

# *In-situ* investigations of $\text{LiMn}_2\text{O}_4$ at high pressure

Paweł Piszora

Laboratory of Magnetochemistry, Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, PL-60780 Poznań, Poland

\* Contact author; e-mail: pawel@amu.edu.pl

**Keywords:** energy-dispersive X-ray powder diffraction, spinel structure, bulk modulus.

**Abstract.** In energy-dispersive X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$  additional diffraction peaks appear for pressures as low as 0.2 GPa. The new diffraction pattern is indexed with the tetragonal  $F4_1/d\text{dm}$  space group. Furthermore, the role of different pressure media is discussed and tested in order to get quasihydrostatic conditions. The calculated parameters of the Vinet equation of state for pseudo-hydrostatic conditions reveal relatively high compressibility of  $\text{LiMn}_2\text{O}_4$ .

## Introduction

Lithium-manganese oxides are of interest as lithium insertion electrodes for rechargeable lithium batteries [1]. The stoichiometric  $\text{LiMn}_2\text{O}_4$  [2], the lithium-deficient  $\text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_4$  [3] and the lithium-excess  $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$  [4] undergo several phase transitions as temperature varies. Moreover, various crystal structures have been observed in the lithium-deficient  $\text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_4$  series [5] and in the lithium-deficient iron-substituted series [6]. A slight lithium-ions deficiency causes the tetragonal phase formation, if the samples obtained at high temperature are rapidly cooled in the solid  $\text{CO}_2$ . On the contrary, a very small amount of excess lithium can influence the cubic→orthorhombic phase transition observed for stoichiometric  $\text{LiMn}_2\text{O}_4$ .

While the temperature-induced phase transitions of  $\text{LiMn}_2\text{O}_4$  have been extensively studied, its behaviour at high pressure and high temperature has not been investigated thoroughly. First high-pressure experiments on lithium manganese spinels have been undertaken by Jak *et al.* [7]. They applied a dynamic compaction method, nevertheless no significant structural changes have been observed after the pressure release from 25 GPa. The preliminary *in-situ* high-pressure experiment, performed on  $\text{LiMn}_2\text{O}_4$  with the energy-dispersive multi-anvil setup under pressure of 0 – 2.6 GPa, revealed a cubic to tetragonal phase transition [8].

The dependence of the diffraction profile on pressure has provided evidence of the phase transition, nevertheless the nature of this transition seems to be not so clear [9]. The reported pressure-dependent cubic→orthorhombic phase transition has been concluded from profile broadening of the cubic 311 and 400 reflections compared to 111 and 222 lines. Unfortunately, low resolution has not permitted to observe the splitting of those lines. Furthermore, asymmetric line profiles were not taken into consideration, which may also suggest the exis-

tence of tetragonal rather than the orthorhombic phase. The transition pressure value at ambient temperature, obtained from the above mentioned relative profile broadening has been estimated at  $1.8 \pm 0.4$  GPa. Based on line broadening after pressure relaxation, those authors have concluded the formation of a metastable non-cubic phase.

## Results

$\text{LiMn}_2\text{O}_4$  sample was prepared by conventional solid-state reaction of  $\text{Li}_2\text{CO}_3$  with  $\alpha\text{-Mn}_2\text{O}_3$  (*Ia3*, bixbyite structure) at 923 K. The energy-dispersive X-ray diffraction experiments were undertaken at beamline F2.1 (DESY/HASYLAB). The sample was mounted in a boron nitride (hBN) cylinder in the middle of a cube of boron-epoxy mixture. The cube was located

