

## Supplementary information

### **LiVPO<sub>4</sub>F<sub>1-y</sub>O<sub>y</sub> Tavorite-type compositions: Influence of the vanadyl-type defects' concentration on the structure and electrochemical performance**

Edouard Boivin <sup>a,b,g</sup>, Rénaud David <sup>b,g</sup>, Jean-Noël Chotard <sup>b,g,h</sup>, Tahya Bamine <sup>a,g</sup>,  
Antonella Iadecola <sup>g</sup>, Lydie Bourgeois <sup>c,d</sup>, Emmanuelle Suard <sup>e</sup>, François Fauth <sup>f</sup>, Dany Carlier <sup>a,g</sup>,  
Christian Masquelier <sup>b,g,h</sup> and Laurence Croguennec <sup>a,g,h,1</sup>

<sup>a</sup> CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France.

<sup>b</sup> Laboratoire de Réactivité et de Chimie des Solides, CNRS UMR 7314,

Université de Picardie Jules Verne, F-80039 Amiens Cedex 1, France.

<sup>c</sup> Université de Bordeaux, ISM, Groupe de Spectroscopie Moléculaire, F-33405 Talence, France.

<sup>d</sup> Bordeaux INP, ISM, CNRS UMR 5255, F-33405, Talence, France.

<sup>e</sup> Institut Laue-Langevin, 71 Avenue des Martyrs, F-38000 Grenoble, France.

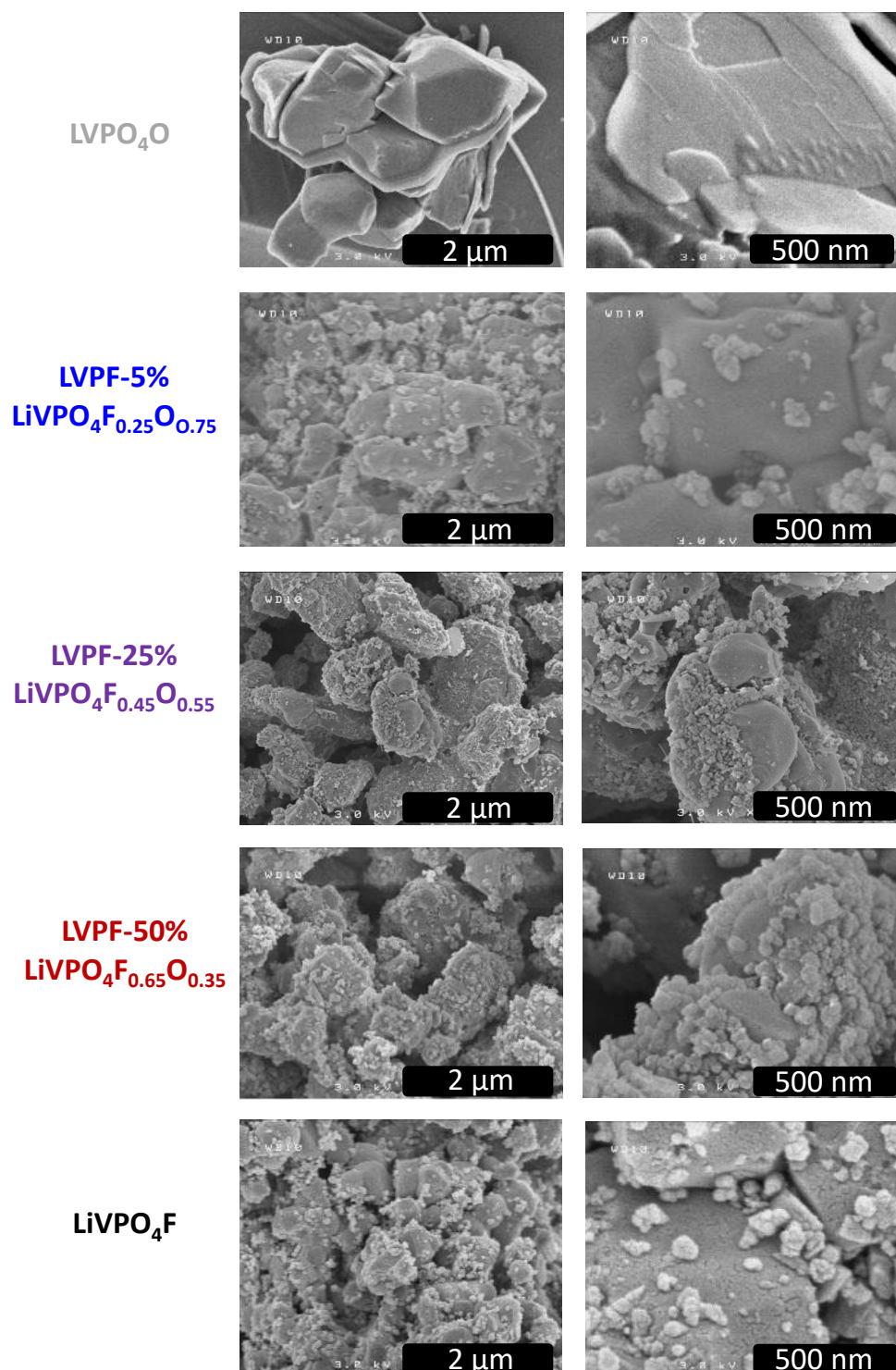
<sup>f</sup> CELLS - ALBA synchrotron, E-08290 Cerdanyola del Vallès, Barcelona, Spain.

