



Journal Name

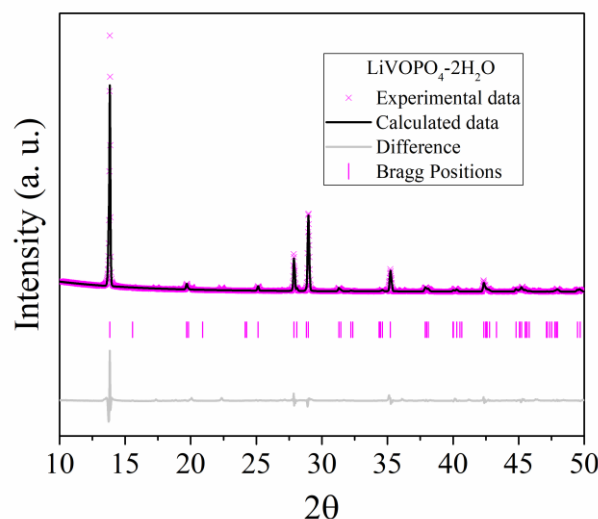
ARTICLE

Supplementary Information

β -LiVOPO ₄		ϵ -LiVOPO ₄	
Facet	Surface energy (J/m ²)	Facet	Surface energy (J/m ²)
(0, 0, 1)	0.656	(0, 0, 1)	1.279
(0, 1, 0)	0.870	(0, 1, 0)	1.299
(0, 1, 1)	0.862	(0, 1, 1)	1.265
(0, 1, 2)	1.111	(0, 1, 2)	1.003
(0, 2, 1)	1.004	(0, 2, 1)	1.097
(1, 0, 0)	1.007	(1, $\bar{1}$, 0)	0.996
(1, 0, 1)	0.976	(1, $\bar{1}$, 1)	1.102
(1, 0, 2)	0.864	(1, $\bar{1}$, 2)	1.024
(1, 1, 0)	1.276	(1, $\bar{2}$, 0)	0.939
(1, 1, 1)	1.132	(1, $\bar{2}$, 1)	1.065
(1, 1, 2)	0.922	(1, $\bar{2}$, 2)	0.957
(1, 2, 0)	1.206	(1, 0, 0)	0.713
(1, 2, 1)	0.957	(1, 0, 1)	0.879
(1, 2, 2)	1.128	(1, 0, 2)	1.032
(2, 0, 1)	1.103	(1, 1, 0)	0.921
(2, 1, 0)	1.205	(1, 1, 1)	0.951
(2, 1, 1)	1.009	(1, 1, 2)	1.078
(2, 1, 2)	0.908	(1, 2, 0)	0.787
(2, 2, 1)	0.976	(1, 2, 1)	1.192
		(1, 2, 2)	1.059
		(2, $\bar{1}$, 0)	1.017
		(2, $\bar{1}$, 1)	1.033
		(2, $\bar{1}$, 2)	0.878
		(2, $\bar{2}$, 1)	1.078
		(2, 0, 1)	0.899
		(2, 1, 0)	0.841
		(2, 1, 1)	0.845
		(2, 1, 2)	1.061
		(2, 2, 1)	0.934

Table S1. Surface energies of symmetrically distinct facets of β - and ϵ -LiVOPO₄ with a maximum Miller index of 2.

(eV)	f_3	f_4	f_5	l_2	l_3	l_4	l_5
β -LiVOPO ₄	2.600	1.426	0.751	1.662	1.292	-0.134	0.556
ϵ -LiVOPO ₄	1.788	0.856	-0.008	-10.000	0.718	1.360	0.682

Table S2. Contributions of various coordinated V (f_i) and Li (l_j) to the surface energy.Figure S2. Rietveld refinement of as-synthesized LiVOPO₄·2H₂O.

Surface energy calculations

For a stoichiometric slab, $\sum_i N_i \mu_i$ is the total energy of a bulk system. However, for a nonstoichiometric slab, the chemical potential accounts for the exchange of atomic species at the surface with an external reservoir. Assuming the surface is in thermodynamic equilibrium with the bulk, μ of all species i will be dependent on each other as such:

$$g^{bulk} = \sum_i n_i \mu_i$$

where g^{bulk} is the bulk energy per formula unit and n_i is the number of species i per formula unit. Using the above expression, μ_O can be used to define μ_P , μ_{Li} , and μ_V in the surface grand potential. As such, we assumed that the surface exchanges O atoms with an external reservoir under an oxidation and reduction process.

