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† SUPPORTING INFORMATION

Structure and electrochemical properties of novel mixed $Li(Fe_{1-x}M_x)SO_4F$ (M = Co, Ni, Mn) phases fabricated by low temperature ionothermal synthesis†

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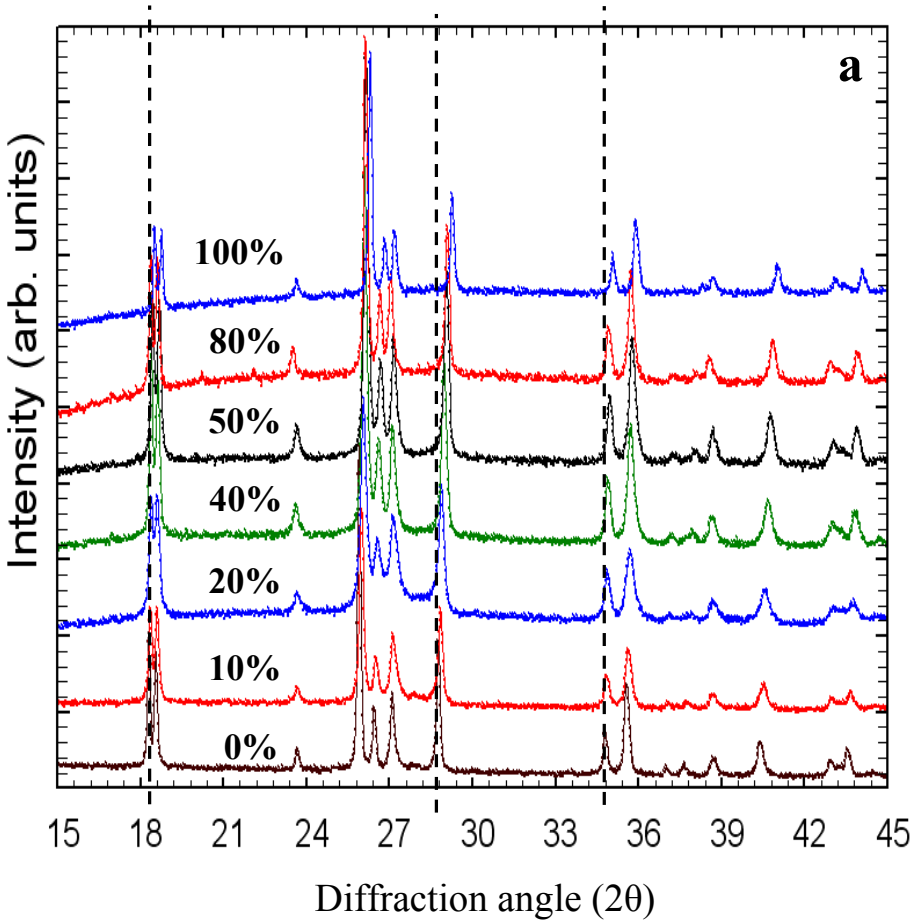
List of Supporting Information