<sup>g</sup> RS2E, Réseau Français sur le Stockage Electrochimique de l'Énergie, FR CNRS 3459,  
F-80039 Amiens Cedex 1, France.

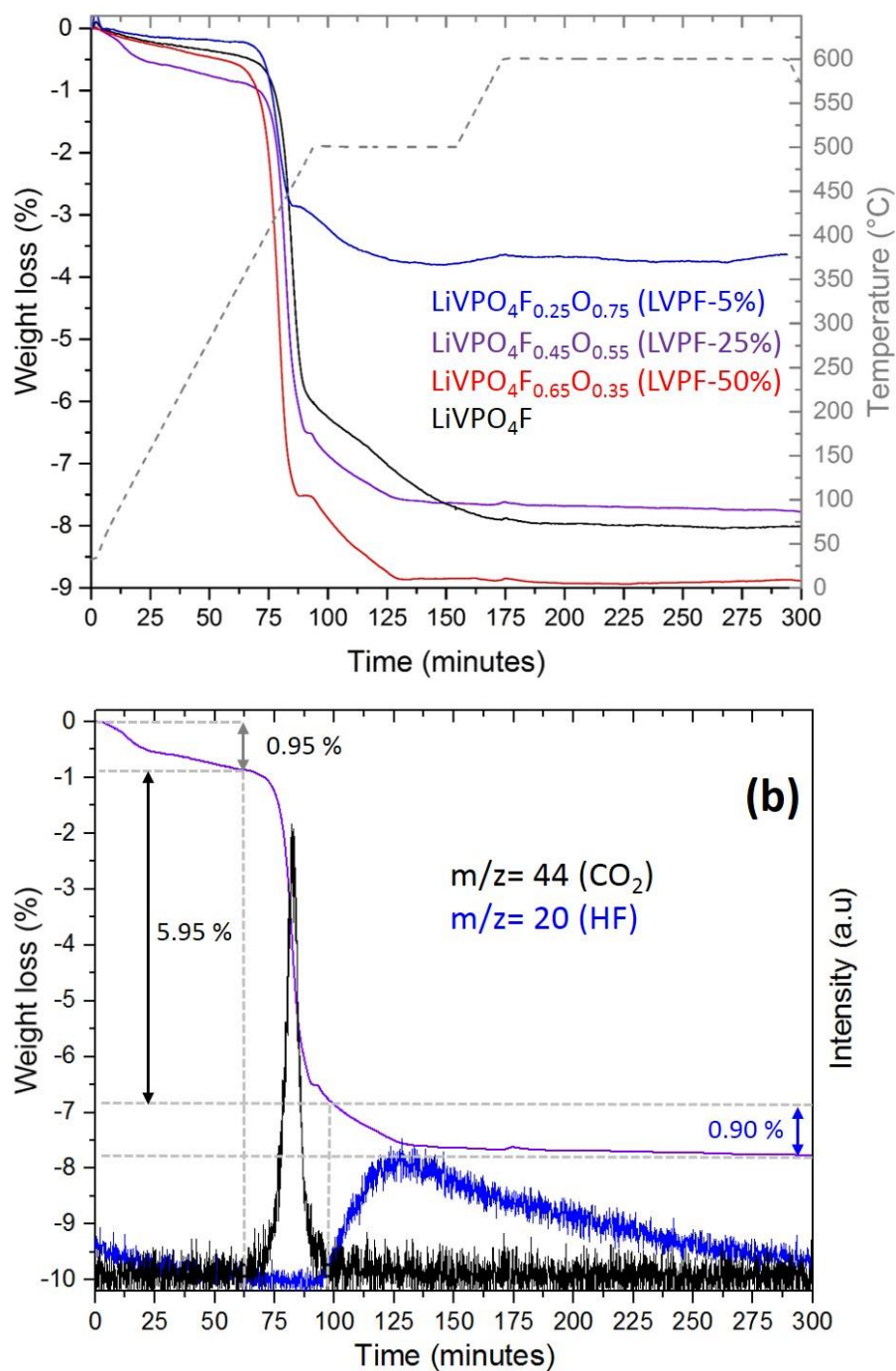
<sup>h</sup>ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France.

