

Fig. S3 MnO₆ octahedra in Li₂MnO₃ (Sample d): (a) Mn at Mn (4g) site, (b) Mn at Li (2b) site in [Li_{1/3}Mn_{2/3}] layer and (c) Mn at Li (4h) site in the interslab. Mn-O bond lengths and octahedral distortion parameter Δ are indicated. $\Delta = 1/6 \sum \{ (r - \langle r \rangle) / \langle r \rangle \}^2 \cdot 10^3$ where r is bond length and $\langle r \rangle$ is average bond length.

Fig. S4 Excitation and Emission spectra of Li₂MnO₃ (Sample c). Calculated energy levels of Mn(IV) in Mn(IV) site (4g) are shown by black vertical bars (|).

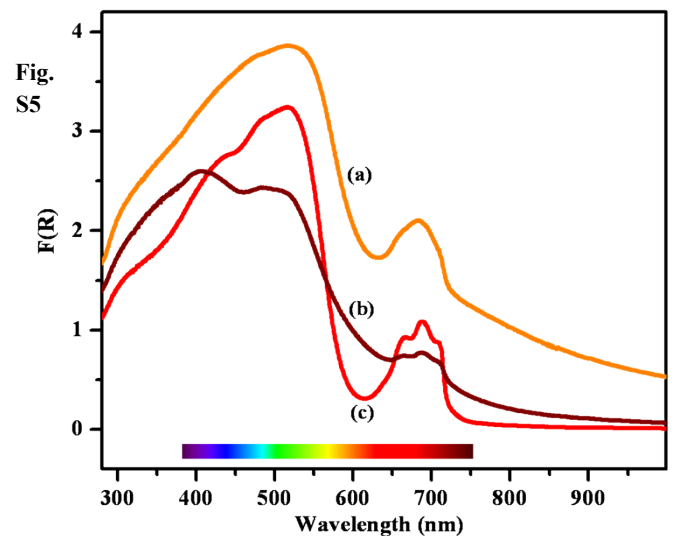
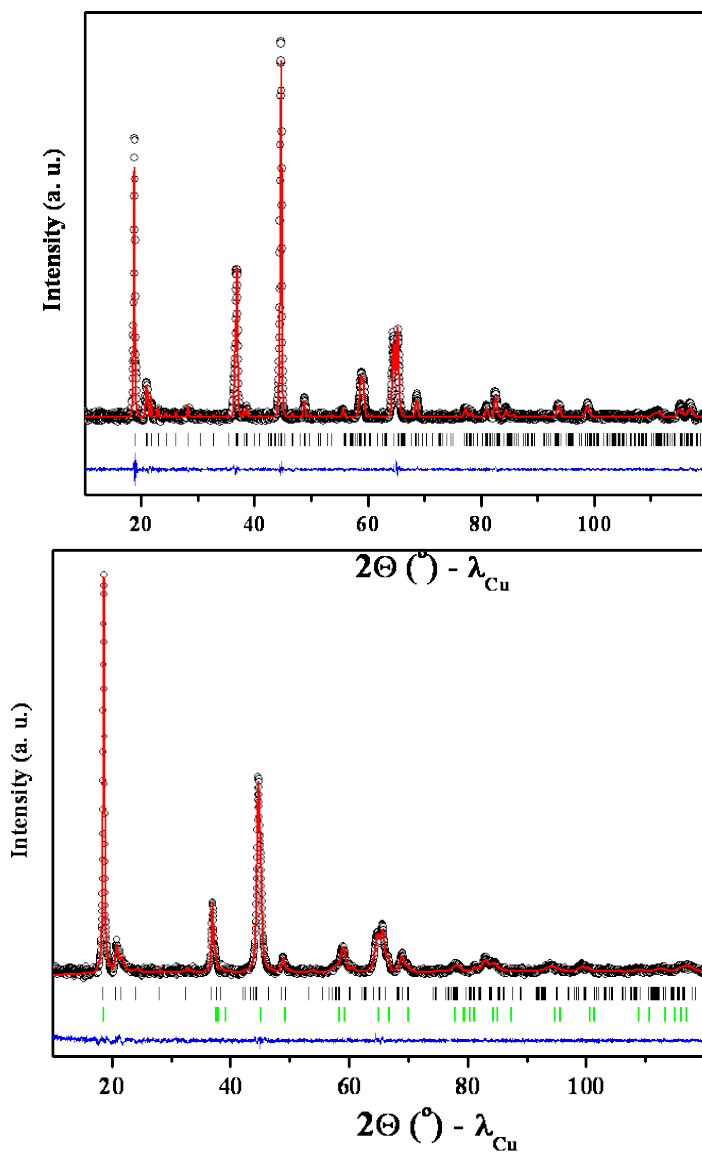


Fig. S5 Rietveld refinement of Li₂Mg_{0.67}Al_{0.66}Mn_{0.67}O₄. Observed (o), calculated (—) and difference (bottom blue line) profiles are shown. The vertical bars (|) indicate Bragg reflections.

