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Synthesis and magnetic properties of Li–Mn–Zn spinel oxides

H. Demidzu, T. Nakamura*, Y. Yamada

Division of Electronic Materials and Devices, Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

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ABSTRACT

$LiMn_{2-X}Zn_XO_4$ ($X<0.5$) compounds were prepared by sol–gel method. The specimens with a large substitution degree ($X>0.2$) led to symmetry reduction from $Fd\bar{3}m$ to $P2_13$ in the spinel oxide, while those with a small substitution degree ($X<0.1$) had $Fd\bar{3}m$ cubic symmetry. The Zn^{2+}-substitution led to the enhancement of the low-temperature magnetic susceptibility and a shift in the Weiss constant from negative to positive, indicating that the dominant exchange interaction changed from antiferromagnetic to ferromagnetic. For the compounds with $X=0.5$, the spontaneous magnetization was $4.48\mu_B$ and the Curie temperature was approximately 21 K. The experimentally obtained magnetization value was close to the value calculated under the assumption that the spins of the Mn^{4+} ions were aligned in ferromagnetic form. In addition, the magnetic properties of Li–Mn–Zn spinel oxides were briefly discussed, and compared with those of Li–Mn–M (M=Ni, Mg) spinel oxides.

1. Introduction

Lithium-containing transition metal oxides, which are known as cathode materials for lithium ion secondary batteries, have been studied extensively. They have a large non-stoichiometry and high-valence state of transition metal ions; therefore the magnetic properties, which are very sensitive to the variations of the non-stoichiometric degree and valence state of the transition metal ions, provide useful information. $LiNiO_2$ layered rock-salt compound has a two-dimensional triangular sub-lattice accommodating Ni^{3+} ions. It is known that the difficulty of complete oxidation of Ni^{2+} to Ni^{3+} brings about the non-stoichiometric compound $Li_{1-X}Ni_{1+X}O_2$, in which the Li^+ evaporation loss occurs simultaneously with Ni^{2+} formation [1–5]. A small deviation X strongly depends on the sample preparation, and this deviation yields a remarkably wide variation in the magnetic properties [6–16].

Another lithiated transition-metal compound is lithium manganese spinel oxide, which also has non-stoichiometry and defect structures [17–22]. This compound exists with the ternary system of $LiMn_2O_4$, $Li_4Mn_5O_{12}$ and $Li_2Mn_4O_9$, and contains cation vacancies, a situation of which is similar to the solid solution between Fe_3O_4 and γ-Fe_2O_3. Apart from the non-stoichiometry affecting the magnetic properties, one of the edge components, $LiMn_2O_4$, has geometrical frustration in the octahedral sub-lattice occupied by both Mn^{3+} and Mn^{4+}, resulting in spin-glass freezing at low temperatures [23–28]. The spin-glass freezing feature is significantly influenced by the compositional deviation from the $LiMn_2O_4$ stoichiometric point.

Similar to the spinel iron oxide system (ferrite), it is thought that the magnetic properties of the lithium manganese spinel oxides may be controlled with the appropriate cation substitution. We have previously studied the divalent cation substitution in lithium manganese spinel oxides and its influence on the structural and magnetic properties [29–31]. The lithium manganese spinel oxides all have the following cation distribution: Li^+ in tetrahedral sites and M^{3+}, Mn^{4+} and M^{2+} in octahedral interstices. In the $LiMn_{2-X}Ni_XO_4$ system, both the ferromagnetic couplings of Mn^{4+}–Mn^{4+} and Ni^{2+}–Ni^{2+} and the antiferromagnetic Mn^{4+}–Ni^{2+} coupling increased with X, and the ferrimagnetic collinear spin structure is established at $X=0.5$, which had a Curie temperature of 146 K and a saturation magnetization of $3.40\mu_B$ at 4.2 K. A similar variation of the magnetic properties was also observed in the $LiMn_{2-X}Cu_XO_4$ system; the Curie temperature was 39 K and the saturation magnetization at 4.2 K was $3.99\mu_B$ for $LiMn_{1.5}Cu_{0.5}O_4$. Additionally, the 1:3 cation ordering in the octahedral sub-lattice yields a space group transformation from $Fd\bar{3}m$ to $P4_332$, which results in some extra reflections in the power X-ray diffraction pattern. In the case that the divalent cation is non-magnetic Mg^{2+}, the substitution brings about the Mn^{4+}–Mn^{4+} ferromagnetic ordering; however, the magnetic dilution causes a lowering of the magnetic transition temperature: high saturation magnetization of $4.68\mu_B$ at 4.2 K but low Curie temperature of 23 K for $LiMn_{1.5}Mg_{0.5}O_4$.