Coordination loss model for surface energy

We were able to determine the contributions of each type of i -fold V and j -fold Li (per unit area) on surface energy by adopting the coordination loss model developed by Wang et al.^{53, 54} given by the following:

$$\Delta E = \sum_{i=2}^5 m_i f_i + \sum_{j=3}^5 n_j l_j = AX$$

where i (j) is the O coordination of V (Li) at the surface. i and j starting from 2 and 3 respectively as those are the lowest coordination numbers for V and Li at the surface. A is the summation of m_i and n_j in matrix form and X is the energetic contributions, f_i and l_j in array form. We determined X using a least-squares approximation and its individual components are summarized in Table S2. Contributions of various coordinated V (f_i) and Li (l_j) to the surface energy.

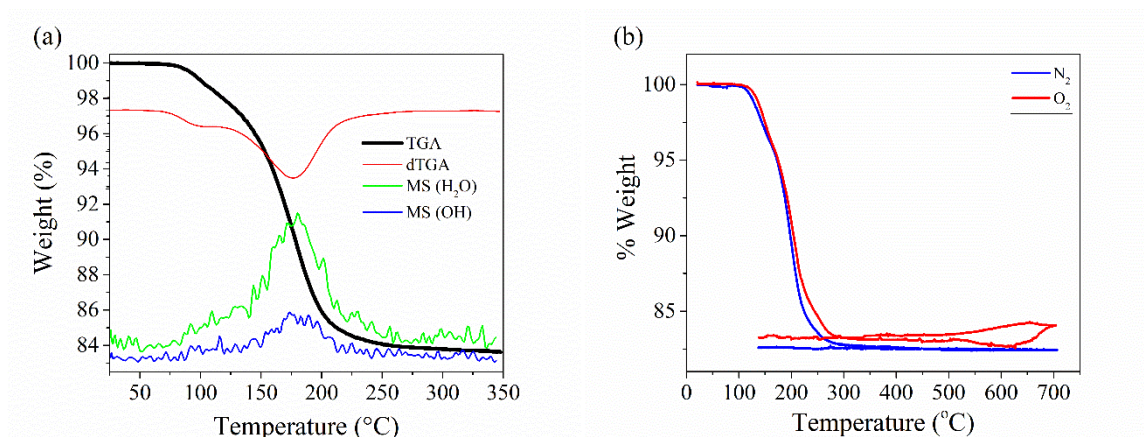


Figure S3. Thermal studies of $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$ via (a) TG-MS in Ar, showing loss of water, and (b) TGA in different atmospheres.

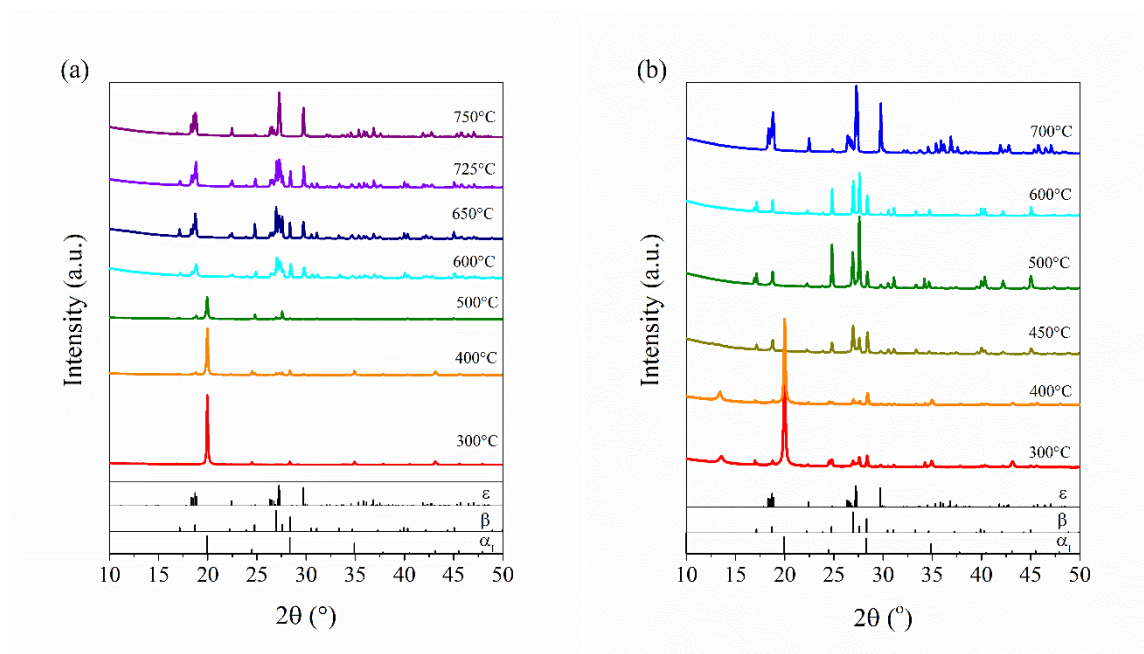


Figure S4. Ex-situ XRD of heated $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$ in (a) Ar and (b) air.

