Electronic Supplementary Information (ESI):

Size Dependent Electronic Structure of $LiFePO_4$ probed by X-ray Absorption and Mössbauer Spectroscopy

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From the Rietveld refinement we have estimated the lattice parameters which were initially taken from the literature.[1] The fitting was done for the entire data set collected in the 2θ range. Further insightful structural details have been analysed by refining the site occupancies for lithium and iron as well as the atomic positions. During the first stage of the refinement, all the parameters including the atomic positions of respective atoms were kept as reported in the literature and all the occupancies to their nominal values. The Li and Fe occupancies were allowed to vary free of constraint and after each step the value obtained were used as starting parameters for the next step. Same procedure was opted for the refinement of the atomic positions and the profile fitting. To get a better refinement or in other words we can say, to achieve a better fit between the experimental and the calculated pattern, all the parameters were refined sequentially, and we were able to get the best fit as evident from the goodness of fit values (1 for an ideal case). Refined profile obtained from the Rietveld analysis for 50 nm CS LFP is shown in the Figure S2 with a χ^2 value of 2.494.

1 P. Gibot, M. Casas-cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J. M. Tarascon and C. Masquelier, Nat. Mater., **7**, (2008) 741–747.

Table TS1 Rietveld Refinement parameters for bulk (50 nm) and 25 nm crystallite sizes.

Crystallite Size			**50 nm**		
Wavelength (Å)			*0.78799*		
Space Group			*Pmna*		
					Errors (%)
a (Å)			10.33917		*1.6E-4*
b (Å)			6.02085		*1E-4*
c (Å)			4.69319		*1.8E-4*
V (Å^3)			*292.14415*		*0.02251*
Li$^+$ Vacancies (%)			*6.7*		*1.56*
R_p (%)			*4.61*		
R_{wp} (%)			*5.30*		
GOF (χ2)			*2.494*		
Site	**Wyck.**	**x/a**	**y/b**	**z/c**	**Occupancy**
Li	4a	0.0000	0.0000	0.0000	0.9330
Fe	4c	0.2823	0.2500	0.9737	0.9977
P	4c	0.0959	0.2500	0.4192	1.0000
O	4c	0.0949	0.2500	0.7414	1.0000
O	4c	0.4590	0.2500	0.2065	1.0000
O	8d	0.1653	0.0481	0.2849	1.0000
Fe	4a	0.0000	0.0000	0.0000	0.0023

Crystallite Size			**25 nm**		
Wavelength (Å)			*0.78799*		
Space Group			*Pmna*		
					Errors (%)
a (Å)			*10.31511*		*2.22E-4*
b (Å)			*6.0010*		*1.48E-4*
c (Å)			*4.70095*		*1.11E-4*
V (Å^3)			*290.99339*		*0.02031*
Li$^+$ Vacancies (%)			*17.1*		*1.87*
R_p (%)			*3.42*		
R_{wp} (%)			*4.55*		
GOF (χ2)			*1.25*		
Site	**Wyck.**	**x/a**	**y/b**	**z/c**	**Occupancy**
Li	4a	0.0000	0.0000	0.0000	0.8291
Fe	4c	0.2820	0.25	0.9731	0.9964
P	4c	0.0953	0.25	0.4193	1.0000
O	4c	0.0962	0.25	0.7404	1.0000
O	4c	0.4579	0.25	0.2056	1.0000
O	8d	0.1653	0.0491	0.2828	1.0000
Fe	4a	0.0000	0.0000	0.0000	0.0050

Table TS2 Crystallite size dependent unit cell parameters and lithium vacancy concentration for LFP extracted through Rietveld refinement analysis.

Crystallite Size (nm)	Lattice parameters			Cell Volume (Å^3)	Lithium ion vacancy (%)
	a (Å)	b (Å)	c (Å)		
50 ± 1.9	10.3391	6.0208	4.6931	292.144	6.70
40 ± 1.7	10.3357	6.0162	4.6940	291.8786	8.23
35 ± 2.0	10.3328	6.0133	4.6968	291.8351	13.03
31 ± 1.6	10.3227	6.0070	4.6992	291.3867	14.76
25 ± 2.19	10.3151	6.001	4.7009	290.9933	17.1

Table TS3 Lattice parameters along with Lithium vacancy calculated from the Rietveld refinement for $LiFePO_4$ with different crystallite sizes.

