

Unusual compressional behavior of lithium-manganese oxides: A case study of $\text{Li}_4\text{Mn}_5\text{O}_{12}$

Jolanta Darul, Waldemar Nowicki and Paweł Piszora*

Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University,
Grunwaldzka 6, 60-780 Poznań, Poland

*Corresponding Author: Phone: +48 61 8291236; E-mail: jola@amu.edu.pl (J. Darul)

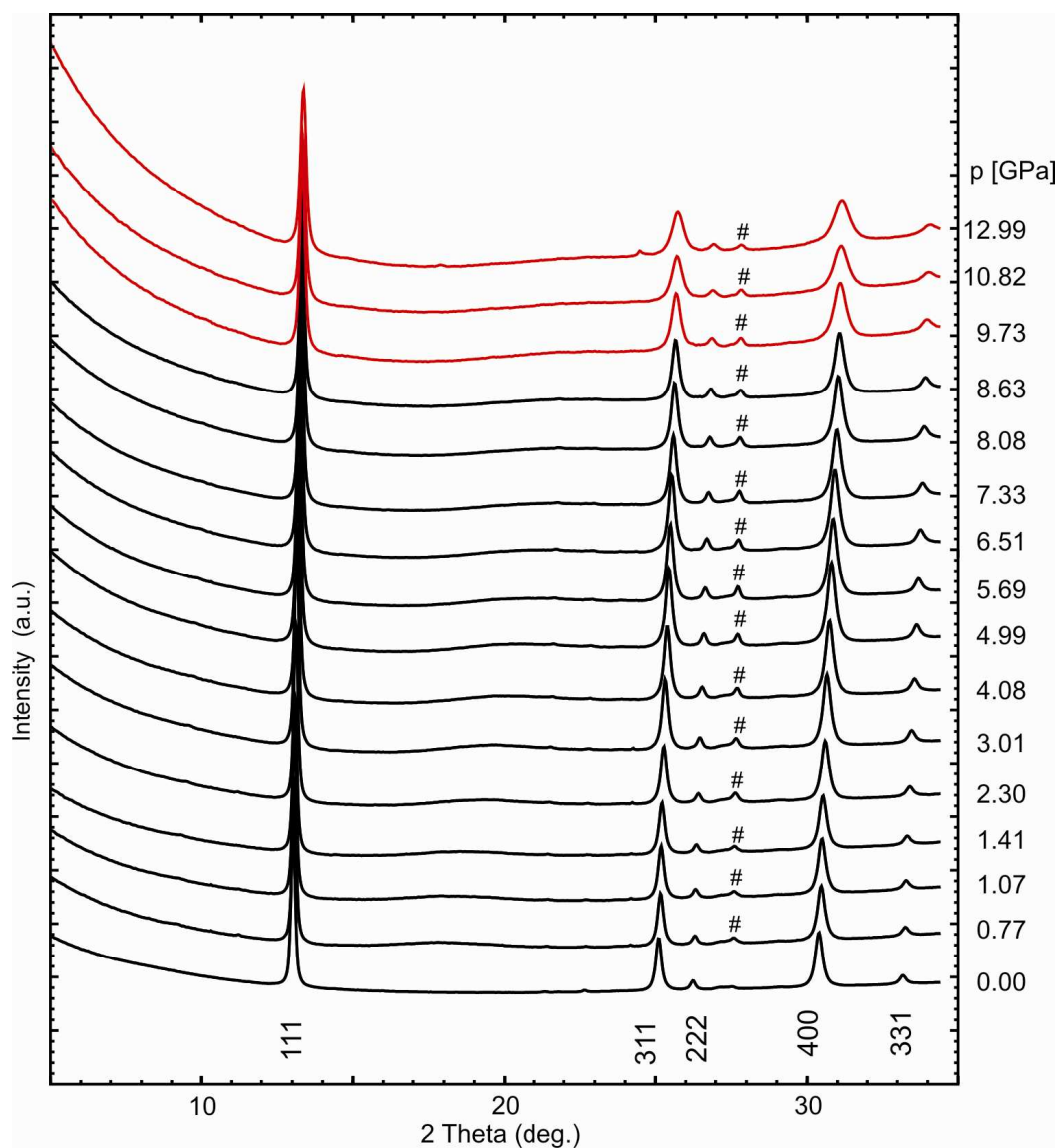


Figure S1. Evolution of the X-ray diffraction patterns of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ powder in a mixture of methanol–ethanol as a function of pressure up to ~ 13 GPa. Systematic shifts toward higher 2θ (smaller d-spacing) were observed at pressures below 8.63 GPa due to the compression of the cubic lattice. Patterns in red are obtained under nonhydrostatic compression. # represents the peak from the tungsten gasket. Miller indices for the spinel cubic phase are given at the bottom.