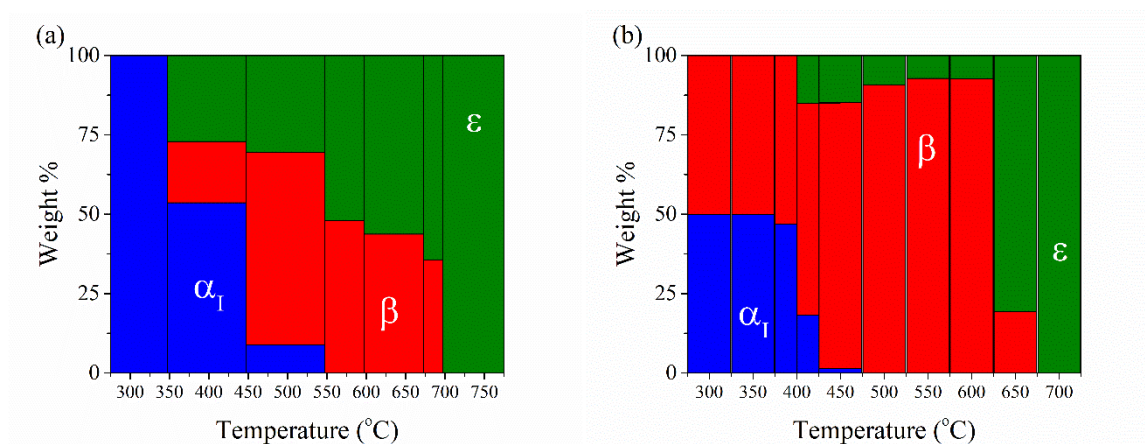


Figure S5. Phase quantification of ex-situ XRD of $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$ heated in (a) Ar and (b) air.

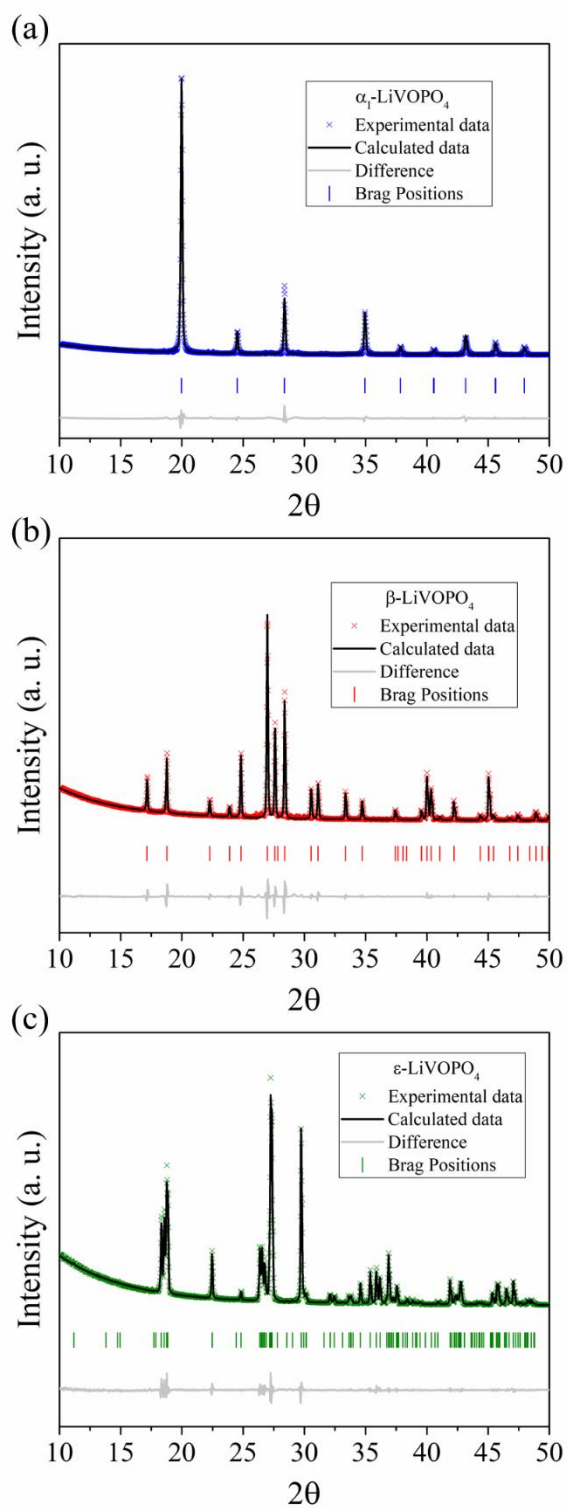


Figure S6. Rietveld refinement of purest phase (a) α -, (b) β -, and (c) ϵ - LiVOPO_4 .

