Nature of Local Disorder in β-$NaYF_4$-based Near-Infrared Upconverting Core Nanocrystals due to Deliberate Incorporation of Symmetry Perturbing Agent

Panchanan Pandey[a], S.D. Kaushik[b], Parasmani Rajput[c,d], Manvendra Narayan Singh[e], Rajendra Kumar Sharma[f], and Supratim Giri[*, a,g]

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

[b]UGC – DAE Consortium for Scientific Research Mumbai Centre, 246 C Common Facility Building, Bhabha Atomic Research Centre, Mumbai-400085, India

[c]Beamline Development and Application Section, Bhabha Atomic Research Centre, Mumbai 400085, India

[d]Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094, India

[e]Hard X-ray Applications Lab., Accelerator Physics and Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore - 452013, India

[f]Technical Physics Division, Bhabha Atomic Research Centre, Trombay Mumbai-400085, India

[g]Centre for Nanomaterials, National Institute of Technology, Rourkela, 769008, India

Characterization

Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was conducted using a PerkinElmer Optima 2100DV instrument, with a detection range of 0.005−100.00 mg/L. XRD measurements were conducted at the BL-12[1] beamline of the Indus-2 synchrotron radiation source (SRS) at RRCAT, Indore, using an image plate detector (mar345dtb) in transmission mode. The NIST standard LaB_6 XRD was used for the energy calibration of a highly monochromatic beam and the exact distance of the detector from the sample. The two-dimensional data was converted into intensity versus 2θ using image processing software FIT2D. Rietveld refinement and Atomic Pair Distribution Function (PDF) analysis were performed from synchrotron X-ray (λ = 0.568473 Å) diffraction data. For transmission electron microscopy (TEM) studies, n-hexane dispersed nanoparticles were drop-cast over the carbon-coated copper grid and dried in a vacuum overnight. TEM experiments were carried out in FEI, 300 kV TECNAI F30 G2 S-Twin, and were used to see the bright field image, selected area electron diffraction (SAED), and high-resolution image. To gain a microscopic understanding of the crystal structure, a neutron diffraction (ND) study was conducted at room temperature using a multi-position sensitive detector (PSD) based focusing crystal diffractometer at the National Facility for Neutron Beam Research (NFNBR), Dhruva reactor, Mumbai, India installed by UGC-DAE CSR Mumbai Centre.[2] The UC powder samples were filled in the vanadium can and placed for diffraction. The neutron beam of wavelength 1.48 Å was used to achieve a diffraction pattern, and data was refined in the FullProf program.[3] X-ray photoelectron spectroscopy (XPS) measurements were conducted at the Hard X-ray Photoelectron Spectroscopy (HAXPES) beamline BL-14 at Indus-2 SRS, RRCAT, Indore to

determine the oxidation state and binding energy. BL-14 is equipped with a double crystal monochromator [DCM, Si (111)] and a hemispherical electron energy analyzer (HSA) along with a detector system (Phoibos 225, Specs make). This system is made up of stainless steel (SS304) and features Mu metal interior shielding to protect against magnetic fields. It is designed to achieve a pressure $\geq 5 \times 10^{-9}$ bar in the experimental station, ensuring clean conditions for the sample analysis. The X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) measurement was performed for the Y K-edge and Yb L_{III}-edge at the Scanning EXAFS beamline (BL-9), Indus-2 SRS, RRCAT, Indore, which covered the energy range of 4-25 keV with the help of DCM. EXAFS measurement was performed for both the edges in transmission mode. The energy range of X-ray absorption fine structure (XAFS) was calibrated from their corresponding oxides Y_2O_3 and Yb_2O_3 at 17038 and 8944 eV, respectively. The EXAFS data has been analyzed using FEFF 6.0 code,[4] which includes background reduction and Fourier transform to derive the $\chi(R)$ versus R spectra from the absorption spectra (using ATHENA software).[5] The EXAFS fitting was done by the same crystallographic information obtained from Rietveld's refinement of SRS XRD data in the Artemis module.[5] Upconversion luminescence (UCL) spectra were recorded in Horiba Jobin Yvon (USA) Fluoromax Plus spectrofluorometer using a 750 nm cutoff filter. This cutoff filter was used to avoid the unwanted laser scattering of photons towards the detector. All the spectra were recorded by a 980 nm continuous wave (CW) fiber laser with an output power density of 2.5 W/cm^2 (Aimil Ltd., India).

