Electronic Supplementary Information

Hooked on switch: Strain managed cooperative Jahn–Teller effect in $Li_{0.95}Mn_{2.05}O_4$ spinel

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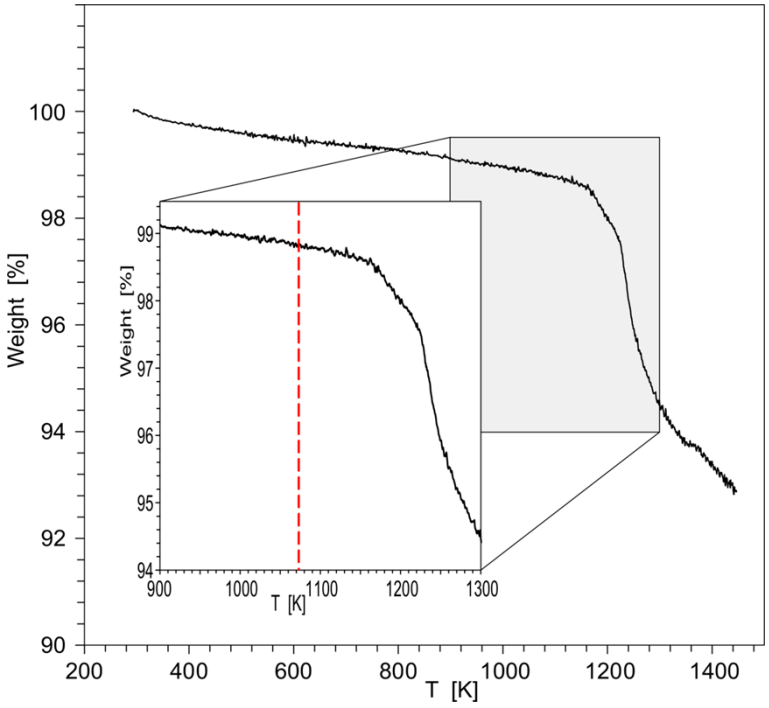

Figure S1. TG curve for $Li_{0.95}Mn_{2.05}O_4$. A dashed line indicates the sintering temperature.

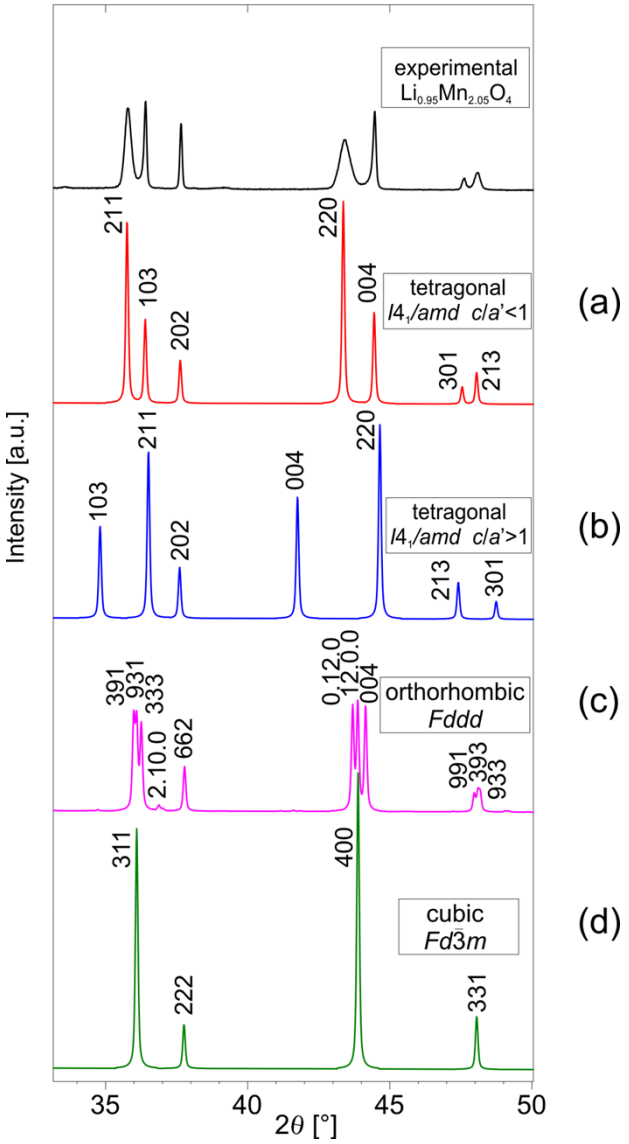

Figure S2. Comparison of the experimental XRD pattern with the patterns calculated for typical structures of lithium-manganese oxides: tetragonal ($I4_1/amd$) $Li_{0.95}Mn_{2.05}O_4$ sample quenched from 1073 K – this study (a); tetragonal ($I4_1/amd$) $LiMn_2O_{3.86}$ synthesized at 1193 K and quenched in liquid N_2 (b)[S1];. orthorhombic (*Fddd*) $LiMn_2O_4$ refined at 230 K (c)[S2]; cubic ($Fd\square m$) $LiMn_2O_4$ obtained at 1173 K in O_2 atmosphere and slowly cooled to room temperature (d)[S1]; Profile function for all calculated patterns is pseudo-Voight without any corrections for microstrain.

