

Hydrothermal Soft Chemical Reaction for Formation of Sandwich Layered Manganese Oxide

Qi Feng,* Chiaki Honbu, Kazumichi Yanagisawa, and Nakamichi Yamasaki

Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University,
2-5-1 Akebono-cho, Kochi-shi 780-8520, Japan

Received March 4, 1999. Revised Manuscript Received June 21, 1999

Lithiophorite with a sandwich layered structure, which consists of stacked MnO_6 octahedral sheets and $\text{LiAl}_2(\text{OH})_6$ octahedral sheets, was prepared from a birnessite-type sodium manganese oxide with a layered structure, by using a hydrothermal soft chemical process. In the first step, lithium–aluminum hydroxide complex ions ($\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$) were inserted into the interlayer space of the manganese oxide layers by an ion-exchange reaction. In the second step, the ion-exchanged manganese oxide was hydrothermally treated to polymerize the complex ions in the interlayer space, forming the sandwich layered structure. The formation reaction of the sandwich layered structure was investigated by XRD, TG-DTA, chemical analyses, and FT-IR spectroscopy. $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ can be formed by dropping a LiOH solution into an $\text{Al}(\text{NO}_3)_3$ solution with Li/Al mole ratio = 2, at 60 °C. A mixed layered phase of manganese oxide with basal spacings of 0.72 and 0.95 nm was obtained after the ion-exchange treatment of the birnessite-type manganese oxide with $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ solution. The mixed layered phase transforms to a 0.95-nm layered phase which corresponds to lithiophorite, with a sandwich-layered structure, under hydrothermal conditions. If a Keggin ion ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) solution was used instead of the $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ solution, the pure 0.95-nm phase cannot be obtained. In the formation reaction of the sandwich layered structure, the layered structure of the manganese oxide acts as a template under hydrothermal conditions for the two-dimensional polymerization of $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ to a $\text{LiAl}_2(\text{OH})_6$ octahedral sheet in the interlayer space.

Introduction

Manganese oxides with layered and tunnel structures constitute a large family of porous materials with pore sizes from the micropore to the mesopore range.^{1,2} The structures of the manganese oxides consist of MnO_6 octahedral units sharing corners and edges,³ which are different to aluminosilicates with SiO_4 tetrahedron– AlO_6 octahedron structural frameworks. Since the manganese oxides show excellent ion exchange, molecular adsorption, electrochemical, and magnetic properties, they can be used as ion sieves,^{4–9} molecular sieves,^{10,11} catalysts,^{11–14} cathode materials of lithium batteries,^{15–18}

and as new magnetic materials.¹⁹ Lithiophorite is a naturally occurring manganese oxide mineral with a sandwich layered structure, as shown in Figure 1.²⁰ The structure consists of stacked $\text{LiAl}_2(\text{OH})_6$ octahedral cation sheets and MnO_6 octahedral anion sheets. Since the MnO_6 octahedral sheet shows semiconductive and magnetic properties, this special structure can cause the sandwich layered compound to show special electrical and magnetic properties, such as two-dimensional conductivity and low-dimensional magnetic properties.^{21,22}

Giovanoli et al.²³ have studied the preparation of lithiophorite and found that lithiophorite can be obtained by hydrothermally treating a layered manganese oxide with Al_2O_3 in a LiOH solution. However, the detailed formation reaction mechanism is unclear. Recently, we have studied the synthesis of tunnel

- (1) Feng, Q.; Kanoh, H.; Ooi, K. *J. Mater. Chem.* **1999**, *9*, 319.
- (2) Brock, S. L.; Duan, N.; Tian, Z.-R.; Giraldo, O.; Zhou, H.; Suib, S. L. *Chem. Mater.* **1998**, *10*, 2619.
- (3) Burns, R. G.; Burns, V. M. *Manganese Dioxide Symposium*; Tokyo: 1998; Vol. 2, p 97.
- (4) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. 1995 Int. Conf. Ion exchange, Proc., 1995, p 141.
- (5) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Langmuir* **1992**, *8*, 1861.
- (6) Tsuji, M.; Abe, M. *Solvent Extr. Ion Exch.* **1984**, *2*, 253.
- (7) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Chem. Mater.* **1995**, *7*, 148.
- (8) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Chem. Mater.* **1995**, *7*, 1226.
- (9) Feng, Q.; Kanoh, H.; Miyai, Y.; Ooi, K. *Chem. Mater.* **1995**, *7*, 1722.
- (10) Shen, Y. F.; Zerger, R. P.; DeGuzman, R. N.; Suib, S. L.; McCurdy, L.; Potter, D. I.; O'Young, C. L. *Science* **1993**, *260*, 511.
- (11) Tian, Z.-R.; Tong, W.; Wang, J.-Y.; Duan, N.-G.; Krishnan, V. V.; Suib, S. L. *Science* **1997**, *276*, 926.
- (12) Cao, H.; Suib, S. L. *J. Am. Chem.* **1994**, *116*, 5334.
- (13) Matsuo, K.; Nitta, M.; Aomura, K. *J. Jpn. Pet. Inst.* **1979**, *22*, 212.

