

Table A Rietveld refinement results of ${}^7\text{LiMn}_2\text{O}_4$ synthesized at 900°C with a cooling rate of $60^\circ\text{C}/\text{h}$ and a Li/Mn ratio of $1/2$ from the starting materials, Li_2CO_3 and Mn_2O_3 (sample B).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	$8a$	1	$1/8$	$1/8$	$1/8$	0.0121(10)
Mn(1)	$16d$	1	$1/2$	$1/2$	$1/2$	0.0094
O(1)	$32e$	0.971(6)	0.26262(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0154
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.0094(4)	$= U_{11}$	$= U_{11}$	-0.0027(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0153(4)	$= U_{11}$	$= U_{11}$	-0.0040(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24781(15) \text{\AA}$, $R_{\text{wp}} = 4.47$,
 $R_{\text{p}} = 3.84$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1230$, $R_{\text{I}} = 1.20$, $R_{\text{F}} = 1.94$.

Table B Rietveld refinement results of ${}^7\text{LiMn}_2\text{O}_4$ synthesized at 900°C with a cooling rate of $100^\circ\text{C}/\text{h}$ and a Li/Mn ratio of $1/2$ from the starting materials, Li_2CO_3 and Mn_2O_3 (sample C).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	$8a$	1	$1/8$	$1/8$	$1/8$	0.0117(11)
Mn(1)	$16d$	1	$1/2$	$1/2$	$1/2$	0.0072
O(1)	$32e$	0.973(6)	0.26306(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0125
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.0072(5)	$= U_{11}$	$= U_{11}$	-0.0023(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0125(3)	$= U_{11}$	$= U_{11}$	-0.0027(3)	$= U_{12}$	$= U_{12}$

Note : This sample contains 1.8% Li_2MnO_3 as the impurity phase.

Phase 1 : LiMn_2O_4 , space group $Fd\bar{3}m$, $a = 8.24709(12) \text{\AA}$, $R_{\text{I}} = 1.47$, $R_{\text{F}} = 2.46$.

Phase 2 : Li_2MnO_3 space group $C2/c$, $a = 4.9185(15) \text{\AA}$, $b = 8.6821(19) \text{\AA}$, $c = 9.455(2) \text{\AA}$, $\beta = 100.23(3)^\circ$, $R_{\text{I}} = 4.64$, $R_{\text{F}} = 4.16$. $R_{\text{wp}} = 4.93$, $R_{\text{p}} = 4.23$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1690$.

Table C Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 800°C in O_2 (sample D).

Atom	site	g	x	y	z	$U/\text{Å}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0132(11)
Mn(1)	16d	1	1/2	1/2	1/2	0.0099
O(1)	32e	0.980(6)	0.26273(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0159
Atom	$U_{11}/\text{Å}^2$	$U_{22}/\text{Å}^2$	$U_{33}/\text{Å}^2$	$U_{12}/\text{Å}^2$	$U_{13}/\text{Å}^2$	$U_{23}/\text{Å}^2$
Mn(1)	0.0099(4)	$= U_{11}$	$= U_{11}$	-0.0021(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0163(3)	$= U_{11}$	$= U_{11}$	-0.0038(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24260(14)$ Å, $R_{\text{wp}} = 5.54$,

$R_{\text{p}} = 4.71$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1817$, $R_{\text{I}} = 1.08$, $R_{\text{F}} = 1.91$.

Table D Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 750°C in O_2 (sample E).

Atom	site	g	x	y	z	$U/\text{Å}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0110(10)
Mn(1)	16d	1	1/2	1/2	1/2	0.0092
O(1)	32e	0.990(6)	0.26274(5)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0160
Atom	$U_{11}/\text{Å}^2$	$U_{22}/\text{Å}^2$	$U_{33}/\text{Å}^2$	$U_{12}/\text{Å}^2$	$U_{13}/\text{Å}^2$	$U_{23}/\text{Å}^2$
Mn(1)	0.0092(4)	$= U_{11}$	$= U_{11}$	-0.0030(3)	$= U_{12}$	$= U_{12}$
O(1)	0.0160(3)	$= U_{11}$	$= U_{11}$	-0.0040(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24060(15)$ Å, $R_{\text{wp}} = 5.47$,

$R_{\text{p}} = 4.65$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1730$, $R_{\text{I}} = 1.24$, $R_{\text{F}} = 1.79$.