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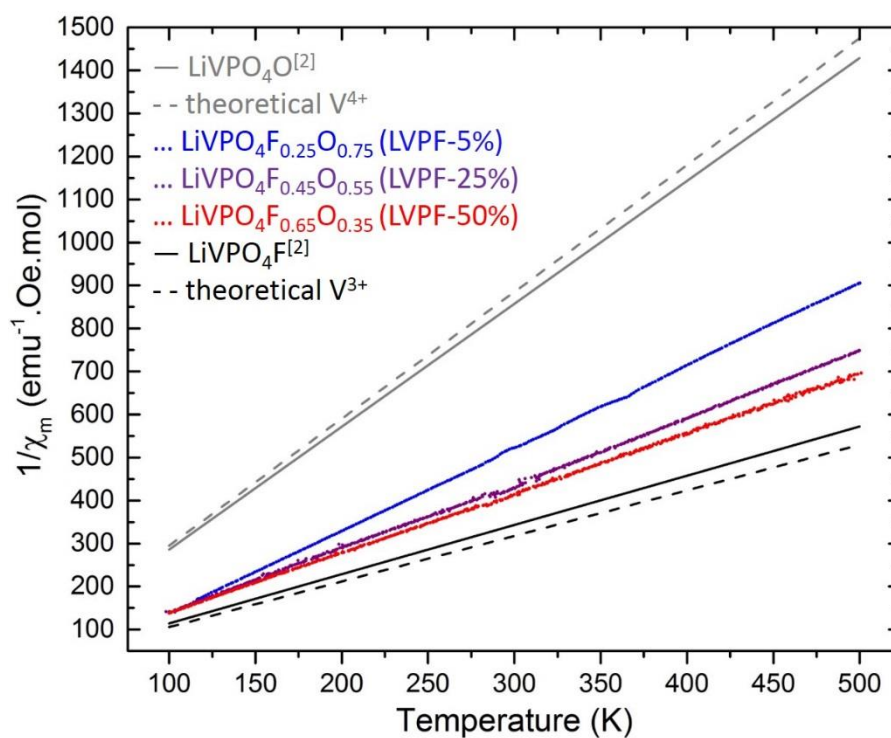
<sup>1</sup> Corresponding author : L. Croguennec (Laurence.Croguennec@icmcb.cnrs.fr)



**Figure S1:** SEM images of the LiVPO<sub>4</sub>F<sub>1-y</sub>O<sub>y</sub> series of materials.



**Figure S2:** (a) TGA data obtained under air for all the  $\text{LiVPO}_4\text{F}_{1-y}\text{O}_y$  samples, (b) The corresponding TGA-MS data for  $\text{LiVPO}_4\text{F}_{0.45}\text{O}_{0.55}$  (LVPF-25%) as function of time (purple line) and the corresponding MS intensities (blue line for HF and black line for  $\text{CO}_2$ ).



**Figure S3:** Temperature dependence of the inverse of the magnetic susceptibilities for the  $\text{LiVPO}_4\text{F}_{1-y}\text{O}_y$  materials.

**Table S1:** Structural parameters obtained by combined Rietveld refinement of the structure of  $\text{LiVPO}_4\text{F}_{0.45}\text{O}_{0.55}$  (LVPF-25%) based on synchrotron XRD and Neutron Diffraction Data.

