Synthesis of Lithiophorite with Sandwich Layered Structure by Hydrothermal Soft Chemical Process

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Lithiophorite with a sandwich layered structure which is constituted by stacking MnO_6 octahedral and $LiAl_2(OH)_6$ octahedral sheets was prepared from a layer manganese oxide by using hydrothermal soft chemical process. In the first step lithium-aluminum hydroxide complex ions were inserted into the interlayer space of the layer manganese oxide by an ion-exchange reaction, and in the second step the ion-exchanged manganese oxide was hydrothermally treated to polymerize the complex ions in the interlayer space to form the sandwich layered structure.

Manganese oxides with layered and tunnel structures show similar properties as zeolites and clay minerals. Since metal ions and organic molecules can be topotactically inserted/extracted into/from the interlayer space and the tunnel of the manganese oxides, these oxides can be used as an ion-sieve,[1-6] molecule-sieve,[7,8] catalysts[9,10] and cathode material of lithium battery.[11-13] Lithiophorite is a naturally occurring manganese oxide mineral with a sandwich layered structure, as show in Figure 1(a).[14] The structure is constituted by stacking $LiAl_2(OH)_6$ octahedral cation sheets and MnO_6 octahedral anion sheets. Since manganese oxides show semiconducting and magnetic properties, this sandwich layer compound may be used as two-dimensional conductor and show specific magnetic properties such as low-dimensional magnetic property similar to layer silicate intercalation compounds with divalent transition metal hydroxides.[15] Wadsley has reported that the lithiophorite can be obtained by hydrothermally treating birnessite-type manganese oxide with Al_2O_3 in LiOH solution.[16] However, the reaction mechanism is not clear.

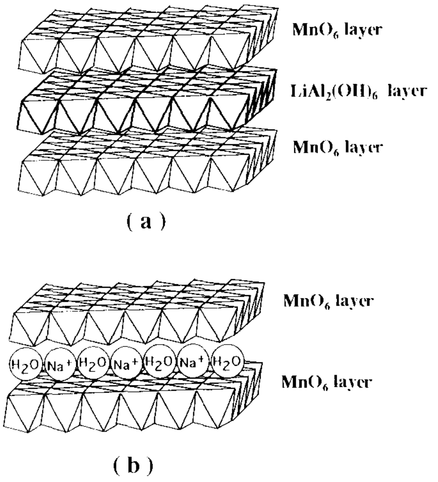

Figure 1. Structure of (a) lithiophorite and (b) birnessite-type sodium manganese oxide.

Recently, we have proposed a hydrothermal soft chemical process for synthesis tunnel manganese oxides from a layer manganese oxide.[17,18] This process comprises two steps: the first step being preparation of a framework precursor with layered structure and insertion of template ions or molecules (structure-directing agents) into its interlayer space by a soft chemical reaction, and the second step transformation of the template-inserted precursor into a tunnel structure by hydrothermal treatment. The dimension of the resulting tunnel can be controlled by the size of the used template. We think that this process is useful not only for the synthesis of tunnel materials but also for other materials. The present paper describes the synthesis of lithiophorite from a layered manganese oxide by using the hydrothermal soft chemical process.

A Na^+-form birnessite-type manganese oxide (NaBIR) which was used as a precursor was prepared by pouring a mixed solution (100 mL) of 3% H_2O_2 and 0.6 M NaOH into a solution (50 mL) of 0.3 M $Mn(NO_3)_2$ with stirring, as described previously.[6] X-Ray diffraction analysis (Figure 2(a)) indicated that NaBIR has a layered structure with a basal spacing of 0.72 nm, which contains two-dimensional sheets of edge-shared MnO_6 octahedra with single crystal water sheets and Na^+ between the sheets of the MnO_6 octahedra (Figure 1(b)).[5,6] A solution of lithium-aluminum hydroxide complex ion ($Li_xAl_n(OH)_m^{z+}$) was prepared by slowly dropping a solution of 0.5 M LiOH (800 mL) into a solution of 0.2 M $Al(NO_3)_3$ (1000 mL) (Li/Al mole ratio = 2.0) at 60 °C with stirring. The solution was aged at 60 °C for 2 h, and filtered to remove precipitate.

NaBIR was treated with the solution of lithium-aluminum hydroxide complex ion at room temperature for 1 day to exchange Na^+ in the interlayer space of NaBIR with $Li_xAl_n(OH)_m^{z+}$ complex ions. The ion-exchange treatment was repeated for two-times to complete the ion-exchange reaction. The layered structure retains after the ion-exchange treatment. Two layer phases with basal spacings of about 0.72 and 0.95 nm, respectively, were observed in the ion-exchanged sample (Figure 2(b)). The phase with 0.72 nm basal spacing corresponds to a layer phase with a single crystal water sheet between the sheets of the MnO_6 octahedra, and that with 0.95 nm basal spacing to that with $Li_xAl_n(OH)_m^{z+}$ complex ions between the sheets of the MnO_6 octahedra. The low crystallinity of the ion-exchanged sample is due to coexistence of both 0.72 and 0.95 nm phases in the same crystal particle.

