

## Supporting information

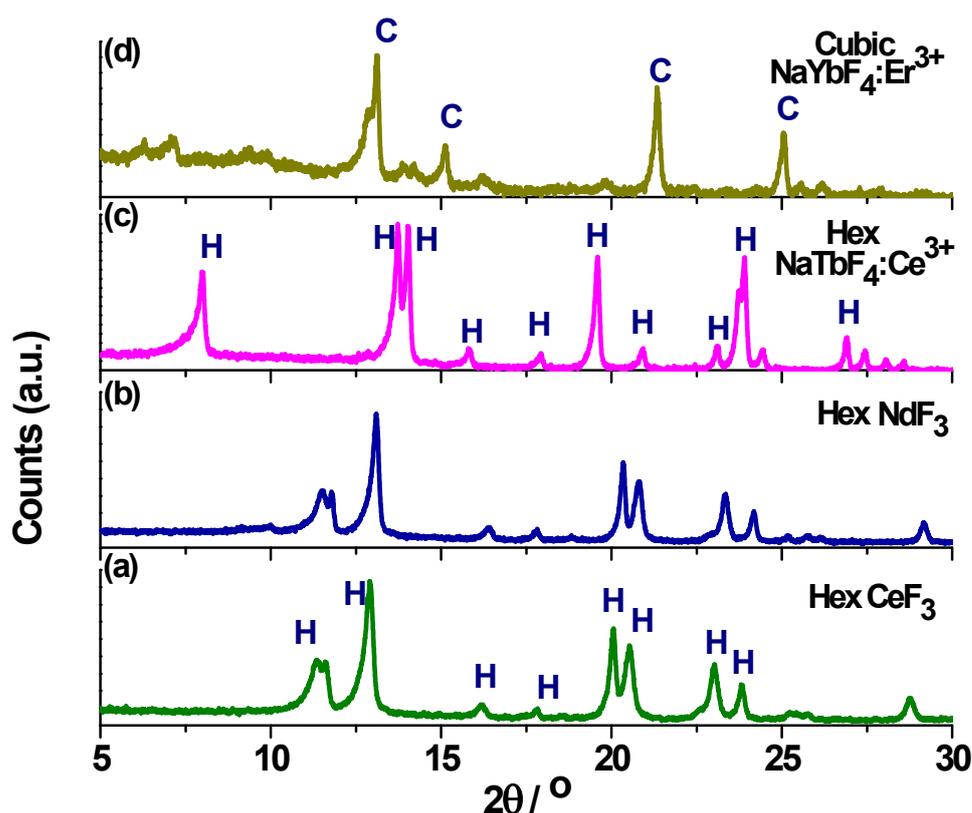
### Size of the rare-earth ions: A key factor in phase tuning and morphology control of binary and ternary rare-earth fluoride materials

Pushpal Ghosh<sup>a\*</sup> Rahul Kumar Sharma<sup>a</sup>, Yogendra NathChouryal<sup>a</sup> and Anja-Verena Mudring<sup>b\*\*†</sup>

<sup>1</sup>School of Chemical Science and Technology, Department of Chemistry, Dr. H.S. Gour University (A Central University), Sagar-470003, Madhya Pradesh, India.

<sup>2</sup>Materials Science and Engineering, Iowa State University, Ames, IA 50014 and Critical Materials Institute, Ames Laboratory, Ames, IA, 50011,

\*Address correspondence to: [mudring@iastate.edu](mailto:mudring@iastate.edu); [pushpalghosh27@gmail.com](mailto:pushpalghosh27@gmail.com)



**Figure S1.** PXR D pattern of (a)  $\text{CeF}_3$  nanocrystals prepared by solvothermal technique at  $200^\circ\text{C}$  for 4 hour reaction time; (b), (c) and (d) PXR D patterns of hexagonal  $\text{NdF}_3$ , hexagonal  $\text{NaTbF}_4:\text{Ce}^{3+}$  and cubic  $\text{NaYbF}_4:\text{Er}^{3+}$  prepared at similar condition but only changing the respective cations such as  $\text{Ce}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Yb}^{3+}$ . In all cases,  $\text{Ln}^{3+}/\text{F}^-$  ratio is taken as 1:8.

