Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information:

Size Induced Structural Changes in Maricite-NaFePO$_4$: An In-Depth Study by Experimental and Simulations

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Experimental Methods

Ex situ Synchrotron XRD and Rietveld refinement

Angle dispersive X-ray diffraction measurements were performed with the synchrotron radiation source having the wavelength of 0.78792 Å at BL-12 in Indus-2 at RRCAT, Indore. The beam size was 0.5 mm x 0.5 mm equipped with double crystal monochromator by covering the spectral range between 5 and 20 keV. The energy resolution of monochromator was 1eV at 10 keV and by having angle resolution of 0.06 degrees. The XRD pattern was recorded in the form of concentric circles on the image plate set up and each circle corresponds to a particular diffraction peak. The image is converted into the diffraction pattern using a freeware handy software fit2D [1], which includes the details of the instrument set up and the calibration standard sample of LaB$_6$. Afterwards the XRD pattern was analysed by using TOPAS software to obtain the structural details [2]. The initial refinement step for the bulk was taken from the JCPDS pattern and subsequent refinement was continued to obtain the best fit between the observed and the calculated spectrum.

Maricite NFP crystallizes in the orthorhombic unit cell with 4 formula units and *Pmnb* space group with the site reversal of Na and Fe in comparison to the olivine structure. Each unit cell has 4 formula units of m-NFP with 4 Na, 4 Fe, 4 P and 16 oxygen atoms and the refinement was done in two steps. The first step is termed as Le-bail refinement, which involves the refinement of all the basic parameters related to the unit cell. The second step includes detailed structural analysis by specifying the atomic positions. Initially, the crystal structure refinement was performed using the Le bail and the lattice parameters were extracted with an appropriate R-parameters and goodness of fit. After completing the Le-bail refinement for the bulk sample with the lattice parameters similar to those found from the literature, the structural refinement was carried out by providing the atomic positions along with their nominal occupancy. All the atomic occupancies and positions are refined step by step for each atom by keeping all other occupancies to their nominal value according to the allowed Wyckoff position. Subsequently, the atomic positions are allowed to vary together with the occupancies of other atomic positions. The best fit between the experimental and the calculated curve have been obtained when all the atomic parameters are allowed to vary simultaneously. Finally, all the atomic positions and the occupancies with the minimal error values are considered for further analysis. Similar procedure has been adopted for other crystallite sizes in the present work, resulting into the deviation in the sodium occupancy. The final refinement parameters based on the goodness of fit and the minimum possible difference curve was considered for the further analysis.

Electron Microscopy

The particle size and morphology of the as synthesised samples has been examined with Field Emission Scanning Electron Microscopy (FESEM) GeminiSEM instrument by ZEISS. Further, the analysis of the images was done using the ImageJ software which has features of enhancing the image quality. Additionally, confirmation of the crystallite size estimated by XRD was done by high resolution transmission electron microscope (HRTEM), TECNAI G2 T30 U-TWIN attached with a double slit holder and an accelerating voltage of 300 kV. A suspension solution of the various crystallite sized samples with the ethanol was dispersed on the carbon coted grid with 300 meshes per mm. The phase contrast images have been recorded using the CCD camera by GATAN which were further analysed for d spacing estimation with the digital micrograph software.

Ex situ soft X-ray absorption

Soft x-ray absorption spectroscopy has been performed with the synchrotron source at the SXAS beamline in Indus-2 at RRCAT, Indore. The operating energy of Indus-2 is 2.5 GeV with the storage current of 150 mA. The measurements were performed at room temperature under ultra-high vacuum (10^{-10} Torr) in the total electron yield (TEY) mode. Iron L-edge and oxygen K-edge were recorded in the energy range of 700-740 eV and 500-580 eV respectively with the energy resolution of 0.3 eV. Grating with 1500 grooves per mm with the entrance and exit slit size of 1000 and 100 μm was used for collecting the spectra in the energy ranges of 500−580 eV for O 1s and 700−740 eV for Fe L-edge. The energy resolution was 0.2 and 0.3 eV for O 1s and Fe L-edge, respectively. The recorded raw was corrected with the Athena software [3] using the pre edge, post edge and normalization corrections with respect to incident photon flux. Further, the individual spectra were deconvoluted using the Kolxpd software which includes the baseline correction and peak identification different features. We also simulated Fe L-edge spectra by using CTM4XAS software to estimate various parameters like crystal field strength, covalency by comparing with the experimental spectra.

