

# Hexagonal Boron Nitride as the Pressure Medium in Examination of High-Pressure Structure of $\text{LiMn}_2\text{O}_4$

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Lithium-manganese oxides with the spinel structure are of interest as lithium insertion electrodes for rechargeable lithium batteries [1]. It is established that at ambient pressure the cubic-orthorhombic phase transition for pure  $\text{LiMn}_2\text{O}_4$  occurs at about 280 K. Lithium deficient  $\text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_4$  samples obtained at 800°C and quenched rapidly in the solid  $\text{CO}_2$  exhibit two kind of tetragonal structures with  $c/a > 1$  and  $c/a < 1$  [2]. First high-pressure experiments on lithium manganese spinels had been undertaken by Jak *et al.* [3], and no significant structural changes had been observed after the sample relaxation from as high pressure as 25 GPa. 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  $\text{LiMn}_2\text{O}_4$  [4,5]. Later experiments have suggested a cubic→orthorhombic phase transition, similar to that observed during cooling of  $\text{LiMn}_2\text{O}_4$ , nevertheless the nature of this transition seemed to be not clear [6]. The high-pressure high-temperature structure of lithium manganese oxide has been studied recently *ex-situ* by X-ray diffraction method after compression at 6 GPa and heating above 1100°C [7].

In the high-pressure investigations a level of the pressure hydrostaticity due to applied pressure medium is very important. The hexagonal boron nitride is considered to be a relatively ‘soft’ material and has been often used as the pressure medium.

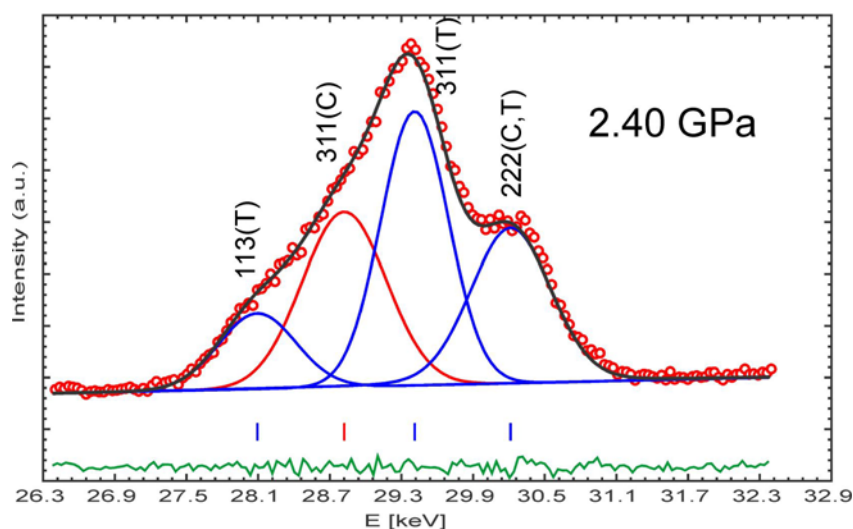


Figure 1. Section of the energy-dispersive X-ray diffraction pattern of  $\text{LiMn}_2\text{O}_4$ , diluted with h-BN (1:5), fitted with the Fullprof program. T – tetragonal phase ( $F4_1/d\bar{d}m$ ); S – cubic phase ( $Fd\bar{3}m$ ).

$\text{LiMn}_2\text{O}_4$  ( $Fd\bar{3}m$  space group) sample was obtained by conventional solid state reaction of  $\text{Li}_2\text{CO}_3$  with  $\alpha\text{-Mn}_2\text{O}_3$  ( $Ia\bar{3}$ , bixbyite structure) at 1073 K. The synchrotron X-ray powder diffraction data at ambient conditions confirmed the cubic spinel structure. The samples were mounted in a boron nitride (h-BN) cylinder, in boron-epoxy cube with the edge length 8 mm. The cube was located in between six anvils of the MAX80 press. The samples were diluted with either sodium chloride or h-BN in order to get quasihydrostatic conditions. The measurements were carried out at room temperature in the pressure range from ambient to 4.59 GPa. The measurements were performed with the energy dispersive experimental setup and a white synchrotron radiation at F2.1 beamline (Hasylab). The X-ray detection system was based on a germanium solid-state detector of resolution 135eV at 6.3 keV.

At the pressure above 2 GPa the experiments with  $\text{LiMn}_2\text{O}_4$  diluted with h-BN showed the line broadening (Figure 1). Looking for the better pressure medium we have performed an experiment with lithium manganese spinel diluted with NaCl. Despite better hydrostaticity, diffraction lines of this crystal phase, much higher in magnitude than of diluted spinel sample, coincide with reflections of the spinel. Therefore, we decided to return back to hexagonal boron nitride as the pressure medium, and to perform high-pressure experiments on  $\text{LiMn}_2\text{O}_4/\text{h-BN}$  with three weight ratio: 1:1, 1:2, and 1:5. A reduction of the h-BN concentration did not significantly improve the hydrostaticity. The pressure of phase transition in the lithium-manganese spinel was not affected by the concentration, as it could be expected (Figure 2).

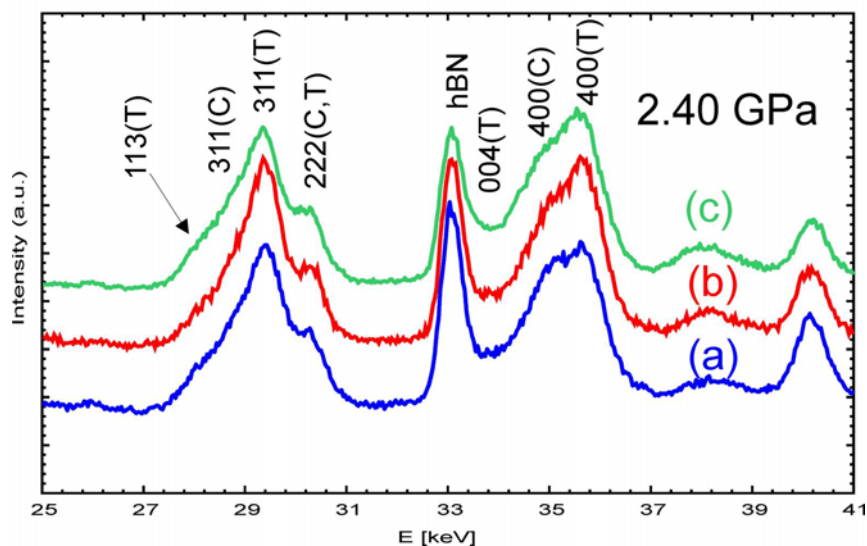


Figure 2. Section of the energy-dispersive X-ray diffraction pattern of  $\text{LiMn}_2\text{O}_4$ , diluted with different sample to h-BN ratio: 1:1 (a); 1:2 (b); 1:5 (c).

The symmetry lowering, arising in the compressed  $\text{LiMn}_2\text{O}_4$  sample, can be attributed to a pressure-induced orientation of  $\text{Mn}^{3+}\text{O}_6$  octahedra in the  $c$ -axis direction, similar to that observed in lithium-deficient  $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$  samples. The observed  $c/a$  axial ratio suggests the structure deformation analogous to that induced by the lithium deficit. Comparison of X-ray diffraction results collected during compression of  $\text{LiMn}_2\text{O}_4$  in sodium chloride and in h-BN, suggest significant sensitivity of the pressure phase transition to a pressure medium. However, there are no difference in pressure of the phase transition if concentration of the lithium-manganese spinel is between 1:1 and 1:5.

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