LiVPO <sub>4</sub> F <sub>0.45</sub> O <sub>0.55</sub>							
SG : <i>P</i> -1		$a = 5.1629 (1) \text{ \AA}$		$\alpha = 107.227 (1)^\circ$		synchrotron: $\chi^2 = 26.5 \%$	
$Z = 2$		$b = 5.2949 (1) \text{ \AA}$		$\beta = 107.612 (1)^\circ$		$R_{\text{Bragg}} = 5.35 \%$	
		$c = 7.1907 (1) \text{ \AA}$		$\gamma = 98.658 (1)^\circ$		neutrons: $\chi^2 = 2.68 \%$	
		$V = 172.612 (6) \text{ \AA}^3$		$V/Z = 86.306 (6) \text{ \AA}^3$		$R_{\text{Bragg}} = 4.56 \%$	
Atoms	Wickoff position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	Biso	BVS
V(1)	1 <i>a</i>	0	0	0	0.99(1)	0.97(1)	3.15(1)
V(2)	1 <i>b</i>	0	0	1/2	1.00(1)	1.29(1)	3.35(1)
P(1)	2 <i>i</i>	0.323(1)	0.647(1)	0.253(1)	1.00(1)	0.75(1)	4.97(1)
O(1)	2 <i>i</i>	0.374(2)	0.239(1)	0.588(1)	1.00(1)	1.12(2)	1.95(1)
O(2)	2 <i>i</i>	0.108(2)	0.671(1)	0.358(1)	1.00(1)	0.92(2)	1.94(1)
O(3)	2 <i>i</i>	0.687(2)	0.655(2)	0.860(1)	1.00(1)	1.05(2)	1.96(1)
O(4)	2 <i>i</i>	0.273(1)	0.797(1)	0.094(1)	1.00(1)	0.53(2)	1.93(1)
O(5)	2 <i>i</i>	0.897(2)	0.081(1)	0.245(1)	0.55	0.38(2)	1.42(1)
F(1)	2 <i>i</i>	0.897(2)	0.081(1)	0.245(1)	0.45	0.38(2)	1.23(1)
Li(1)	2 <i>i</i>	0.732(6)	0.390(6)	0.209(6)	0.97(4)	3.7(3)	0.89(3)