The transition metal oxides with octahedral symmetry, if the degeneracy of the d orbital is lifted then it leads to the splitting of d orbital into two groups with different energies (t_{2g} and e_g) levels. The difference in energy between t_{2g} and e_g level is called as crystal-field splitting energy (10Dq or Δ_o) and it is strongly depend on nature of the ligand and charge state of the metal ion. Such a simple picture does not hold good for the present case due to the distorted octahedral symmetry of transition metal ion. In this case, we found transition metal ion in the D_{3d} symmetry with trigonal distortion. Further, the trigonal distortion results into the splitting of the degenerate t_{2g} level further into two groups namely a singlet a_{1g} and a doublet e_g^{π}component, summing into the overall three set of energy levels in the 3d orbitals. Hence, 10Dq signifies the energy difference between the t_{2g} (π) component (chosen as the centre of a_{1g} (π) and e_g (π) components) and e_g (σ). Typically, the trigonal field defined in terms of the D_σ and D_τ parameters. The D_σ and D_τ signifies the same meaning as the D_s and D_t in the tetragonal distortion.

DFT Methodology

Spin polarized density functional theoretical calculations were carried out using the projector-augmented plane-wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP) [4]. The crystal lattice parameters and atomic structures have been computed using the Perdew-Burke–Ernzerhof (PBE) functional [5] with the Hubbard U parameter [6] ($U_{\mathrm{eff}} = U\text{-}J$, the Dudarev approach). We have studied the influence of U value on the structural parameters. A U value of 5.0 eV was then chosen on the basis of periodic structure resemblance with the literature and experimental results. The applied unit cell parameters and Monkhorst–Pack *k*-point meshes for various vacancy concentrations (modelled with various unit cell sizes) are listed in Table TS5. The wave function has been expanded using a plane wave basis set with an energy cut-off of 520 eV for all the calculations. The atomic structures were visualized by the VESTA software [7].

References

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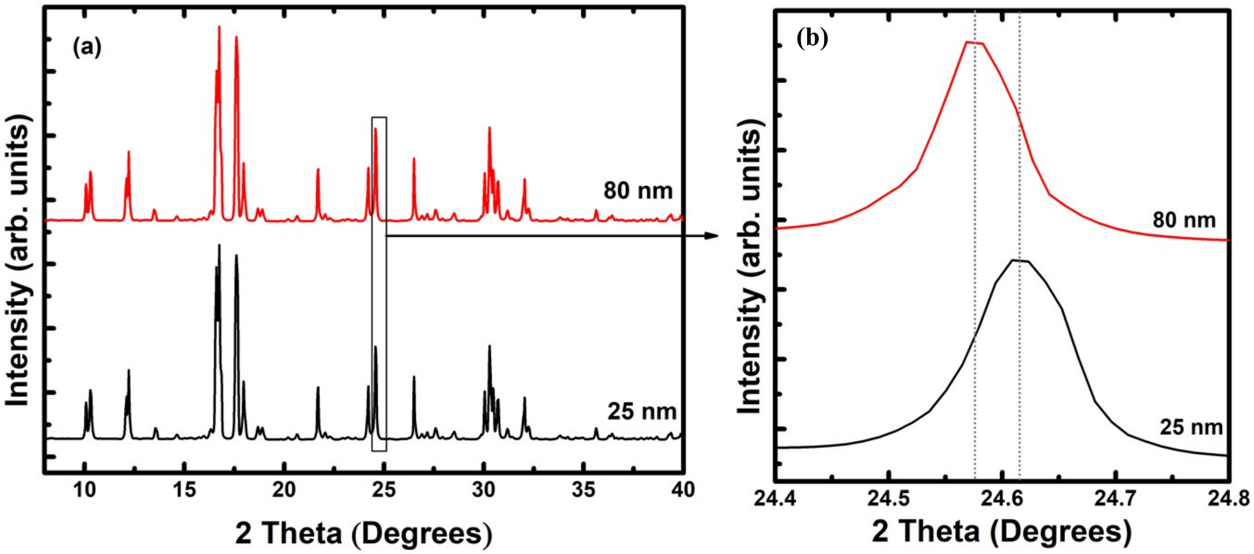

Figure S1: (a) XRD pattern of maricite-NFP for 80 and 25 nm crystallite sizes measured at the room temperature with the synchrotron source (λ=0.78792 Å), (b) Magnification of (122) diffraction peak shows the broadening and shift towards higher angle with decrease in the crystallite size.

