Electronic Supplementary Information (ESI)

Effect of Crystallite Size on the Phase Transition Behavior of Heterosite $FePO_4$

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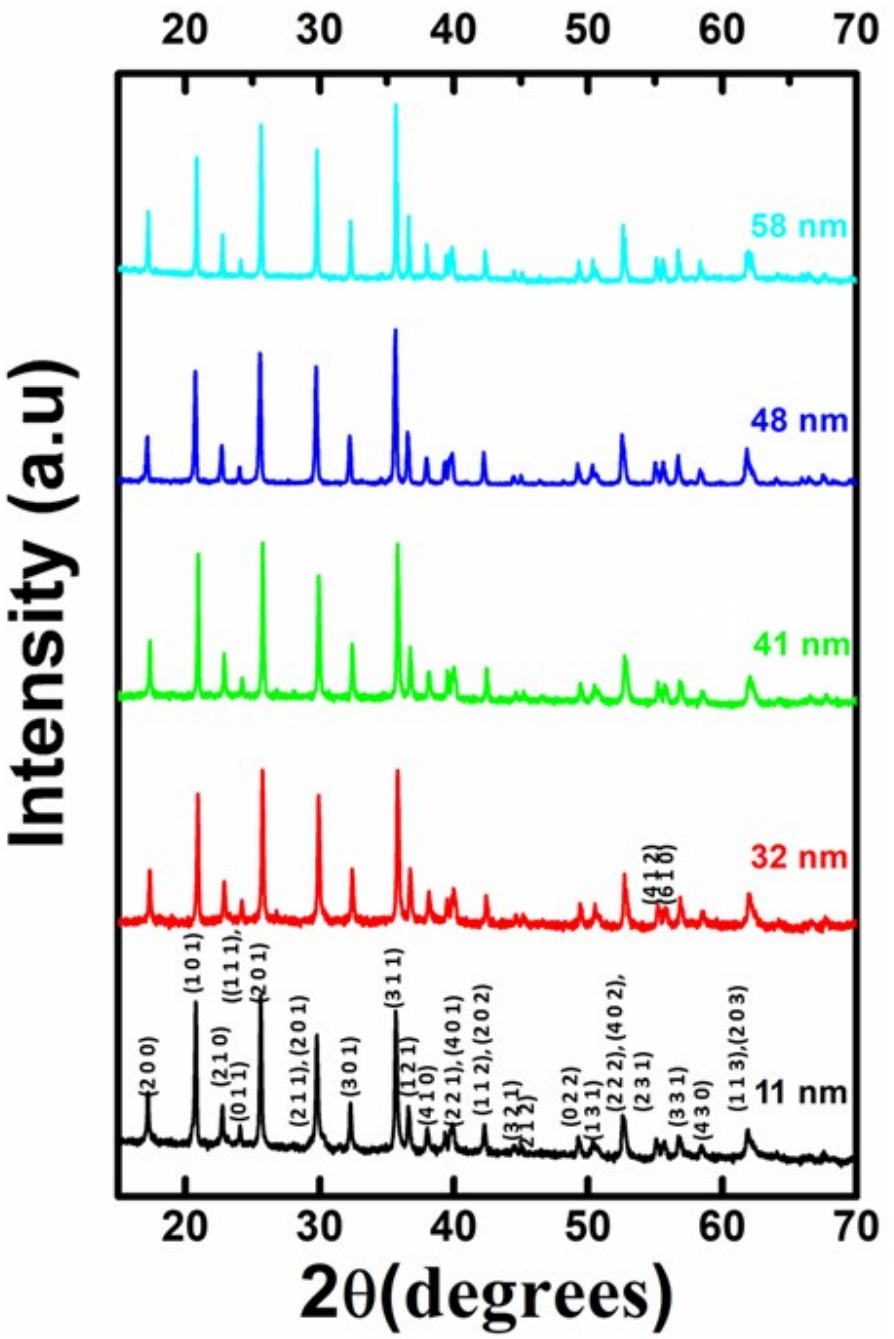

Fig. S1: XRD patterns of as-prepared different crystallite sized $LiFePO_4$ samples before chemical delithiation.