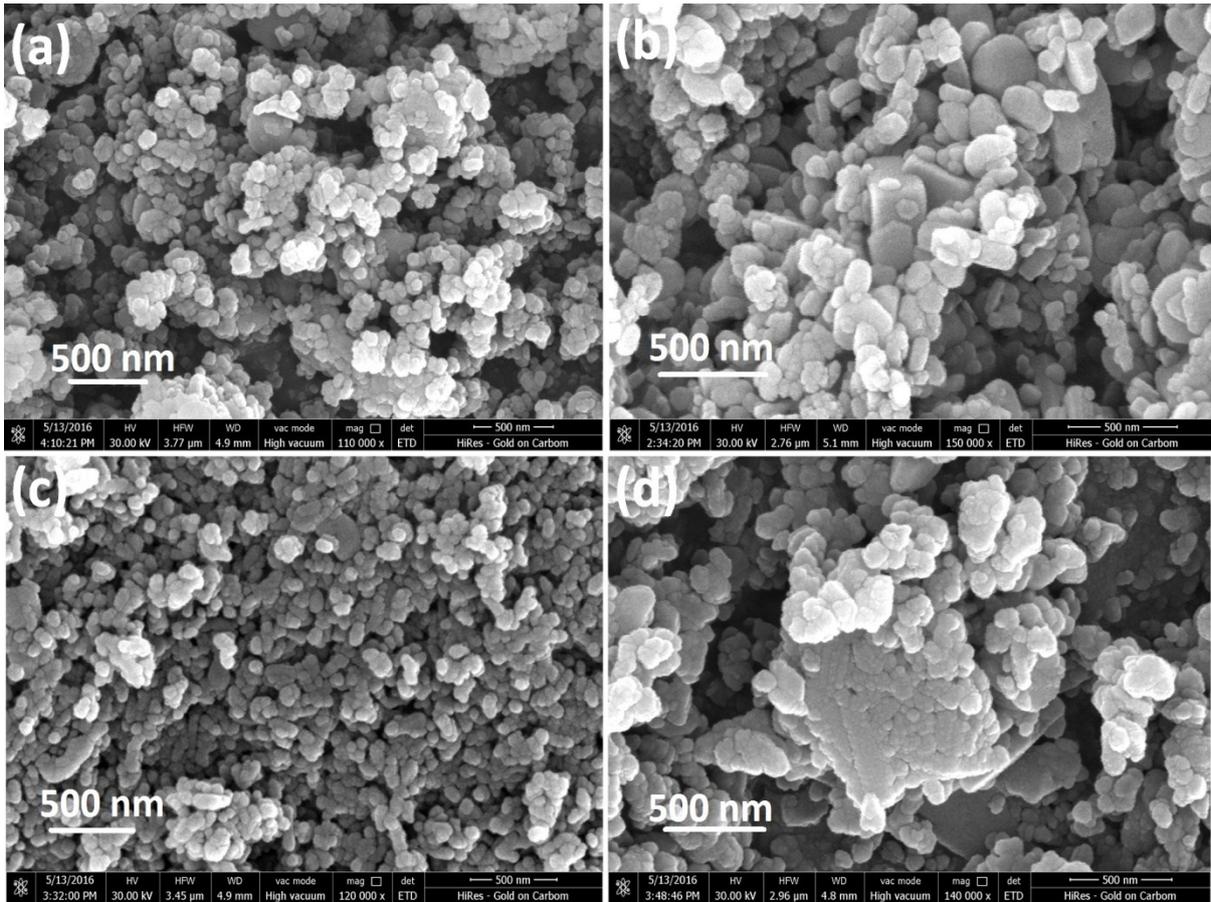
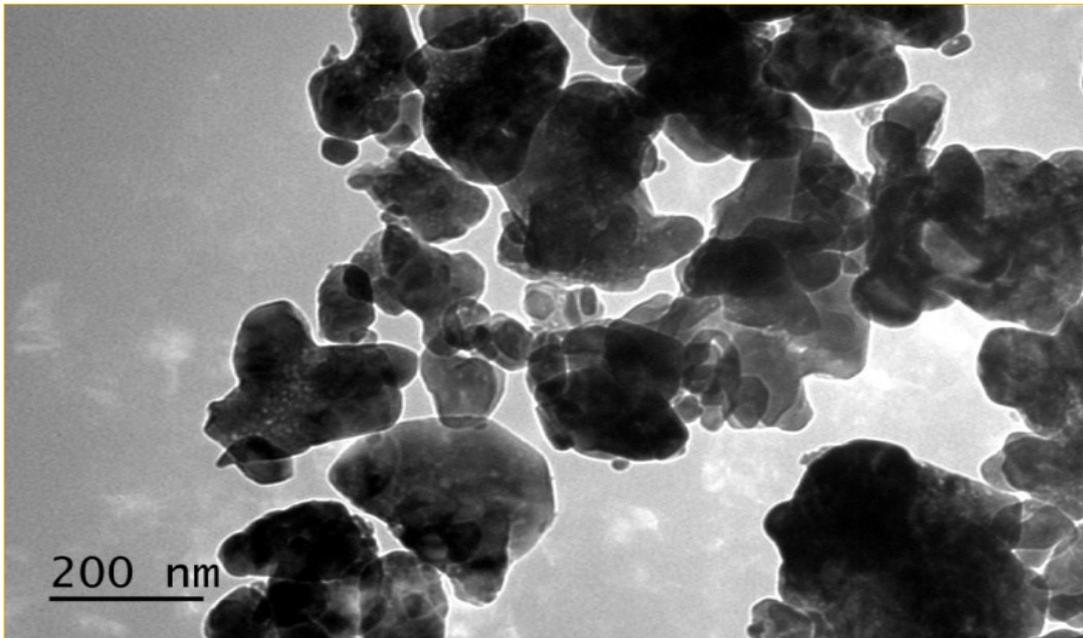