Another divalent and non-magnetic cation substituted system is $LiMn_{2-X}Zn_XO_4$, in which the Zn^{2+} ion has a strong preference to the tetrahedral sites. It is likely that the magnetic behavior of the Zn^{2+}-substituted system is similar to that of the Mg^{2+} substituted

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* Corresponding author. Tel.: +81 79 267 4867; fax: +81 79 267 4855.
E-mail address: tatsuya@eng.u-hyogo.ac.jp (T. Nakamura).

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spinel. The first report of Li–Mn–Zn cubic spinel oxides was given by Blasse [32], who showed that $LiMn_{1.5}Zn_{0.5}O_4$ has a space group $P2_13$ and is ferromagnetic. Lee et al. [33] measured magic angle spinning NMR spectra of $LiMn_{2-X}Zn_XO_4$; they reported a gradual change in the nature of the interactions between Mn ions, from antiferromagnetic at low doping levels to ferromagnetic when $X=0.5$. Here, the preparation conditions, crystal structure and magnetic properties of Li–Mn–Zn spinel oxides are studied. The magnetic behavior is discussed through the magnetic interactions between the spin of transition metal ions, and compared with our previous studies.

2. Experimental

$LiMn_{2-X}Zn_XO_4$ ($X<0.5$) spinel oxides were synthesized by the sol–gel method. Reagent grade $LiNO_3$ (Nakarai tesque, purity above 98%), $Zn(CH_3COO)_2\cdot 4H_2O$ (Nakarai tesque, purity above 99%) and $Mn(CH_3COO)_2\cdot 4H_2O$ (Nakarai tesque, purity above 99%) were utilized as raw materials. 0.101 mol of $LiNO_3$, $(2-X)/10$ mol of $Mn(CH_3COO)_2\cdot 4H_2O$, and $X/10$ mol of $Zn(CH_3COO)_2\cdot 4H_2O$ were dissolved in 300 ml of ethanol and distilled water mixed solvent (ratio of water to ethanol was 3), where 1% excess amount of $LiNO_3$ was applied taking into account the Li evaporation loss. The solution was heated at 75 °C using a rotary evaporator until a viscous transparent gel was obtained. The obtained gel precursors were thermally decomposed at 300 °C for 1 h in ambient atmosphere. The decomposed powders were ground and press-compacted into pellets (30 mm in diameter and approximately 2 mm thick) at a pressure of approximately 500 kg/cm^2, where the green density of the pellets was approximately 2.3 g/cm^3. Finally, the pellets were annealed at a certain temperature in the range of 500–800 °C for 10 h in oxygen flow, followed by furnace cooling. The annealing temperature was selected so as to obtain a single-phase compound.

Powder X-ray diffraction patterns were measured with an X-ray diffractometer (RIGAKU, RINT-1500, Cu-K_α radiation at 40 kV and 200 mA). X-ray diffraction data was collected under the following conditions: diffraction angle between 10 and 120°, scanning step of 0.02° and scanning rate of 1.2 °/min. The generated phase was identified from full X-ray diffraction patterns, and the Rietveld refinement (Rietan-2000 [34]) was carried out in order to obtain the lattice parameters and the ionic distribution. Magnetization of the powder samples was measured using a magnetic balance (SHIMADZU) in the temperature range from 4.2 to 300 K. The sample was placed in a glass tube and an external applied magnetic field was adjusted to be less than 10 kOe. After identifying the temperature region where the magnetization was proportional to the magnetic field, the Weiss constant was evaluated by numerical fitting of the high-temperature susceptibility to the Curie–Weiss expression. Both spontaneous magnetization and Curie temperature were obtained using the Arrot plot technique [35].