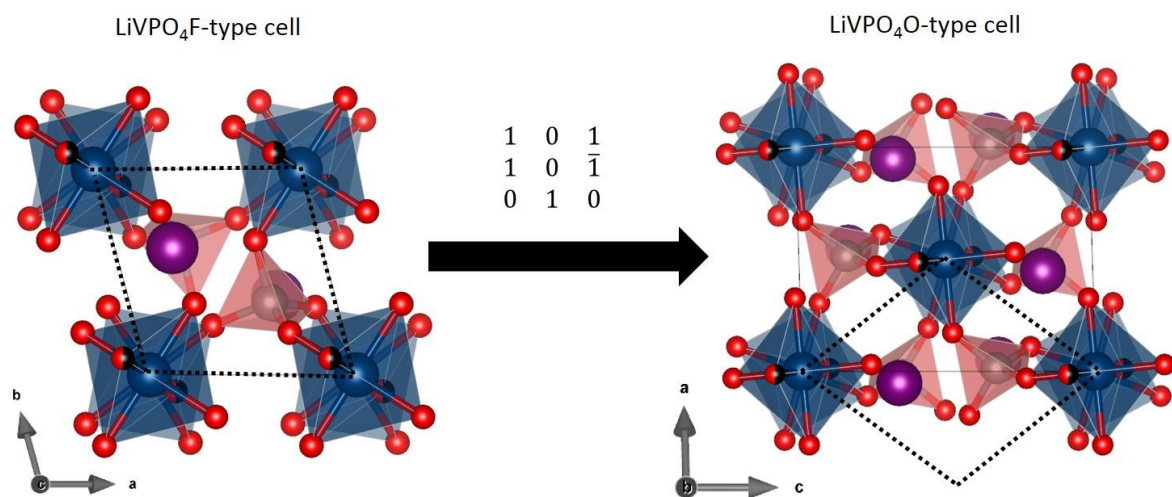
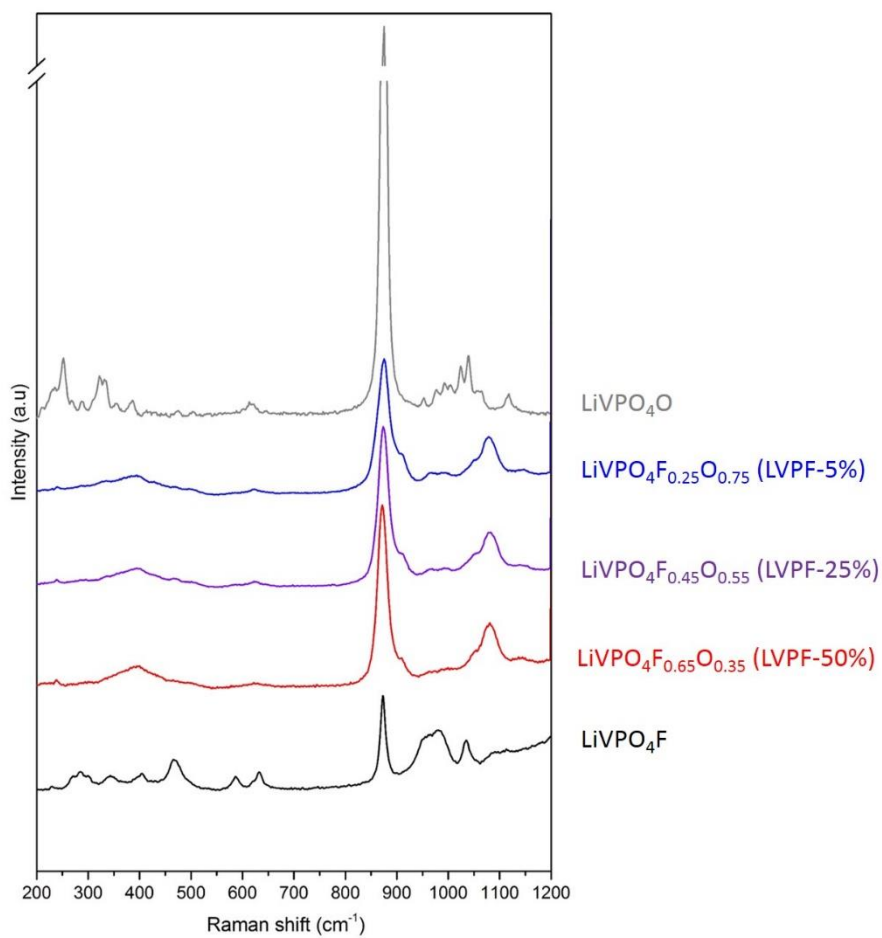
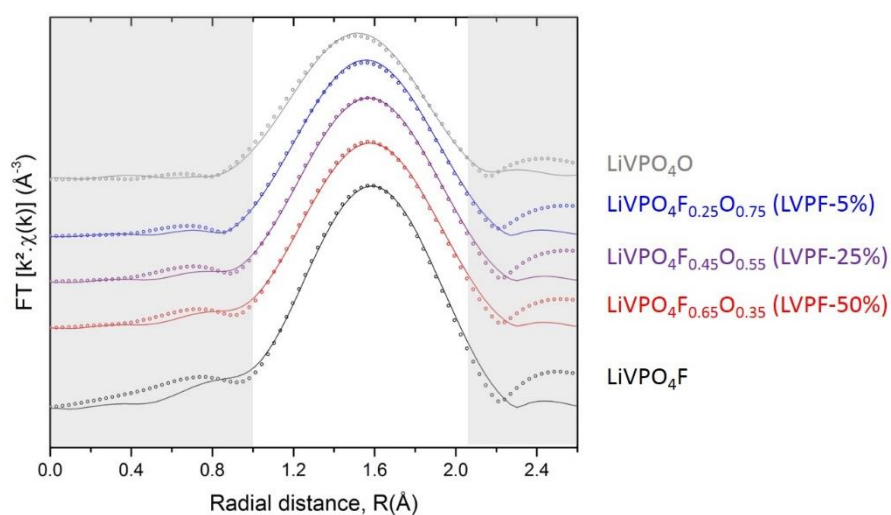


Figure S4: structural relationship between the LiVPO<sub>4</sub>F-type cell (left, Z=2) and LiVPO<sub>4</sub>O-type cell (right, Z=4)



**Figure S5:** Raman spectra of LiVPO<sub>4</sub>O (grey line), LiVPO<sub>4</sub>F<sub>0.25</sub>O<sub>0.75</sub> (blue line), LiVPO<sub>4</sub>F<sub>0.45</sub>O<sub>0.55</sub> (purple line), LiVPO<sub>4</sub>F<sub>0.65</sub>O<sub>0.35</sub> (red line) and LiVPO<sub>4</sub>F (black line).