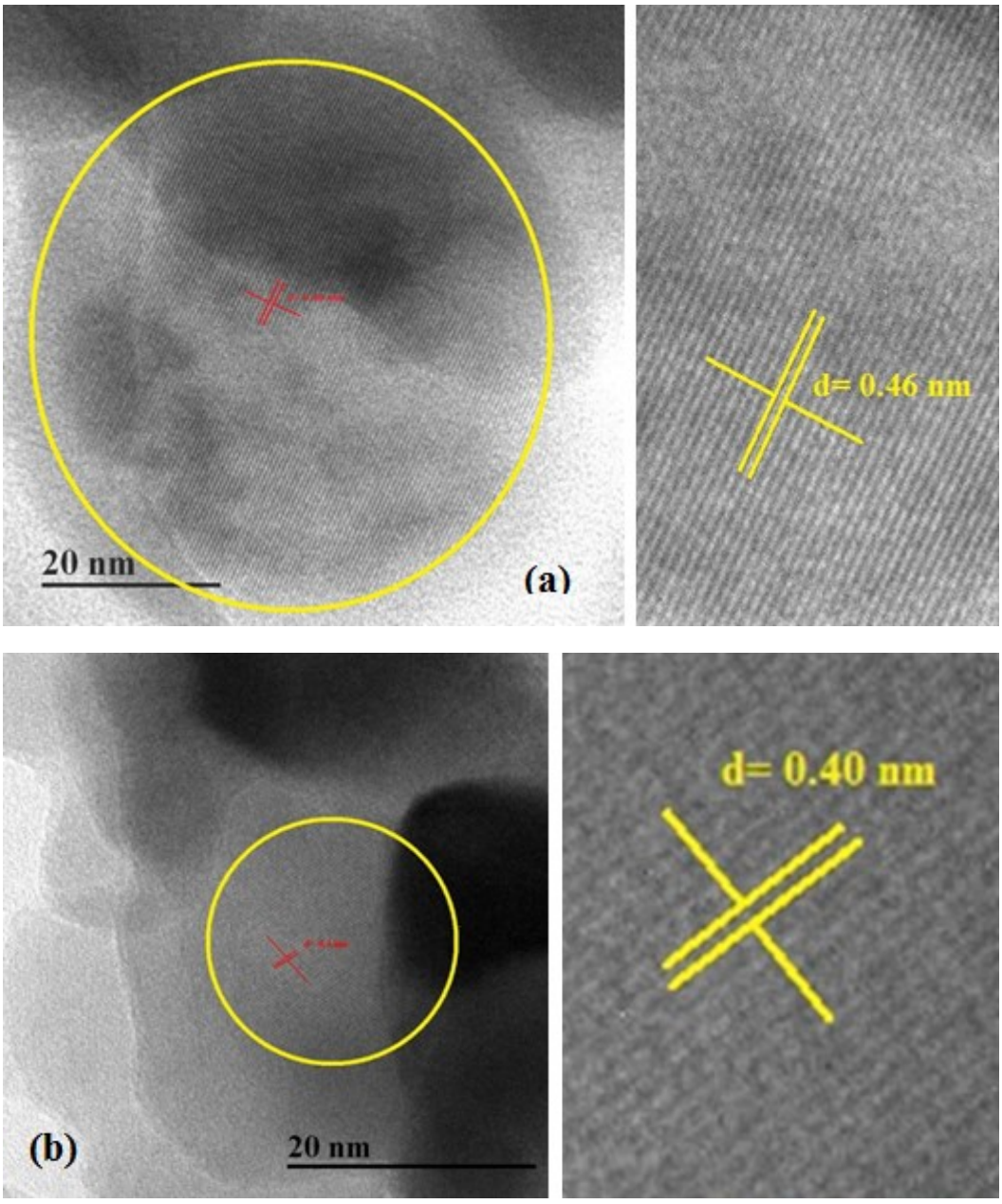

Fig. S2: TEM images along with its HRTEM pattern for (a) 59 nm, and (b) 21 nm crystallite sizes of h-FP.