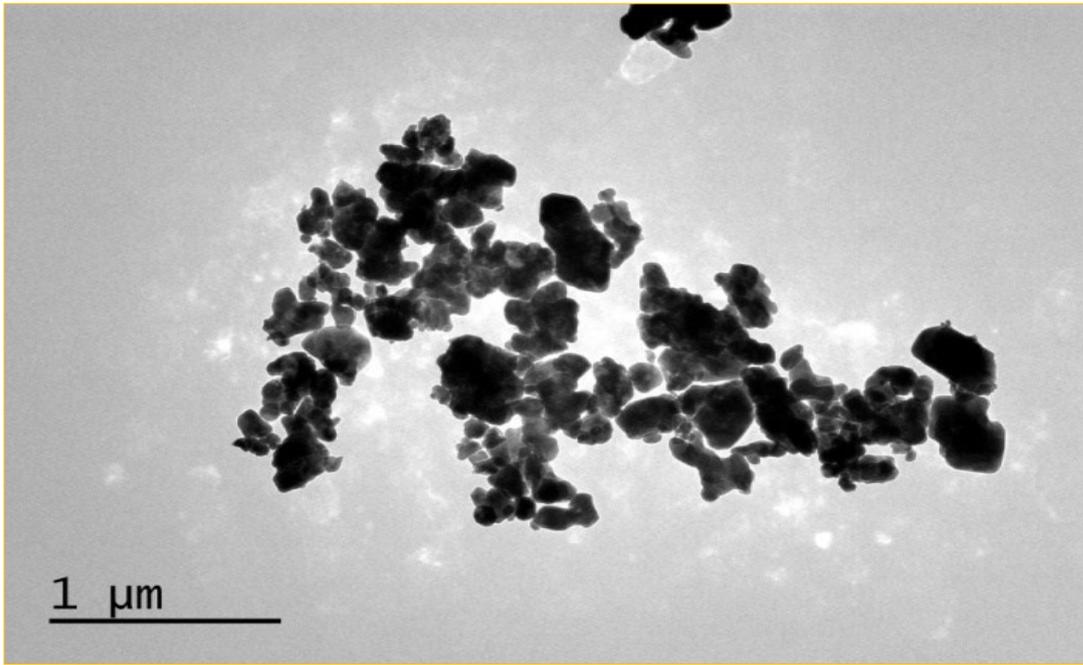
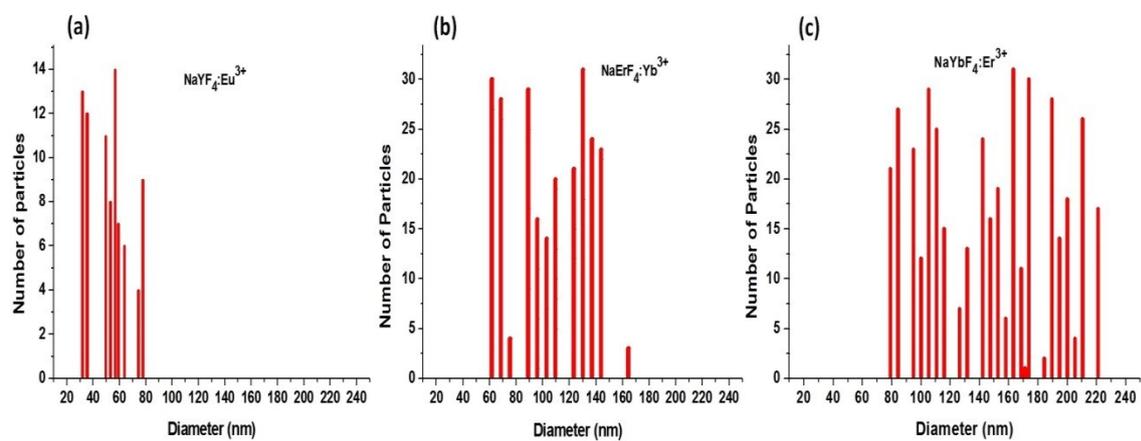