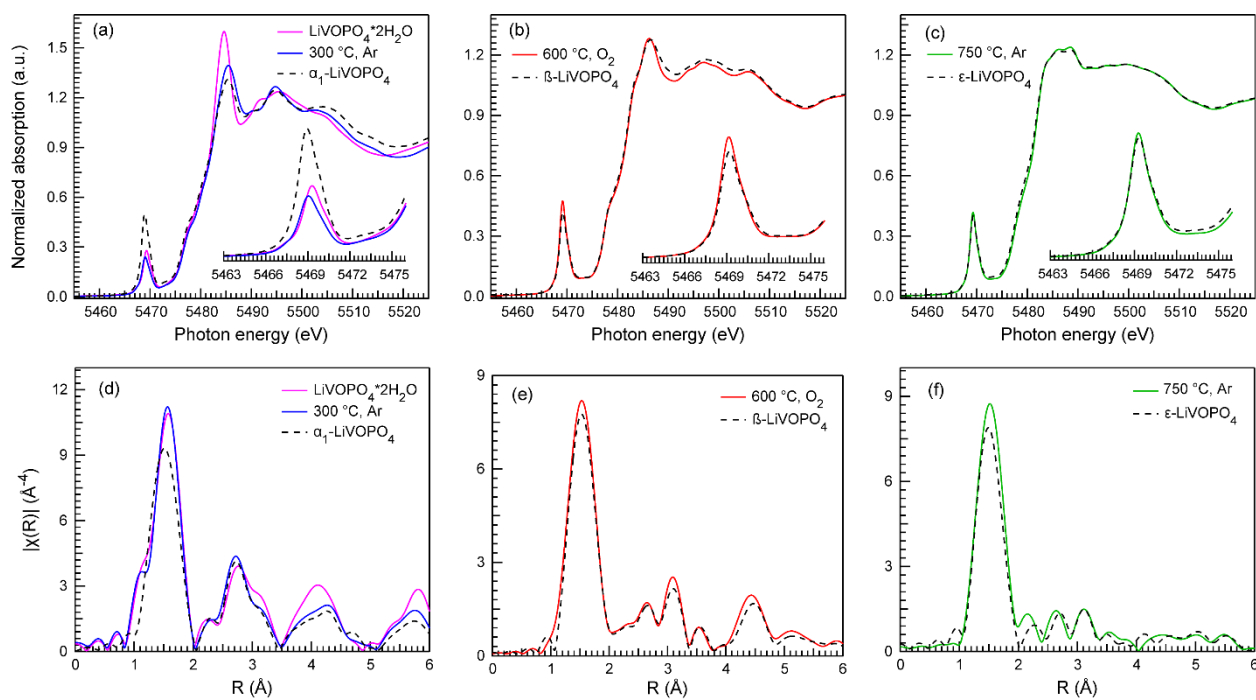


Figure S7. Normalized XANES data (top) and the Fourier-transformed EXAFS data of LiVOPO_4 samples obtained by heating at 300 °C (a,d), 600 °C (b, e), and 750 °C (c, f). For comparison, the data of phase-pure α_1 -, β -, and ϵ - LiVOPO_4 polymorphs are also shown.