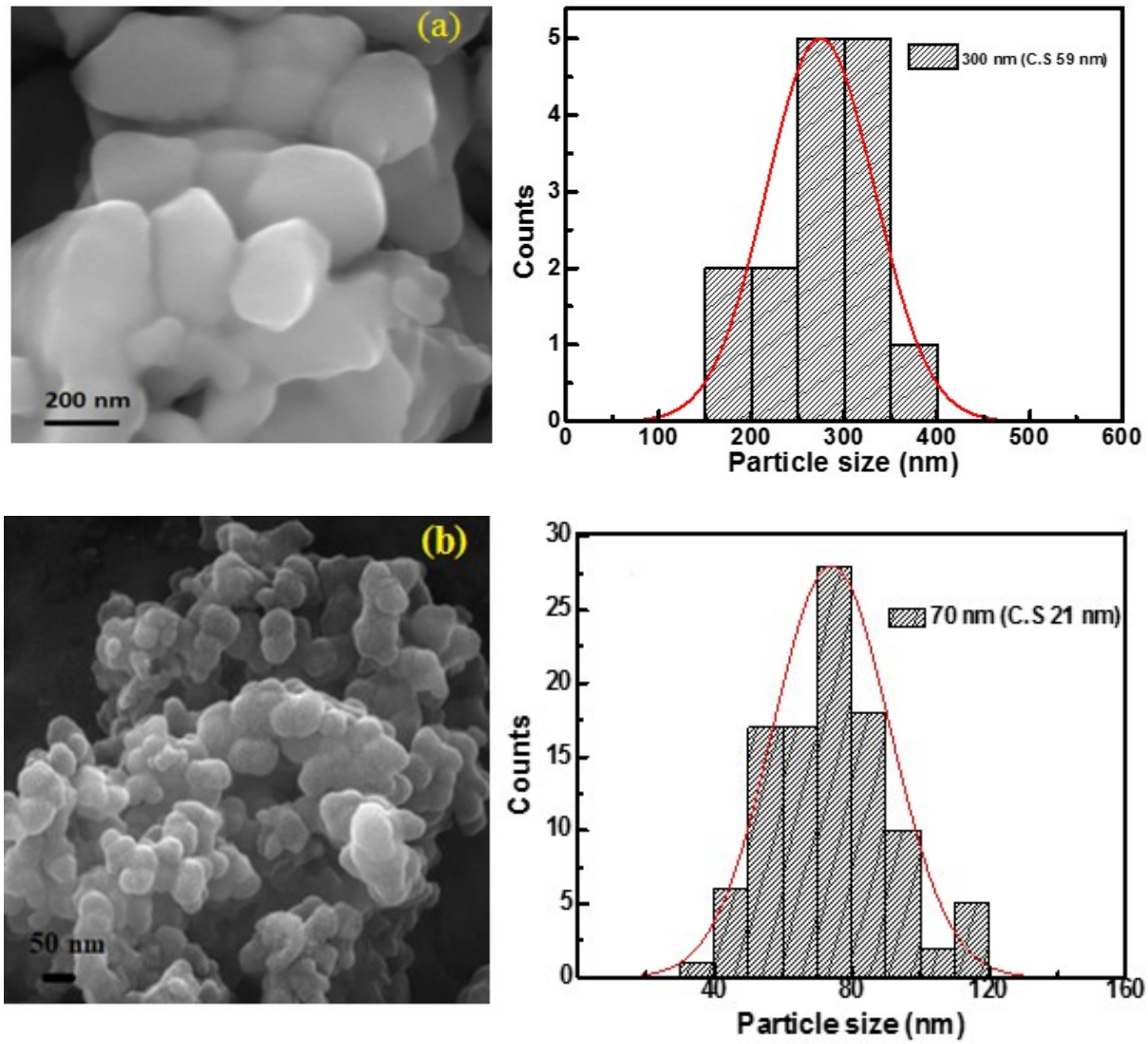

Fig. S3: FESEM images of (a) 59 nm, and (b) 21 nm crystallite sizes of h-FP along with the particle size distribution histograms.