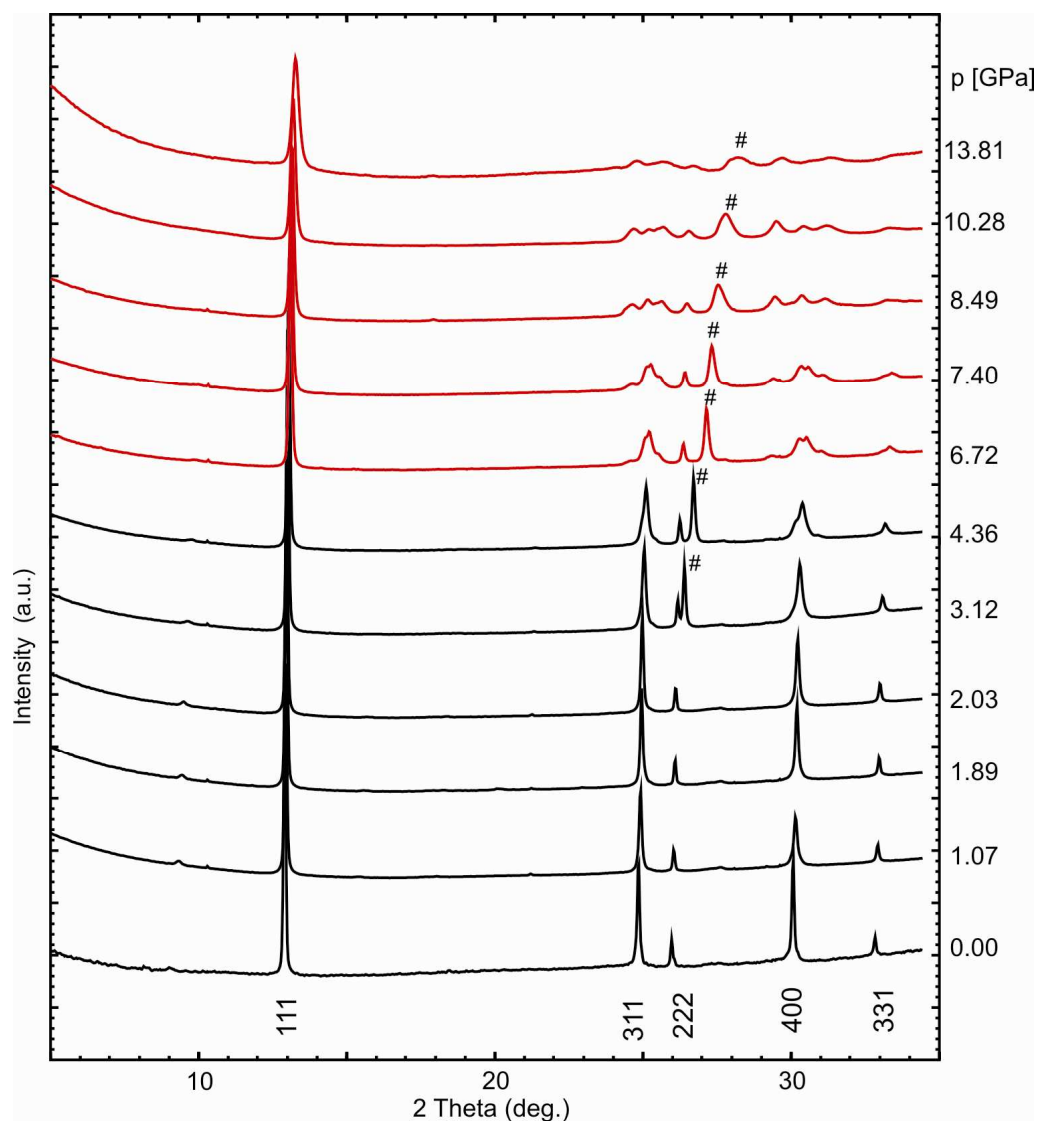


Figure S2. Evolution of the X-ray diffraction patterns of LiMn_2O_4 powder in a mixture of methanol–ethanol as a function of pressure up to ~ 13.8 GPa. Systematic shifts toward higher 2θ (smaller d-spacing) were observed at pressures below 4.36 GPa due to the compression of the cubic lattice. Patterns in red