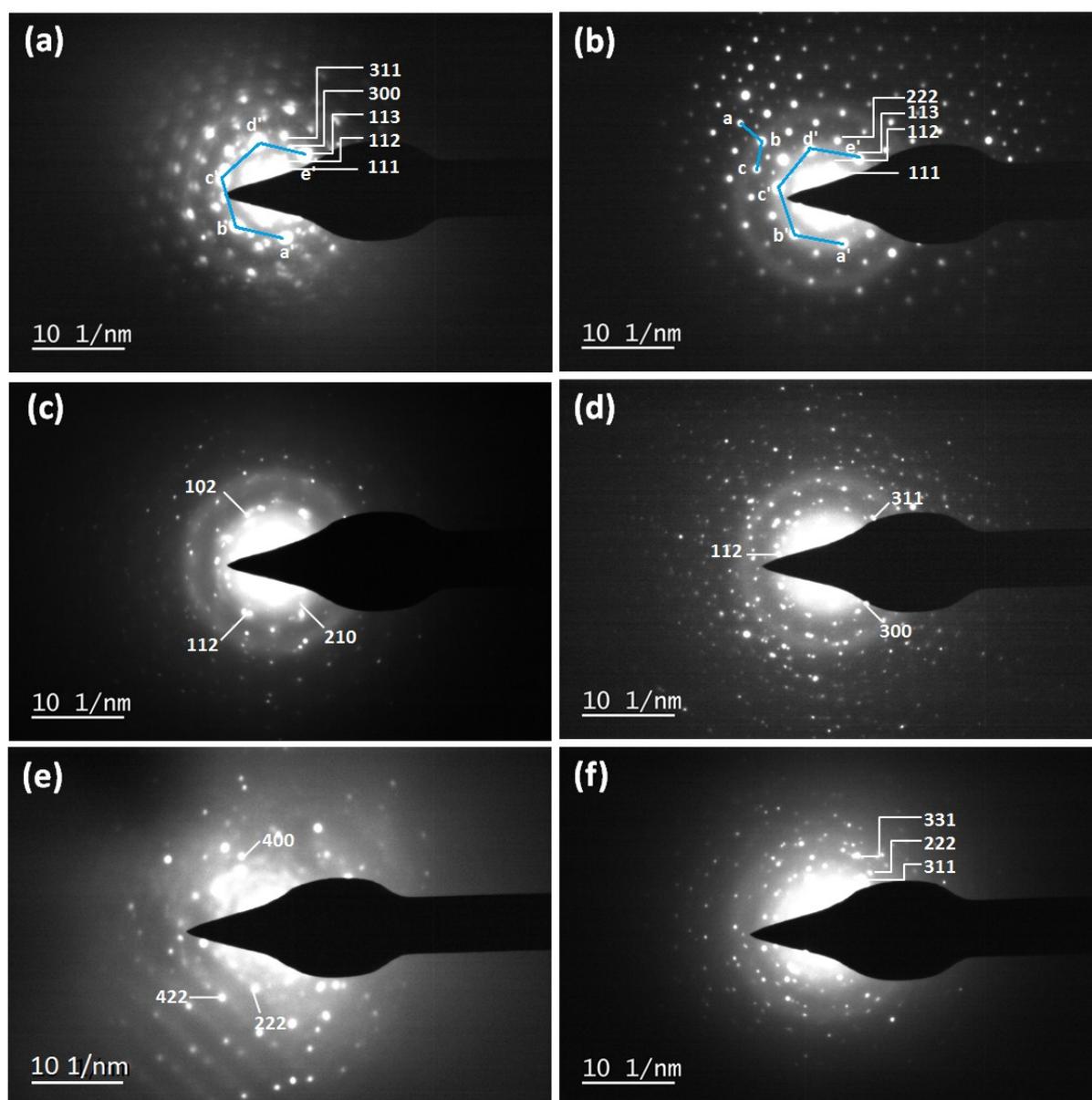
Figure S2. Low magnification FESEM images: a)  $\text{LaF}_3:\text{Dy}^{3+}$  b)  $\text{NdF}_3$  c)  $\text{NaSmF}_4$  d)  $\text{NaTbF}_4:\text{Ce}^{3+}$ ; inset is the high magnification FESEM image of  $\text{LaF}_3:\text{Dy}^{3+}$ , Nanocrystals prepared IL assisted solvothermal method at  $200^\circ\text{C}$ .