Table E Rietveld refinement results for ${}^7\text{LiMn}_2\text{O}_4$ (Li/Mn = 0.5) synthesized at 800°C in Air (sample F).

Atom	site	g	x	y	z	$U/\text{Å}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0109(9)
Mn(1)	16d	1	1/2	1/2	1/2	0.0079
O(1)	32e	0.982(6)	0.26274(5)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0140
Atom	$U_{11}/\text{Å}^2$	$U_{22}/\text{Å}^2$	$U_{33}/\text{Å}^2$	$U_{12}/\text{Å}^2$	$U_{13}/\text{Å}^2$	$U_{23}/\text{Å}^2$
Mn(1)	0.0078(3)	$= U_{11}$	$= U_{11}$	-0.0025(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0140(3)	$= U_{11}$	$= U_{11}$	-0.0039(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24648(11)$ Å, $R_{\text{wp}} = 4.19$,

$R_{\text{p}} = 3.61$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1946$, $R_{\text{I}} = 1.28$, $R_{\text{F}} = 2.20$.

Table F Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 800°C in Air (sample G).

Atom	site	g	x	y	z	$U/\text{Å}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0115(11)
Mn(1)	16d	1	1/2	1/2	1/2	0.0076
O(1)	32e	0.978(6)	0.26266(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0143
Atom	$U_{11}/\text{Å}^2$	$U_{22}/\text{Å}^2$	$U_{33}/\text{Å}^2$	$U_{12}/\text{Å}^2$	$U_{13}/\text{Å}^2$	$U_{23}/\text{Å}^2$
Mn(1)	0.0076(3)	$= U_{11}$	$= U_{11}$	-0.0028(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0143(3)	$= U_{11}$	$= U_{11}$	-0.0039(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24330(13)$ Å, $R_{\text{wp}} = 5.09$,

$R_{\text{p}} = 4.32$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1658$, $R_{\text{I}} = 1.50$, $R_{\text{F}} = 2.33$.

Table G Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 470°C, 1 times and 750°C, 1 time in air (sample H).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0110(11)
Mn(1)	16d	1	1/2	1/2	1/2	0.0078
O(1)	32e	0.986(6)	0.26274(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0138

Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.0078(4)	$= U_{11}$	$= U_{11}$	-0.0022(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0130(8)	$= U_{11}$	$= U_{11}$	-0.0037(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24075(13)\text{\AA}$, $R_{\text{wp}} = 4.73$,

$R_{\text{p}} = 4.06$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1792$, $R_{\text{I}} = 1.53$, $R_{\text{F}} = 2.36$.

Table H Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 470°C, 1 times and 750°C, 1 time in O_2 (sample I).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0101(11)
Mn(1)	16d	1	1/2	1/2	1/2	0.0079
O(1)	32e	0.990(7)	0.26275(13)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0140

Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.0078(4)	$= U_{11}$	$= U_{11}$	-0.0019(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0140(4)	$= U_{11}$	$= U_{11}$	-0.0036(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.23803(13)\text{\AA}$, $R_{\text{wp}} = 4.53$,

$R_{\text{p}} = 3.94$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1243$, $R_{\text{I}} = 1.08$, $R_{\text{F}} = 1.92$.

Table I Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 470°C, 3 times and 750°C, 1 time in O_2 (sample J).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0106(11)
Mn(1)	16d	1	1/2	1/2	1/2	0.0075
O(1)	32e	0.996(6)	0.26275(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0143

Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.0075(4)	$= U_{11}$	$= U_{11}$	-0.0023(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0143(3)	$= U_{11}$	$= U_{11}$	-0.0039(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.23785(13)$ \AA, $R_{\text{wp}} = 4.29$,

$R_{\text{p}} = 3.94$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1520$, $R_{\text{I}} = 1.27$, $R_{\text{F}} = 2.00$.