3. Results and discussion

First, synthesis conditions for the single phase of Li–Mn–Zn spinel oxides were examined. In the case of the substitution degree $X<0.4$, the single-phase spinel compounds were easily obtained by selecting an annealing temperature around 700 °C; these compounds have no impurity phase such as $ZnMn_2O_4$ and Li_2MnO_3 as reported by Lee et al. [33]. For the specimen with $X=0.5$, it was necessary to carefully select the annealing temperature. Fig. 1 shows the X-ray diffraction patterns for $LiMn_{1.5}Zn_{0.5}O_4$ annealed at 500, 650 and 800 °C, respectively. An impurity phase ZnO was observed at an annealing temperature below 600 °C, while the impurity phase $ZnMn_2O_4$ was detected at calcination temperatures higher than 700 °C. Therefore, it was found that the single phase spinel oxide was obtained only in the case of an annealing temperature around 650 °C.

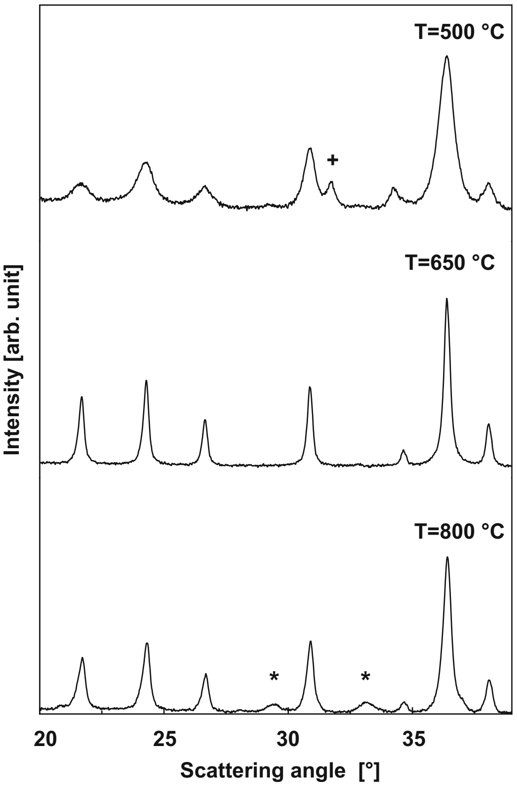

Fig. 1. X-ray diffraction patterns for $LiMn_{1.5}Zn_{0.5}O_4$ compounds annealed at: 500, 650 and 800 °C, respectively. The cross denotes the X-ray diffraction peak resulting from ZnO, and the asterisks denote the diffraction peaks of $ZnMn_2O_4$.

In order to discuss the effect of substitution on the structural parameters and magnetic properties of $LiMn_{2-X}Zn_XO_4$, we selected the single phase specimens annealed at 700 °C for the specimens with $X<0.4$ and at 650 °C for the specimen of $X=0.5$. The powder X-ray diffraction patterns for $LiMn_{2-X}Zn_XO_4$ spinel oxides with $X=0.0$–0.5 are shown in Fig. 2. It is possible that all diffraction patterns are indexed as cubic spinel structures. The obtained specimen for $X<0.1$ consisted of a spinel structure with $Fd\overline{3}m$ space group. However, further substitution yielded extra reflections, which were related to the cation ordering within tetrahedral 8a and octahedral 16d sites [33,36–38]. This indicated a change in the space group from $Fd\overline{3}m$ to $P2_13$. A similar situation was observed in the system of Mg^{2+}-substituted Li–Mn spinel oxides, which were reported in our previous study [31]. In the system of Mg^{2+} substituted Li–Mn spinel oxides, the 1:3 cation ordering of Mg^{2+} and Mn^{4+} in the 16d octahedral site produced the extra reflections. But the number of the extra reflection peaks in the Zn^{2+}-substituted Li–Mn spinel oxide system was remarkably higher than that in the Mg^{2+}-substituted Li–Mn spinel oxide system. The difference was attributed to the cation ordering form; the Zn^{2+}-substituted Li–Mn spinel oxide has $P2_13$ space group, whereas the Mg^{2+}-substituted Li–Mn spinel oxide has a different symmetry of $P4_332$. In the system of Zn^{2+}-substituted Li–Mn spinel oxides, the 1:1 cation ordering of Li^+ and Zn^{2+} in the 8a octahedral site (split into 4a and 4a' sites) occurs in addition to the 1:3 cation ordering of Li^+ and Mn^{4+} in the 16d octahedral site (split into 4a and 12d sites). The origin of this type