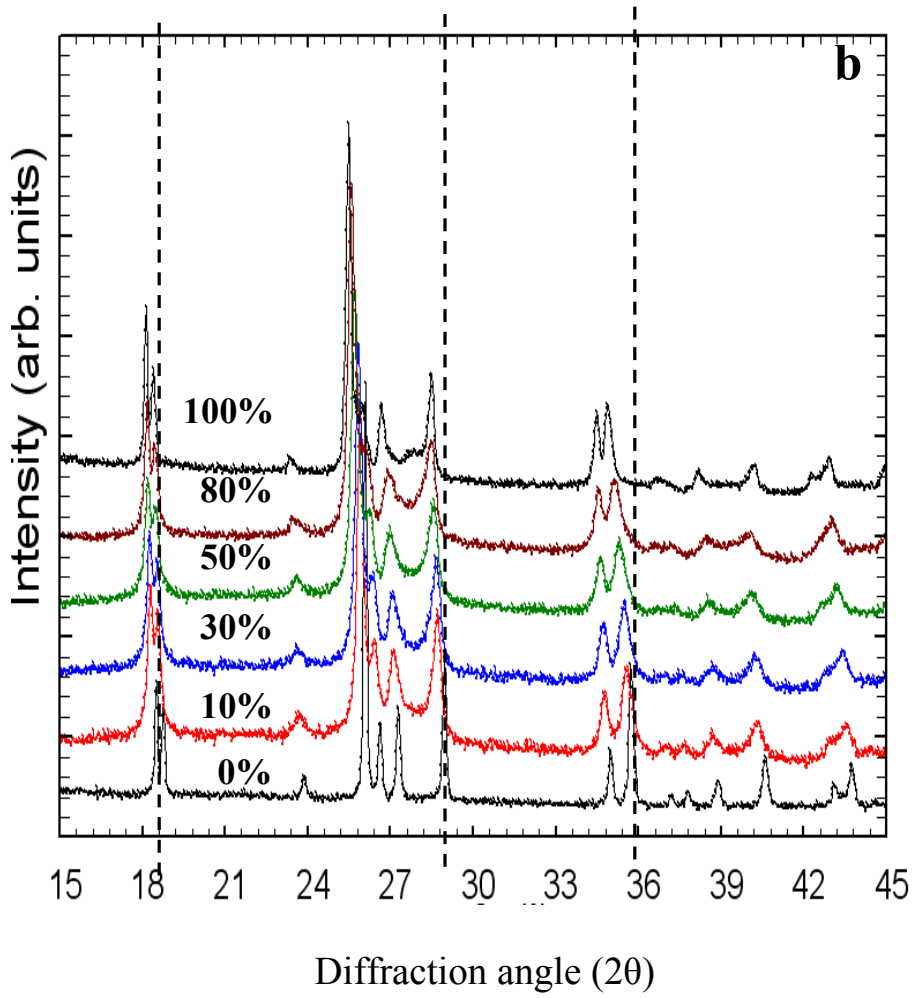


Fig. S1 X-ray diffraction patterns of (a) $(Fe_{1-x}Co_x)SO_4.H_2O$ and (b) $(Fe_{1-x}Mn_x)SO_4.H_2O$ monohydrate precursors varying the Co or Mn doping content from 0 to 100 wt%. The numbers alongside the diffraction patterns present the Co or Mn dopant content (wt%). As shown, increasing Co content gradually leads to lower lattice volume as indicated by peak shift towards higher diffraction angle (or lower *d* value) due to the lower ionic radii of Co wrt Fe (similar to Ni doping in the manuscript Fig 2). On the other hand, Mn doping shifts the XRD peaks towards lower angle (or higher *d* value) reflecting the larger ionic radii of Mn wrt Fe. The dashed lines are shown to guide eyes about the gradual peak shift upon varying the precursor composition.

Table S1 Lattice parameters and cell volume of $(Fe_{1-x}Co_x)SO_4.H_2O$ solid-solution precursors having monoclinic (*C*2/*c*) symmetry.

Materials	a (Å)	b (Å)	c (Å)	V (Å^3)	β (°)
$FeSO_4.H_2O$	7.0918(3)	7.5352(2)	7.7822(2)	364.67(2)	118.72(2)
$(Fe_{0.90}Co_{0.10})SO_4.H_2O$	7.0845(2)	7.5429(1)	7.7645(1)	364.09(1)	118.66(1)
$(Fe_{0.60}Co_{0.40})SO_4.H_2O$	7.0904(2)	7.5864(2)	7.7145(1)	362.36(1)	119.16(5)
$(Fe_{0.50}Co_{0.50})SO_4.H_2O$	7.0405(2)	7.5553(2)	7.6875(1)	357.80(1)	118.95(1)
$(Fe_{0.40}Co_{0.60})SO_4.H_2O$	7.0246(1)	7.5620(1)	7.6753(1)	356.77(1)	118.86(2)
$(Fe_{0.20}Co_{0.80})SO_4.H_2O$	6.9866(6)	7.5498(6)	7.6353(4)	352.93(4)	118.80(1)
$CoSO_4.H_2O$	6.9542(8)	7.5731(1)	7.6242(1)	351.72(3)	118.68(1)

Table S2 Lattice parameters and cell volume of $(Fe_{1-x}Mn_x)SO_4.H_2O$ solid-solution precursors having monoclinic (*C*2/*c*) symmetry.

Materials	a (Å)	b (Å)	c (Å)	V (Å^3)	β (°)
$FeSO_4.H_2O$	7.0918(3)	7.5352(2)	7.7822(2)	364.67(2)	118.72(2)
$(Fe_{0.90}Mn_{0.10})SO_4.H_2O$	7.1279(2)	7.5305(2)	7.7921(1)	366.37(2)	118.84(5)
$(Fe_{0.70}Mn_{0.30})SO_4.H_2O$	7.1342(2)	7.4689(2)	7.8862(1)	367.19(1)	119.09(5)
$(Fe_{0.50}Mn_{0.50})SO_4.H_2O$	7.1592(3)	7.5473(3)	7.8404(2)	370.35(2)	119.05(2)
$(Fe_{0.20}Mn_{0.80})SO_4.H_2O$	7.1425(2)	7.4985(2)	7.7248(2)	372.48(2)	115.80(3)
$MnSO_4.H_2O$	7.1241(6)	7.6631(4)	7.7642(7)	381.44(3)	115.85(12)