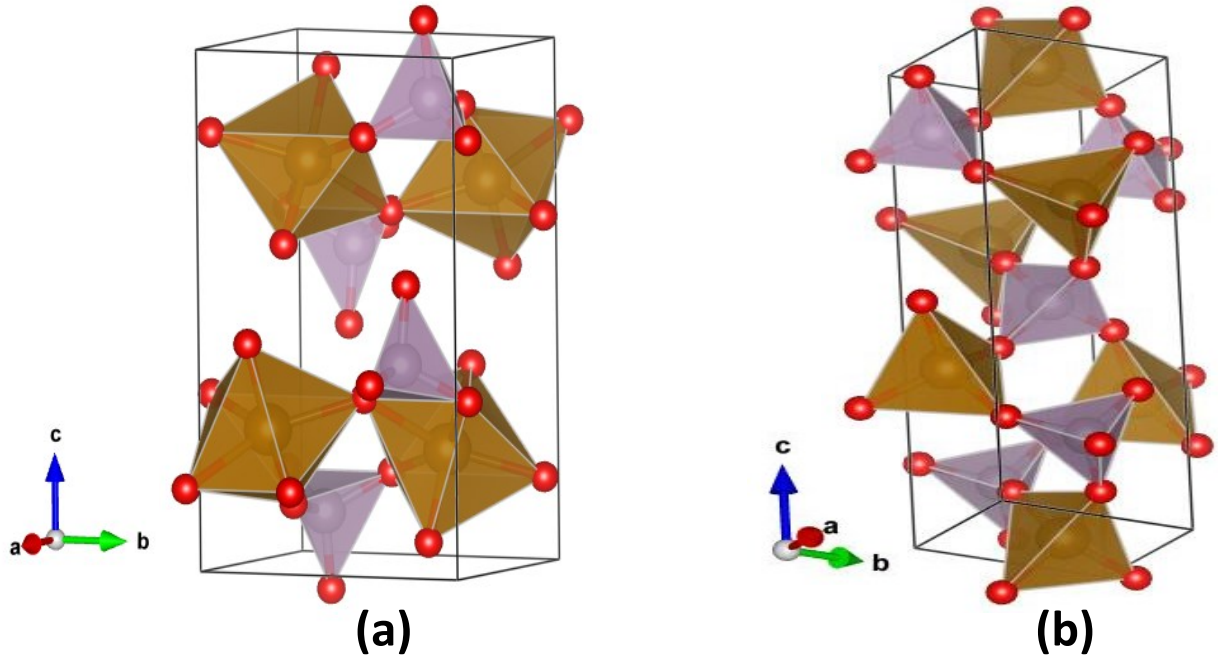

Fig. S4: Crystal structure of (a) heterosite $FePO_4$ and (b) trigonal $FePO_4$ as visualized by using VESTA software

