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IN-SITU HIGH-PRESSURE OBSERVATION OF JAHN-TELLER EFFECT IN LITHIUM-MANGANESE OXIDES

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A secondary battery is a crucial part of portable and high-performance electrical devices such as personal computers, mobile phones, digital cameras, and video movies. The high cost and high toxicity of cobalt has created enormous interest in development of less expensive, environmentally benign manganese-based cathodes as an alternative to cobalt-based cathodes for rechargeable lithium batteries. The spinel oxides, $Li_xMn_{3-x}O_4$ are being intensively pursued in this regard.

$LiMn_2O_4$ shows two plateaus in voltage versus capacity plots. For one of them, around 3 V, one can observe drastic capacity fading upon cycling due to the macroscopic volume change associated with a cooperative Jahn-Teller distortion. The cyclability can be improved by increasing the average oxidation state of manganese through a substitution of lithium for manganese in $Li_{1+x}Mn_{2-x}O_4$. Such substitutions suppress Jahn-Teller distortions. $Li_4Mn_5O_{12}$ is known to show better cyclability in the 3 V region than $LiMn_2O_4$. Likewise, a cubic symmetry can be preserved at low temperature due to lithium insertion into the manganese lattice sites.

Table 1. Selection of the high-pressure experiments and the average valency of manganese.

Li-Mn oxides	Mn valency	HP Ref.
$LiMn_2O_4$	3.5	[1, 2]
$LiMnO_2$	3	[3]
$Li_xMn_{3-x}O_4$	3.35 - 3.50	[4]
$Li_{0.92}Mn_2O_4$	3.54	[5]
$Li_4Mn_5O_{12}$	4	–

The relevance of the lithium manganese oxides to electrochemistry and to many another applications merits a deeper understanding of the materials. Among several kinds of lithium manganese oxides, the high pressure (HP) properties of the end member of the spinel structure type, $Li_4Mn_5O_{12}$, is of high interesting. In compounds with average valency of manganese less than 4, Mn^{3+} ions give a Jahn-Teller distortion to the regular MnO_6 octahedron, as Mn^{3+} ions are in a high-spin state with the electronic configuration $t_{2g}^3e_g^1$. The cooperative Jahn-Teller distortion due to Mn^{3+} ions plays a significant role in determining the high-pressure crystal structure of many lithium-manganese oxides (Table 1). $Li_4Mn_5O_{12}$ is in this context an ideal reference material for the high-pressure experiments (Fig. 1).

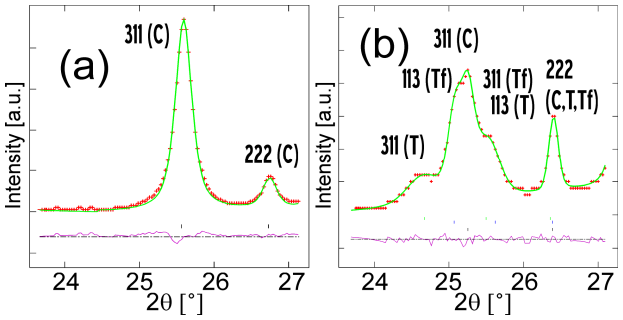

Figure 1. The most representative 2Θ region of the Rietveld refinement of $Li_4Mn_5O_{12}$ (a) and $LiMn_2O_4$ (b) at 7.5 GPa. Indices refer to $Fd3m$ (C) and $F4_1/ddm$ (T and Tf) space groups.

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References

[1] A. Paolone, A. Sacchetti, P. Postorino, R. Cantelli, A. Congeduti, G. Rousse, C. Masquelier, "Stabilization of an orthorhombic phase in $LiMn_2O_4$ by means of high pressure", *Solid State Ionics* **176** (2005) 635-639.

[2] P. Piszora, "*In-situ* investigations of $LiMn_2O_4$ at high pressure", *Z. Kistallogr.* **S26** (2007) 387-392.

[3] J. Sugiyama, T. Noritake, T. Hioki, T. Itoh, T. Hosomi, H. Yamauchi, "A new variety of $LiMnO_2$: high-pressure synthesis and magnetic properties of tetragonal and cubic phases of $Li_xMn_{1-x}O$ (x~0.5)", *Mat. Sci. Eng. B* **84** (2001) 224–232.

[4] P. Piszora, W. Nowicki, J. Darul, "High-pressure metaelastic properties of $Li_xMn_{3-x}O_4$ (x=0.87; 0.94; 1.00)" *J. Mater. Chem.* **18** (2008) 2447-2452.

[5] K. Yamaura, Q. Huang, L. Zhang, K. Takada, Y. Baba, T. Nagai, Y. Matsui, K. Kosuda, E. Takayama-Muromachi, "Spinel-to-$CaFe_2O_4$-type structural transformation in $LiMn_2O_4$ under high pressure", *J. Am. Chem. Soc.* **9** (2006) 9449-9456.