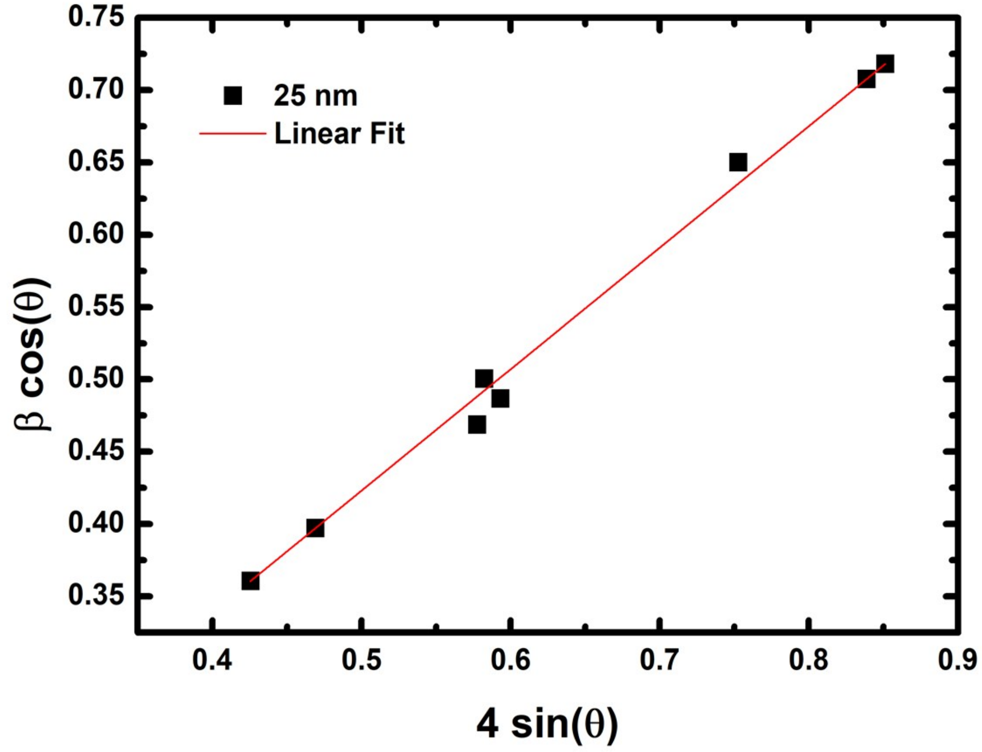

Figure S2: Williamson Hall plot for the representative 25 nm crystallite size sample. Fit to the experimental data points, the crystallite size is extracted from the y-intercept and the strain is obtained from the slope.

