Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Crystal chemistry of Mg substitution in $NaMnPO_4$ olivine: concentration limit and cation distribution

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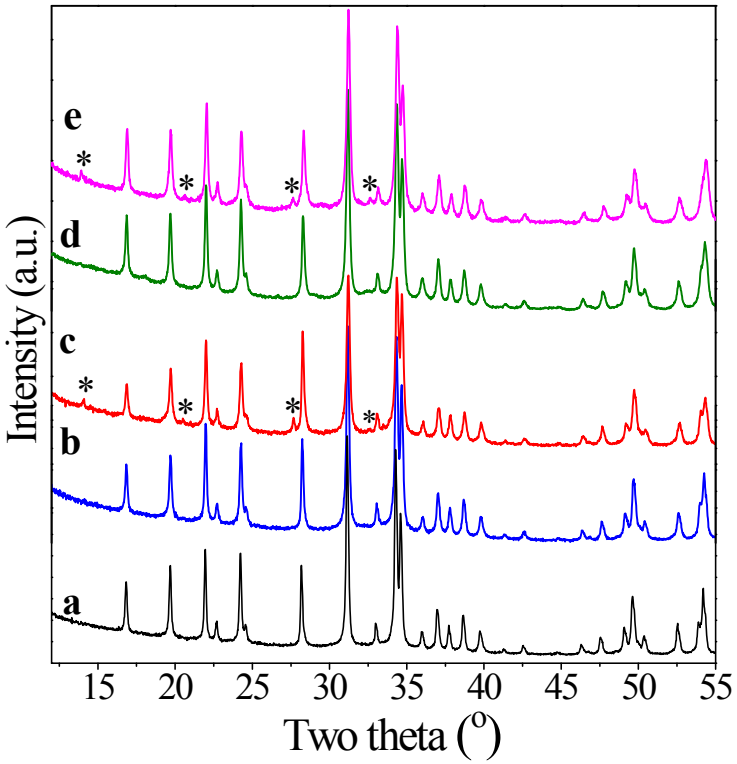

Fig. S1. Powder XRD patterns of $NaMn_{1-x}Mg_xPO_4$ compositions obtained at 200 °C: (a) x = 0 ; (b) x = 0.10 ; (c) x = 0.15; and annealed at 400 °C : d) x = 0.10 and (e) x = 0.15. Asterisk denotes peaks due to β-$KMgPO_4$