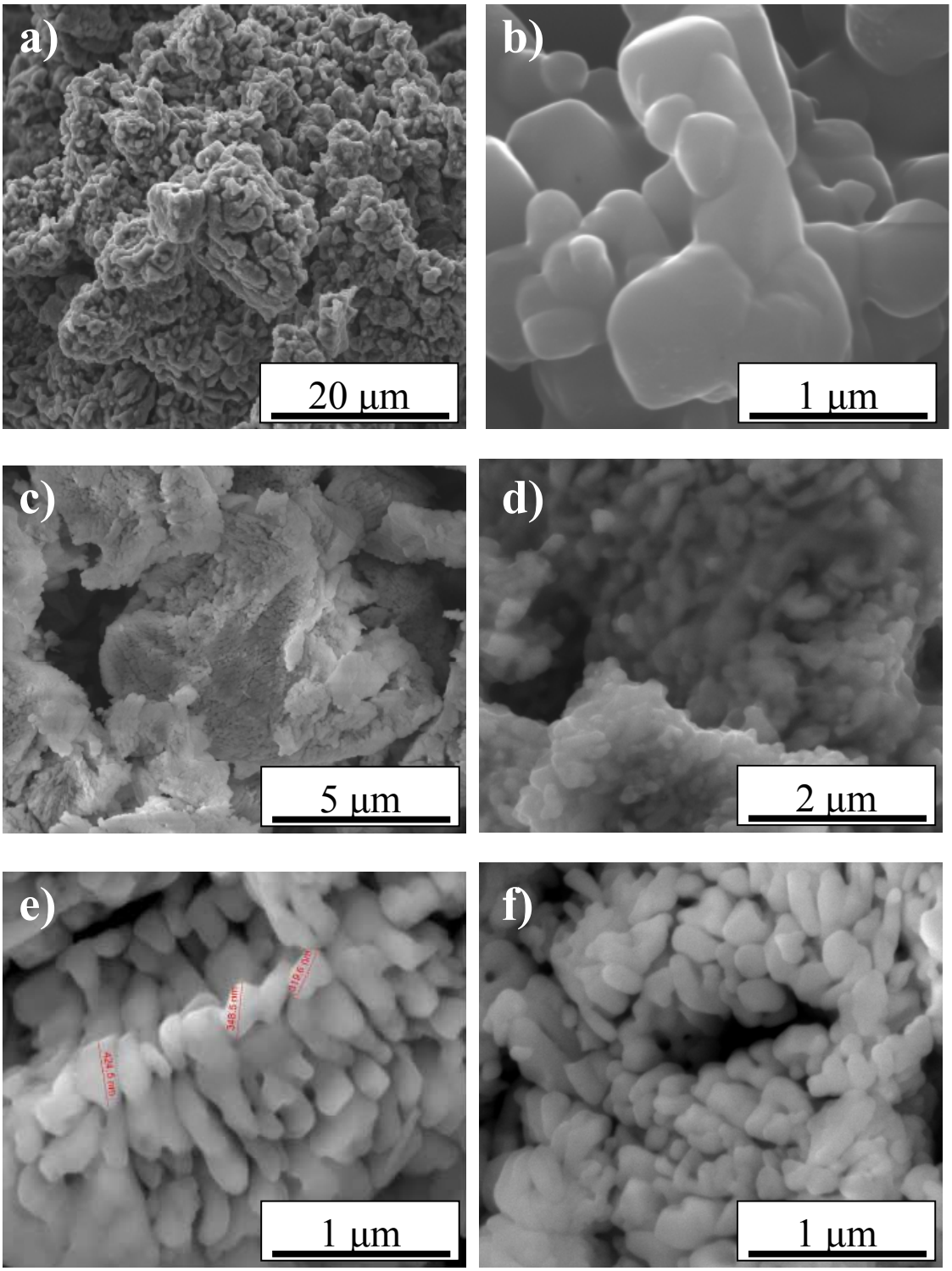


Fig. S2 SEM images showing the topotactic reaction involving initial $(Fe_{1-x}M_x)SO_4.H_2O$ precursor and final $Li(Fe_{1-x}M_x)SO_4F$ products with similar morphology. (a) $(Fe_{0.80}Co_{0.20})SO_4.H_2O$, (b) $Li(Fe_{0.80}Co_{0.20})SO_4F$, (c) $(Fe_{0.80}Ni_{0.20})SO_4.H_2O$, (d) $Li(Fe_{0.80}Ni_{0.20})SO_4F$, e) $(Fe_{0.90}Ni_{0.10})SO_4.H_2O$ and f) $Li(Fe_{0.90}Ni_{0.10})SO_4F$.