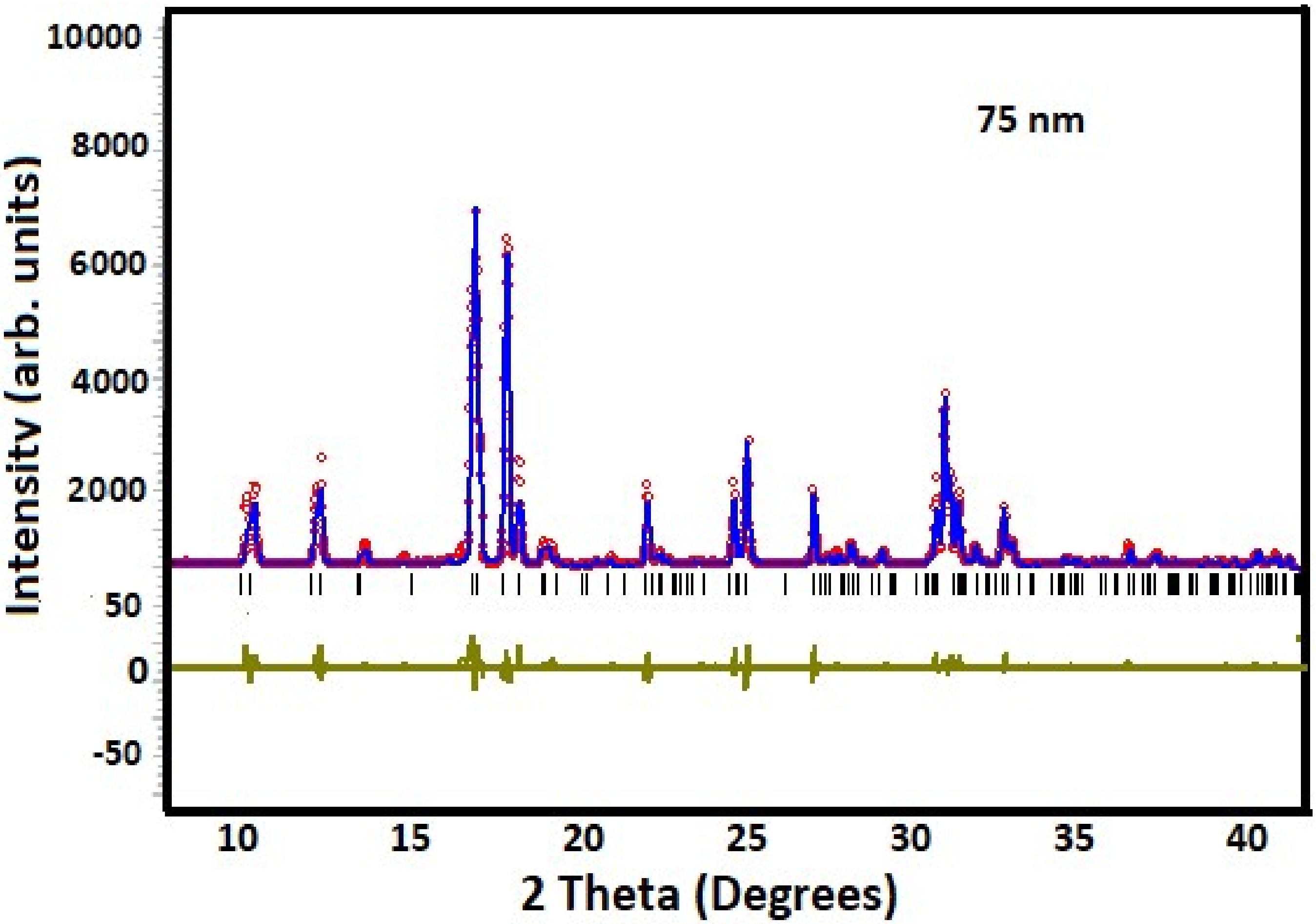

Figure S3: Fitted experimental data for the sample with 75 nm crystallite size of m-NFP. The experimental curve has been shown with the open red circles where the solid blue line represents the Rietveld calculated diffractogram. Below are the markers (black) according to the JCPDS pattern with the space group *Pmnb* and the difference curve between the experimental and fitted curve has been plotted in the solid green colour.