Table J Rietveld refinement results for ${}^7\text{LiMn}_2\text{O}_4$ (Li/Mn = 0.5) synthesized at 470°C, 1 times and 750°C, 1 time in O_2 (sample K).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0100(9)
Mn(1)	16d	1	1/2	1/2	1/2	0.0087
O(1)	32e	0.989(6)	0.26282(5)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0142

Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.0087(4)	$= U_{11}$	$= U_{11}$	-0.0025(4)	$= U_{12}$	$= U_{12}$
O(1)	0.0142(3)	$= U_{11}$	$= U_{11}$	-0.0033(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24165(12)$ \AA, $R_{\text{wp}} = 4.66$,

$R_{\text{p}} = 3.99$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1196$, $R_{\text{I}} = 1.06$, $R_{\text{F}} = 1.80$.

Table K X-ray Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 800°C 1 in air (sample G).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.01554(8)
Mn(1)	16d	1	1/2	1/2	1/2	0.0089
O(1)	32e	0.978	0.26261(8)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0147
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.00889(6)	$= U_{11}$	$= U_{11}$	-0.00232(9)	$= U_{12}$	$= U_{12}$
O(1)	0.0147(2)	$= U_{11}$	$= U_{11}$	-0.0042(3)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24463(2)\text{\AA}$, $R_{\text{wp}} = 3.99$,
 $R_{\text{p}} = 3.13$, $S = R_{\text{wp}}/R_{\text{e}} = 2.0168$, $R_{\text{I}} = 0.61$, $R_{\text{F}} = 0.49$.

Table L X-ray Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 470°C, 1 times and 750°C, 1 time in air (sample H).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	8a	1	1/8	1/8	1/8	0.0139(10)
Mn(1)	16d	1	1/2	1/2	1/2	0.0080
O(1)	32e	0.986	0.26294(8)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0141
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.00796(6)	$= U_{11}$	$= U_{11}$	-0.00179(8)	$= U_{12}$	$= U_{12}$
O(1)	0.0141(2)	$= U_{11}$	$= U_{11}$	-0.0037(3)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24382(2)\text{\AA}$, $R_{\text{wp}} = 3.33$,
 $R_{\text{p}} = 2.54$, $S = R_{\text{wp}}/R_{\text{e}} = 1.9178$, $R_{\text{I}} = 0.62$, $R_{\text{F}} = 0.48$.

Table M Rietveld refinement results for $\text{LiMn}_2\text{O}_4(\text{Li}/\text{Mn} = 0.5)$ synthesized at 470°C , 1 times and 750°C , 1 time in O_2 (sample I).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	$8a$	1	1/8	1/8	1/8	0.0139(8)
Mn(1)	$16d$	1	1/2	1/2	1/2	0.0086
O(1)	$32e$	0.990	0.26269(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0152
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.00860(6)	$= U_{11}$	$= U_{11}$	-0.0019(4)	$= U_{12}$	$= U_{12}$
O(1)	0.01521(18)	$= U_{11}$	$= U_{11}$	-0.0038(3)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24234(2)$ \AA , $R_{\text{wp}} = 3.22$,
 $R_{\text{p}} = 2.50$, $S = R_{\text{wp}}/R_{\text{e}} = 1.8259$, $R_{\text{I}} = 0.61$, $R_{\text{F}} = 0.50$.

Table N X-ray Rietveld refinement results for $\text{LiMn}_2\text{O}_4(\text{Li}/\text{Mn} = 0.5)$ synthesized at 470°C , 3 times and 750°C , 1 time in O_2 (sample J).

Atom	site	g	x	y	z	$U/\text{\AA}^2$
Li(1)	$8a$	1	1/8	1/8	1/8	0.0132(8)
Mn(1)	$16d$	1	1/2	1/2	1/2	0.0086
O(1)	$32e$	0.996	0.26267(6)	$= x(\text{O}(1))$	$= x(\text{O}(1))$	0.0148
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
Mn(1)	0.00863(6)	$= U_{11}$	$= U_{11}$	-0.00204(7)	$= U_{12}$	$= U_{12}$
O(1)	0.01484(18)	$= U_{11}$	$= U_{11}$	-0.0040(2)	$= U_{12}$	$= U_{12}$

Space group $Fd\bar{3}m$, $a = 8.24025(2)$ \AA , $R_{\text{wp}} = 3.00$,
 $R_{\text{p}} = 2.33$, $S = R_{\text{wp}}/R_{\text{e}} = 1.7361$, $R_{\text{I}} = 0.53$, $R_{\text{F}} = 0.48$.

