SUPPORTING INFORMATION

Synchrotron-based X-Ray analysis: Relating Compressive Lattice Strain with the Photoluminescence Intensity of Li⁺ Doped β-NaYF₄:Yb³⁺/Ln³⁺ (Ln³⁺=Ho³⁺/Er³⁺/Tm³⁺) Upconversion Crystals

Preeti Verma[†], Debasish Sarkar^{‡,I}, Parasmani Rajput[¶], Manvendra Narayan Singh[§], Rajendra Sharma[⊥] and Supratim Giri^{*,†}

[†]Department of Chemistry, National Institute of Technology, Rourkela, 769008, India

[‡]Department of Ceramic Engineering, National Institute of Technology, Rourkela, 769008, India

HiLASE Centre, Institute of Physics, Prague, Czech Republic

[¶]Atomic & Molecular Physics Division, Bhabha Atomic Research Centre Trombay, Mumbai-400085, India

[§]Hard X-ray Laboratory, Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore - 452013, India

[⊥]Technical Physics Division, Bhabha Atomic Research Centre, Trombay Mumbai.



Figure S1: Upconversion emission spectra of NaYF₄:Yb³⁺ with different concentrations of Ho³⁺ (a) Concentration above 0.5 mol% (b) Concentration below 0.5 mol%



Figure S2: Pump power dependant UC emission spectra of NaYF₄:Yb³⁺/Ho³⁺ crystals without and with 50% Li⁺ doping excited by 980 nm laser.



Figure S3: SAED pattern of NaYF₄:Yb³⁺/Ho³⁺ crystals doped with different concentrations of Li⁺: a) Ho-0 b) Ho-10 c) Ho-30 d) Ho-50 e) Ho-80 f) Ho-100. The SAED patterns produced from the crystals essentially demonstrate a crystalline structure. The pattern shows clear polycrystalline diffraction rings corresponding to different planes of hexagonal phase NaYF₄ lattice, which was also confirmed from XRD analysis. Ho-100 corresponds to pure tetragonal LiYF₄ phase.



Figure S4: EDAX spectrum of 50 mol% Li⁺ doped NaYF₄:Yb³⁺/Ho³⁺ crystals



Figure S5: XPS spectrum of oleic acid capped 50 mol% Li⁺ doped NaYF₄:Yb³⁺/Ho³⁺ crystals synthesized by thermal decomposition method and cumulative peak fit.



Figure S6: XRD pattern of as synthesized a) β -NaYF₄:Yb³⁺/Ln³⁺ matching with standard diffraction pattern of hexagonal NaYF₄ JCPDS No-16-0334 b) LiYF₄:Yb³⁺/Ln³⁺ matching with standard diffraction pattern of tetragonal LiYF₄ JCPDS No-77-0816

Rietveld refinement method

The Rietveld refinement of the x-ray diffractogram of samples at room temperature was performed using Fullprof software. The fitting method used in Rietveld refinement is the non-linear least squares approach. The hexagonal shape NaYF₄:Yb³⁺/Ln³⁺ (Ln³⁺=Er³⁺ and Ho³⁺) crystals matches well with the P6 space group of NaYF₄. The fitting was obtained refining the scale factor, zero point of the detector, specimen displacement, lattice parameter, FWHM and shape parameters, atomic positions and anisotropic temperature factors. After multiple cycles of refinement, the values of GOF (Goodness of Fit) obtained from Rwp/Rexp indicates appreciable quality of the fitting. The refined lattice parameter and χ^2 for Ho-0 to Ho-80 and Er-10, Er-30 and Er-50 are given in the table below:



Figure S7: Rietveld refinement plot of ADXRD data of a) Ho-10 and b) Ho-80 showing predominantly hexagonal phase.

Table S1. Lists the refinement parameters including χ^2 value, Rwp/Rexp and lattice parameters obtained from Rietveld refinement of Ho-0 to Ho-100

Refinement	Ho-0	Ho-10	Но-50	Ho-80	Ho-100
parameter					
χ2	7.62	3.94	7.02	6.21	10.1
Rwp/Rexp	2.75	1.98	2.65	2.5	3.23
a (Å)	5.9397(6)	5.9893(11)	5.9352(11)	5.9765(7)	5.1654(8)
c (Å)	3.4840(5)	3.5096(7)	3.4779(7)	3.5018(8)	10.7182(3)
V (Å ³)	106.45(2)	109.03(4)	106.12(3)	108.32(3)	285.97(9)