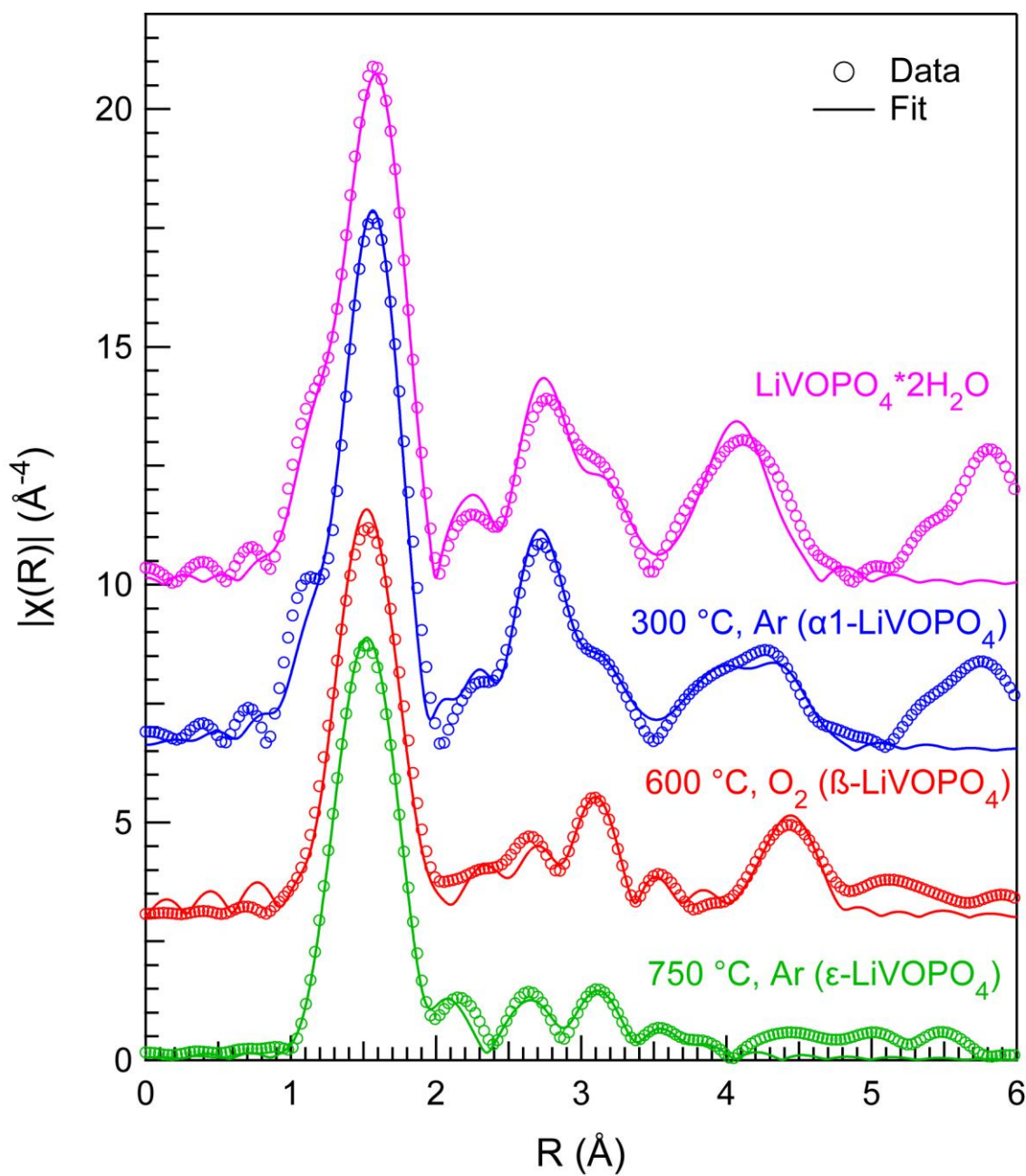


Figure S8. EXAFS fits to the data of the hydrated precursor, $\text{LiVOPO}_4 \cdot 2\text{H}_2\text{O}$, and of the samples synthesized at 300 °C (Ar), 600 °C (O_2), and 750 °C (Ar).

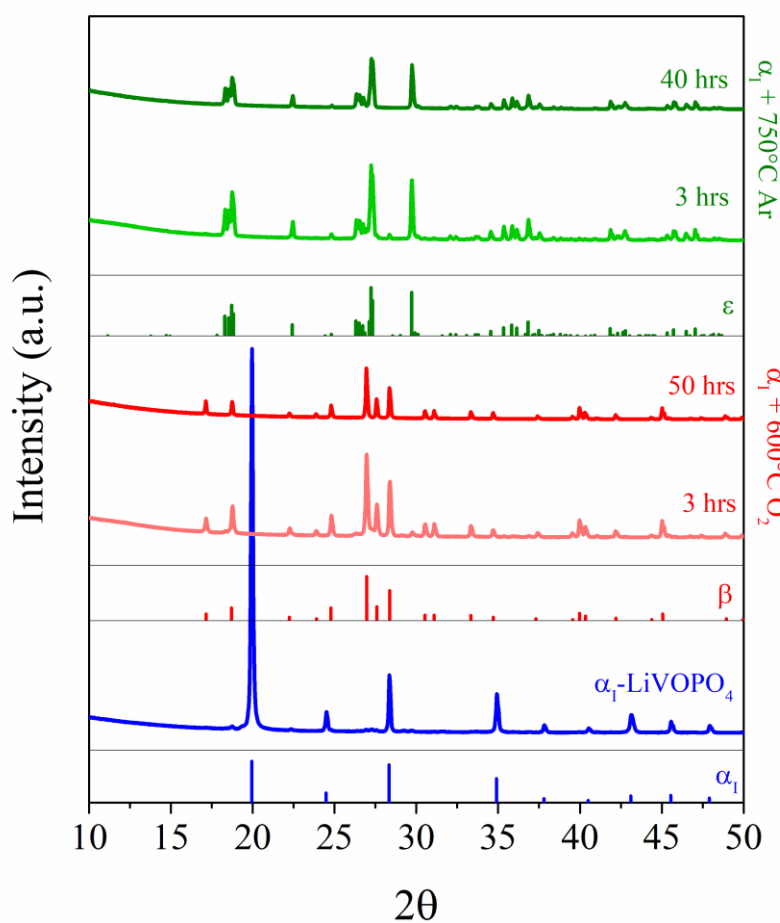


Figure S9. XRD patterns of α_I -LiVOPO₄ heated in conditions to form β - and ϵ -LiVOPO₄.