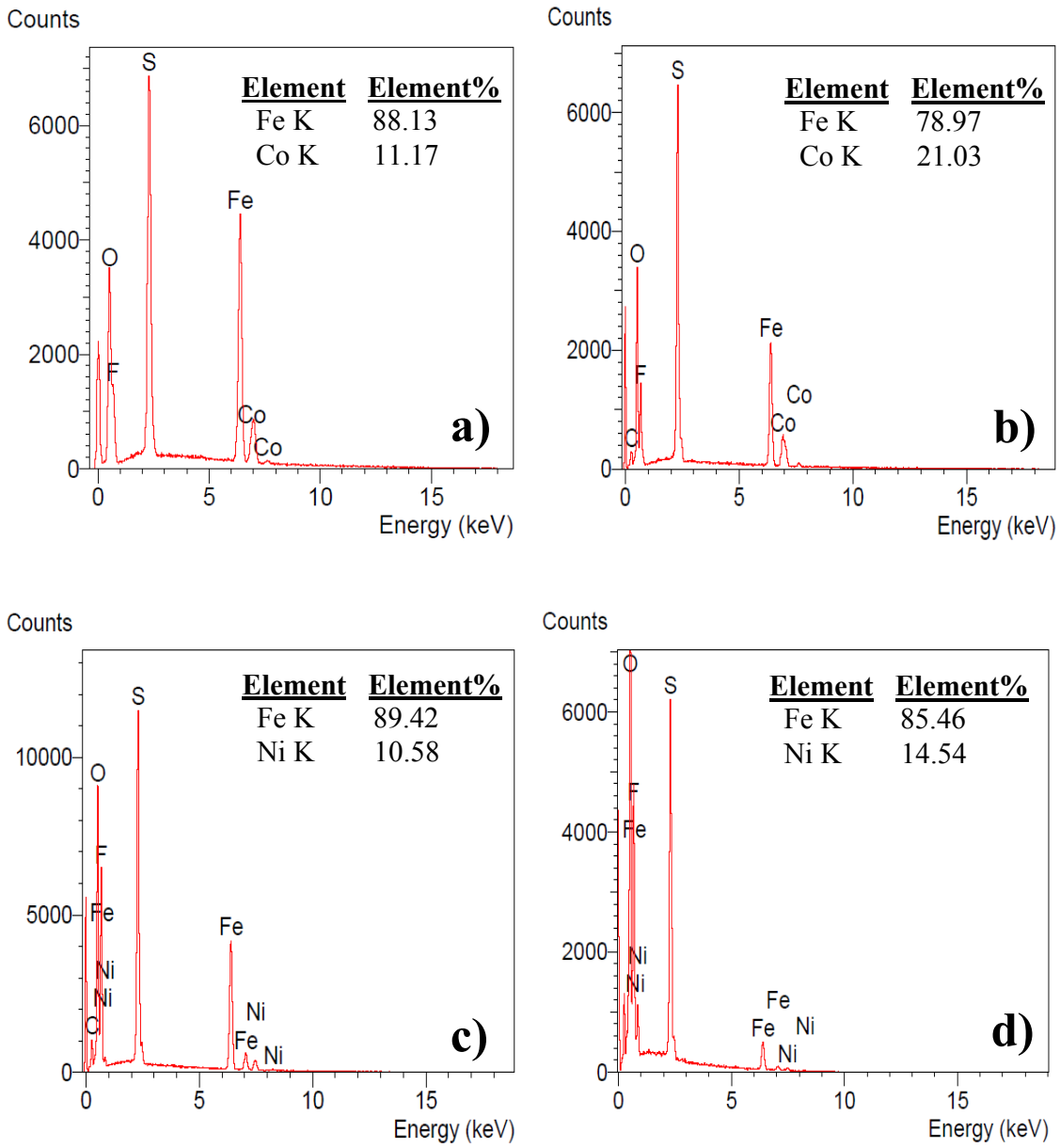


Fig. S3 Some representative EDAX elemental analysis done in conjunction with SEM study to confirm the stoichiometric composition and uniform distribution of individual 3*d* transition metals in $Li(Fe_{1-x}M_x)SO_4F$ products; (a) $Li(Fe_{0.90}Co_{0.10})SO_4F$, (b)

$Li(Fe_{0.80}Co_{0.20})SO_4F$, (c) $Li(Fe_{0.90}Ni_{0.10})SO_4F$ and (d) $Li(Fe_{0.80}Ni_{0.20})SO_4F$ products. The elemental analysis values are enlisted in the inset of each figure.