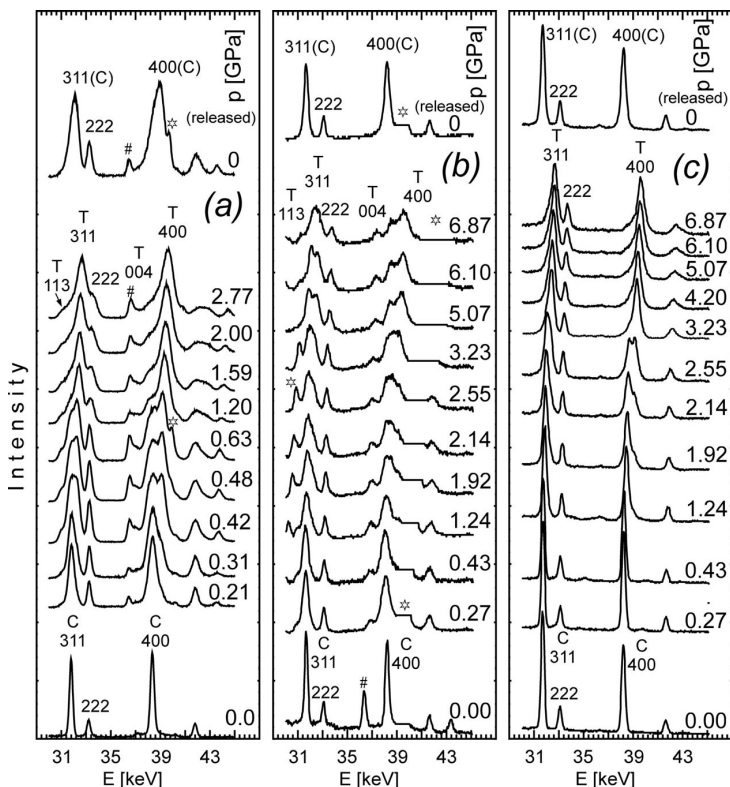


Figure 1. Section of energy-dispersive X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$  for different pressure-transmitting media: (a) – hexagonal boron nitride (hBN); (b) – NaCl; (c) – silicone gel. The reflections marked by \* and # symbols are due to NaCl and hBN respectively. In case of NaCl as the pressure medium, the region of  $220_{\text{NaCl}}$  reflection has been excluded.

between six anvils of the MAX80 press. The measurements were carried out at room temperature, in the pressure range from ambient to 7 GPa. Three different pressure-transmitting media were applied successively: hexagonal boron nitride (hBN), sodium chloride and silicone gel. Le Bail fitting, implemented in FullProf program [10], was used to refine the unit-cell size of sample diluted in hBN. For measurements in NaCl and silicone gel the fitting of single reflections with WinPlotr program was used [11] to obtain the unit-cell volume change with pressure. Phase identification of released samples was based on measurements performed at beamline I711, MAX-lab (Lund).

Non-negligible in these pressure investigations are the role of pressure-transmitting medium, and the level of the pressure hydrostaticity. The hexagonal boron nitride is considered to be a relatively 'soft' material and has been often used as the medium. However, first experiments with  $\text{LiMn}_2\text{O}_4$  diluted with this substance showed significant line broadening at pressures above 2 GPa (Figure 1). The second applied solid pressure-transmitting medium, NaCl, gave better hydrostaticity, but unfortunately the diffraction lines of this crystal phase, much higher in magnitude than of the diluted spinel sample, coincide with reflections of the spinel phases. Finally, the silicone gel was applied, eliminating the above-mentioned disadvantages.

### $\text{LiMn}_2\text{O}_4$ in hBN as pressure-transmitting medium

Le Bail fitting of energy-dispersive X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$  in hBN medium allowed for indexing of high-pressure phase (phase II) with  $F4_1/ddm$  space group (Figure 2). The phase II is detectable for pressure as low as 0.2 GPa, and its concentration increases rapidly with pressure up to 85% for 3.2 GPa (Figure 3). At these non-hydrostatic conditions one can observe deviation of the line-intensity ratio  $I_{400}/I_{004}$  of the phase II from the expected 2:1 value. The reason of this effect is not clear, nevertheless, it could be a consequence of preferred orientation and the  $hkl$  dependent stacking faults. The broadening of lines with indices  $h \neq k \neq l$  can be also observed in the cubic phase I ( $Fd3m$ ). For pressure exceeding 0.36 GPa (over 40% of phase II) the model of initial cubic phase was replaced with