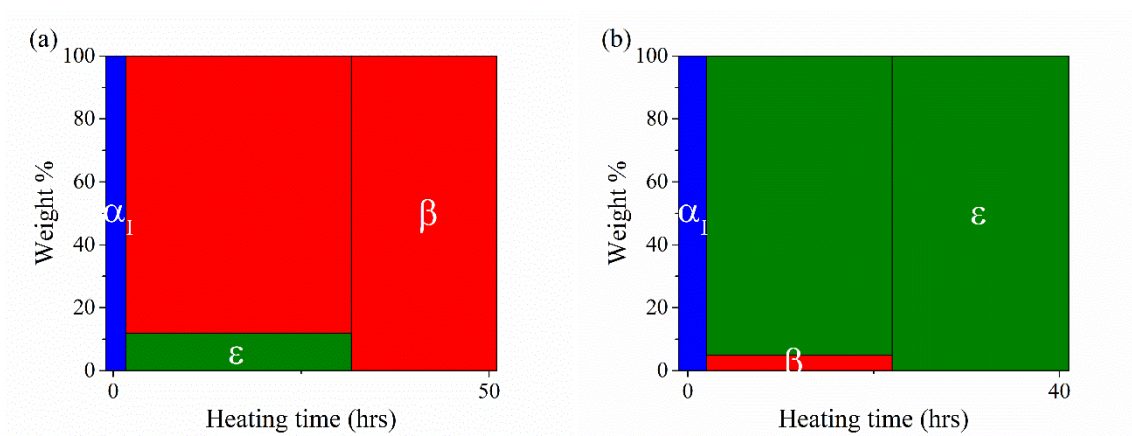


Figure S10. Phase quantification showing α_I -LiVOPO₄ heated in conditions for the formation of (a) β -LiVOPO₄ (600 °C in O₂) and (b) ϵ -LiVOPO₄ (750 °C in Ar).

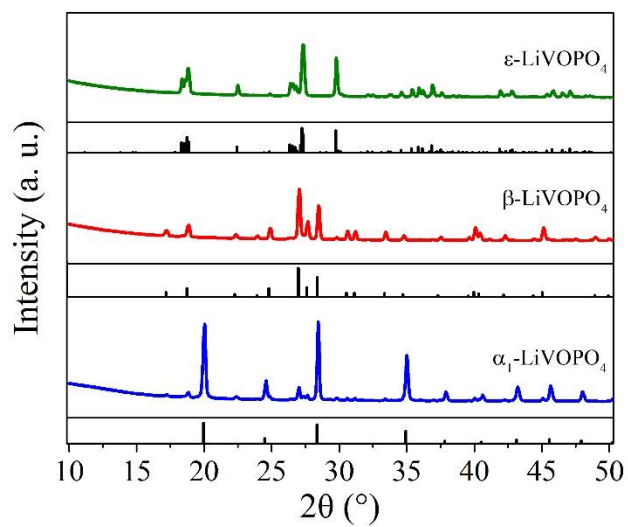


Figure S11. XRD of α_1 -, β -, and ϵ -LiVOPO₄ heated at conditions for the formation of α_1 -LiVOPO₄ (300 $^{\circ}$ C in Ar) for 50 hours.