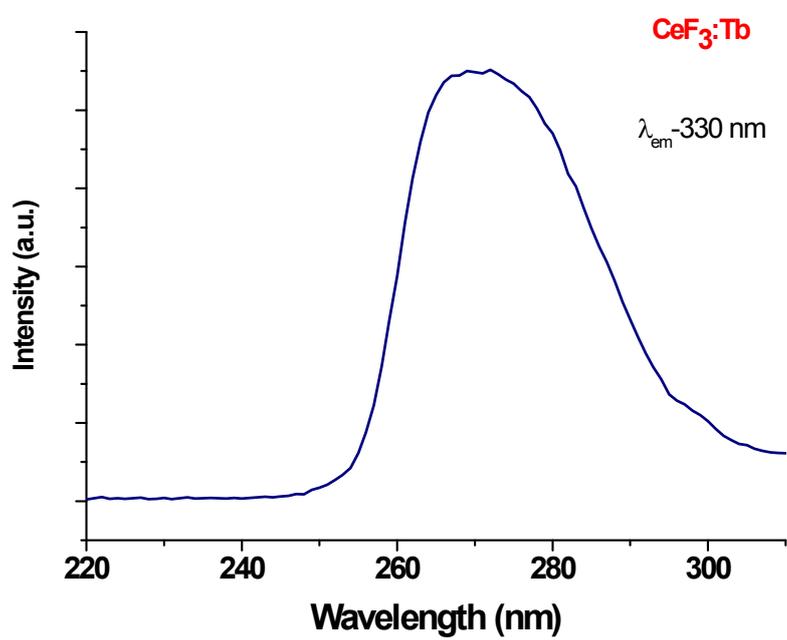
**Figure S3.** TEM images of NaDyF<sub>4</sub> nanoparticles synthesized by solvothermal method at 200°C and was measured at 1 μm and 200 nm scale.