Table O Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5125) synthesized at 900°C in O_2 (sample L).

Atom	site	g	x	y	z	$U(\text{\AA}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0124(15)
Li(2)	16d	0.011	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.989(8)	1/2	1/2	1/2	0.0085
O(1)	32d	0.971(16)	0.26288(6)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0142
Atom	$U_{11}(\text{\AA}^2)$	$U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$	$U_{13}(\text{\AA}^2)$	$U_{23}(\text{\AA}^2)$
Mn(1)	0.0085(4)	= U_{11}	= U_{11}	-0.0029(4)	= U_{12}	= U_{12}
O	0.0142(3)	= U_{11}	= U_{11}	-0.0035(2)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.23845(13) \text{\AA}$, $R_{\text{wp}} = 4.99$,

$R_{\text{p}} = 4.18$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1568$, $R_{\text{I}} = 1.21$, $R_{\text{F}} = 2.17$.

Table P Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.525) synthesized at 900°C in O_2 (sample M).

Atom	site	g	x	y	z	$U(\text{\AA}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0123(15)
Li(2)	16d	0.021	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.979(8)	1/2	1/2	1/2	0.0068
O(1)	32d	0.989(6)	0.26289(6)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0133
Atom	$U_{11}(\text{\AA}^2)$	$U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$	$U_{13}(\text{\AA}^2)$	$U_{23}(\text{\AA}^2)$
Mn(1)	0.0068(4)	= U_{11}	= U_{11}	-0.0023(4)	= U_{12}	= U_{12}
O(1)	0.0133(3)	= U_{11}	= U_{11}	-0.0037(2)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.23222(5) \text{\AA}$, $R_{\text{wp}} = 5.10$,

$R_{\text{p}} = 4.31$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1968$, $R_{\text{I}} = 1.24$, $R_{\text{F}} = 1.72$.

Table Q Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.55) synthesized at 900°C in O_2 (sample N).

Atom	site	g	x	y	z	$U(\text{\AA}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0108(19)
Li(2)	16d	0.045	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.955(8)	1/2	1/2	1/2	0.0062
O(1)	32e	0.998(7)	0.26276(9)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0138
Atom	$U_{11}(\text{\AA}^2)$	$U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$	$U_{13}(\text{\AA}^2)$	$U_{23}(\text{\AA}^2)$
Mn(1)	0.0061(4)	= U_{11}	= U_{11}	-0.0025(4)	= U_{12}	= U_{12}
O	0.0140(4)	= U_{11}	= U_{11}	-0.0038(3)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.21393(15) \text{\AA}$, $R_{\text{wp}} = 5.31$,

$R_{\text{p}} = 4.45$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1699$, $R_{\text{I}} = 1.63$, $R_{\text{F}} = 2.12$.

Table R Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.5) synthesized at 750°C in O_2 (sample O).

Atom	site	g	x	y	z	$U(\text{\AA}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0109(11)
Mn(1)	16d	1	1/2	1/2	1/2	0.0079
O(1)	32e	0.975(8)	0.26280	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0143
Atom	$U_{11}(\text{\AA}^2)$	$U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$	$U_{13}(\text{\AA}^2)$	$U_{23}(\text{\AA}^2)$
Mn(1)	0.071(4)	= U_{11}	= U_{11}	-0.0024(4)	= U_{12}	= U_{12}
O(1)	0.0142(3)	= U_{11}	= U_{11}	-0.0039(2)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.24118(10) \text{\AA}$, $R_{\text{wp}} = 4.75$,

$R_{\text{p}} = 4.49$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1728$, $R_{\text{I}} = 1.85$, $R_{\text{F}} = 2.25$.

Table S Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.515) synthesized at 750°C in O_2 (sample P).