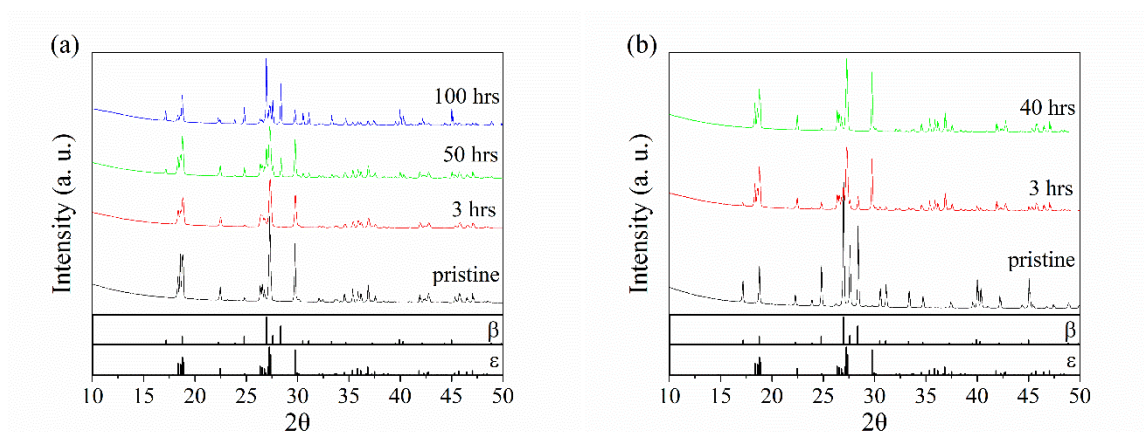


Figure S12. XRD patterns of (a) ϵ -LiVOPO₄ heated at 600 $^{\circ}$ C in O₂ and (b) β -LiVOPO₄ heated at 750 $^{\circ}$ C in Ar.

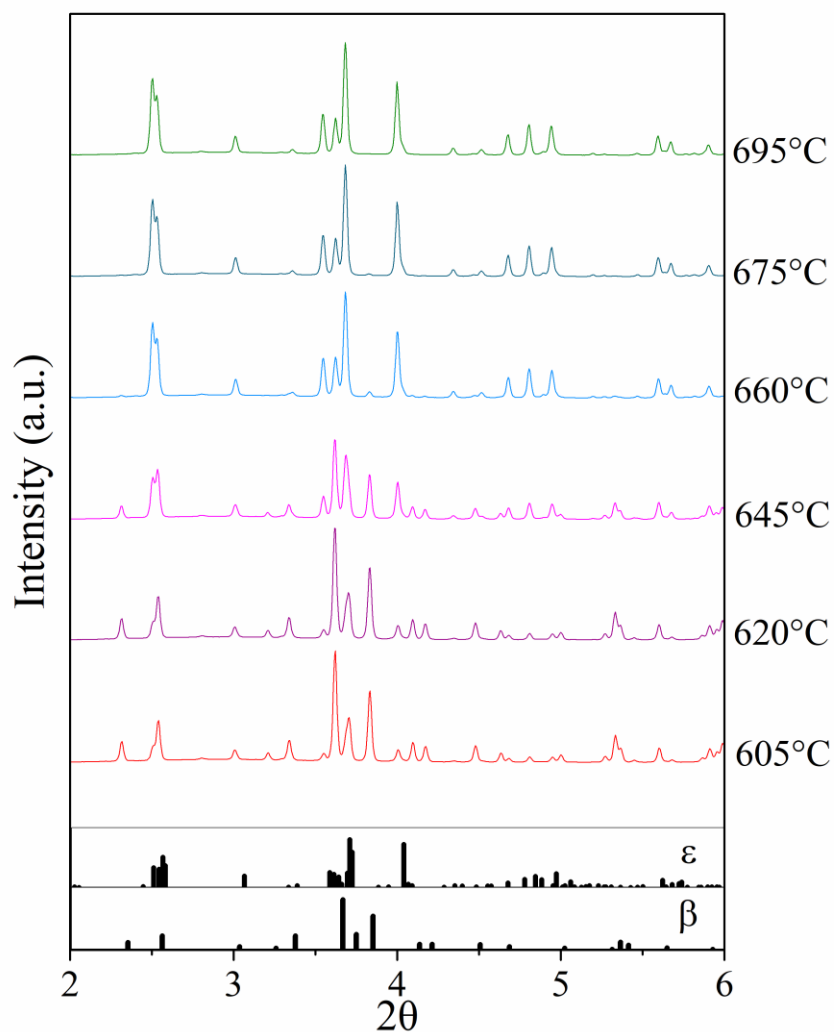


Figure S13. In-situ XRD of β -LiVOPO₄ heated in He.

