Crystal Chemistry and Phase Stability of Ru-doped Layered Monoclinc $LiMnO_2$

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INTRODUCTION

Lithium manganese oxide has received much attention as a potential cathode in rechargeable Li ion batteries due to the low cost and environmentally benign nature of manganese. The main drawback of the manganese system is the difficulty in synthesizing the layered α-$NaFeO_2$ structure, which is the stable phase observed in $LiCoO_2$ and $LiNiO_2$ systems.

The thermodynamically stable state of lithium manganese oxide is the orthorhombic structure with *Pmmn* space group. However, there have been some reports on the successful use of Al and Cr acting as dopants to stabilize the layered monoclinic (*C2/m*) form of $LiMnO_2$ using conventional solid-state reaction. The layered phase of $LiMnO_2$ is an attractive alternative to spinel-type lithium manganese oxide since the stoichiometry offers a capacity double that of the spinel phase. However, its' transition to the commercial battery status has been hindered by its unstability and irreversible transformation to the spinel phase. There is still a need to identify approaches and dopants to stabilize the layered structure.

In this study, ruthenium has been identified as a new dopant for synthesizing the layered form. The present paper will discuss the synthesis, crystal chemistry and phase stability of $LiMn_{(1-x)}Ru_xO_2$ ($0<x<0.25$).

EXPERIMENTAL

$LiMn_{(1-x)}M_xO_2$ (M=Ru) was synthesized by a modified solid-state reaction employing high-energy mechanical milling. Li_2O_2, MnO and RuO_2 were mixed in the stoichiometric ratio and milled in an SPEX-8000 high-energy mechanical mill for 24h. The obtained powder was heated to 1000°C for 8h - 16h in Ar atmosphere. The structure of the resultant powder was characterized using x-ray diffraction (Rigaku, CuKα, θ/θ diffractometer), Rietveld refinement and x-ray simulation.

RESULTS AND DISCUSSION

Fig. 1. shows the powder XRD patterns of the $LiMn_{(1-x)}Ru_xO_2$ (x=5 and 10) compounds. The XRD pattern is identified to be monoclinic and not tetragonal $L_2Mn_2O_4$ (*$F4_1$/ddm*) phase due to minor peaks in the 66-68° 2θ range. The x=5 shows the monoclinic phase with some orthorhombic phase (*Pmmn*) present as well, but the x=10 composition shows the complete formation of the monoclinic phase.

The extent of order-disorder of Li, Mn and Ru atoms can be analyzed from the intensity of peaks in the 30-45° range.

Compared to the other monoclinic-layered $LiMnO_2$ structures synthesized using Al and Cr as dopants, the Ru doped $LiMnO_2$ shows more broad peaks indicating a finer particle size. In addition, the most intense (001) peak at 18.3° is lower in intensity but broader than other peaks, for example, (111). The $(20\bar{1})$ peak observed at ≈ 33° is also broader than the other peaks. From the above results, it is believed that Ru inhibits the particle growth and induces anisotropic crystal growth. Results on the detailed structural characterization of various Ru-doped $LiMnO_2$ compound will be presented and discussed. The potential of some of these doped structures as cathodes will also be discussed.

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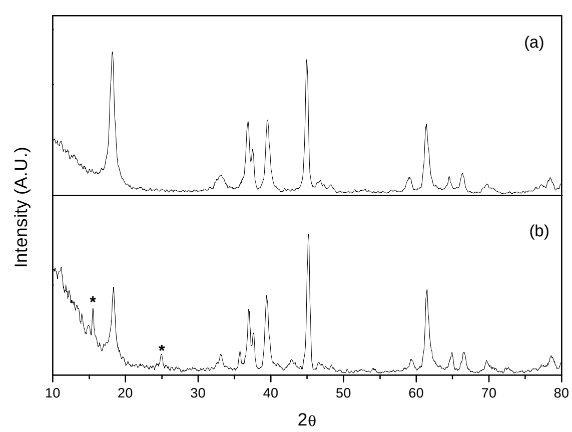

Fig. 1. The XRD pattern of (a) m-$LiMn_{90}Ru_{10}O_2$ (b) m-$LiMn_{95}Ru_5O_2$ (∗-orthorhombic) heated at 1000°C for 8h in Ar.