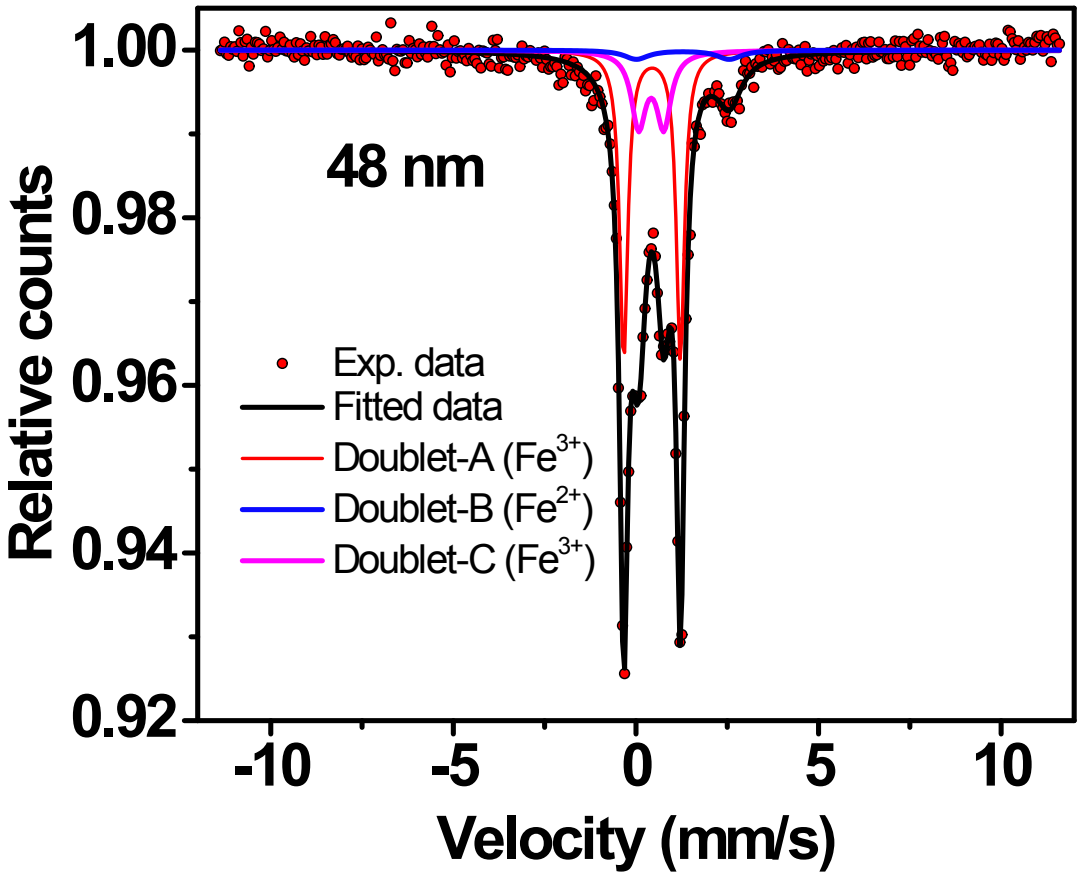

Fig. S5: ^{57}Fe Mössbauer spectra of heterosite $FePO_4$ with 48nm crystallite size recorded at 303 K. Experimental (filled circle) and fitted spectra (black solid line) are represented. Additional solid lines illustrate contributions from the primary Fe^{3+} (doublet-A and C) and secondary Fe^{2+} components (doublet B: blue line) and they are described in the text.

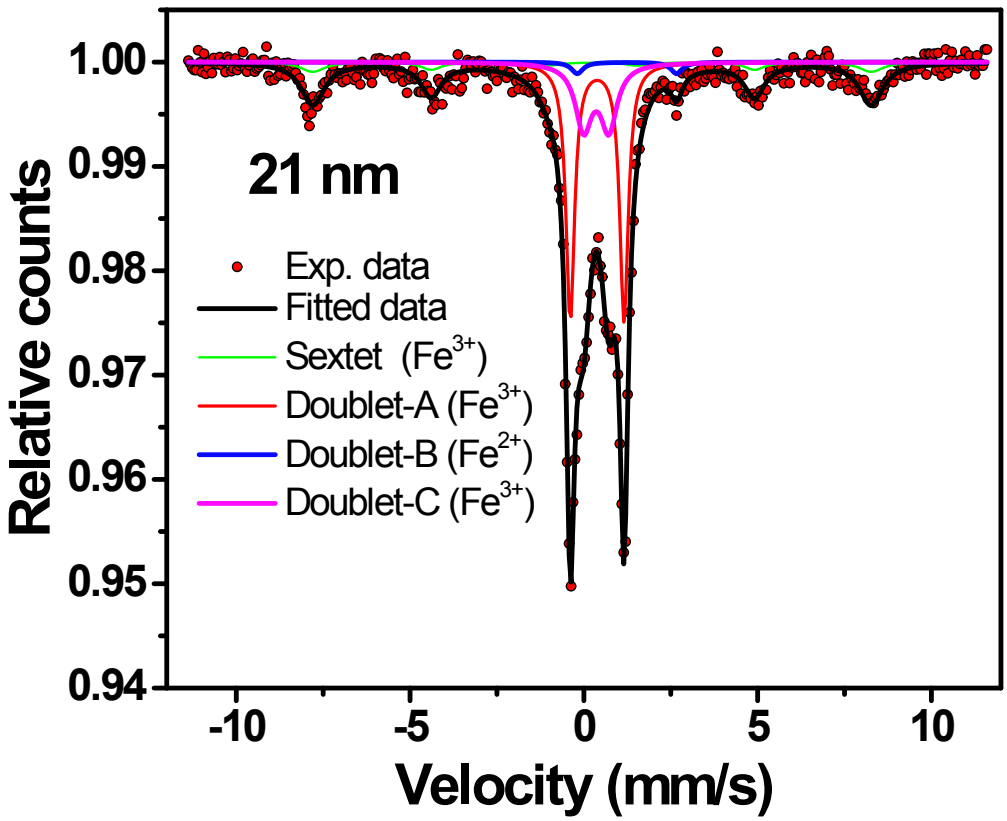

Fig. S6: ^{57}Fe Mössbauer spectra of heterosite $FePO_4$ with 21nm crystallite size recorded at 303 K. Experimental (filled circle) and fitted spectra (black solid line) are represented. Additional solid lines illustrate contributions from the primary Fe^{3+} (doublet-A and C) and secondary Fe^{2+} (doublet-B) components and they are described in the text. The appearance of sextet (green line) is visible for the lower crystallite sized h-FP and is due to the trigonal FP phase.