are obtained under nonhydrostatic compression. # represents the peak from the tungsten gasket. Miller indices for the spinel cubic phase are given at the bottom.

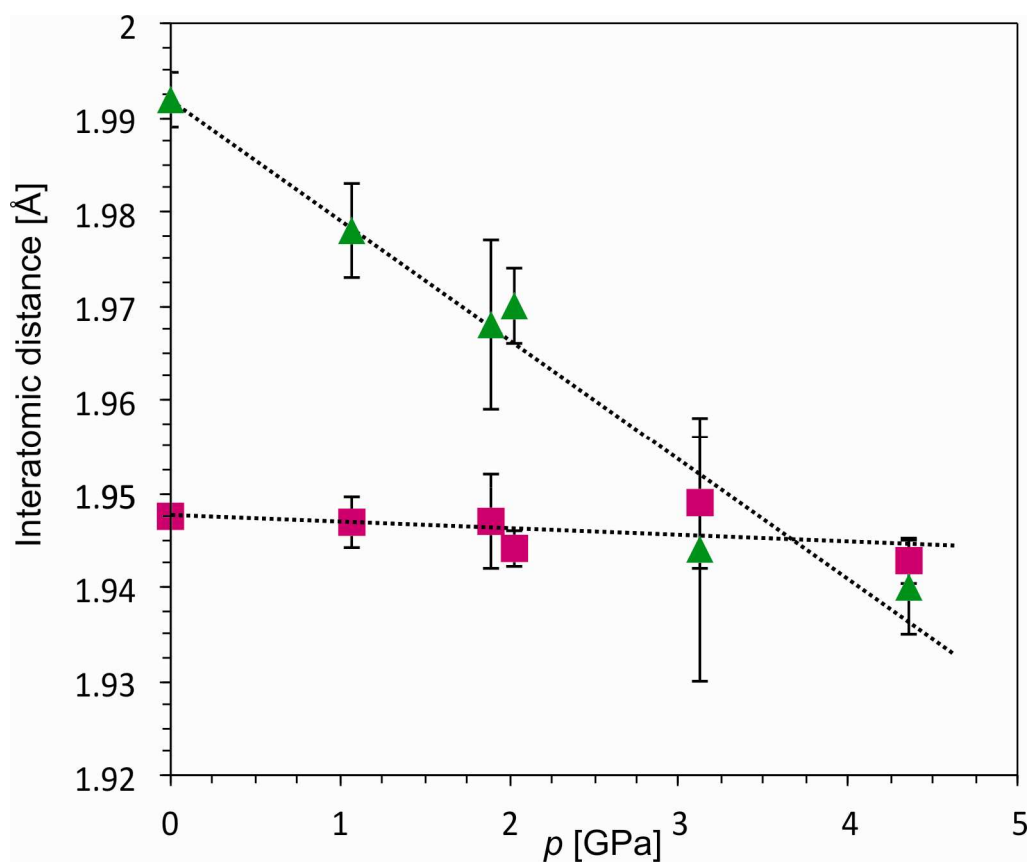


Figure S3. Interatomic distances in LiMn_2O_4 as a function of pressure; square - $(\text{Mn,Li})\text{O}_6$ octahedra, triangle - LiO_4 tetrahedra.