Rietveld refinement of laboratory XRD data collected under ambient conditions.

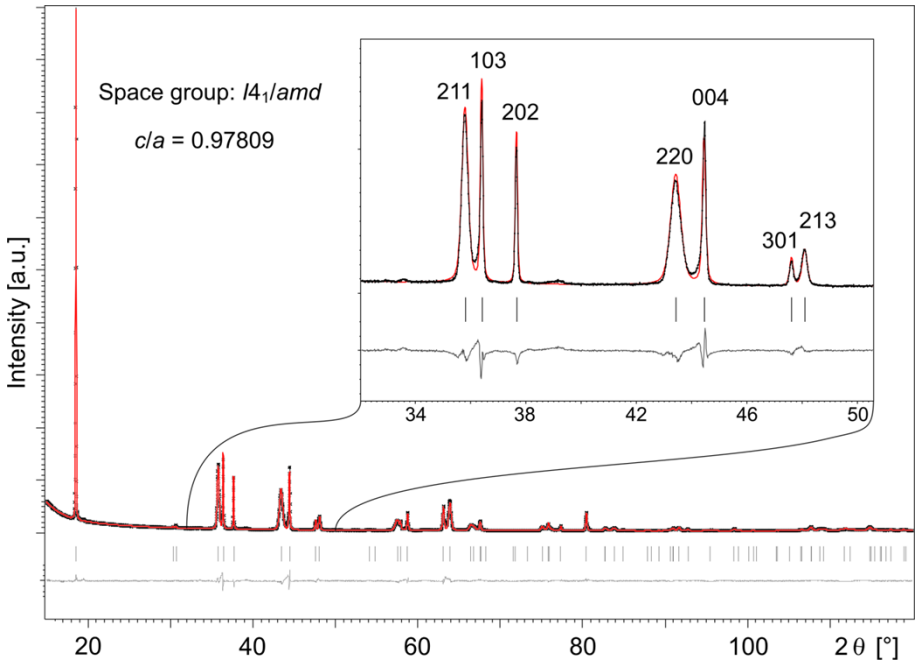

Figure S3. Observed, calculated and difference plot for the tetragonal lithium manganese spinel, $Li_{0.95}Mn_{2.05}O_4$, under ambient conditions.

The unit cell parameters determined under ambient conditions are: a = 5.88602(19) and c = 8.1417(3). Atomic coordinates, selected bond lengths and angles are presented in Tables 3 and 4, respectively. Non negligible discrepancy between expected R and observed Rwp parameters at the final stage of refinement is connected with the use of analytical function to model the pattern. The reason is the observed earlier limitation of using a symmetrical pseudo-Voigt profile function to model the profile function produced by the real system.[S3]

Table S1. Atomic coordinates and displacement parameters resulting from Rietveld refinement of the $Li_{0.95}Mn_{2.05}O_4$ pattern collected under ambient conditions.

	x	*y*	*z*	U_{iso} [Å^2]
Li/Mn (Tetra)	0	0.75	0.125	0.015(2)
Mn (Octa)	0	0	0.5	0.0119(3)
O	0	0.9767(3)	0.7370(2)	0.0185(6)

Space group: $I4_1/amd$; $\chi^2 = 0.0336$, $R_p = 0.0502$, $R_{wp} = 0.0799$; $R_{exp} = 0.0336$

Table S2. Selected interatomic distances and angles resulting from Rietveld refinement of the $Li_{0.95}Mn_{2.05}O_4$ pattern collected under ambient conditions.

Atoms	Distances [Å]
Li(Tetra)–O	1.9623(18)
Mn(Octa)–O1 x2	1.9345(18)
Mn(Octa)–O1 x4	1.9891(12)
	Angles [deg]
O-Li/Mn(Tetra)-O	110.14(7)
O-Li/Mn(Tetra)-O	109.14(4)
O-Mn(Octa)-O	96.06(6)
O-Mn(Octa)-O	180.0(5)
O-Mn(Octa)-O	83.94(6)
O-Mn(Octa)-O	84.25(5)
O-Mn(Octa)-O	95.75(5)

REFERENCES

(S1) R. Kanno, A. Kondo, M. Yonemura, R. Gover, Y. Kawamoto, M. Tabuchi and G. Rousse, The relationships between phases and structures of lithium manganese spinels. *J. Power Sources,* 1999, **81**, 542-546.

(S2) J. Rodriguez-Carvajal, G. Rousse, C. Masquelier and M. Hervieu, Electronic crystallization in a lithium battery material: columnar ordering of electrons and holes in the spinel $LiMn_2O_4$. *Phys. Rev. Lett.,* 1998, **81**, 4660.