Crystallite Size (nm)	Fe-O1 (Å)	Fe-O2 (Å)	Fe-O3 (Å)	Fe-O3' (Å)	Avg. (Å)
50	2.221	2.183	2.233	2.107	2.186
40	2.224	2.192	2.253	2.073	2.185
35	2.215	2.175	2.228	2.121	2.184
31	2.204	2.212	2.220	2.077	2.178
25	2.206	2.153	2.219	2.081	2.159

Table TS4 The isomer shift (δ), quadrupole splitting (ΔE_Q: doublet), 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	ΔE_Q (mms^{-1}) ±0.03	δ (mms^{-1}) ±0.01	Γ (mms^{-1}) ±0.03	R_A (%)	χ^2
25 nm	Doublet-A (Fe^{2+})	2.970	1.216	0.283	87.8	2.76
	Doublet-B (Fe^{3+})	0.808	0.481	0.513	12.2	
31 nm	Doublet-A (Fe^{2+})	2.995	1.225	0.330	94.2	2.59
	Doublet-B (Fe^{3+})	0.724	0.488	0.519	5.8	
35 nm	Doublet-A (Fe^{2+})	2.981	1.247	0.300	94.5	1.95
	Doublet-B (Fe^{3+})	0.850	0.474	0.359	5.5	
40 nm	Doublet-A (Fe^{2+})	2.991	1.225	0.318	95.6	1.38
	Doublet-B (Fe^{3+})	0.812	0.480	0.428	4.4	
50 nm	Doublet-A (Fe^{2+})	2.970	1.217	0.298	97.2	3.0
	Doublet-B (Fe^{3+})	0.608	0.582	0.435	2.8	

Table TS5 Simulation parameters for LFP different crystallite sizes related to the D_{4h} symmetry.

Crystallite Size (nm)	10Dq (eV) (obtained from Fe L edge)	10Dq (eV) (obtained from O K edge)	D_s (eV)	D_t (eV)	Δt_{2g} (eV)	Δe_g (eV)
50	**1.32**	**1.497**	**0.28**	**0.05**	**0.59**	**1.37**
40	**1.30**	**1.381**	**0.48**	**0.09**	**0.99**	**2.37**
35	**1.28**	**1.31**	**0.45**	**0.09**	**0.90**	**2.25**
31	**1.25**	**1.242**	**0.42**	**0.12**	**0.66**	**2.28**
25	**1.27**	**1.272**	**0.48**	**0.09**	**0.99**	**2.37**

Table TS6 Fe 3d orbital energies in LFP with D_{4h} symmetry calculated for different crystallite sizes.

Crystallite Size (nm)	B_{1g} (eV)	a_{1g} (eV)	B_{2g} (eV)	e_g (eV)
50	**1.302**	**-0.068**	**-0.018**	**-0.608**
40	**1.650**	**-0.720**	**0.320**	**-0.640**
35	**1.578**	**-0.672**	**0.298**	**-0.602**
31	**1.470**	**-0.810**	**0.220**	**-0.440**
25	**1.632**	**-0.738**	**0.362**	**-0.628**