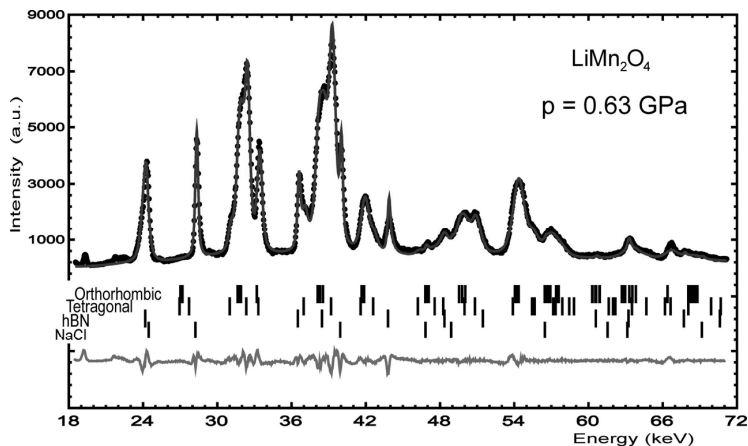


Figure 2. Le Bail fitting of energy-dispersive X-ray diffraction pattern of  $\text{LiMn}_2\text{O}_4$  diluted with hBN.

the orthorhombic one ( $Fddd$ ), what significantly improved the R factors. Notwithstanding, it is not possible to distinguish between the slight peak splitting (as a result of the symmetry lowering to orthorhombic), and the line broadening due to the deviatoric stress. To keep the refinement more reasonable, the  $a$ ,  $b$  and  $c$  unit-cell parameters of this hypothetical orthorhombic phase were linearly constrained 1:1:1 ( $a,b,c$ ).

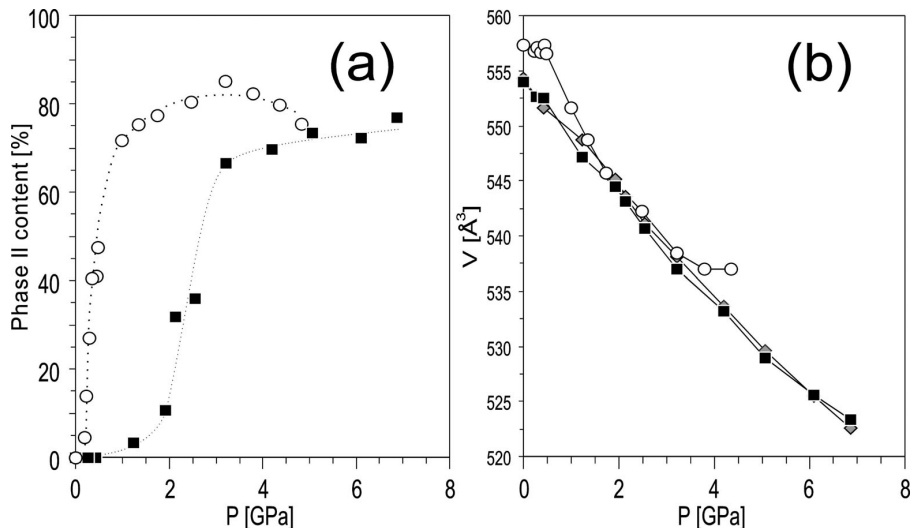


Figure 3. Percentage of phase II (a), and unit cell volume (b) evaluated from  $(I_{113(\sigma)} + I_{311(\sigma)}) / (I_{113(\sigma)} + I_{311(\sigma)} + I_{311(\zeta)}) * 100$  of energy-dispersive X-ray diffraction patterns: ○ – obtained from the Le Bail for LiMn<sub>2</sub>O<sub>4</sub> diluted with hBN; resulting from single reflection fitting with pseudo-Voigt function for LiMn<sub>2</sub>O<sub>4</sub>: ◆ – in NaCl; ■ – in the silicone gel medium.