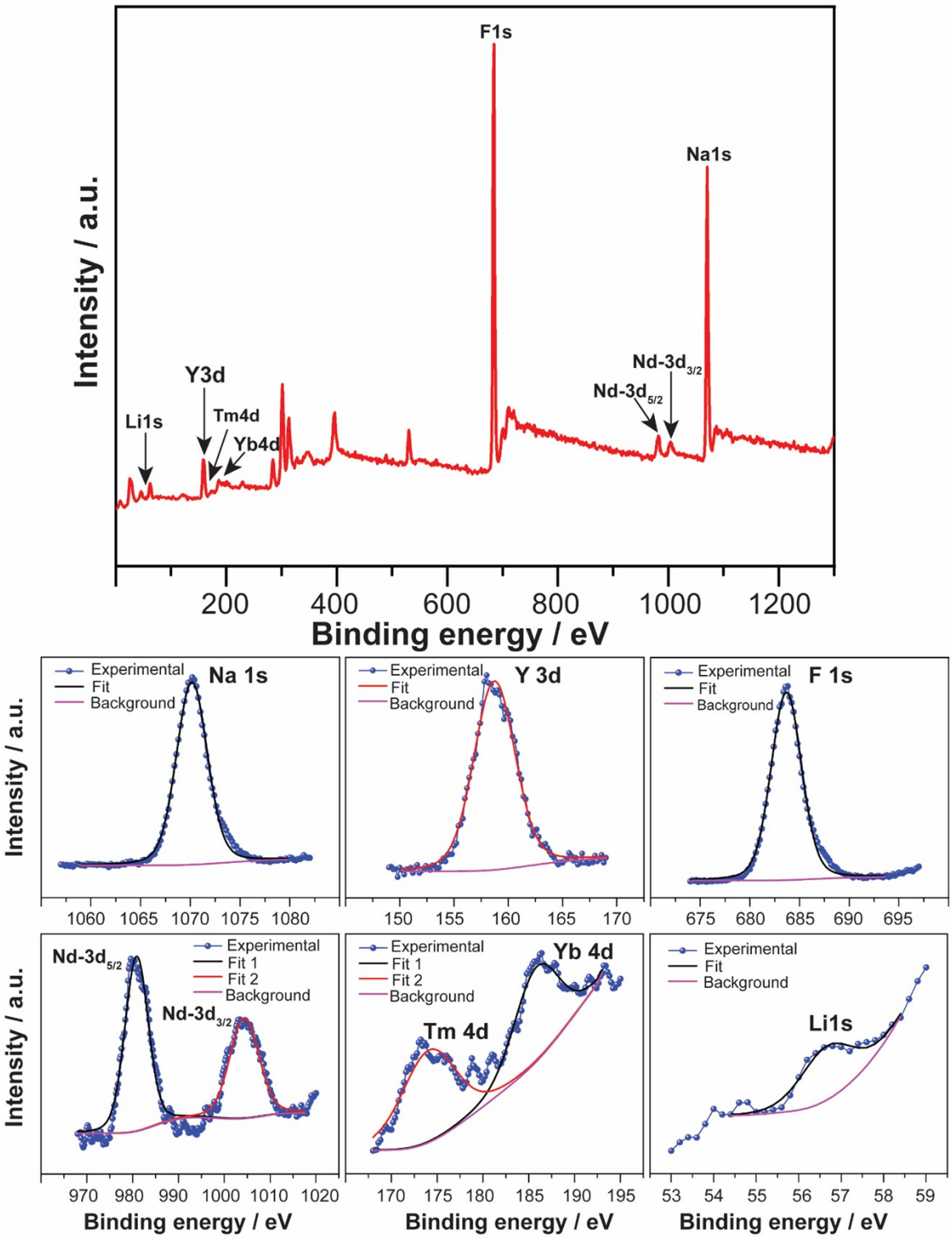

Figure S1. XPS spectrum of survey scan and individual constituent element of oleate capped B50 UCNC synthesized by coprecipitation metho

Table S1 χ^2, R_{wp}/R_{exp}, and lattice parameters obtained from the Rietveld refinement

Sample	χ^2	R_{wp}/R_{exp}	a=b (Å)	c (Å)	V (Å^3)
B0	1.02	1.010	5.9848(3)	3.5245(2)	109.327(9)
B10	1.05	1.027	5.9773(2)	3.5251(2)	109.076(8)
B30	1.05	1.023	5.9724(4)	3.5181(3)	108.679(13)
B50	1.25	1.117	5.9839(4)	3.5202(2)	109.158(12)
B60	1.08	1.039	5.9788(3)	3.5144(2)	108.794(10)
B80*	1.02	1.002	5.99113$^{\#}$ 5.51277 ■ 4.0324▪	3.51340 5.51277 4.0324	109.213 167.537 65.5702
B100♦	5.36	2.32	5.1555(4)	10.6968(2)	284.31(5)

*Mixed phase sample #Hexagonal phase ■Cubic $NaYF_4$ ▪Cubic LiF ♦Tetragonal $LiYF_4$

Table S2A Atomic coordinates of hexagonal $NaYF_4$ ($P\bar{6}$) used for Rietveld refinement