X-ray Absorption near edge structure spectroscopy (XANES) and Extended X-ray absorption fine structure (EXAFS) study

The energy range of XAFS was calibrated using Ho₂O₃, Y₂O₃ and Yb₂O₃ oxide at 8071, 17038 and 8944 eV, respectively. The k-range of all edges 2.5–9Å⁻¹ range has been used for FT of Ho, Y and Yb EXAFS data. The XAFS data has been analysed using FEFF 6.0 code ¹, which includes background reduction and Fourier transform to derive the $\chi(R)$ versus R spectra from the absorption spectra (using ATHENA software) ², generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure and finally fitting of experimental data with the theoretical spectra using ARTEMIS software ⁵.



Figure S8: Figure 1 (a-b) shows normalized Y K edge and Yb L₃-edge XANES data of Ho-0 and Ho-50 samples including Y^{3+} and Yb^{3+} standards. From, the 1st derivative of Y absorption edge, it has been observed that Y +3 reference and Ho-0 and Ho-50 samples comes at 17037.9 eV which confirms that Y is in +3 oxidation state. Similarly, the 1st derivative of Yb absorption edge, it has been observed that Yb 3+ reference comes at 8943.9 eV whereas Ho-0 and Ho-50 samples comes at 8945.5 eV.



Figure S9 (a-b) shows (FT) k^2 -weighted $\chi(k)$ XAFS oscillations of Y K edge and Yb L₃-edge of Ho-0 and Ho-50 samples.

The EXAFS fitting were done using hexagonal structure of NaYF₄ (space group P6) where Yb/Y/Ho has 6 F atoms at 2.3153 Å distance and 3 F atom at 2.3249 in first shell. For the fitting of EXAFS data the coordination numbers (CN), bond distance (*R*) and Debye-Waller factor (σ_2) has been taken as free parameters as a common Yb/Y/Ho-F bond. Figure 2(a-b) also shows the best fitted curves of Ho-0 and Ho-50 samples and best fitted values of the all parameters are listed in table S2

Table S2. From the Ho L₃, Y K and Yb L₃-edges XAFS data fitting, we have obtained variation of CN (coordination number), R (bond distance) and σ 2 (Debye-Waller factor). The numbers in parentheses indicate the uncertainty in the last digit.

	Ho L ₃ -edge		Y K-edge			Yb L ₃ -edge			
Sample	CN _{Ho-F}	R _{Ho-F} (Å)	$\sigma^2_{\text{Ho-F}}(\text{\AA}^2)$	CN _{Y-F}	R _{Y-F} (Å)	$\sigma^2{}_{Y\text{-}F}(\text{\AA}^2)$	CN _{Yb-F}	R _{Yb-F} (Å)	$\sigma^2{}_{Yb\text{-}F}(\text{\AA}^2)$
Но-0	8.7(3)	2.276 (3)	0.0033 (2)	8.9(2)	2.336(3)	0.0035(3)	8.6(3)	2.281(3)	0.0048(3)
Но-50	8.6(2)	2.279 (3)	0.0038(3)	8.7(3)	2.333(2)	0.0042(3)	8.0(2)	2.286(2)	0.0062(3)



Figure S10: a) Raman spectra of β -NaYF₄:Yb³⁺/Ho³⁺ crystals with different concentration of Li⁺ and b) Raman imaging of Ho-0 and Ho-50 crystals



Figure S11: X-ray diffraction patterns of a) Er-0, Tm-0 and W-0 b) Er-100 and Tm-100



Figure S12: UC emission spectra of W-100 *i.e.* LiYF₄:Yb³⁺/Er³⁺/Tm³⁺ crystals

Table S3. Lists the refinement parameters including χ^2 value, Rwp/Rexp and lattice parameters obtained from Rietveld refinement of Er-10, Er-30 and Er-50

Refinement	Er-10	Er-30	Er-50
parameter			
χ^2	7.84	4.71	2.59
Rwp/Rexp	2.79	2.17	1.60
a (Å)	5.9929(17)	5.9854(4)	5.9806(9)
c (Å)	3.5139(14)	3.5069(4)	3.5058(9)
V (Å ³)	109.296(6)	108.803(18)	108.595(4)



Figure S13: Diffraction pattern obtained in image form from ADXRD and Rietveld refinement of the converted (I-2θ) data of NaYF₄:Yb³⁺/Er³⁺ doped with different concentrations of Li⁺: a-b) Er-0 c-d) Er-30 e-f) Er-50