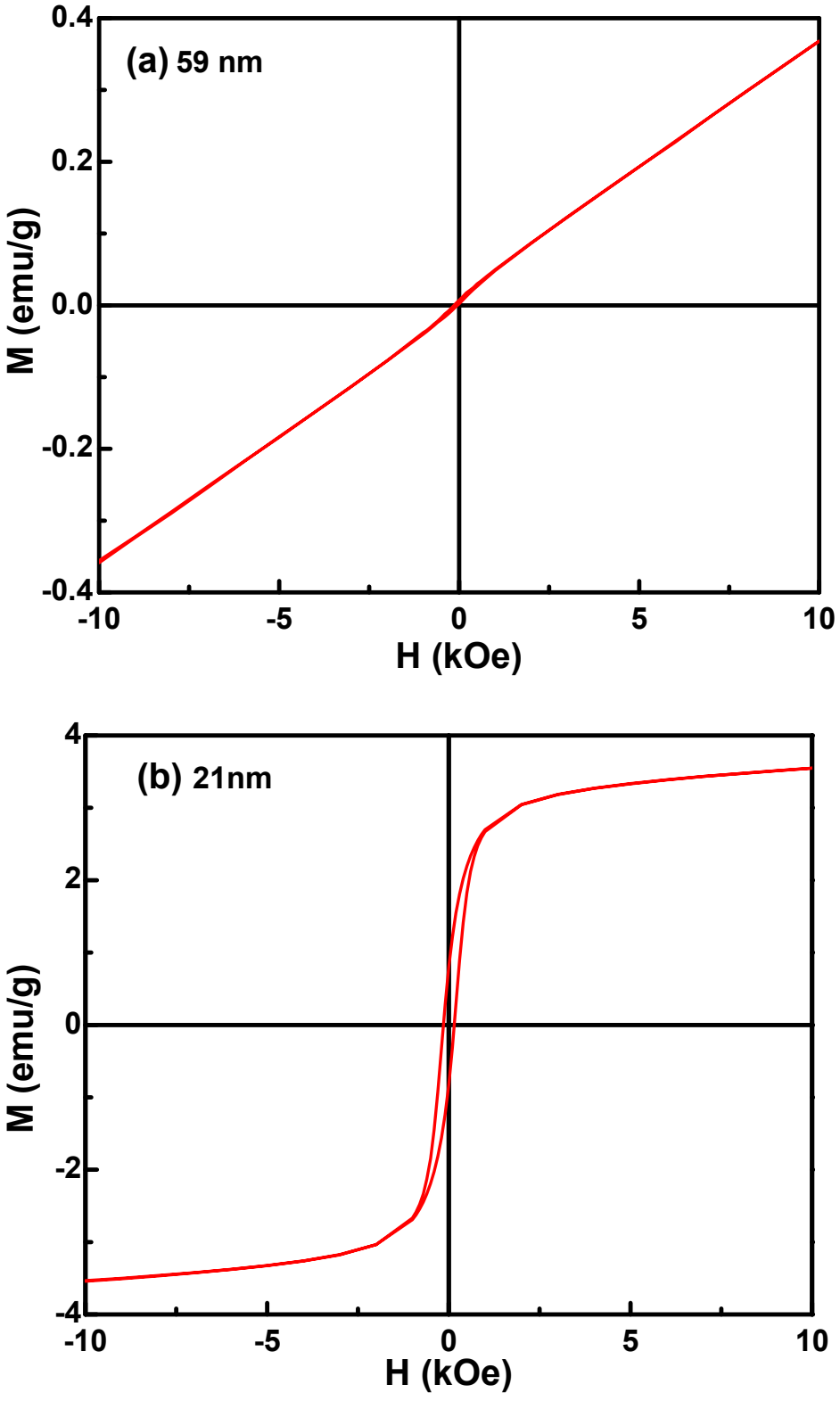

Fig. S7: Magnetic hysteresis (M-H) loops for (a) 59 nm crystallite size sample showing a paramagnetic behaviour and (b) 21nm crystallite size sample showing a weak ferromagnetic behaviour.