Elements	x	y	z	site
Y1	0.00000	0.00000	0.00000	1a
Y2/Na1/Li	0.66667	0.33333	0.50000	1f
Na2/Li	0.33333	0.66667	0.62925	2h
F1	0.61300	0.07600	0.00000	3j
F2	0.68700	0.73863	0.50000	3k

Table S2B Coordinates of different void positions used in refinement of Li+-doped samples

HCP Voids	x	y	z	Site
Tetrahedral	0.00000	0.00000	0.37500	2g
	0.00000	0.00000	0.62500	0
	0.66666	0.33333	0.12500	2i
	0.66666	0.33333	0.87500	2h
Octahedral	0.33333	0.66666	0.25000	2h
	0.33333	0.66666	0.75000	0

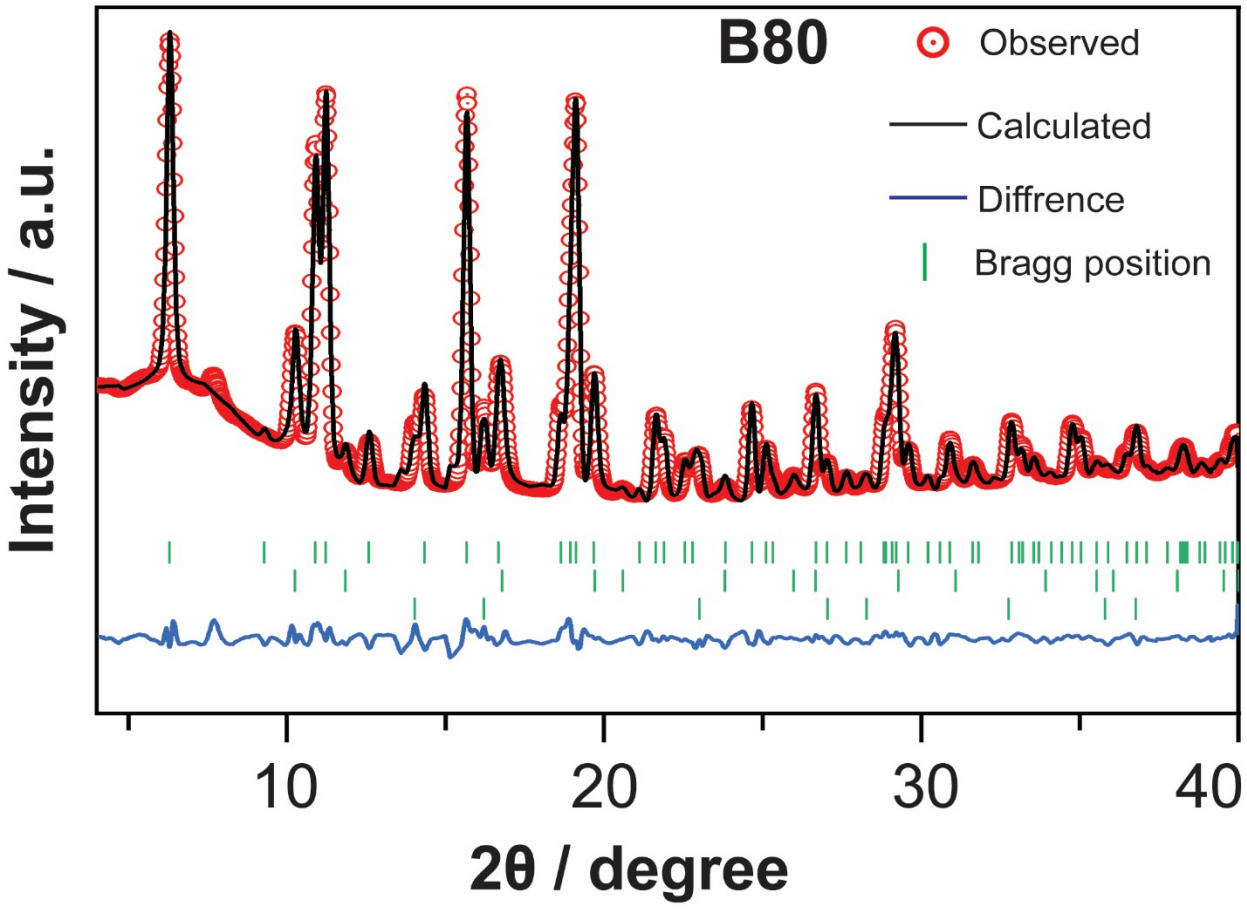

Figure S2. Rietveld refinement plot of the B80 sample

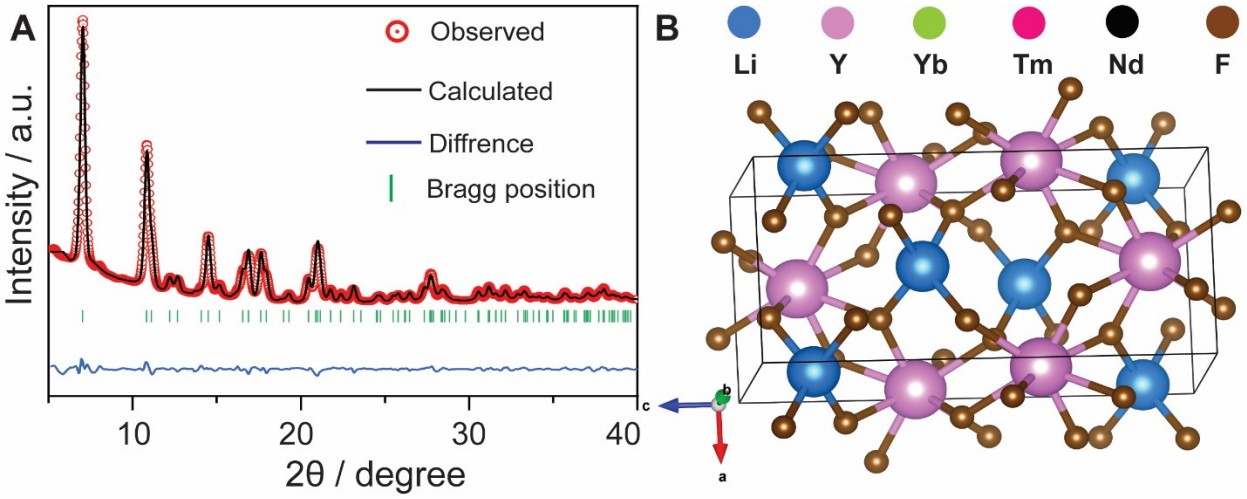

Figure S3. Rietveld refinement plot and crystal structure of the B100 ($LiYF_4$) sample