Atom	site	g	x	y	z	$U(\text{Å}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0110(9)
Li(2)	16d	0.011	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.988(8)	1/2	1/2	1/2	0.0070
O(1)	32d	0.985(7)	0.26274(3)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0143
Atom	$U_{11}(\text{Å}^2)$	$U_{22}(\text{Å}^2)$	$U_{33}(\text{Å}^2)$	$U_{12}(\text{Å}^2)$	$U_{13}(\text{Å}^2)$	$U_{23}(\text{Å}^2)$
Mn(1)	0.0069(4)	= U_{11}	= U_{11}	-0.0024(2)	= U_{12}	= U_{12}
O	0.0143(2)	= U_{11}	= U_{11}	-0.0039(2)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.24185(10)$ Å, $R_{\text{wp}} = 4.99$,

$R_{\text{p}} = 4.18$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1568$, $R_{\text{I}} = 1.21$, $R_{\text{F}} = 2.17$.

Table T Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.525) synthesized at 750°C in O_2 (sample Q).

Atom	site	g	x	y	z	$U(\text{Å}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0118(11)
Li(2)	16d	0.018	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.982(6)	1/2	1/2	1/2	0.0063
O(1)	32d	0.994(6)	0.26274(4)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0138
Atom	$U_{11}(\text{Å}^2)$	$U_{22}(\text{Å}^2)$	$U_{33}(\text{Å}^2)$	$U_{12}(\text{Å}^2)$	$U_{13}(\text{Å}^2)$	$U_{23}(\text{Å}^2)$
Mn(1)	0.0063(4)	= U_{11}	= U_{11}	-0.0025(3)	= U_{12}	= U_{12}
O	0.0137(2)	= U_{11}	= U_{11}	-0.00408(15)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.22889(11)$ Å, $R_{\text{wp}} = 4.99$,

$R_{\text{p}} = 4.18$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1568$, $R_{\text{I}} = 1.21$, $R_{\text{F}} = 2.17$.

Table U Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.54) synthesized at 750°C in O_2 (sample R).

Atom	site	g	x	y	z	$U(\text{Å}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0106(11)
Li(2)	16d	0.034	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.966(6)	1/2	1/2	1/2	0.0065
O(1)	32d	0.996(8)	0.26270(4)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0129
Atom	$U_{11}(\text{Å}^2)$	$U_{22}(\text{Å}^2)$	$U_{33}(\text{Å}^2)$	$U_{12}(\text{Å}^2)$	$U_{13}(\text{Å}^2)$	$U_{23}(\text{Å}^2)$
Mn(1)	0.0059(3)	= U_{11}	= U_{11}	-0.0021(2)	= U_{12}	= U_{12}
O	0.01296(17)	= U_{11}	= U_{11}	-0.00377(14)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.21687(12)$ Å, $R_{\text{wp}} = 5.32$,

$R_{\text{p}} = 5.12$, $S = R_{\text{wp}}/R_{\text{e}} = 1.1628$, $R_{\text{I}} = 2.05$, $R_{\text{F}} = 2.17$.

Table V Rietveld refinement results for LiMn_2O_4 (Li/Mn = 0.55) synthesized at 750°C in O_2 (sample S).

Atom	site	g	x	y	z	$U(\text{Å}^2)$
Li(1)	8a	1	1/8	1/8	1/8	0.0104(10)
Li(2)	16d	0.038	1/2	1/2	1/2	= $U(\text{Mn}(1))$
Mn(1)	16d	0.938(7)	1/2	1/2	1/2	0.0060
O(1)	32d	1	0.26267(4)	= $x(\text{O}(1))$	= $x(\text{O}(1))$	0.0130
Atom	$U_{11}(\text{Å}^2)$	$U_{22}(\text{Å}^2)$	$U_{33}(\text{Å}^2)$	$U_{12}(\text{Å}^2)$	$U_{13}(\text{Å}^2)$	$U_{23}(\text{Å}^2)$
Mn(1)	0.0060(3)	= U_{11}	= U_{11}	-0.0021(2)	= U_{12}	= U_{12}
O	0.0129(2)	= U_{11}	= U_{11}	-0.0037(2)	= U_{12}	= U_{12}

Space group $Fd\bar{3}m$, $a = 8.21218(8)$ Å, $R_{\text{wp}} = 4.59$,

$R_{\text{p}} = 4.05$, $S = R_{\text{wp}}/R_{\text{e}} = 1.2436$, $R_{\text{I}} = 2.05$, $R_{\text{F}} = 2.11$.