(S3) P. Scardi, M. Leoni and Y. H. Dong, Whole diffraction pattern-fitting of polycrystalline fcc materials based on microstructure. *Eur. Phys. J. B,* 2000, **18**, 23-30.

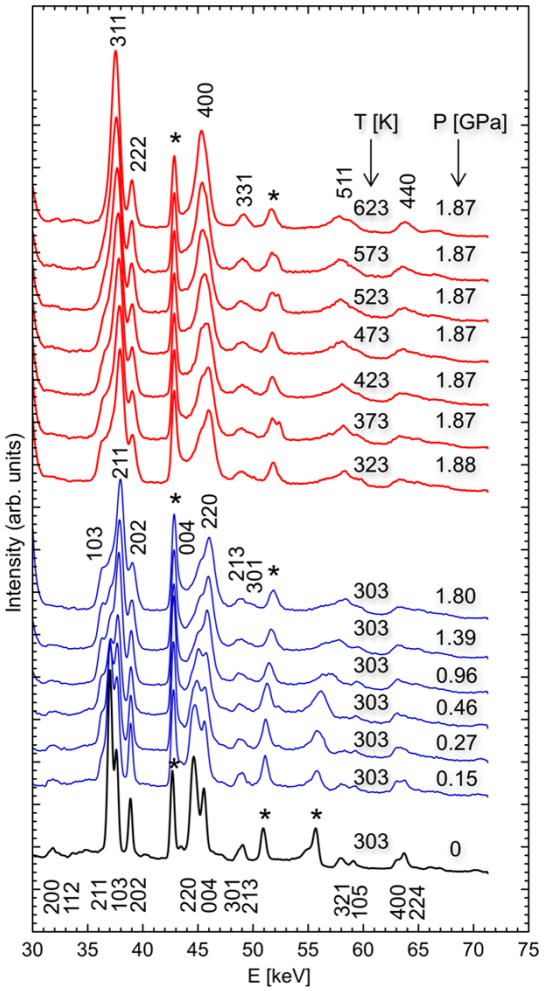

Figure S4. Section of the synchrotron EDXRD patterns obtained *in situ* for $Li_{0.95}Mn_{2.05}O_4$ sample in HP/HT experiment. Indices at the bottom refer to the tetragonal spinel structure ($I4_1/amd$) with $c/a' < 1$, indices in the middle refer to the tetragonal spinel structure ($I4_1/amd$) with $c/a' > 1$, indices above the upper pattern – to the cubic spinel ($Fd\square m$); * indicates the most pronounced reflections of hBN.

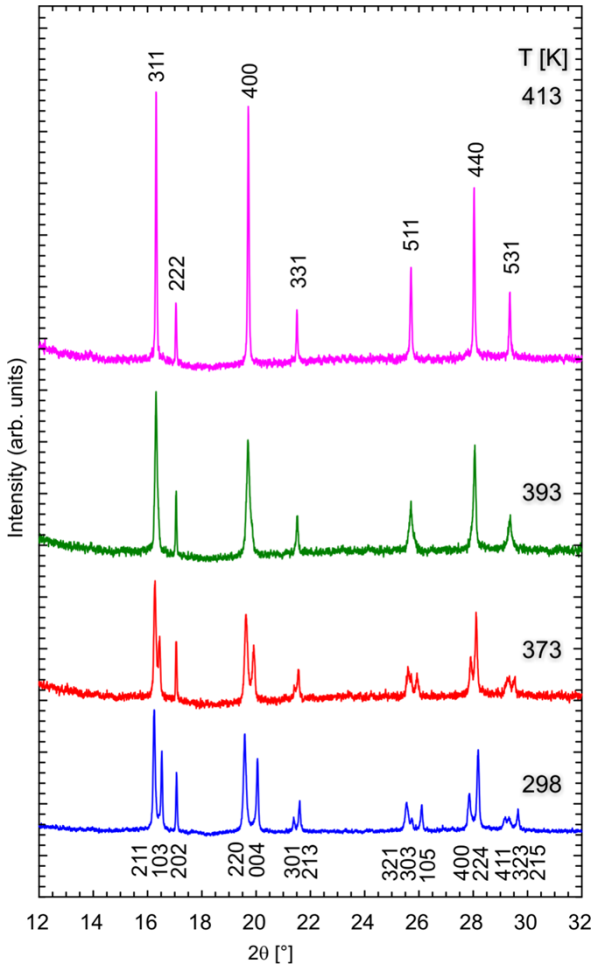

Figure S5. Section of the synchrotron ADXRD patterns obtained *in situ* for $Li_{0.95}Mn_{2.05}O_4$ sample at various temperatures under ambient pressure. Indices at the bottom refer to the tetragonal spinel structure ($I4_1/amd$) with $c/a < 1$, indices above the upper pattern refer to the cubic spinel ($Fd\square m$).