Fig. S6 Rietveld refinement of Li₃AlMnO₅. Observed (o), calculated (—) and difference (bottom blue line) profiles are shown.

profiles are shown. The vertical black bars (|) and green bars (|) indicate Bragg reflections of $\text{Li}_3\text{AlMnO}_5$ and $\alpha\text{-LiAlO}_2$ phases respectively.

Fig. S7 UV-vis spectra of (a) $\text{Li}_2\text{Mg}_{0.67}\text{Al}_{0.66}\text{Mn}_{0.67}\text{O}_4$ (b) $\text{Li}_3\text{AlMnO}_5$ and (c) Li_2MnO_3 (Sample c).

Table S1. Rietveld refinement of $\text{Li}_2\text{Mg}_{0.67}\text{Al}_{0.66}\text{Mn}_{0.67}\text{O}_4$

<i>Atom</i>	<i>Site</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}(Å²)</i>	<i>Occupancy</i>
Li1	4e	0	0.104(10)	0.25	0.059(4)	1.0
Li2	4e	0	0.396(4)	0.25	0.079(2)	1.0
Li3	4e	0	0.7932(4)	0.25	0.029(2)	1.0
Mg1/Al1 /Mn1	4d	0.25	0.25	0.5	0.011(2)	0.34(1)/0.32(1)/0.34(1)
Mg2/Al2/Mn2	8f	0.233(2)	0.075(2)	0.010(1)	0.009(1)	0.33(1)/0.34(1)/0.33(1)
O1	8f	0.171(3)	0.223(3)	0.131(1)	0.010(5)	1
O2	8f	0.169(2)	0.580(4)	0.120(1)	0.021(3)	1
O3	8f	0.138(3)	0.913(4)	0.116(1)	0.010(3)	1

Space group $C2/c$: $a = 4.959(1) \text{ \AA}$, $b = 8.560(1) \text{ \AA}$, $c = 9.609(1) \text{ \AA}$, $\beta = 99.71(1)^\circ$

Reliability Factors (%): $R_p = 2.72$, $R_{wp} = 4.31$, $\chi^2 = 5.62$

$2 \times \text{Li}(1) - \text{O}(1) = 1.896(1) \text{ \AA}$, $2 \times \text{Li}(1) - \text{O}(2) = 1.900(1) \text{ \AA}$, $2 \times \text{Li}(1) - \text{O}(3) = 2.260(1) \text{ \AA}$, $\langle \text{Li}(1) - \text{O} \rangle = 2.019 \text{ \AA}$, BVS $\text{Li}(1) - \text{O} = 1.478$;

$2 \times \text{Li}(2) - \text{O}(1) = 2.061(1) \text{ \AA}$, $2 \times \text{Li}(2) - \text{O}(2) = 2.262(1) \text{ \AA}$, $2 \times \text{Li}(2) - \text{O}(3) = 2.027(1) \text{ \AA}$, $\langle \text{Li}(2) - \text{O} \rangle = 2.117 \text{ \AA}$, BVS $\text{Li}(2) - \text{O} = 1.072$;

$2 \times \text{Li}(3) - \text{O}(1) = 1.895(1) \text{ \AA}$, $2 \times \text{Li}(3) - \text{O}(2) = 2.437(1) \text{ \AA}$, $2 \times \text{Li}(3) - \text{O}(3) = 1.865(1) \text{ \AA}$, $\langle \text{Li}(3) - \text{O} \rangle = 2.066 \text{ \AA}$, BVS $\text{Li}(3) - \text{O} = 1.453$;

$2 \times \text{Mg}(1)/\text{Al}(1)/\text{Mn}(1) - \text{O}(1) = 2.251(1) \text{ \AA}$, $2 \times \text{Mg}(1)/\text{Al}(1)/\text{Mn}(1) - \text{O}(2) = 1.936(1) \text{ \AA}$, $2 \times \text{Mg}(1)/\text{Al}(1)/\text{Mn}(1) - \text{O}(3) = 1.925(1) \text{ \AA}$,