### LiMn<sub>2</sub>O<sub>4</sub> in NaCl and in silicone gel as pressure medium

The  $Fd3m$  phase (phase I), which is stable at ambient conditions, is retained up to at least 6.9 GPa. A transition into a high-pressure phase, with space group  $F4_1/ddm$  (phase II), is observed to occur above 1.2 GPa.

The parameters of the Vinet equation of state (Table 1) calculated for pseudo-hydrostatic conditions (Figure 3b) reveal a relatively high compressibility of LiMn<sub>2</sub>O<sub>4</sub>. Recently, the bulk moduli of spinel type oxides have been discussed [12]. What is interesting, all of those spinels, independent of the cation composition, have bulk modulus value in the range from 196 GPa to 206 GPa. Theoretical calculations have suggested the bulk modulus for LiMn<sub>2</sub>O<sub>4</sub> to be in a similar range [13]. However, another review [14] has revealed that this limit is not fixed for all spinel oxides, and e.g. for hausmannite (Mn<sub>3</sub>O<sub>4</sub>), with the tetragonally deformed spinel structure, bulk modulus can be as low as 137.0(3.8) GPa [15]. The lowest bulk modulus of LiMn<sub>2</sub>O<sub>4</sub> for all compressed spinel oxides could be a consequence of ordering of Mn<sup>3+</sup>O<sub>6</sub> octahedra with pressure.

Rietveld refinement of X-ray diffraction patterns of released samples revealed the presence of pure cubic LiMn<sub>2</sub>O<sub>4</sub> phase, in case of silicone gel as the pressure medium, and a profile

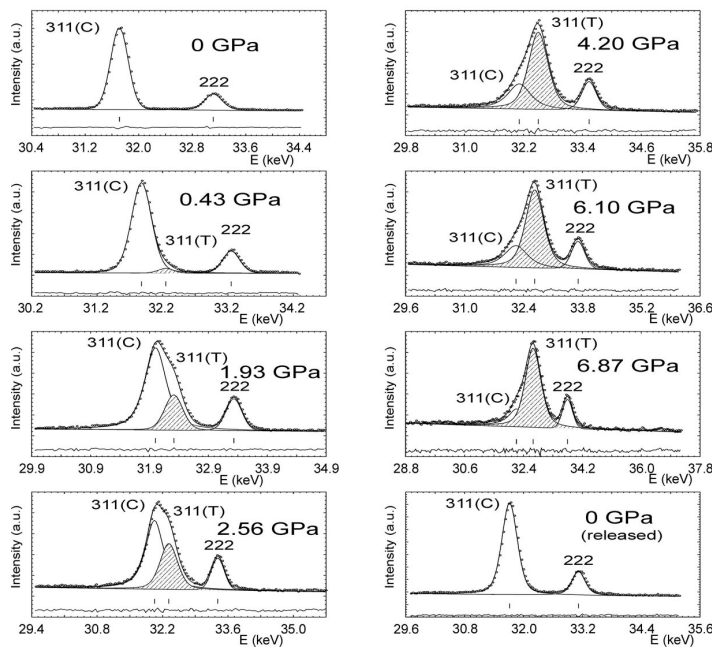


Figure 4. The range of 311 and 222 cubic spinel lines and results of fitting with the pseudo-Voigt function for  $\text{LiMn}_2\text{O}_4$  diluted with silicone gel medium.

Table 1. Parameters of the Vinet equation of state for the two high-pressure phases of  $\text{LiMn}_2\text{O}_4$ , calculated with EOS program [16]. Bulk moduli  $K_0$  are in GPa.