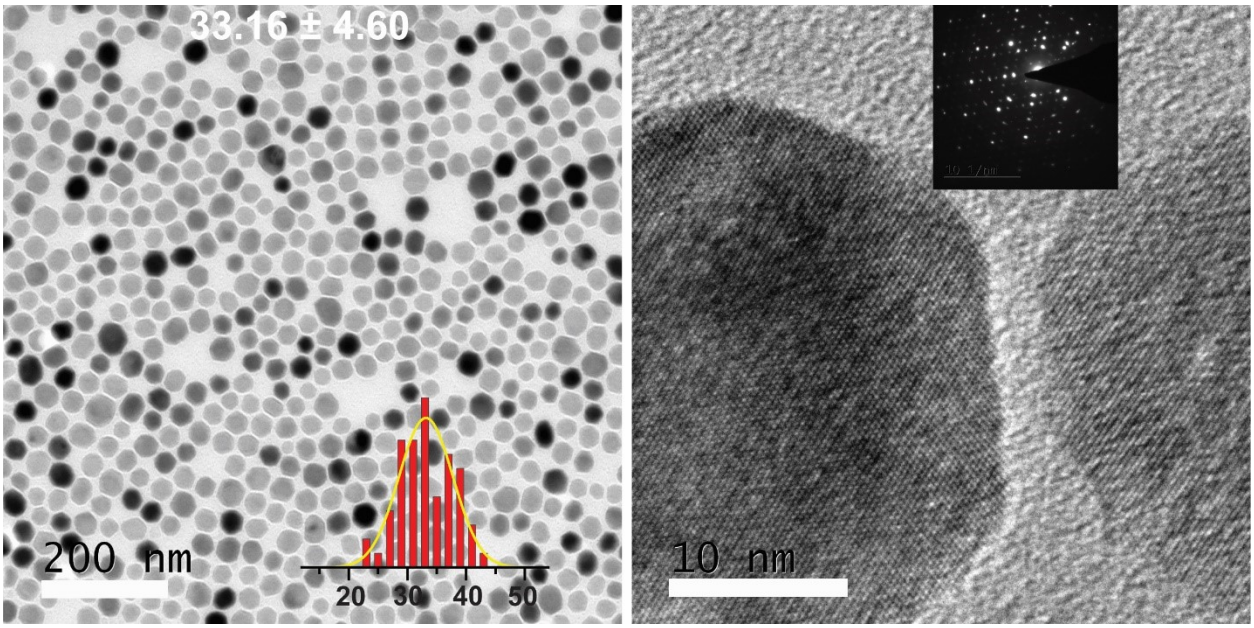

Figure S4 Bright field, high resolution TEM image and SAED of B80 sample

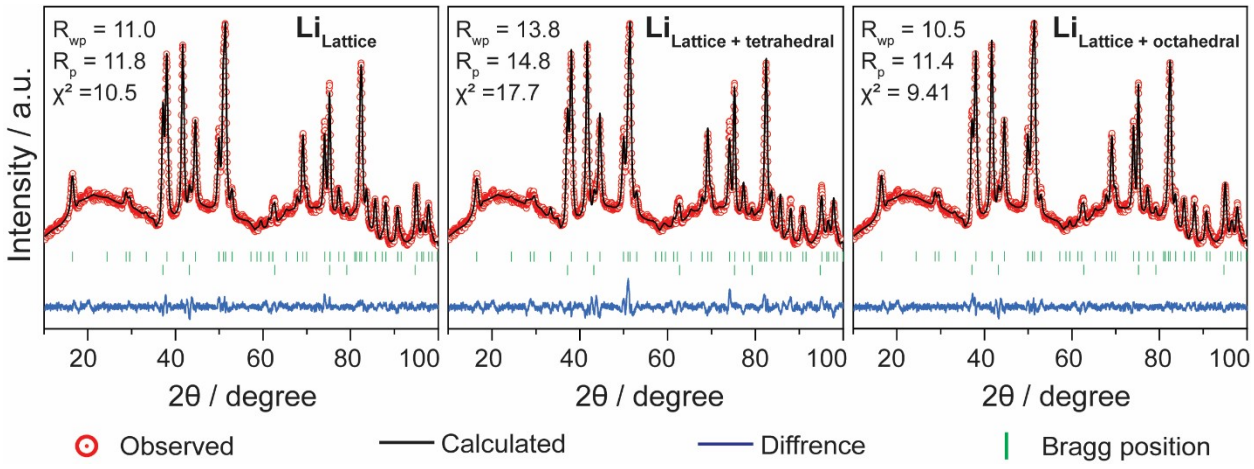

Figure S5. Rietveld refinement plot of ND data for Li positions at lattice ($Li_{Lattice}$), lattice + tetrahedral ($Li_{Lattice + Tetrahedral}$), and lattice + octahedral ($Li_{Lattice + Octahedral}$)

B0

```
 ------------------------------------------------------
 BRAGG R-Factors and weight fractions for Pattern #  1
 ------------------------------------------------------

=> Phase:  1     HexagonalNaYF4
=> Bragg R-factor:   2.31       Vol:  107.867( 0.017)  Fract(%):  100.00( 0.48)
=> Rf-factor=  1.91             ATZ:         435.054   Brindley:  1.0000
```

B50

```
 ------------------------------------------------------
 BRAGG R-Factors and weight fractions for Pattern #  1
 ------------------------------------------------------

=> Phase:  1     HexagonalNaYF4
=> Bragg R-factor:   1.84       Vol:  108.023( 0.000)  Fract(%):   91.20( 0.00)
=> Rf-factor=  1.47             ATZ:         368.280   Brindley:  1.0000

=> Phase:  2     LIFcubic
=> Bragg R-factor:   4.12       Vol:   65.160( 0.000)  Fract(%):    8.80( 0.00)
=> Rf-factor=  2.82             ATZ:      239057.500   Brindley:  1.0000
```

Figure S6. Phase purity result obtained from the Rietveld refinement of ND data

Table S3 Lattice parameters and exact R_w values obtained from PDF analysis

Sample	R_w	a=b (Å)	c (Å)	V (Å^3)

B0	0.163522	5.96392	3.50415	107.938641
B10	0.187938	5.97011	3.50691	108.248010
B30	0.214003	5.95569	3.50126	107.552164
B50	0.218301	5.97699	5.97699	108.429278
B60	0.212431	5.96842	3.49728	107.889649
B100	0.246416	5.15369	10.71170	284.508325