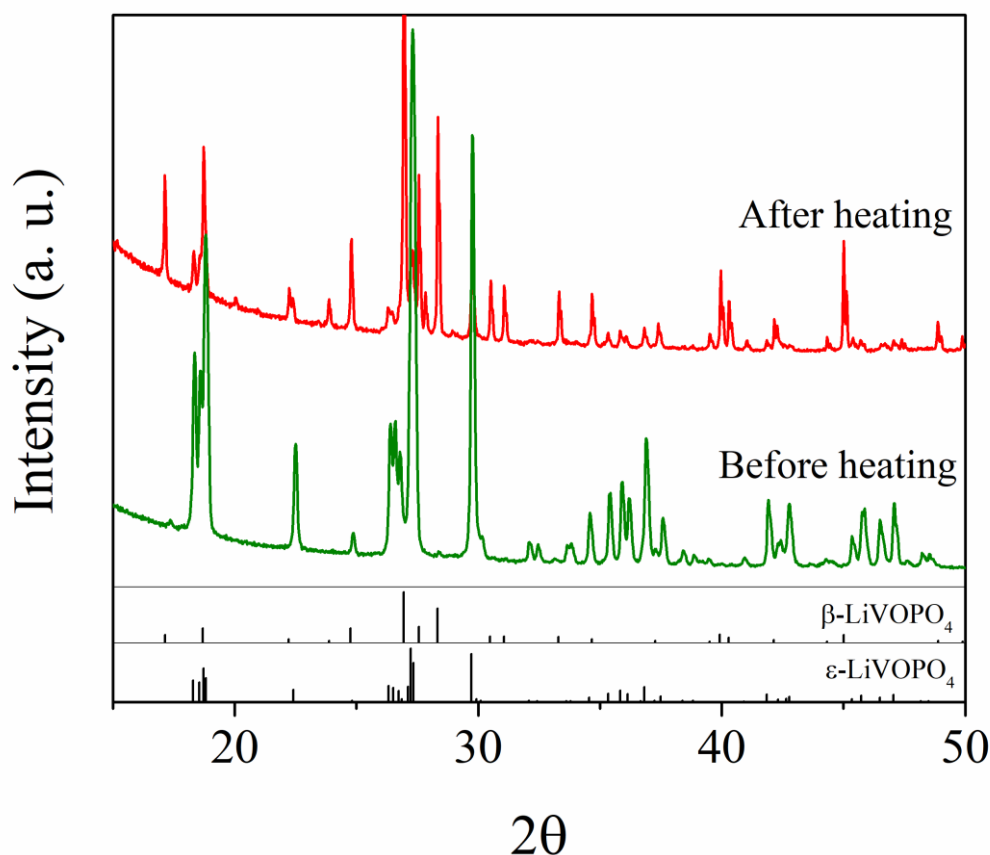


Figure S14. XRD of ϵ -LiVOPO₄ after heating in a TGA for 50 hours in O₂.

Figure S15 plots the surface energy as a function of the relative O chemical potential ($\Delta\mu_O$) for different facets on the Wulff shapes of β - and ϵ -LiVOPO₄. Stoichiometric or clean surfaces maintain a constant surface energy while the surface energy of oxidized surfaces vary with the chemical potential of O. We limit the range of $\Delta\mu_O$ such that the upper bounds ensures that the surface energy is always positive while the lower bounds are set to show the transition from oxidized to stoichiometric surfaces for all facets. Bulk LiVOPO₄ is stable when the value of $\Delta\mu_O$ is between -2.1 and -0.7 eV. Therefore, the $\Delta\mu_O$ range of stability for slabs with stable β - and ϵ -LiVOPO₄ are -2.1 eV < $\Delta\mu_O$ < -1.5 eV and -2.1 eV < $\Delta\mu_O$ < -1.3 eV, respectively.

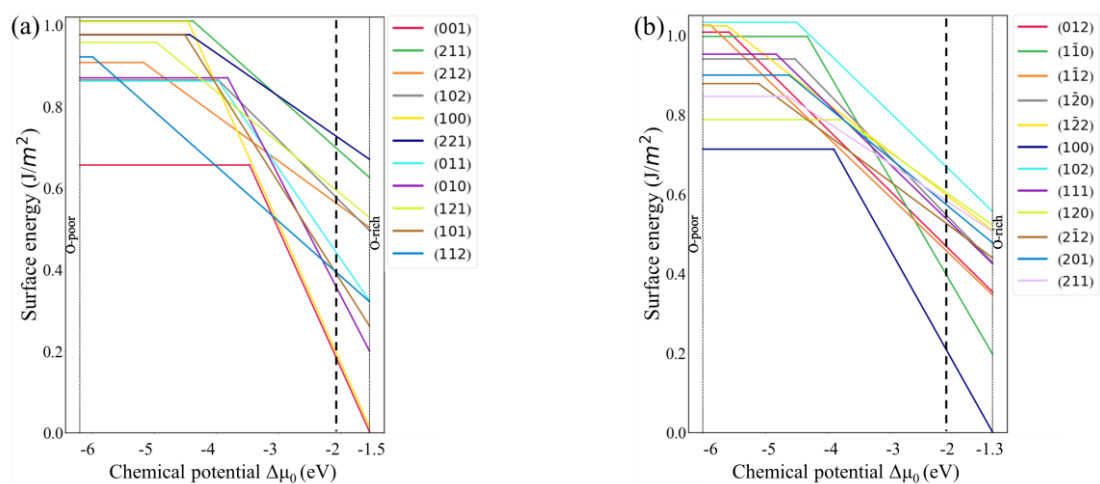


Figure S15. The evolution of surface energy of different facets with $\Delta\mu_0$ for (a) β - and (b) ϵ -LiVOPO₄.