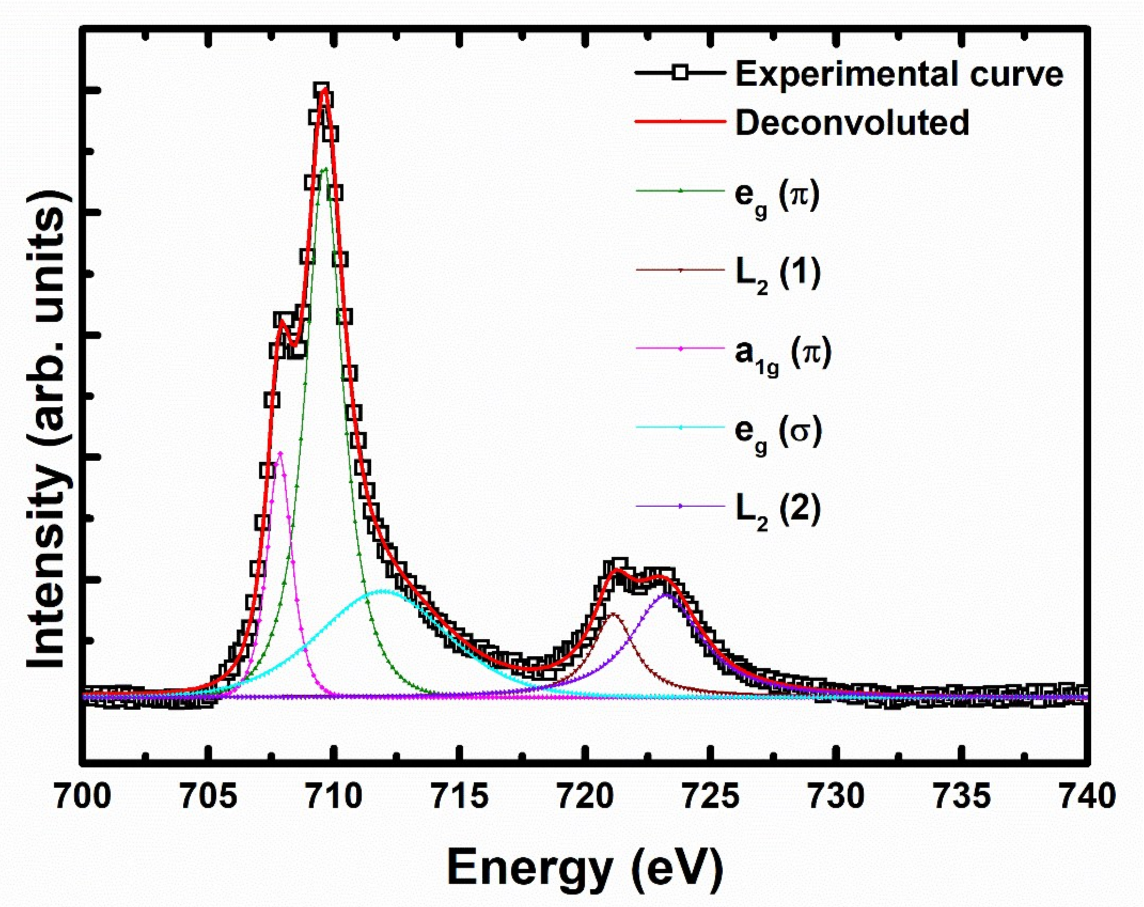

Figure S4: Deconvoluted XAS spectra for the Fe L-edge recorded at room temperature showing different orbital contributions in the overall spectra for 80 nm crystallite size.