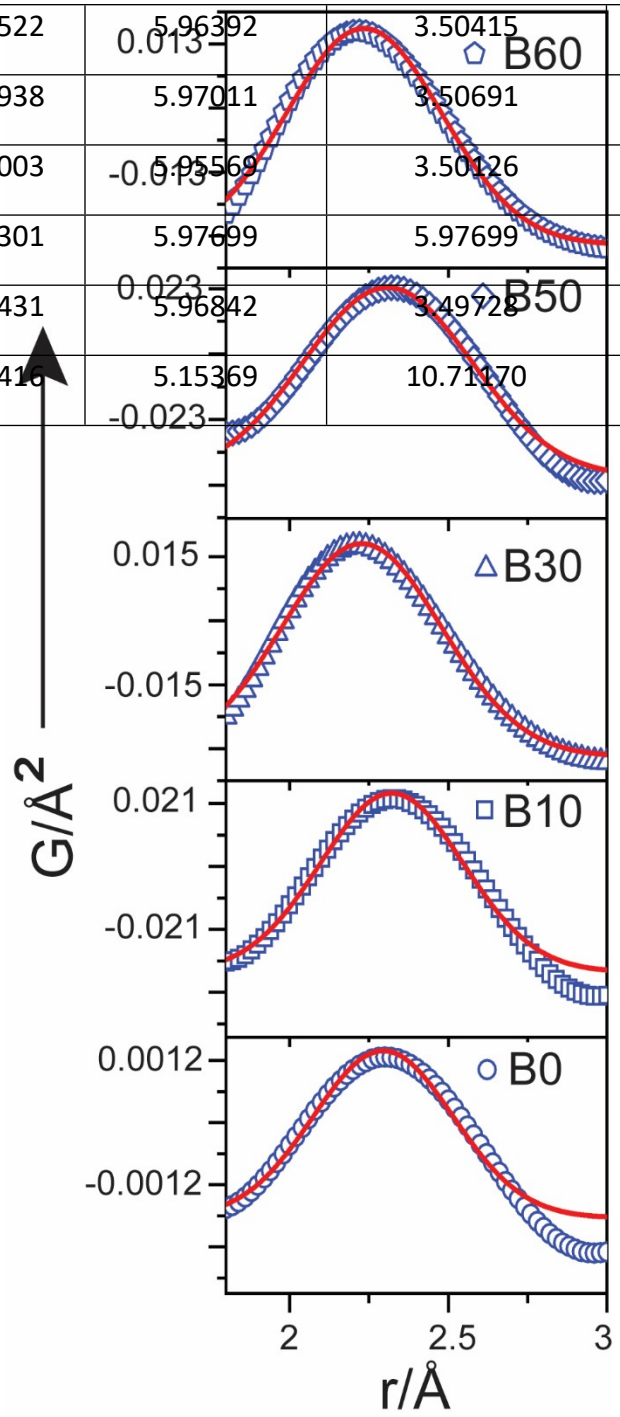

Figure S7. Gaussian fitting of experimental PDF for different samples. Red line is Gaussian fit over experimental PDF peak at ~2.29 Å