**Figure S4.** Histogram images of particle size distribution: (a) NaYF<sub>4</sub>:Eu<sup>3+</sup>, (b) NaErF<sub>4</sub>:Yb<sup>3+</sup> and (c) NaYbF<sub>4</sub>:Er<sup>3+</sup> of nanoparticles synthesized by solvothermal method at 200°C.



**Figure S5.** Selected Area Electron Diffraction (SAED) images of: (a)  $\text{LaF}_3:\text{Dy}^{3+}$ , (b)  $\text{CeF}_3:\text{Tb}^{3+}$ , (c)  $\text{NaGdF}_4:\text{Eu}^{3+}$ , (d)  $\text{NaDyF}_4$ , (e)  $\text{NaErF}_4:\text{Yb}^{3+}$  and (f)  $\text{NaYbF}_4:\text{Er}^{3+}$  nanoparticles synthesized by solvothermal method at  $200^\circ\text{C}$ .



**Figure S6.**Excitation spectrum of CeF<sub>3</sub>:Tb nanoparticles (λ<sub>em</sub>= 330 nm).

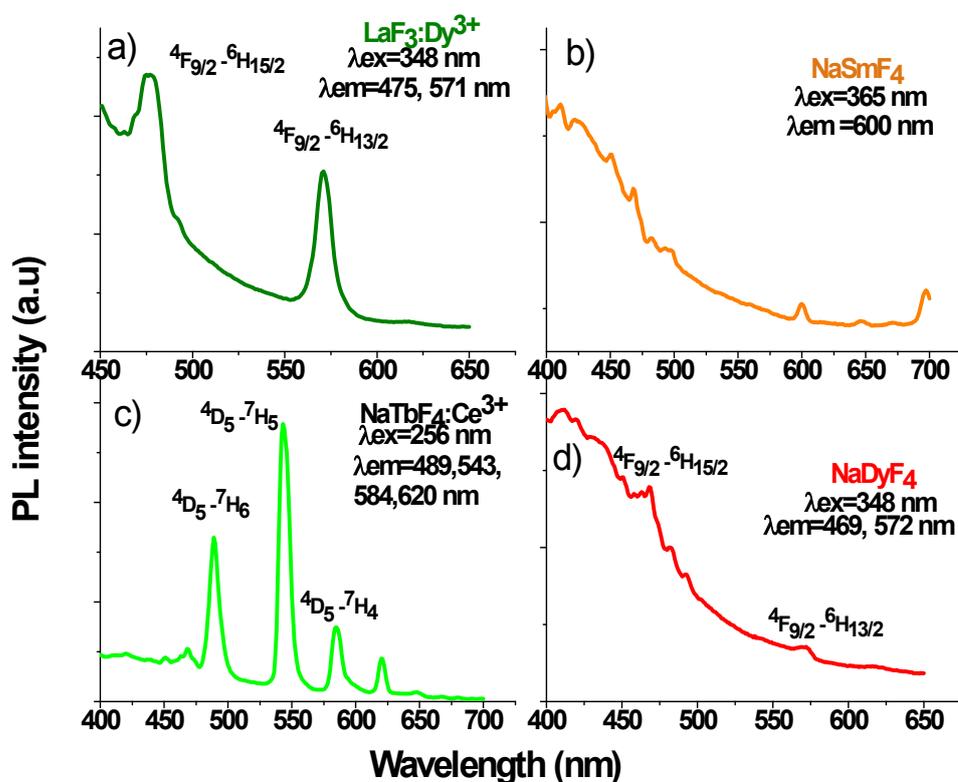


Figure S7: PL emission spectra of RE<sup>3+</sup>-doped rare-earth fluorides; a) LaF<sub>3</sub>:Dy<sup>3+</sup> excited at 348 nm, b) NaSmF<sub>4</sub> ( $\lambda_{ex}$ =365 nm), c) NaTbF<sub>4</sub>:Ce<sup>3+</sup> ( $\lambda_{ex}$ =256 nm) and d) NaDyF<sub>4</sub> ( $\lambda_{ex}$ =348 nm) synthesized at 200°C for 4 hours.

SI Table 1. Optoelectronic applications of the as-prepared RE<sup>3+</sup> ion-doped binary/ternary rare earth fluorides nanoparticles under similar reaction conditions.

