

Thermal and elastic microstrain in lithium-manganese oxide

J. Darul¹, C. Popescu², F. Fauth² and P. Piszora^{1*}

¹Department of Materials Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań
²CELLS-ALBA Synchrotron Light Facility, 08290 Cerdanyola, Barcelona, Spain

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*e-mail: pawel@amu.edu.pl

Ternary oxides of the form Li_xMn_{3-x}O₄ have been extensively studied for their interesting physical properties, in particular, as cathode materials for rechargeable lithium secondary batteries [1]. When pressure is applied to some lithium-manganese spinels, a phase transition to the so-called “post-spinel” phase is induced [2]. During the last decade, high-pressure (HP) studies of Li_xMn_{3-x}O₄ under the nonhydrostatic stress condition have generated a large amount of attention, with stress being an efficient tool in transforming crystal structure of this materials [3,4]. Strain measurement is possible i.a. with the electrochemical strain microscopy and it allows probing a wide range of functional properties of lithium-manganese spinels at the nanoscale [5].

The Li_{0.95}Mn_{2.05}O₄ spinel sample was obtained from the appropriate amounts of thoroughly mixed powders of α-Mn₂O₃ and Li₂CO₃ (99.0% Merck) by thermal treatment in air at 1048 K. After heating, the specimen was quenched rapidly in solid CO₂. Structural analyses showed the expected stoichiometry of the obtained powder and confirmed that no spurious phases were present.

The microstructural properties of Li_{0.95}Mn_{2.05}O₄ under pressure and at elevated temperature were studied up to 13 GPa by X-ray powder diffraction at the MSPD-BL04 beamline of the ALBA synchrotron [6]. Diffraction patterns were recorded on image plates and then integrated to yield intensity vs 2θ diagrams. Synchrotron X-ray diffraction experiments were conducted using a polydimethyl-siloxane oil as the pressure-transmitting medium. The lithium manganese oxide in a powder form was studied at room temperature and at elevated temperature in pressure loading cycles using DAC. Gold has been chosen as a pressure standard because of its moderate compressibility, chemical inertness, and large

X-ray scattering power. A small lump of gold with a purity of 999.9 and an average particle size of about 30 μm was put in the hole of a rhenium gasket. Rietveld refinements were performed using the program GSAS.

Anisotropic peak broadening mainly caused by lattice strain was observed with broadening of the diffraction peaks. The phenomenological microstrain model of Stephens with 4 and 2 refinable parameters for tetragonal and cubic symmetry respectively was used to model the anisotropy in FWHM of the individual peak profiles. This microscopic picture is completed by analyzing the isosurface of the anisotropic microstrain which reflects the strong shear strain of neighboring coordination polyhedra in the lithium manganese structure.

We apply a comparative approach for microstrain analysis between the sample at HP/HT and at HP condition to illustrate the differences between microcrystalline properties of the high-pressure crystalline phase with and without thermal treatment.

It is important to note that, although the overall deformation during the experiments should be quasi-hydrostatic, individual powder particles experience a very heterogeneous deformation because of possible point contacts between the particles. We conjectured that grain-to-grain interactions and nonhydrostatic stress component induced a phase transition because of high stress concentration during powder compaction. It is quite possible that a limited hydrostaticity of the pressure transmitting medium and the grain boundaries in the polycrystalline aggregates play a decisive role in defining the sample microstructural properties at high pressure.

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