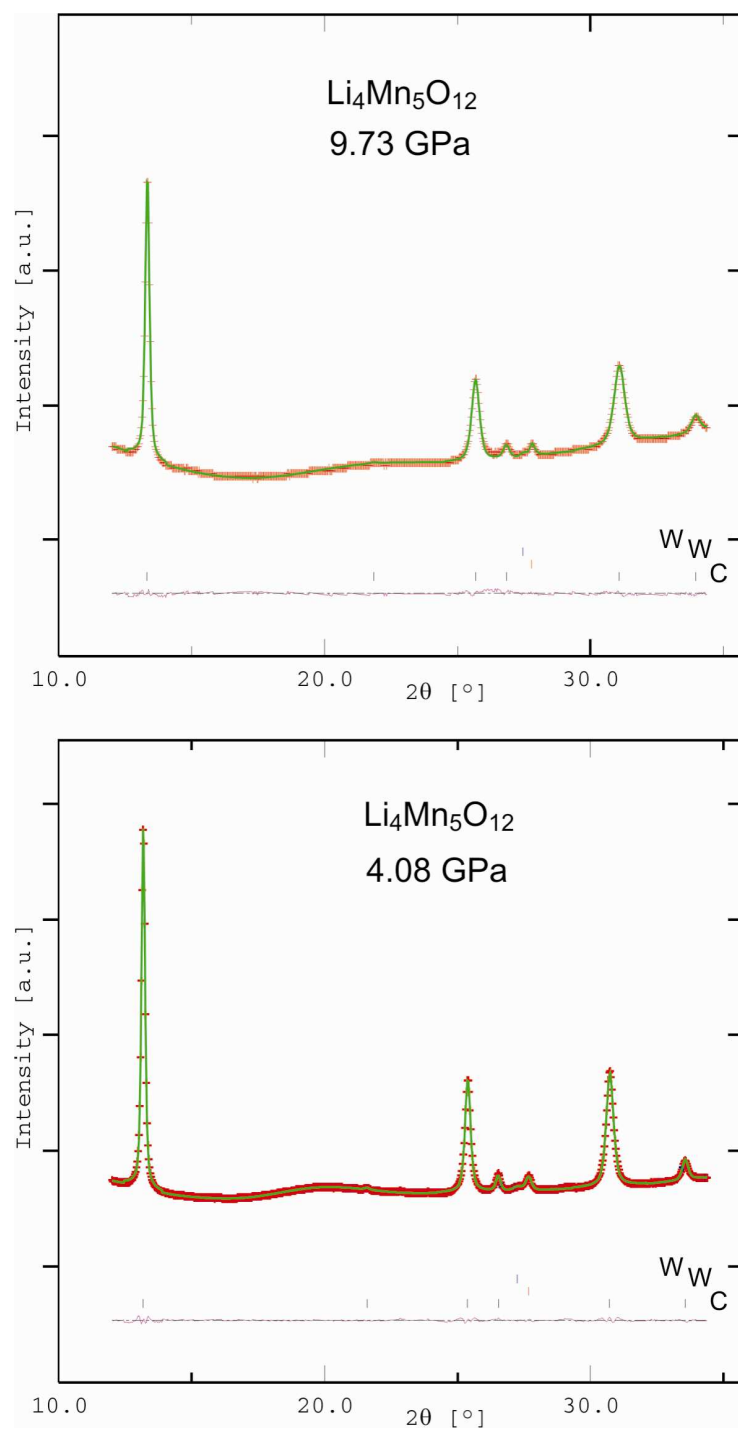


Figure S4. Structure refinement of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ spinel ($Fd3m$, Nr. 227; $Z = 8$; pressure 4.08 GPa: $a = 8.05873$ (9) Å, $u = 0.26154$ (9); pressure 9.73 GPa: $a = 7.9707$ (6) Å, $u = 0.2606$ (1)) showing observed (red crosses) and calculated (green solid line) intensities. Tick marks refer to $\text{Li}_4\text{Mn}_5\text{O}_{12}$ – C and tungsten gasket – W.