Vinet EoS	$V_0(\text{\AA})^*$	$K_0(\text{GPa})$	$K'(\text{fixed})$	$R_w(\%)$
Whole range 0 – 6.87 GPa	560.8(2)	103(1)	4	2.77
Pressure range with major phase I 0 – 1.92 GPa	560.66(6)	111(2)	4	1.92
Pressure range with major phase II 2.14 – 6.87 GPa	560.3(5)	105(3)	4	1.96

\* corrected for the ambient-pressure unit cell volume from [3]

splitting of the cubic spinel lines, for the sample that had been compressed in hBN. The sample from these non-hydrostatic conditions could be considered in Rietveld refinement as the mixture of cubic and tetragonal polymorphs of this lithium manganese oxide.

### Concluding remarks

The high-pressure phase transition was predefined as the cubic→tetragonal symmetry reduction. The zero-pressure bulk modulus,  $K_0$ , of  $\text{LiMn}_2\text{O}_4$  was experimentally determined for the first time and found to be much lower than that seen for common spinel oxides.

## References

1. Tarascon, J.M., & Armand, M., 2001, *Nature*, **414**, 359.
2. Rodríguez-Carvajal, J., Rousse, G., Masquelier, C., & Hervieu, M., 1998, *Phys. Rev. Lett.*, **81**, 4660.
3. Piszora, P., 2005, *J. Alloys Compd.*, **401**, 34.
4. Wolska, E., Piszora, P., Darul, J., & Nowicki, W., 2004, *J. Phys. Chem. Solids*, **65**, 223.
5. Piszora, P., 2006, *Chem. Mater.*, **18**, 4802.
6. Piszora, P., Nowicki, W., Darul, J., & Wolska, E., 2004, *Mater. Lett.*, **58**, 1321.
7. Jak, M.J.G., Kelder, E.M., Stuivinga, M., & Schoonman, J., 1996, *Solid State Ionics*, **86-88**, 897.
8. Piszora, P., Paszkowicz, W., Nowicki, W., Minikayev, R., & Lathe, C., 2003, *HASYLAB Annual Report*, p. 309.
9. Paolone, A., Sacchetti, A., Postorino, P., Cantelli, R., Congeduti, A., Rousse, G., & Masquelier, C., 2005, *Solid State Ionics*, **176**, 635.
10. Rodríguez-Carvajal, J., FULLPROF version June 2005, ILL (unpublished).
11. Roisnel, T., & Rodríguez-Carvajal, J., 2000, *Mater. Sci. Forum*, **321-324**, 118.
12. Gerward, L., Jiang, J.Z., Olsen, J.S., Recio, J.M., & Waśkowska, A., 2005, *J. Alloys Compd.*, **401**, 11.
13. Grechnev, G.E., Ahuja, R., Johansson, B., & Eriksson, O., 2002, *Phys. Rev. B*, **65**, 174408.
14. Knittle, E., 1995, in *Mineral Physics and Crystallography: A Handbook of Physical Constants*, edited by T.J. Ahrens (Washington: American Geophysical Union Press.), pp. 98.
15. Paris, E., Ross, C.R., & Olijnyk, H., 1992, *Eur. J. Mineral.*, **4**, 87.
16. R. Angel, 2000, in *High-pressure and High-temperature Crystal Chemistry. MSA Reviews in Mineralogy and Geochemistry*, edited by R.M. Hazen, & R.T. Downs, vol. **41**, p. 35.

**Acknowledgements.** Fruitful discussions with Prof. E. Wolska are gratefully acknowledged. The author would like to thank Dr. Thomas Ursby from MAX-lab (Lund), Dr. Christian Lathe from DESY/HASYLAB, Dr. Jolanta Darul and Dr. Waldemar Nowicki for assistance during the measurements. This work was partially supported by The Committee for Scientific Research (KBN) under grant No 128/E-336/SPB/DESY/KN/DWM/08/2005-2006. The author is grateful for the support from the European Community - Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science".) by DESY/HASYLAB and by MAX-Lab (Contract RII3-CT-2004-506008).