1.3 of 10 Gd^{3+} ions in the excited ${}^{6}G_{J}$ states transfers all its energy to a high energy levels of Eu^{3+} resulting in the emission of one visible photon. In this way, a visible quantum efficiency of 187% is achieved which is very close to the theoretical maximum value of 200%. Similarly, the quantum yield for the sample containing both cubic and hexagonal NaGdF₄:Eu was determined (Fig. 5) to

127% which is much less compared to the pure hexagonal phase signifying the importance of preparing pure hexagonal Eu^{3+} doped NaGdF₄.

References

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