S.No.	Name of the Sample	Optical Applications
1.	1 NaYF <sub>4</sub> :Eu <sup>3+</sup> (P1)	Normal luminescence
2.	LaF <sub>3</sub> :Dy <sup>3+</sup> (P2)	Normal luminescence
3.	CeF <sub>3</sub> (P3)	Normal luminescence
4.	CeF <sub>3</sub> :Tb <sup>3+</sup> (P4)	Energy Transfer
5.	NdF <sub>3</sub> (P5)	Normal luminescence
6.	NaSmF <sub>4</sub> (P6)	Normal luminescence
7.	NaGdF <sub>4</sub> :Eu <sup>3+</sup> (P7)	Quantum Cutting Downconversion
8.	NaTbF <sub>4</sub> :Ce <sup>3+</sup> (P8)	Energy Transfer
9.	NaDyF <sub>4</sub> (P9)	Normal luminescence
10.	NaErF <sub>4</sub> :Yb <sup>3+</sup> (P10)	Upconversion
11.	NaYbF <sub>4</sub> :Er <sup>3+</sup> (P11)	Upconversion

## Judd-Ofelt parameter calculation

Judd-Ofelt (J-O) parameters are calculated to get more information into the structural changes surrounding the  $\text{Eu}^{3+}$  ion due to change of crystal phases, morphology etc.<sup>1-3</sup> The J-O parameter ( $\Omega_2$ ) gives insights on the nature of the hypersensitive transitions of the  $\text{Eu}^{3+}$  ion. The experimental asymmetry parameters ( $\Omega_2$ ) were determined from the emission spectra for  $\text{Eu}^{3+}$  ion based on the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  magnetic dipole transitions as the reference and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  electric-dipole transition and are estimated according to the equation

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

Where  $A$  is the coefficient of spontaneous emission,  $e$  is the electronic charge,  $\omega$  is the angular frequency of the transition,  $h$  is Plank's constant,  $c$  is the velocity of light,  $\chi$  is the Lorentz local field correction and is expressed as  $\chi = \eta(\eta^2+2)^2 / 9$  where  $\eta$  is the refractive index of the sample which is experimentally determined,  $\langle {}^5D_0 \| U^{(2)} \| {}^7F_2 \rangle^2$  is the squared reduced matrix elements whose value is independent of the chemical environment of the ion and it is 0.0039 for  $J=2$ .<sup>1</sup> Normally magnetic dipole transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) is relatively insensitive to the chemical environment around the  $\text{Eu}^{3+}$  ion, and can be considered as a reference for the whole spectrum. The coefficient of spontaneous emission is calculated according to the relation

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

where  $\gamma_{01}$  and  $\gamma_{0j}$  are the energy baricenters of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions, respectively.  $A_{01}$  is the Einstein's coefficient between  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  levels and it is calculated

using  $A_{01} = \eta^3(A_{0-1})_{\text{vac}}$ ; where  $\eta$  is the refractive index of the sample and  $(A_{0-1})_{\text{vac}} = 14.65 \text{ sec}^{-1}$ .<sup>1</sup> J-O parameters ( $\Omega_2$ ) for the  $\text{Eu}^{3+}$  doped hexagonal  $\text{NaGdF}_4$  and cubic  $\text{NaYF}_4$  samples are calculated by the above explained method. The values of J-O parameter ( $\Omega_2$ ) are  $11.6 \times 10^{-20} \text{cm}^2$ ,  $3.75 \times 10^{-20} \text{cm}^2$  for hexagonal  $\text{NaGdF}_4$  and cubic  $\text{NaYF}_4$  sample doped with  $\text{Eu}^{3+}$  ions. These points to a less symmetric environment for  $\text{Eu}^{3+}$  ion for the hexagonal  $\text{NaGdF}_4$  sample.

## References

- 1 P. Ghosh and A-V Mudring, Phase Selective Synthesis of Quantum Cutting Nanophosphors and the Observation of a Spontaneous Room Temperature Phase Transition, *Nanoscale*, 2016,**8**,8160.
- 2 P. Ghosh, S. Tang and A-V. Mudring, Efficient Quantum Cutting in Hexagonal  $\text{NaGdF}_4:\text{Eu}^{3+}$  Nanorods. *J. Mater. Chem.* 2011, **21**, 8640-8644.
- 3 P. Ghosh and A. Patra, Influence of Crystal Phase and Excitation Wavelength on Luminescence Properties of Eu-Doped Sodium Yttrium Fluoride Nanocrystals. *J.Phys.Chem C*, 2008, **112**, 19283-19292.