Lattice strain calculation using Williamson hall Plot

Crystallite size and lattice strain affect the Bragg peak in different ways. Both these effects leads to increase in the peak. The micro strain present in the lattice of materials were calculated by Williamson Hall (W-H) plot governed by the mathematical equation:

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin\theta}{\lambda}$$

Where, λ is the wavelength of radiation (x-ray from synchrotron radiation= 0.75428 Å), β is full width at half maximum (FWHM) of diffraction peak, D is the crystallite size in Å, θ is the peak position and ϵ is the micro strain present in the sample. Plots are drawn between $\sin\theta/\lambda$ and $\beta\cos\theta/\lambda$ and micro strain is calculated from slope and particle size from intercept at Y-axis of the fit.



Figure S14: Williamson-Hall analysis of Li⁺ doped NaYF₄:Yb³⁺/Ho³⁺, NaYF₄:Yb³⁺/Er³⁺, NaYF₄:Yb³⁺/Tm³⁺ and NaYF₄:Yb³⁺/Er³⁺/Tm³⁺ systems. Strain is obtained from the slope of the fit.

Sample	Adj. R square	Slope	Standard error	Intercept	Standard error
Но-10	0.9975	-4.1108 E ⁻⁴	8.3936 E ⁻⁶	0.00275	7.7326 E ⁻⁶
Но-50	0.9901	-3.944 E ⁻⁴	1.9626 E ⁻⁵	0.00261	1.9495 E ⁻⁵
Но-80	0.9737	-10.0 E ⁻⁴	7.3513 E ⁻⁵	0.00347	7.8068 E ⁻⁵
Er-10	0.9739	-8.2573 E ⁻⁴	6.0236 E ⁻⁵	0.00309	6.0170 E ⁻⁵
Er-30	0.9949	-3.7011 E ⁻⁴	1.5281 E ⁻⁵	0.00259	1.2314 E ⁻⁵
Er-50	0.9702	-39.9 E ⁻⁴	2.4652 E ⁻⁴	0.00766	2.1744 E ⁻⁴
Tm-30	0.9577	-29.6 E ⁻⁴	2.1910 E ⁻⁴	0.00596	1.9919 E ⁻⁴
Tm-50	0.9738	-4.3596 E ⁻⁴	2.9075 E ⁻⁵	0.00263	2.6795 E ⁻⁵
Tm-80	0.9503	-20.0 E ⁻⁴	1.6131 E ⁻⁴	0.00482	1.6274 E ⁻⁴
W-10	0.9786	-4.7668 E ⁻⁴	3.1458 E ⁻⁵	0.00263	2.4531 E ⁻⁵
W-50	0.9505	-3.7679 E ⁻⁴	4.9186 E ⁻⁵	0.00279	3.9747 E ⁻⁵
W-70	0.9887	-1.6227 E ⁻⁴	9.9896 E ⁻⁶	0.00242	9.5105 E ⁻⁶

Table S4: Data of linear fitting corresponding to Figure S14



Figure S15: Particle size distribution curve of NaYF₄:Yb³⁺/ Ho³⁺ with different concentrations of Li⁺



Figure S16. Schematic energy-level diagram of Yb³⁺ and Ho³⁺, and the proposed mechanism of upconversion luminescence. For the Yb³⁺/Ho³⁺ co-doped β -NaYF₄ based UCNP under NIR irradiation, Yb³⁺ ion can be excited to the ${}^{2}F_{5/2}$ from ${}^{2}F_{7/2}$ state by ground state absorption. The excited Yb³⁺ ion transfers its energy to the nearby Ho³⁺ ion through successive two-step energy transfer processes to populate ${}^{5}I_{6}$ and ${}^{5}S_{2}/{}^{5}F_{4}$ states of Ho³⁺ ion. Through multi-phonon relaxation process it gives rise to green (539 nm) and red (650 nm) emissions. This intense green and red emissions were attributed to the efficient non-radiative cross-relaxation process ${}^{5}F_{4+}{}^{5}S_{2} \rightarrow {}^{5}I_{8}$ and ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ of Ho³⁺, which consequently leads to the dominant population of the Ho³⁺.

References

1. Zabinsky, S.; Rehr, J.; Ankudinov, A.; Albers, R.; Eller, M. Multiple-scattering calculations of X-ray-absorption spectra. *Phys. Rev. B* **1995**, *52* (4), 2995.

2. Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Syn. Rad.* **2005**, *12* (4), 537-541.