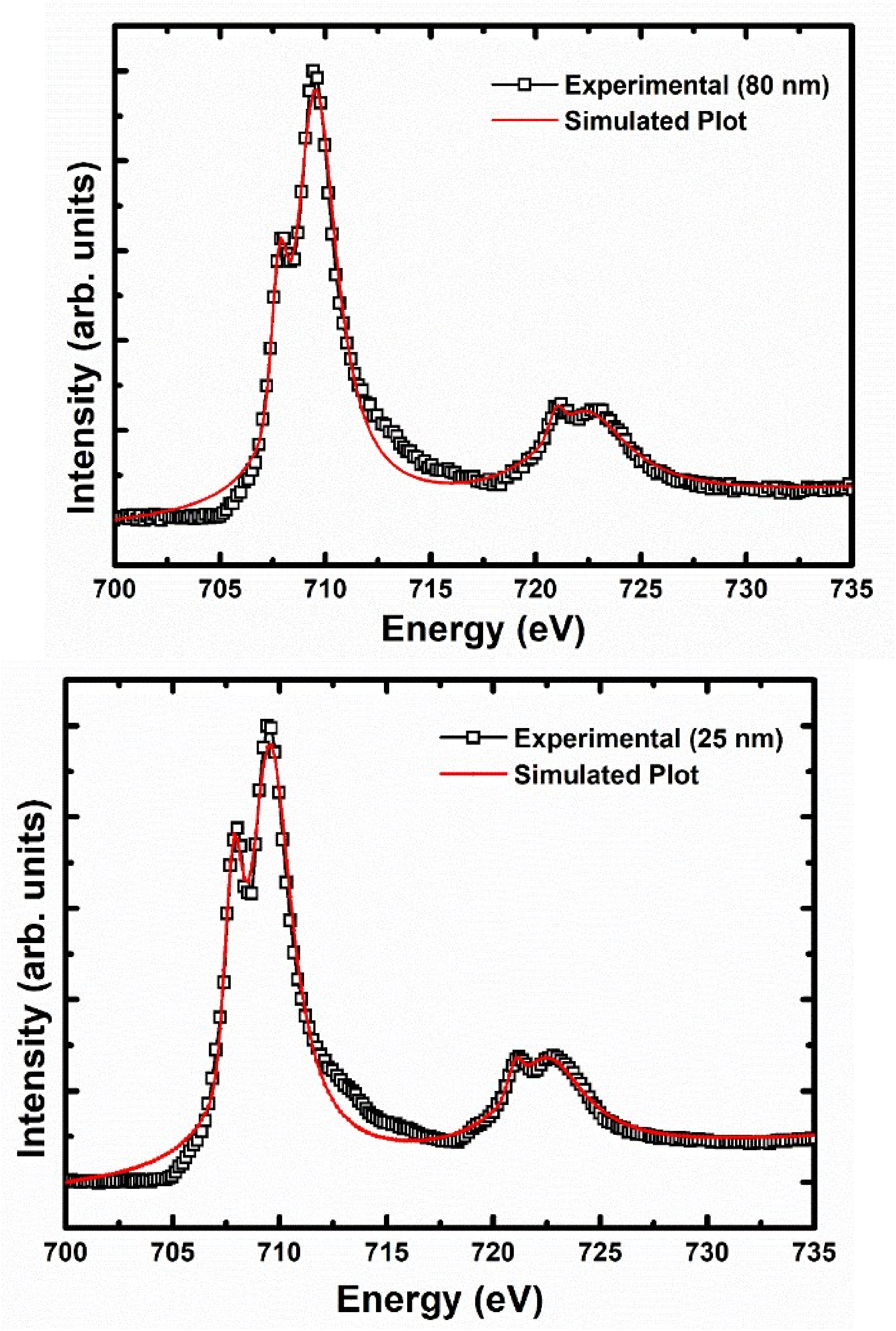

Figure S5: Experimental XAS spectra fitted with the simulation curve for (a) bulk 80 nm and (b) 25 nm crystallite size.