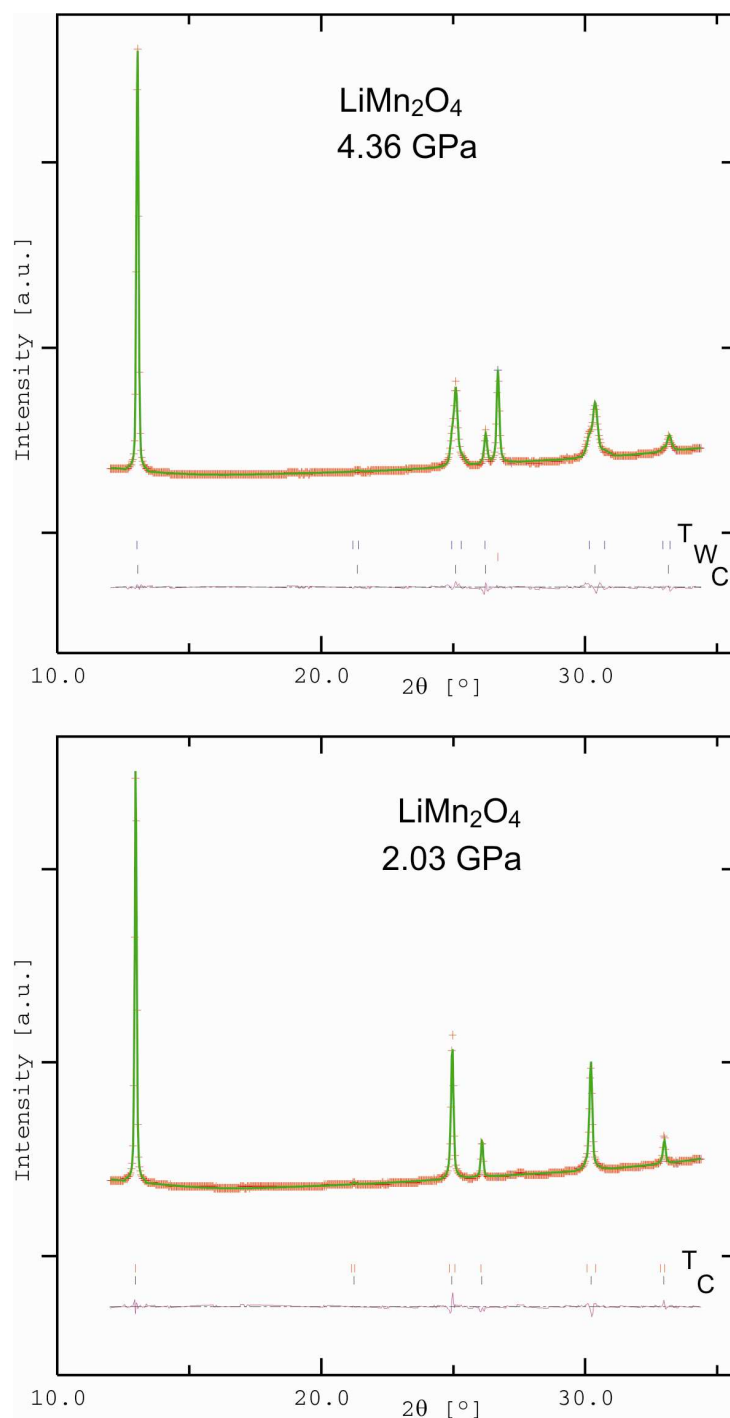


Figure S5. Structure refinement of LiMn_2O_4 spinel showing observed (red crosses) and calculated (green solid line) intensities. Tick marks refer to $\text{LiMn}_2\text{O}_4 - \text{C}$ ($Fd3m$, Nr. 227; pressure 2.03 GPa: $a = 8.1992(2)$ Å, $u = 0.2636(3)$; pressure 4.36 GPa: $a = 8.1544(3)$ Å, $u = 0$).

2624(3)), – T ($I4_1/amd$, Nr. 141; pressure 4.36 GPa: $a = 5.8078(6)$ Å, $c = 8.060(2)$) and tungsten gasket – W.