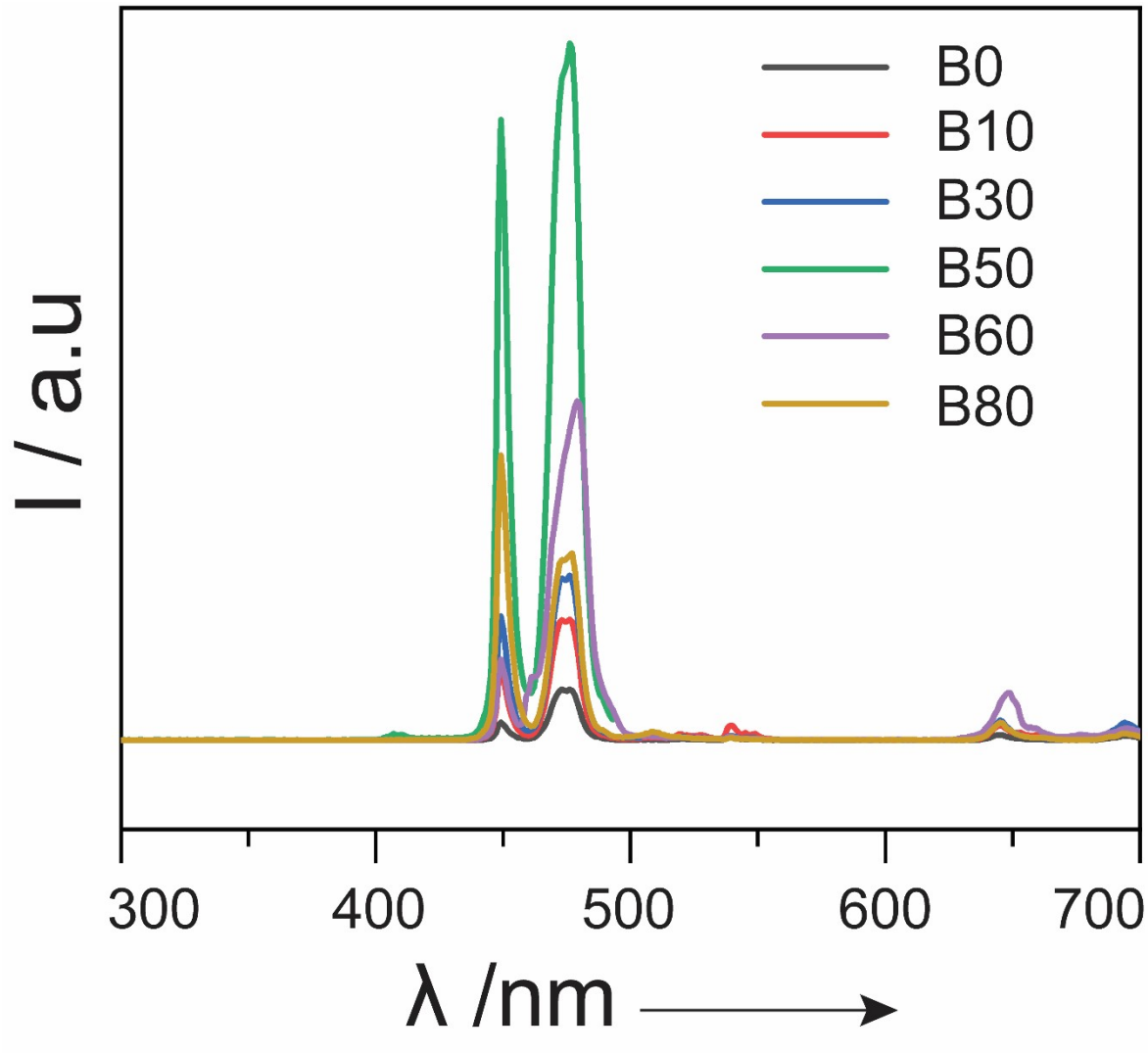

Figure S8. 2D-plot of UCL spectra of all the samples

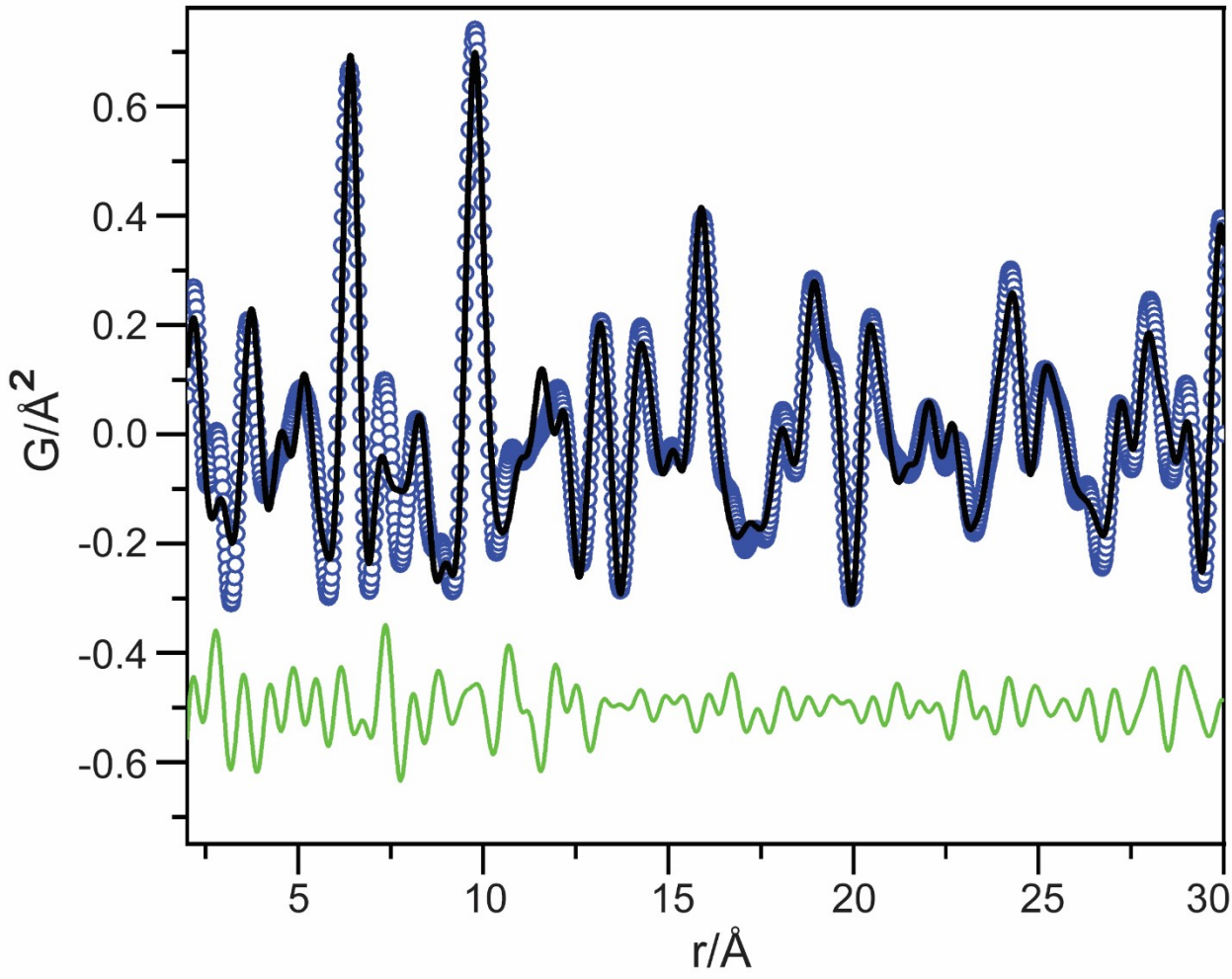

Figure S9. PDF plot of B100 sample ($LiYF_4$). Blue circle is experimental PDF and black line is calculated PDF. the green line is difference between experimental and calculated PDF.