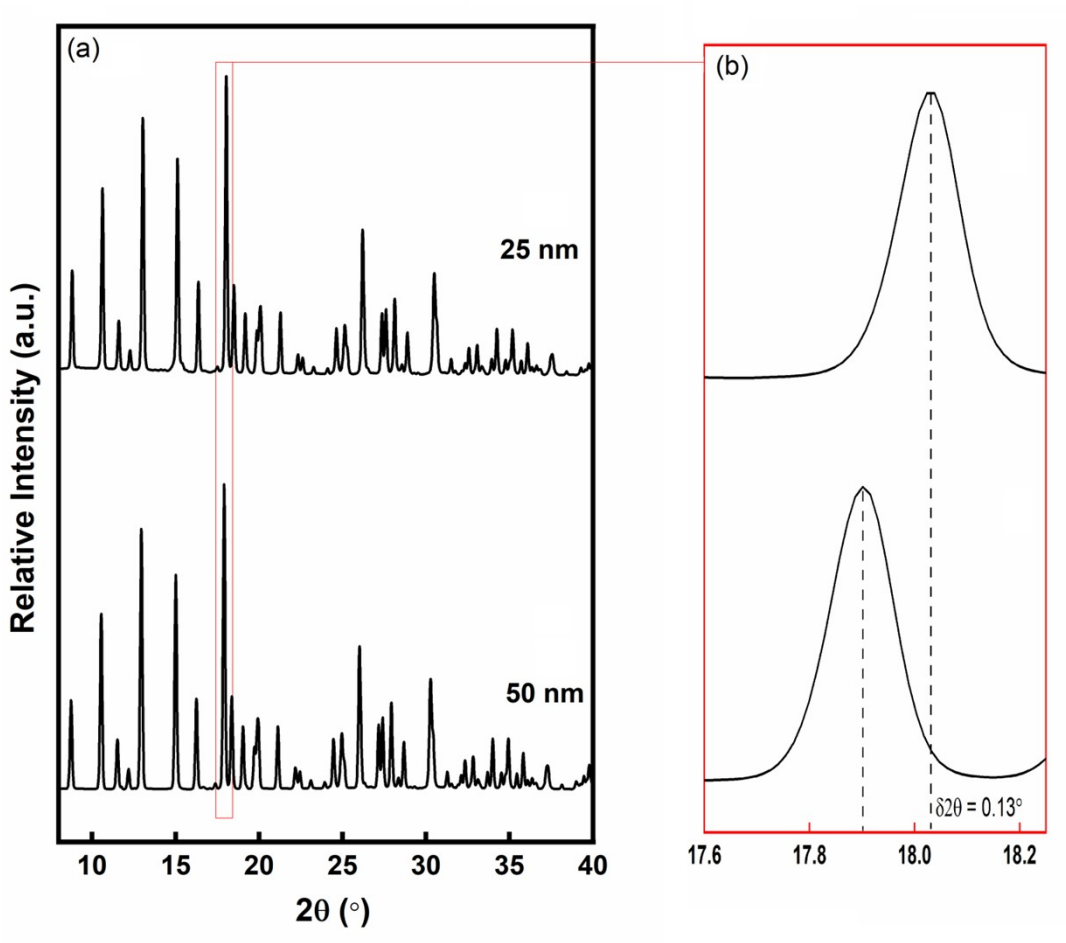

Fig. S1 (a) XRD pattern of olivine $LiFePO_4$ for 50 and 25 nm crystallite sizes measured at the room temperature with the synchrotron source (λ=0.78799 Å), (b) Magnification of (211/020) diffraction peak shows the broadening and shift towards higher angle with decrease in the crystallite size.

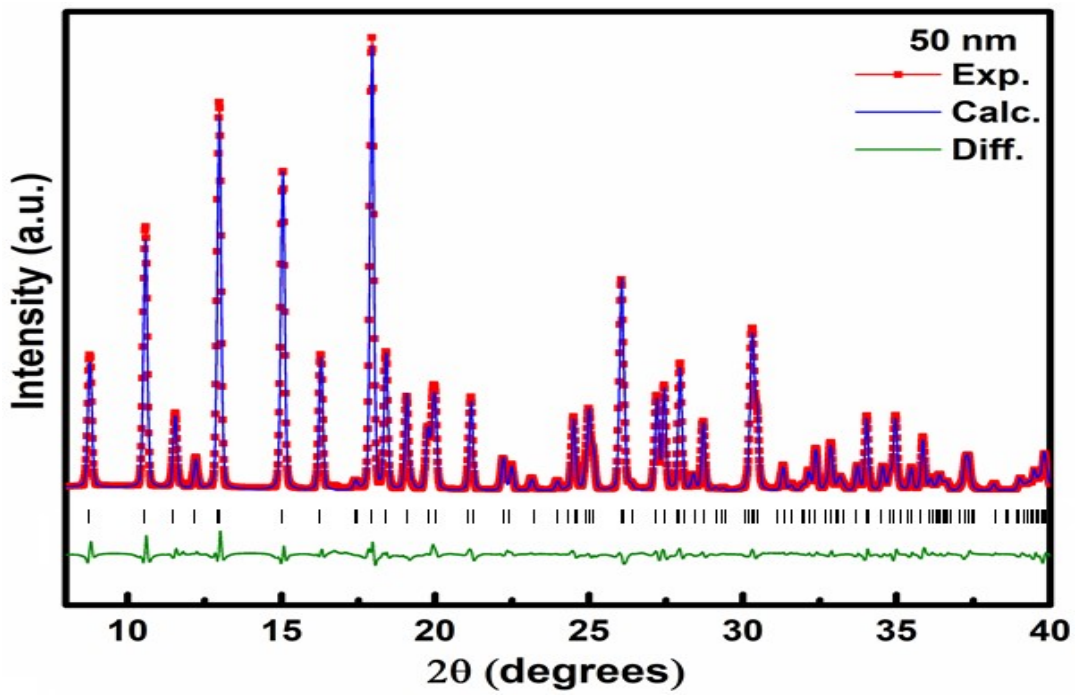

Fig. S2 Experimental X-ray powder diffraction pattern (filled square with red colour) of $LiFePO_4$ sample is compared to the Rietveld refined profile (continuous blue line) and the difference curve (bottom green curve) taken at room temperature. The vertical markers (black) below the diffraction pattern indicate positions of possible Bragg reflections for $LiFePO_4$.