The ion-exchanged sample was hydrothermally treated in distilled water at 100 and 150 °C, respectively, for 1 day under autogeneous pressure. The X-ray diffraction studies on the ion-exchanged and hydrothermally treated samples indicated that the amount of 0.72 nm layer phase decrease and that of the 0.95 nm layer phase increase after the hydrothermal treatment (Figure 2). The X-ray diffraction pattern of the hydrothermally treated sample at 150°C corresponds to that of natural lithiophorite (JCPDS 41-1378), except a small diffraction peak with a d value of 0.62 nm which corresponds to γ-AlOOH. The lithiophorite

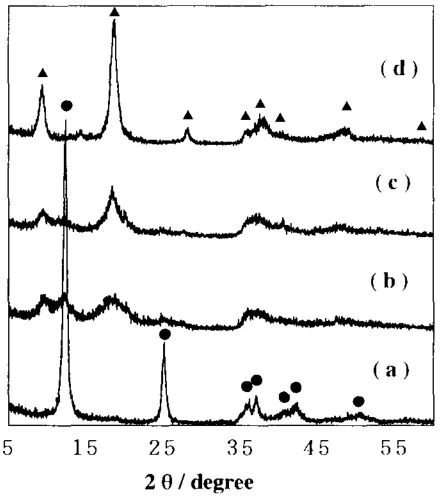

Figure 2. X-Ray diffraction patterns of starting material, ion-exchanged sample, and hydrothermally treated samples. (a) NaBIR (birnessite) used as starting material; (b) ion-exchanged sample; (c) and (d) hydrothermally treated samples at 100 and 150oC. ●: birnessite phase, ▲: lithiophorite phase.

has a sandwich layered structure, as shown in Figure 1(a), which belongs to hexagonal system (R3m) with lattice constants of **a** = 0.292 nm and **c** = 2.85 nm. The formation of the lithiophorite can be confirmed also by a FT-IR spectrum study. The IR spectrum of the ion-exchanged sample varies after the hydrothermal treatment, and the sample hydrothermally treated at 150 °C showed same IR spectrum as the natural lithiophorite.[19] These facts suggest that lithiophorite can be obtained by the hydrothermal treatment at 150 °C.

The compositional analysis indicated that all Na^+ in the NaBIR were exchanged with the $Li_xAl_n(OH)_m^{z+}$ complex ions by the ion-exchange treatment. The compositional analysis results for the ion-exchanged sample (Ion-exch) and hydrothermally treated samples at 100 and 150°C (Hydro-100 and Hydro-150) are shown in Table 1. The Li/Mn and Al/Mn mole ratios slightly decrease after the hydrothermal treatments. The smaller mole ratio of Li/Al (=0.34) for Hydro-150 than the theoretical value (=0.5) is due to formation of smal amount of γ-AlOOH and that there may be some Li^+ vacancies in the $LiAl_2(OH)_6$ octahedral sheet. DTA-TG study revealed that the hydrothermal treatment causes a large decrease in water content of the sample. There is almost no crystal water molecule in the hydrothermally treated sample at 150 °C. The sandwich layered structure of the lithiophorite is stable until heating at 400 °C in air. The -OH groups of $LiAl_2(OH)_6$ layer in the lithiophorite structure dehydrate over 400°C, accompanying destruction of the sandwich layered structure.

Table 1. Compositions of ion-exchanged and hydrothermally treated samples

sample	Li/Mn mole ratio	Al/Mn mole ratio	H_2O cont. (%)
Ion-ex	0.295	0.896	18
Hydro-100	0.292	0.831	12
Hydro-150	0.282	0.836	3.8

The reaction of transformation from the ion-exchanged birnessite to the lithiophorite can be described as follows. The $Li_xAl_n(OH)_m^{z+}$ complex ions in the interlayer space are unstable, and polymerize together to form large complex ions under the hydrothermal conditions. Since the layered structure of birnessite acts as a template (structure-directing agent) in the polymerization reaction, the polymerization occurs in two-dimension, and forms the $LiAl_2(OH)_6$ octahedral cation sheet between the MnO_6 octahedral sheets of the birnessite structure. The polymerization accompanies hydrolysis of $Li_xAl_n(OH)_m^{z+}$ ions and dehydration of the crystal water from the interlayer space of the birnessite. Since there is almost no crystal water molecule in the lithiophorite prepared here, most of the space between MnO_6 sheets is occupied by $LiAl_2(OH)_6$ sheet.

The above facts suggest that the hydrothermal soft chemical process is useful not only for the synthesis of tunnel oxides but also for the sandwich layer oxides at low temperature conditions. Other types of sandwich layer compounds may be also prepared by using this process.

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