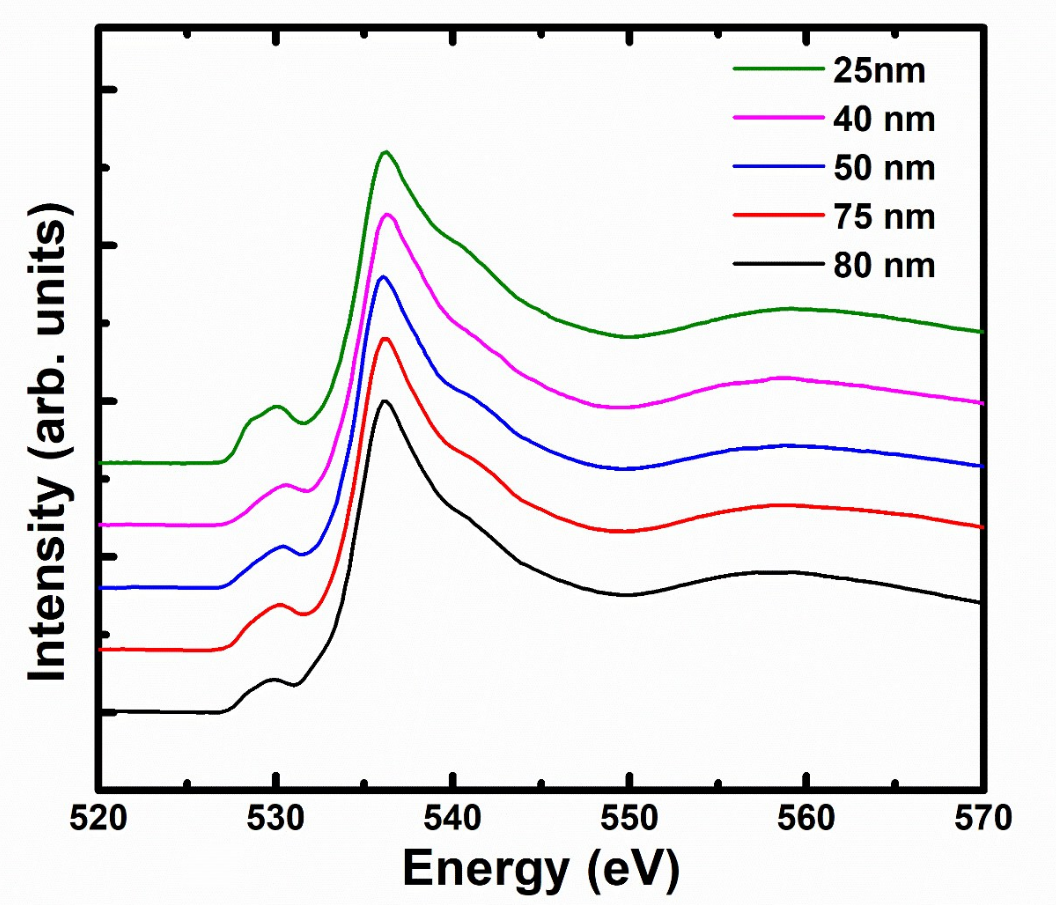

Figure S6: The soft X-ray absorption spectra of oxygen K-edge for different crystallite sizes of m-NFP recorded at room temperature.

Table TS1: Parameters for the preparation of different crystallite sized m-NFP samples.

Crystallite Size (nm)	**Temperature (K)**	**Time (min)**
25	923	120
40	973	240
50	1023	360
75	1073	360
80	1123	480

Table TS2: Rietveld Refinement parameters for bulk (80 nm) and 25 nm crystallite sizes.

Crystallite Size	***Bulk (80 nm)***	***(±) Error***	***25 nm***	***(±) Error***
Wavelength (Å)	*0.79792*	*0.01*	*0.79792*	*0.01*
Space Group	*Pmnb*		*Pmnb*	
a (Å)	*5.047*	*0.002*	*5.004*	*0.004*
b (Å)	*6.884*	*0.0015*	*6.812*	*0.0032*
c (Å)	*8.994*	*0.0008*	*8.986*	*0.003*
V $(\AA^3)$	*312.6*	*0.012*	*306.1*	*0.046*
Na^+ ***Vacancies (%)***	*0.01*	*0.003*	*14.2*	*0.006*
R_p ***(%)***	*11.70*		*9.94*	
R_{wp} ***(%)***	*13.70*		*12.43*	
GOF $(\chi 2)$	*1.17*		*1.25*	
Strain	*0.001*	*0.0004*	*0.820*	*0.0024*

Table TS3: Comparison of crystallite size along with d-spacing calculated from XRD and HRTEM.

Crystallite size (nm) ± 2nm		**Lattice spacing (nm) ± 0.001nm**	
XRD	**HRTEM**	**XRD**	**HRTEM**
80	83	0.3708	0.370
75	78	0.3724	0.370
50	52	0.3688	0.368
40	43	0.3668	0.366
25	28	0.3621	0.365

Table TS4: Simulation parameters for different crystallite sizes related to the D_{3d} symmetry.

Crystallite size (nm)	**10 Dq (eV)**	**D_σ (eV)**	**D_τ (eV)**	D_{trig}^{0}	**% Fe^{3+} sites**
80	1.30	0.3	0.18	-2.1	*0.01*
75	1.34	0.38	0.13	-1.998	1.3
50	1.45	0.43	0.10	-1.952	4.6
40	1.52	0.49	0.07	-1.931	9.3
25	1.62	0.55	0.03	-1.848	16

Table TS5: Parameters related to deconvolution for iron L edge with different crystallite size.

Crystallite Size (nm)	**10 Dq (eV)**	**Δ(eV)**	e_g **((σ)eV)**	$e_g((\pi)eV)$	**a_{1g} ((π) eV)**
80	1.30	1.67	0.780	0.038	-1.632
75	1.34	1.678	0.804	0.033	-1.708
50	1.45	1.778	0.870	0.028	-1.806
40	1.52	1.909	0.912	0.022	-1.868
25	1.62	1.939	0.972	0.015	-1.954

Table TS6: k-points chosen for the supercell structure mentioned with the lattice parameters.

Super cell	**a (Å)**	**b (Å)**	**c (Å)**	**K POINTS**	**Na^+ vacancies (%) (expt. value)**	**Crystallite size (nm) (expt. value)**
3x3x2	15.312	20.721	18.188	1x1x1	0.01	80
3x2x2	15.312	13.814	18.188	3x3x3	1.75	75
3x2x1	15.312	13.814	9.094	3x3x6	6	50
2x2x1	10.208	13.814	9.094	3x3x6	9.5	40
1x2x1	5.104	13.814	9.094	9x3x6	14.2	25