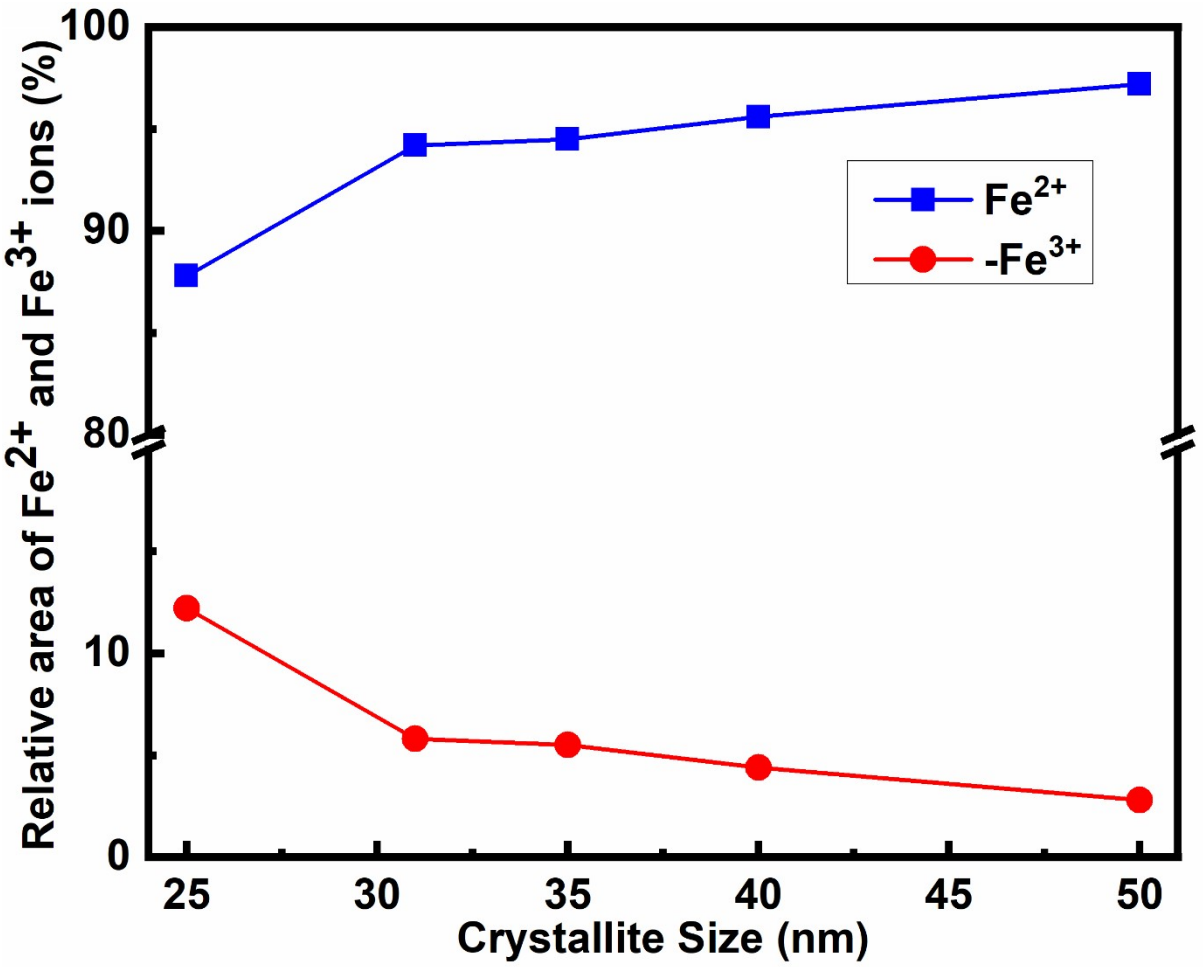

Fig. S3 Change in relative areas in percentage of different sites of Fe^{3+} and Fe^{2+} ions with respect Crystallite Size (nm) fitted from Mössbauer spectra in Fig. 3.