Table S1: The synthesis parameters used for different crystallite sized LFP samples

Crystallite Size (nm)	Temperature (K)	Time period (Hour)
58	1023	6
48	1023	4
41	973	12
32	823	12
11	823	2

Table S2 (a): Crystal structure related parameters obtained from the Rietveld refinement method for h-FP phase with 59 nm crystallite size

Wavelength (Å)	0.78283
Space group (No.)	Pnma(62)
a (Å)	9.81067
b (Å)	5.78954
c (Å)	4.77567
V ($Å^3$)	271.25431
R_p (%)	14.8
R_{wp} (%)	12.8
R_{exp} (%)	5.69
GoF (χ^2)	5.07

Atomic coordinates

Site	Wyck.	x/a	y/b	z/c	S.O.F	B_{iso}
Fe	4c	0.27191	0.25000	0.94371	0.995	0
P	4c	0.09254	0.25000	0.39859	1	0
O(1)	4c	0.13851	0.25000	0.70173	0.996	0
O(2)	4c	0.44726	0.25000	0.15682	1	0
O(3)	8d	0.17660	0.00834	0.25362	0.995	0

Table S2 (b): Crystal structure related parameters obtained from the Rietveld refinement method for h-FP phase with 21 nm crystallite size

Wavelength (Å)	0.78283
Space group (no.)	Pnma(62)
a (Å)	9.84573
b (Å)	5.81157
c (Å)	4.79143
V ($Å^3$)	274.16139
R_p (%)	6.00
R_{wp} (%)	6.84
R_{exp} (%)	2.37
GoF (χ^2)	8.31

Atomic coordinates

Site	Wyck.	x/a	y/b	z/c	S.O.F	B_{iso}
Fe	4c	0.27055	0.25000	0.94550	0.9601	0
P	4c	0.09622	0.25000	0.39354	1	0
O(1)	4c	0.12821	0.25000	0.69517	1.0085	0
O(2)	4c	0.44169	0.25000	0.14165	0.9383	0
O(3)	8d	0.17093	0.02245	0.24205	0.9962	0

Table S3: Summary of extracted particle and crystallite size from FESEM, XRD and HRTEM method.

Particle size (nm) ± 15 nm		**Crystallite size (nm) ± 2 nm**	
FESEM	TEM	Scherrer's formula	HRTEM
300	300	59	60
220	200	48	46
120	105	40	42
80	85	29	27
70	65	21	20

Table S4: The Hyperfine magnetic field (H_{hf}), isomer shift (δ), quadrupole splitting (ΔE_Q: doublet and Δ: sextet), outer linewidth (Γ) and relative areas (R_A) in percentage of different sites of Fe^{3+} or Fe^{2+} ions for all five samples derived from Mössbauer spectra recorded at room temperature. Isomer shift values are relative to Fe metal foil (δ = 0.0 mms^{-1}). χ^2: goodness of fit.

Sample (code)	**Iron Sites**	H_{hf} **(Tesla)** ±0.01	ΔE_Q **(mms^{-1})** ±0.01	δ **(mms^{-1})** ±0.01	Γ **(mms^{-1})** ±0.03	R_A **(%)**	χ^2
21 nm	Sextet (Fe^{3+})	49.82	-0.023	0.246	0.818	35.8	1.328
	Doublet-A (Fe^{3+})	--	1.549	0.383	0.297	32.1	
	Doublet-B (Fe^{2+})	--	2.858	1.240	0.40	2.6	
	Doublet-C (Fe^{3+})	--	0.724	0.356	0.569	29.5	
29 nm	Sextet (Fe^{3+})	50.18	0.031	0.329	0.681	26.3	1.148
	Doublet-A (Fe^{3+})	--	1.547	0.440	0.286	40.9	
	Doublet-B (Fe^{2+})	--	2.558	1.231	0.482	11.4	
	Doublet-C (Fe^{3+})	--	0.633	0.436	0.451	21.4	
40 nm	Doublet-A (Fe^{3+})	--	1.562	0.437	0.287	46.1	1.115
	Doublet-B (Fe^{2+})	--	2.375	1.258	0.652	7.1	
	Doublet-C (Fe^{3+})	--	0.702	0.415	0.336	46.8	
48 nm	Doublet-A (Fe^{3+})	--	1.555	0.442	0.269	49.4	1.275
	Doublet-B (Fe^{2+})	--	2.543	1.283	0.820	13.4	
	Doublet-C (Fe^{3+})	--	0.689	0.418	0.478	37.2	
59 nm	Doublet-A (Fe^{3+})	--	1.562	0.436	0.270	28.0	1.390
	Doublet-B (Fe^{2+})	--	2.538	1.196	0.489	9.7	
	Doublet-C (Fe^{3+})	--	0.662	0.435	0.474	62.3	