

DIFFRACTION HP/HT STUDY OF  $\text{LiMn}_2\text{O}_4$ P. Piszora<sup>1\*</sup>, J. Darul<sup>1</sup>, W. Nowicki<sup>1</sup>, and C. Lathe<sup>2</sup><sup>1</sup> Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland<sup>2</sup> GeoForschungsZentrum Potsdam, Telegrafenberg A17, D-14473 Potsdam, Germany

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Rechargeable lithium batteries with lithium-manganese spinel as a cathode material are state-of-the-art power sources for consumer electronics and automotive applications [1]. Knowledge of the properties of the lithium-manganese oxides under the conditions of high temperatures and pressures is of fundamental concern to solid-state chemistry and is important for the battery materials manufacturing. The *in-situ* high-pressure experiment, performed on  $\text{LiMn}_2\text{O}_4$  with the energy-dispersive multi-anvil setup, have revealed cubic to tetragonal phase transition of  $\text{LiMn}_2\text{O}_4$  [2]. The effect of a hydrostatic pressure on the crystal structure of  $\text{LiMn}_2\text{O}_4$  has been studied by measuring the X-ray diffraction pattern along three isotherms at 350, 385 and 415 K [3], whereas pressure has been obtained with a diamond anvil cell in the range between 0 and 20 GPa. At the pressure of 1.8 GPa and at 350 K the cubic→orthorhombic phase transition, similar to that observed during cooling of  $\text{LiMn}_2\text{O}_4$ , has been reported, nevertheless the nature of this transition seemed to be not clear. Rietveld refinement of the X-ray diffraction pattern collected of the  $\text{LiMn}_2\text{O}_4$  sample mounted in a diamond-anvil cell revealed that the high-pressure polymorphs have tetragonal structures ( $F4_1/ddm$ ) [4]. However, it has been also observed by Paolone *et al.* [3] that at ~10 GPa and at 415 K,  $\text{LiMn}_2\text{O}_4$  transformed into a new phase,

which persisted also when the external pressure was released. The high-pressure high-temperature structure of lithium manganese oxide has been studied *ex-situ* by X-ray diffraction method after compression at 6 GPa and heating above 1373 K [5]. The new  $\text{CaFe}_2\text{O}_4$ -type ( $Pnma$ ) structure of the lithium-manganese oxide, stable at ambient condition, has been reported.

$\text{LiMn}_2\text{O}_4$  sample was obtained by the solid state reaction of  $\text{Mn}_2\text{O}_3$  with  $\text{Li}_2\text{CO}_3$  at 1073 K. The phase transitions in  $\text{LiMn}_2\text{O}_4$  were investigated at high pressure and high temperature (HP/HT) up to 4 GPa and 1500 K with *in-situ* X-ray diffraction measurements at the synchrotron beamline F2.1 (DESY/HASYLAB).

The cubic ( $Fd3m$ ) lithium-manganese spinel transforms to the tetragonal phase ( $F4_1/ddm$ ) at 3 GPa and 300 K. The tetragonal phase transforms again to a cubic HP/HT structure at about 4 GPa and at 648 K. Some new additional diffraction peaks were observed at about 4 GPa and in the temperature region of 748 – 773 K. Subsequently, at 873 K diffraction lines from the spinel-like phase vanished and some new intense diffraction lines of the HP/HT phase can be observed. Neither  $\text{CaFe}_2\text{O}_4$ -type nor orthorhombic structures, previously proposed as HP or HP/HT phase, were observed in the applied pressure and temperature range.

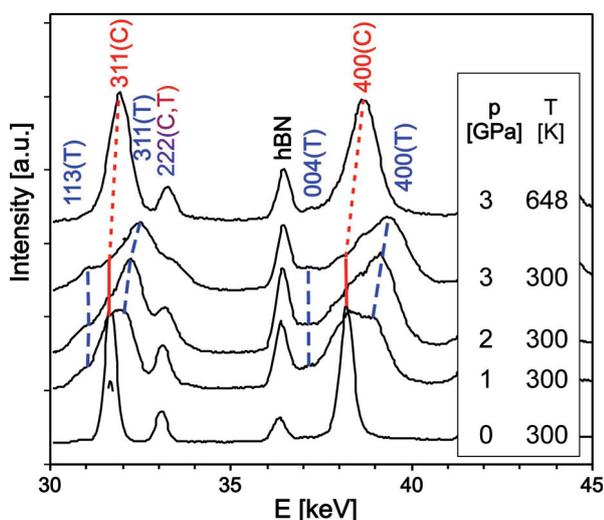


Figure 1. Section of the energy-dispersive X-ray diffraction pattern of  $\text{LiMn}_2\text{O}_4$  at varied pressure and temperature. C and T are for cubic ( $Fd3m$ ) phase and tetragonal phase with  $c/a > 1$  ( $F4_1/ddm$ ), respectively.

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