Synthesis, Structure, Magnetic Properties, and Phase Relationship in Lithium Manganese Oxide Spinel

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Introduction

Lithium manganese oxide spinels are a promising candidate as cathodes in rechargeable lithium batteries. Cathodic properties of the lithium manganese spinels were influenced by synthesis conditions. For example, the chage-discharge capacities of the spinel cathodes increase with decreasing x in $Li_{1+x}Mn_{2-x}O_4$ and the highest capacities of ~140mAh/g was obtained for the stoichiometric composition, $LiMn_2O_4$, while cycling characteristics improved with decreasing *x*.

Although many studies have been tried to clarify the relationship between these cathodic properties and synthesis procedures, and optimize the synthesis conditions. The spinels are usually discussed in the ternary phase diagram, $LiMnO_2$ - Li_2MnO_3 - MnO_2. The composition variety resulted from the synthesis at various temperatures and Li/Mn ratio could be interpreted in the triangle region of $LiMn_2O_4$ - $Li_4Mn_5O_{12}$ - $Li_2Mn_4O_9$. Change in the Li/Mn ratio in the starting materials leads to the composition varieties in the spinel from $LiMn_2O_4$ to $Li_4Mn_5O_{12}$, and the decrease in synthesis temperature gives compositions from $LiMn_2O_4$ to $Li_2Mn_4O_9$. The structure is complicated due to the existence of Jahn-Teller trivalent manganese ions. Furthermore, oxygen vacancies have also been reported. Therefore, the structures and the relation to the $LiMn_2O_4$ - $Li_4Mn_5O_{12}$ - $Li_2Mn_4O_9$ phase diagram are still ambiguous.

In this study, phase relationships, structures, magnetic properties and the phase transitions in the lithium manganese oxide spinels were studied using samples synthesized at various conditions. Their structures were discussed based on the structure date determined by TOF neutron and synchrotron X-ray Rietveld analysis. The oxygen vacancy was confirmed, and its amount varied with the synthesis condition. The relationship between the composition, structure, and phase transition will be discussed.

Experimental

The lithium manganese spinels were synthesized by various molar ratios of Li_2CO_3 and Mn_2O_3. They were mixed, pelleted and then heated at 750 – 900ºC in oxygen or air. The spinels close to the stoichiometric compositions were prepared from the manganese oxides obtained by thermal decomposition of $Mn(HCOO)_2$ as the starting materials. Neutron diffraction data for the spinels were taken on time-of-flight (TOF) neutron powder diffractomters, VEGA and Sirius, at the KENS pulsed spallation neutron source at the High Energy Accelerator Research organization(KEK). Magnetization was measured by a SQUID magnetometer (Quantum Design, MPMS2) between 5 and 300K in a field of 10 Oe and 1 KOe.

Results and Discussion

The neutron diffraction results indicated that the compositions of the lithium manganese spinels are dependent upon the synthesis conditions. The spinels synthesized in this study were classified into four categories; stoichiometric spinels, oxygen deficient spinels, lithium-substituted spinels, and cation deficient spinels. Most of the samples showed oxygen vacancy with an amount of 1-7%. The details of structure analysis for typical examples will be presented in our poster. Fig.1 summarized the phase relationships of the lithium manganese oxide spinel. The spinel ($LiMn_2O_{4-\delta}$ system) with oxygen vacancy is situated above the $LiMn_2O_4$ – $Li_2Mn_4O_9$ – $Li_4Mn_5O_{12}$ triangle region. For the spinel with oxygen vacancy, Li and Mn occupied the 8*a* and 16*d* site, respectively, and oxygen vacancy was confirmed. Oxygen vacancy also exists at shallow *x* regions in $Li_{1+x}Mn_{2-x}O_{4-\delta}$, and the δ value decreased with increasing excess lithium content.

There are three type of transition, charge-ordering transition(T_{CO}), anti-ferromagnetic transition(T_{AF}), and spin glass like transition(T_{SG}). The transition temperatures of T_{CO} and T_{AF} decrease with decreasing oxygen vacancy in $LiMn_2O_{4-\delta}$, and the spin glass-like transition increases with *x* in $Li_{1+x}Mn_{2-x}O_{4-\delta}$. The magnetic susceptibility χ increases with *x* in $Li_{1+x}Mn_{2-x}O_{4-\delta}$, while in the oxygen vacancy spinel, the χ value increases with increasing oxygen vacancy. These values also increase in the cation deficient spinels from $LiMn_2O_4$ to $Li_2Mn_4O_9$. The stoichiometric $LiMn_2O_4$ spinel may have the smallest χ values.

The low-temperature structure of the spinels, and the relationship between the oxygen composition and the charge-ordering phase transition will also be discussed.

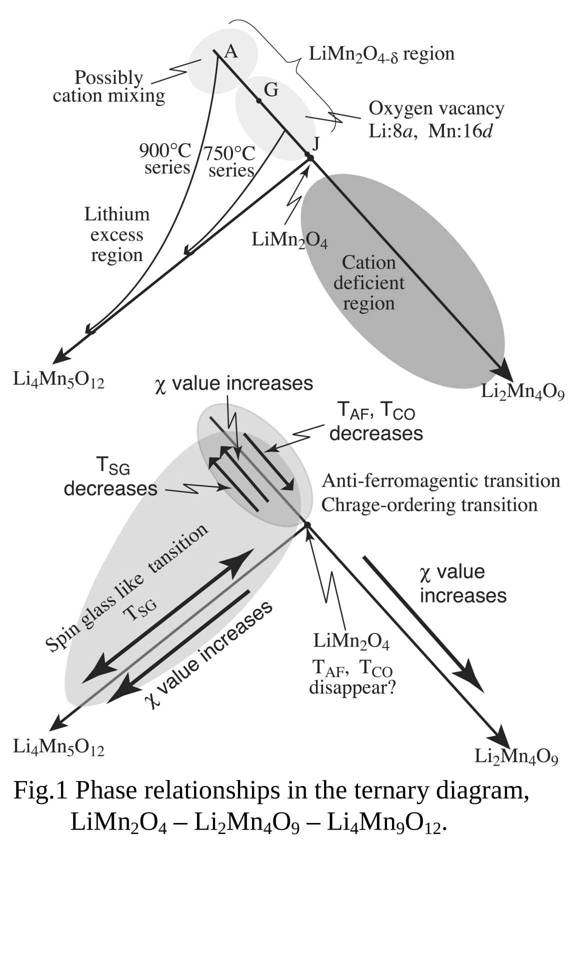

Fig.1 Phase relationships in the ternary diagram, $LiMn_2O_4$ – $Li_2Mn_4O_9$ – $Li_4Mn_9O_{12}$.