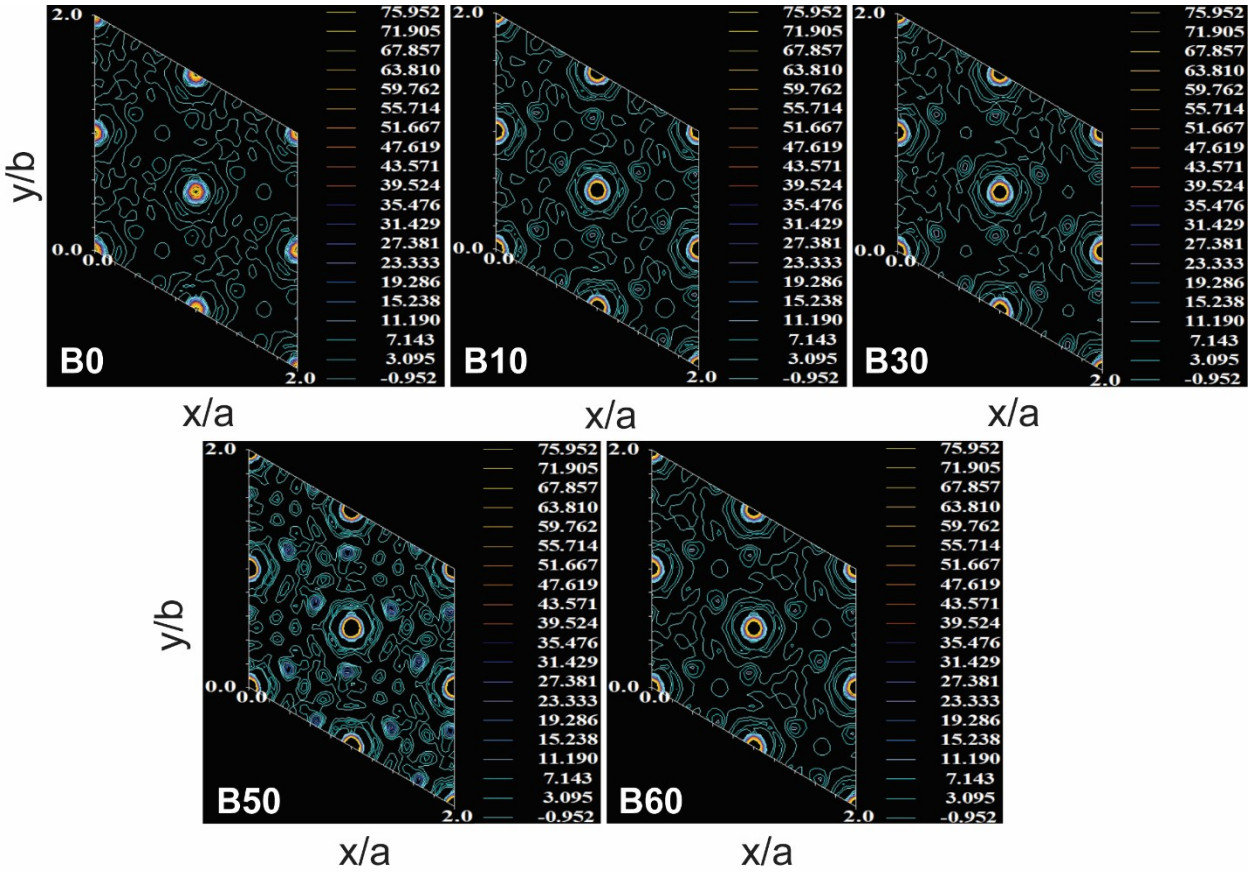

Figure S10. Electron density contour map obtained from Synchrotron XRD refinement of different samples

References

1. A. Sinha, A. Sagdeo, P. Gupta, A. Upadhyay, A. Kumar, M. Singh, R. Gupta, S. Kane, A. Verma and S. Deb, Deb, S. In Angle dispersive X-ray diffraction beamline on indus-2 synchrotron radiation source: commissioning and first results, *Journal of Physics: Conference Series*, 425(7):072017, 2013.
2. V. Siruguri, P. Babu, M. Gupta, A. Pimpale and P. Goyal, *Pramana,* A high resolution powder diffractometer using focusing optics. 2008, **71**, 1197-1202.
3. J. Rodríguez-Carvajal, *Physica B Condens. Matter*, Recent advances in magnetic structure determination by neutron powder diffraction. 1993, **192**, 55-69.
4. S. Zabinsky, J. Rehr, A. Ankudinov, R. Albers and M. Eller, *Physical Review B*, Multiple-scattering calculations of X-ray-absorption spectra.1995, **52**, 2995.
5. B. Ravel and M. Newville, *J Synchrotron Radiat.*, data analysis for X-ray absorption spectroscopy using IFEFFIT. 2005, **12**, 537-541.