**Figure S6:** The Fourier transforms of the  $k^2$ -weighted V K-edge EXAFS oscillations ( $k$ -range:  $3.7\text{--}11.0 \text{ \AA}^{-1}$ , sine window) were fitted in the R space (R range:  $1.0\text{--}2.05 \text{ \AA}$ ,  $dR = 0.1 \text{ \AA}$ , Hanning window) for the whole series of  $\text{LiVPO}_4\text{F}_{1-y}\text{O}_y$ . The circles represent the experimental data and the solid lines represent the fits. The parameters thus extracted are provided in **Table S2**.



**Table S2:** Structural parameters obtained by the EXAFS analysis. The parameters marked by \* or # in the same sample have been refined together. The average XRD distance is compared with the average one found by EXAFS. The associated BVS are also compared.

Sample	V <sup>n+</sup> -X	Coordination number, N	R (Å)	σ <sup>2</sup> (10 <sup>-3</sup> Å <sup>2</sup> )	BVS
LiVPO <sub>4</sub> F R <sub>f</sub> = 3.9.10 <sup>-4</sup>	V <sup>4+</sup> =O	/	/	/	
	V <sup>4+</sup> --O	/	/	/	2.92(8)
	V <sup>4+</sup> -F	/	/	/	vs 3.00
	V <sup>3+</sup> -F	2	2.00(2)*	4.3(3)#	theoretically
	V <sup>3+</sup> -O	4	2.00(2)*	4.3(3)#	
Average EXAFS		6	2.00(2)	4.3(3)	/
Average XRD		6	1.972(7)	/	3.06(2)
LiVPO <sub>4</sub> F <sub>0.65</sub> O <sub>0.35</sub> LVPF-50% R <sub>f</sub> = 2.1.10 <sup>-3</sup>	V <sup>4+</sup> =O	0.35	1.648(9)	5.4(4)#	
	V <sup>4+</sup> --O	0.1	2.19(8)	5.4(4)#	3.31(8)
	V <sup>4+</sup> -F	0.25	2.01(3)*	5.4(4)#	vs 3.35
	V <sup>3+</sup> -X	1.3	2.01(3)*	5.4(4)#	theoretically
	V <sup>3/4+</sup> -O	4	2.01(3)*	5.4(4)#	
Average EXAFS		6	1.99(3)	5.4(4)	/
Average XRD		6	1.965(9)	/	3.23
LiVPO <sub>4</sub> F <sub>0.45</sub> O <sub>0.55</sub> LVPF-25% R <sub>f</sub> = 4.3.10 <sup>-4</sup>	V <sup>4+</sup> =O	0.55	1.642(6)	4.9(2)#	
	V <sup>4+</sup> --O	0.2	2.20(6)	4.9(2)#	3.51(8)
	V <sup>4+</sup> -F	0.35	2.03(3)*	4.9(2)#	vs 3.55
	V <sup>3+</sup> -X	0.9	2.03(3)*	4.9(2)#	theoretically
	V <sup>3/4+</sup> -O	4	2.03(3)*	4.9(2)#	
Average EXAFS		6	2.00(2)	4.9(2)	/
Average XRD		6	1.965(8)	/	3.25(2)
LiVPO <sub>4</sub> F <sub>0.25</sub> O <sub>0.75</sub> LVPF-5% R <sub>f</sub> = 4.4.10 <sup>-4</sup>	V <sup>4+</sup> =O	0.75	1.642(3)	4.3(3)#	
	V <sup>4+</sup> --O	0.45	2.20(3)	4.3(3)#	3.68(8)
	V <sup>4+</sup> -F	0.30	2.01(1)*	4.3(3)#	vs 3.75
	V <sup>3+</sup> -X	0.5	2.01(1)*	4.3(3)#	theoretically
	V <sup>3/4+</sup> -O	4	2.01(1)*	4.3(3)#	
Average EXAFS		6	1.98(1)	4.3(3)	/
Average XRD		6	1.962(9)	/	3.31(2)
LiVPO <sub>4</sub> O R <sub>f</sub> = 3.3.10 <sup>-3</sup>	V <sup>4+</sup> =O	1	1.642(8)	4.9(2)#	
	V <sup>4+</sup> --O	1	2.25(3)	4.9(2)#	3.77(8)
	V <sup>4+</sup> -F	/	/	/	vs 4.00
	V <sup>3+</sup> -F	/	/	/	theoretically
	V <sup>4+</sup> -O	4	2.00(3)*	4.9(2)#	
Average EXAFS		6	1.98(3)	4.9(2)	/
Average XRD		6	1.968(9)	/	3.82(3)