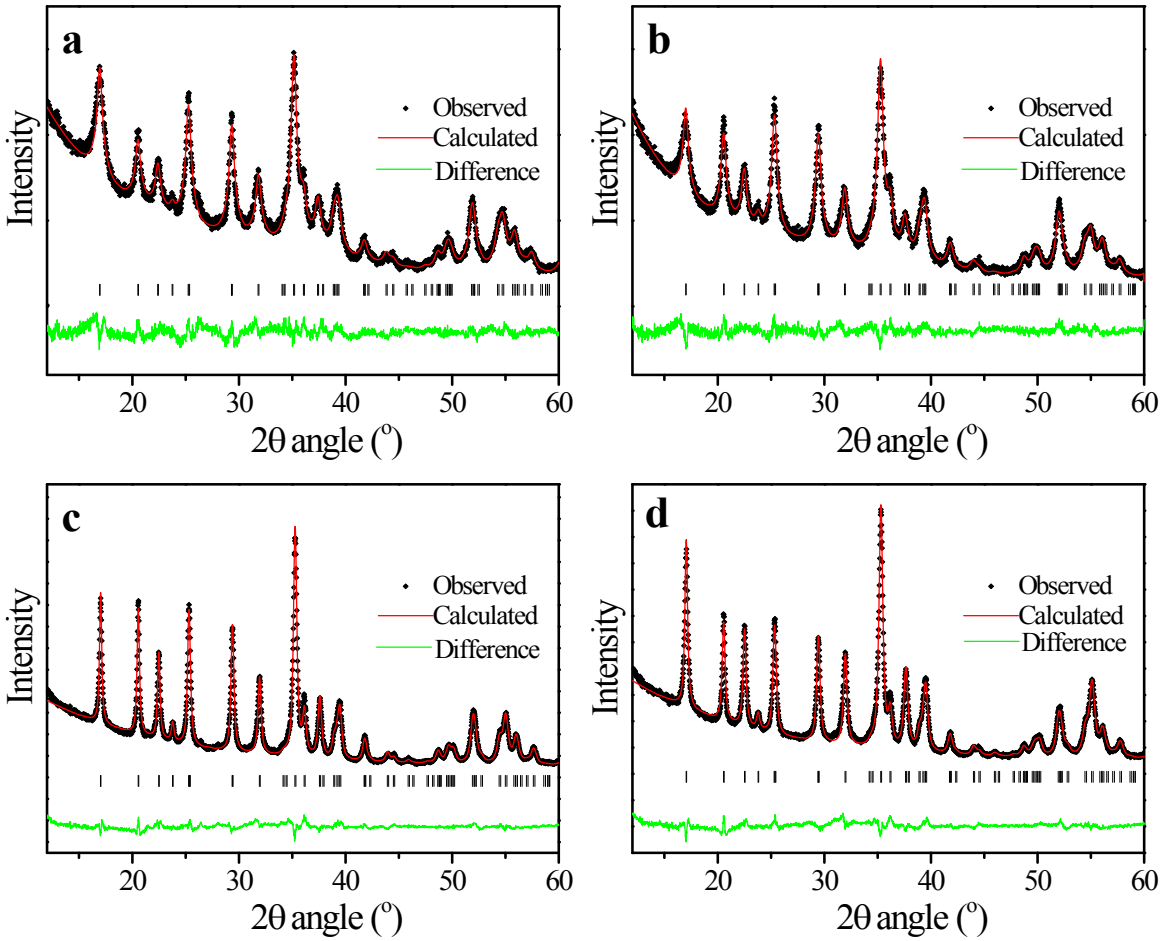

Fig. S2. XRD patterns and their Rietveld refinements according to the structural Model 1 for $LiMg_xMn_{1-x}PO_4$ obtained at 200 °C: (a) x = 0.10, (b) x = 0.15 and annealed samples at 500 °C: (c) x = 0.10, (d) x = 0.15.

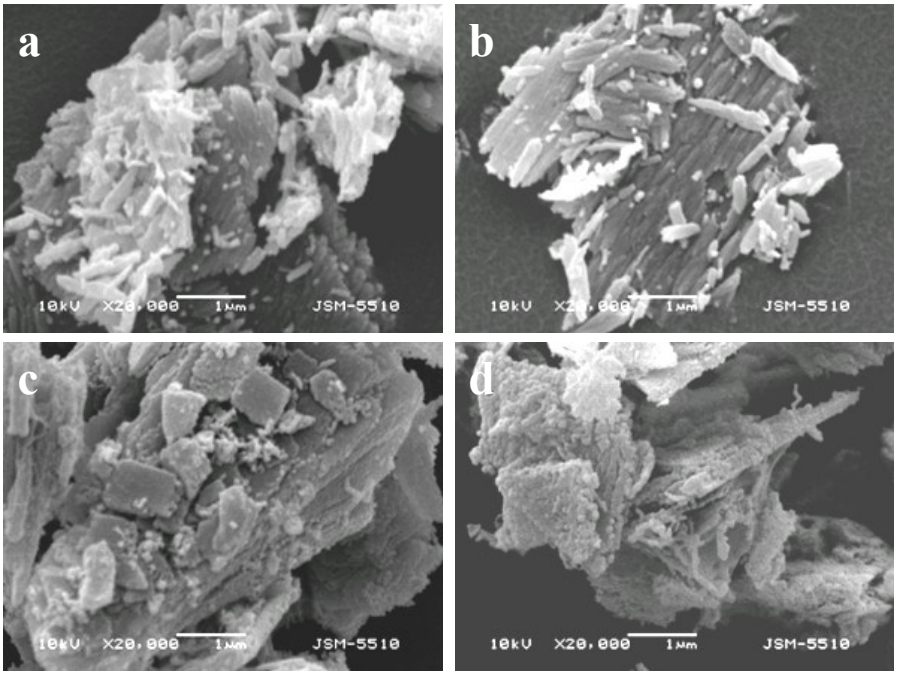

Fig. S3. SEM images of $NaMn_{1-x}Mg_xPO_4$ annealed at 400 °C: (a) x= 0.10 and (b) x = 0.15 and $LiMn_{1-x}Mg_xPO_4$ annealed at 500 °C: (c) x= 0.10 and (d) x = 0.15;