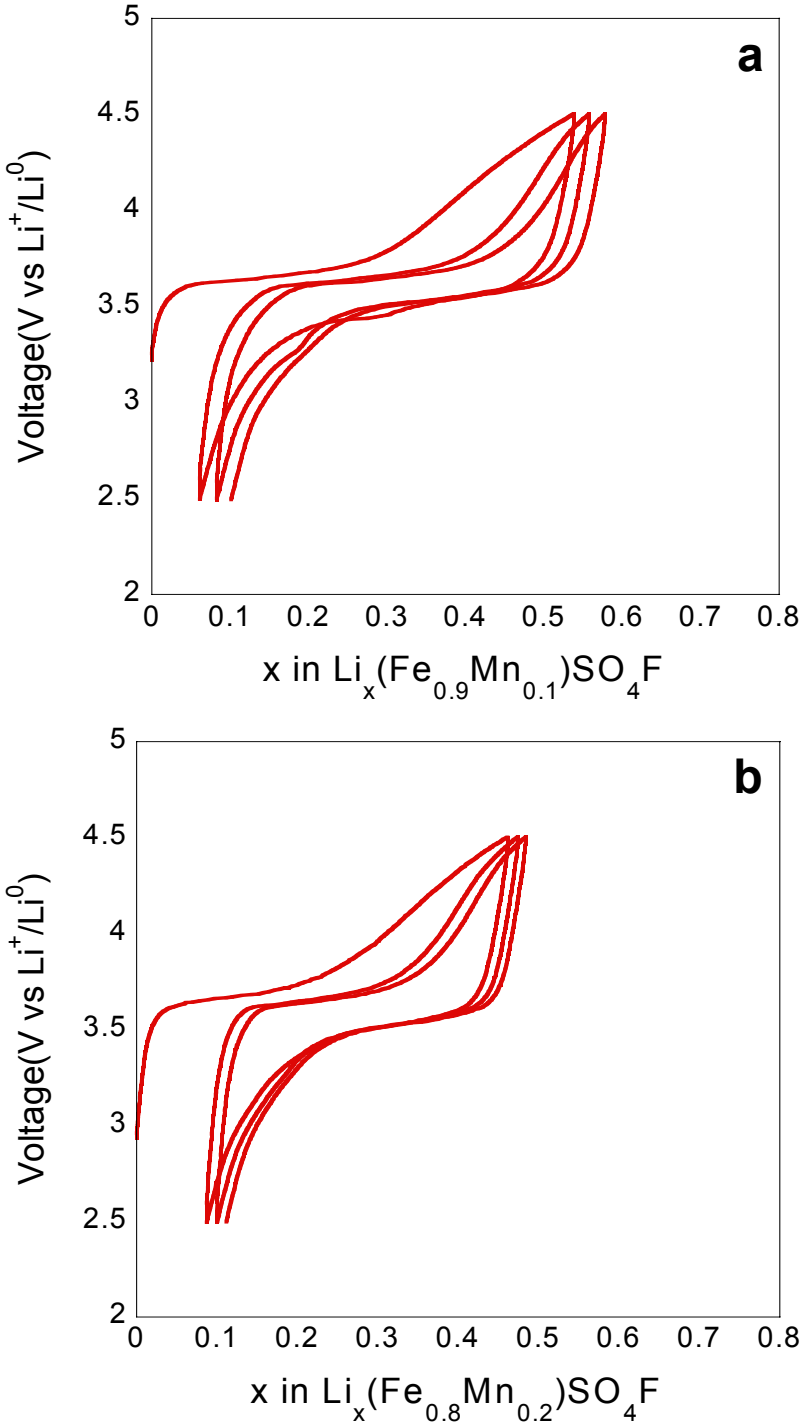


Fig. S4 Galvanostatic electrochemical cycling profiles of (a) $Li(Fe_{0.9}Mn_{0.1})SO_4F$, (b) $Li(Fe_{0.8}Mn_{0.2})SO_4F$ compounds, cycled between 2.5 to 4.5 V at C/10 (1 Li in 10 hours) in Li-half cell swagelok setting. The electrodes were prepared by ball-milling

$Li(Fe_{1-x}Mn_x)SO_4F$ and carbon black (85:15 weight ratio) for 15 minutes. A 3.6 V plateau is observed in both cases with excellent cycling stability.