$\langle \text{Mg}(1)/\text{Al}(1)/\text{Mn}(1) - \text{O} \rangle = 2.037 \text{ \AA}$, BVS $\text{Mg}(1)/\text{Al}(1)/\text{Mn}(1) - \text{O} = 2.554$;

$\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O}(1) = 1.854(1) \text{ \AA}$, $\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O}(1) = 2.216(1) \text{ \AA}$, $\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O}(2) = 2.240(1) \text{ \AA}$, $\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O}(2) = 1.940(1) \text{ \AA}$, $\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O}(3) = 1.835(1) \text{ \AA}$, $\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O}(3) = 2.031(1) \text{ \AA}$, $\langle \text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O} \rangle = 2.019 \text{ \AA}$, BVS

$\text{Mg}(2)/\text{Al}(2)/\text{Mn}(2) - \text{O} = 2.707$;

Table S2. Rietveld refinement of $\text{Li}_3\text{AlMnO}_5$

Atom	Site	x	y	z	$U_{iso}(\text{Å}^2)$	Occupancy
Li1/Mn1/Al1	2b	0	0.5	0	0.022(2)	0.80(1)/0.10(1)/0.10(1)
Li2	2c	0	0	0.5	0.033(8)	1.0
Li3	4h	0	0.713(2)	0.5	0.031(6)	1.0
Li4/Mn2/Al2	4g	0	0.175(1)	0	0.026(1)	0.10(1)/0.55(1)/0.35(1)
O1	4i	0.209(2)	0	0.207(1)	0.010(2)	0.95(1)
O2	8j	0.250(1)	0.338(1)	0.238(1)	0.012(1)	0.93(1)

Space group $C2/m$: $a = 4.994(1) \text{ \AA}$, $b = 8.530(1) \text{ \AA}$, $c = 5.028(1) \text{ \AA}$, $\beta = 109.15(1)^\circ$

Reliability Factors (%): $R_p = 1.66$, $R_{wp} = 2.18$, $\chi^2 = 1.73$

$2 \times \text{Li}(1)/\text{Mn}(1)/\text{Al}(1) - \text{O}(1) = 2.032(1) \text{ \AA}$, $4 \times \text{Li}(1)/\text{Mn}(1)/\text{Al}(1) - \text{O}(2) = 1.979(1) \text{ \AA}$; $\langle \text{Li}(1)/\text{Mn}(1)/\text{Al}(1) - \text{O} \rangle = 1.997 \text{ \AA}$, BVS $\text{Li}(1)/\text{Mn}(1)/\text{Al}(1) - \text{O} = 1.675$;

$2 \times \text{Li}(2) - \text{O}(1) = 2.059(1) \text{ \AA}$; $4 \times \text{Li}(2) - \text{O}(2) = 2.030(1) \text{ \AA}$, $\langle \text{Li}(2) - \text{O} \rangle = 2.040 \text{ \AA}$, BVS $\text{Li}(2) - \text{O} = 1.274$;

$2 \times \text{Li}(3) - \text{O}(1) = 2.479(1) \text{ \AA}$; $2 \times \text{Li}(3) - \text{O}(2) = 2.127(1) \text{ \AA}$, $2 \times \text{Li}(3) - \text{O}(2) = 1.825(1) \text{ \AA}$, $\langle \text{Li}(3) - \text{O} \rangle = 2.144 \text{ \AA}$, BVS $\text{Li}(3) - \text{O} = 1.22$;

$2 \times \text{Li}(4)/\text{Mn}(2)/\text{Al}(2) - \text{O}(1) = 1.920(1) \text{ \AA}$, $2 \times \text{Li}(4)/\text{Mn}(2)/\text{Al}(2) - \text{O}(2) = 1.977(1) \text{ \AA}$, $2 \times \text{Li}(4)/\text{Mn}(2)/\text{Al}(2) - \text{O}(3) = 1.982(1) \text{ \AA}$, $\langle \text{Li}(4)/\text{Mn}(2)/\text{Al}(2) - \text{O} \rangle = 1.960 \text{ \AA}$, BVS $\text{Li}(4)/\text{Mn}(2)/\text{Al}(2) - \text{O} = 1.585$;