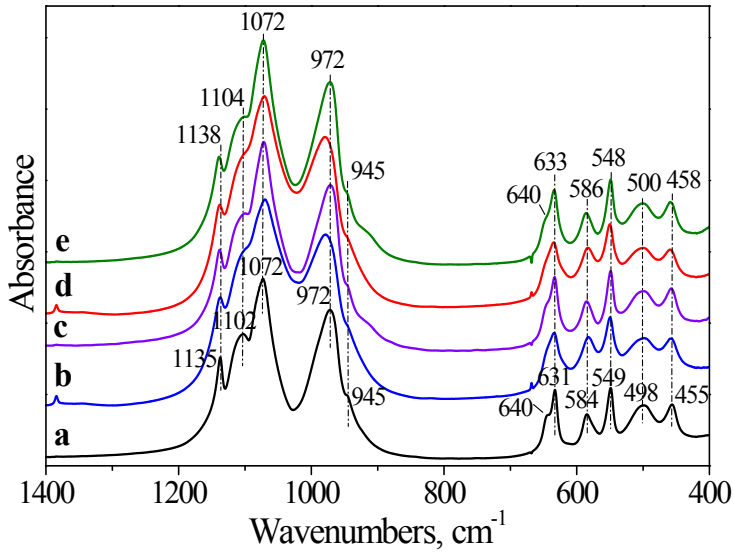

Fig. S4. IR spectra of $LiMg_xMn_{1-x}PO_4$: (a) x = 0; (b) x = 0.10 (200 °C); (c) x = 0.10 (400 °C); (d) x = 0.15 (200 °C); (e) x = 0.15 (400 °C).

Table S1 Reliability factors from Rietveld analysis of structural models 1, 2, and 3 with different distribution of A^+ (A = Li, Na), Mn^{2+} and Mg^{2+} ions over *4a* and *4c* crystallographic sites in the olivine structure.

	$LiMn_{1-x}Mg_xPO_4$				**$NaMn_{1-x}Mg_xPO_4$**			
	T=200 °C		T=500 °C		T=200 °C		T=400 °C	
	x=0.0	x=0.10	x=0.0	x=0.10	x=0.0	x=0.10	x=0.0	x=0.10
Model 1 : $[A]_{4a}[Mn_{1-x}Mg_x]_{4c}PO_4$								
R_b	3.9	2.5	5.2	5.00	7.8	8.35	3.9	5.4
R_{wp}	12.9	11.9	12.8	10.6	13.3	15.0	10.4	11.6
R_p	11.5	11.6	12.1	9.9	13.0	14.3	9.2	10.7
R_e	8.1	8.5	8.8	5.7	5.9	6.2	5.7	6.2
Model 2 : $[A_{1-\delta}Mn_\delta]_{4a}[Mn_{1-\delta-x}A_\delta Mg_x]_{4c}PO_4$								
R_b	2.5	2.2	5.1	5.4	7.6	8.1	3.9	5.4
R_{wp}	12.7	11.8	13.4	11.2	13.2	14.9	10.4	12.3
R_p	11.9	11.5	14.5	10.7	12.9	14.3	9.2	12.0
R_e	8.4	8.6	8.8	5.7	5.9	6.3	5.6	6.2
δ_{Mn}	0.04	0.01	0.0	0.0	0.02	0.02	0.0	0.01
***Model 3 (EPR)*: $[Na_{1-2x/(1-x)}Mg_{x/(1-x)}\square_{x/(1-x)}]_{4a}[Mn]_{4c}PO_4$**								
R_b	-	-	-	-	-	10.3	-	6.8
R_{wp}						15.7		13.3
R_p						15.4		12.8
R_e						6.3		6.2