- (14) Yin, Y.-G.; Xu, W.-Q.; Shen, Y.-F.; Suib, S. L. *Chem. Mater.* **1994**, *6*, 1808.
- (15) Koksang, R.; Barker, J.; Shi, H.; Saidi, M. Y. *Solid State Ionics* **1996**, *84*, 1.
- (16) Feng, Q.; Kanoh, H.; Ooi, K.; Tani, M.; Nakacho, Y. *J. Electrochem. Soc.* **1994**, *141*, L135.
- (17) Armstrong, A. R.; Bruce, P. G. *Nature* **1996**, *381*, 499.
- (18) Goff, P. L.; Baffier, N.; Bach, S.; Pereira-Ramos, J. P. *Mater. Res. Bull.* **1996**, *31*, 36.
- (19) Rao, C. N. R.; Cheetham, A. K.; Mahesh, R. *Chem. Mater.* **1997**, *8*, 2421.
- (20) Giovanoli, R. *Chem. Erde* **1985**, *44*, 227.
- (21) Takahashi, M.; Ishio, S.; Onuki, S.; Ohtsuka, K.; Suda, M.; Ono, M. *J. Appl. Phys.* **1988**, *64*, 5766.
- (22) Richard-Plouet, M.; Vilminot, S. *J. Mater. Chem.* **1998**, *8*, 131.
- (23) Giovanoli, R.; Buhler, H.; Sokolowska, K. *J. Microscopie* **1973**, *18*, 271.

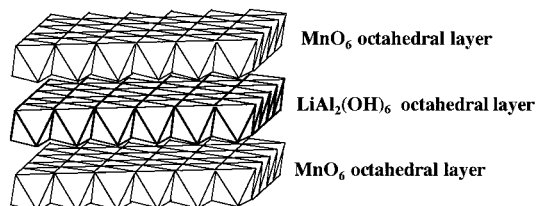


Figure 1. Sandwich layered structure of lithiophorite.

manganese oxides from a layered manganese oxide by hydrothermal reaction and proposed this method as a hydrothermal soft chemical process.^{24,25} This process comprises of two steps: the first step being preparation of a framework precursor with a layered structure, and insertion of template ions or molecules (structure-directing agents) into its interlayer space by a soft chemical reaction. The second step, is the transformation of the template-inserted precursor into a tunnel structure by hydrothermal treatment. The dimensions of the resulting tunnel can be controlled by the size of the template used. Six kinds of tunnel manganese oxides with different tunnel forms have been obtained from a layered manganese oxide by using this process with metal ions as the templates.

Our preliminary study²⁶ indicated that if a lithium–aluminum hydroxide complex ion was used as the insertion ion, a tunnel manganese oxide was not formed, but instead a lithiophorite with a sandwich layered structure was obtained from the layered manganese oxide. This suggests that it is possible to use the hydrothermal soft chemical process in the synthesis of sandwich layered compounds. However, the reaction mechanism and detailed conditions for the formation of lithiophorite has not yet been clarified.

The present paper describes the formation mechanism and necessary formation conditions of lithiophorite from a birnessite-type manganese oxide with a layered structure by a hydrothermal soft chemical process.

Experimental Section

Sample Preparation. A Na^+ form of birnessite-type manganese oxide (NaBIR), which was used as a precursor, was prepared by pouring a mixed solution of 3% H_2O_2 and 0.6 M NaOH (100 mL) into a solution of 0.3 M $\text{Mn}(\text{NO}_3)_2$ (50 mL) with stirring, as described previously.²⁵ Solutions of lithium–aluminum hydroxide complex ions ($\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$) were prepared by slowly dropping a solution of 0.5 M LiOH into a solution of 0.2 M $\text{Al}(\text{NO}_3)_3$ at 60 °C with stirring. Three kinds of the solutions with different Li/Al mole ratios (1.5, 2.0, and 2.5) were prepared. The solutions were aged at 60 °C for 2 h and filtered to remove any precipitate formed. The solutions showed pH values of 3.6, 3.8, and 4.0, respectively. A solution of Keggin ions ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) was prepared by slowly dropping a solution of 0.4 M NaOH (1000 mL) into a solution of 0.4 M $\text{Al}(\text{NO}_3)_3$ (500 mL) (Na/Al mole ratio = 2.0) at 60 °C with stirring, followed aging at 60 °C for 2 h.²⁷

NaBIR was treated with the solution of lithium–aluminum hydroxide complex ions or the solution of Na⁺ ions at room temperature for 1 day to exchange Na⁺ ions in the interlayer

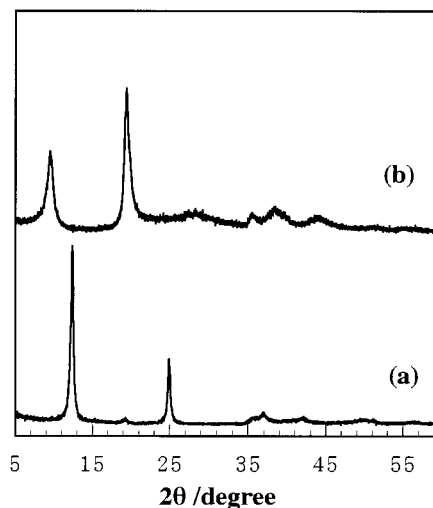


Figure 2. X-ray diffraction patterns of (a) NaBIR and (b) $\text{LiAl}_2(\text{OH})_6\text{NO}_3 \cdot n\text{H}_2\text{O}$.

space of NaBIR with $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ or $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ complex ions. The ion-exchange treatment was repeated twice to complete the ion-exchange reaction. The ion-exchanged sample was washed with distilled water and hydrothermally treated in distilled water at 100 or 150 °C, for 1 day under autogenous pressure. The samples treated with the solutions of Li/Al mole ratio = 1.5, 2.0, and 2.5 were designated as BIR-LA1.5, BIR-LA2.0, and BIR-LA2.5, respectively, and the hydrothermally treated samples at 100 and 150 °C as HyLAX-100 and HyLAX-150, respectively, where x corresponds to the Li/Al mole ratio of the solution used in the ion-exchange treatment. The sample treated with the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ solution was designated as BIR-NA2.0, and the hydrothermally treated sample at 150 °C, as HyNA2.0-150.

Chemical Analysis. The lithium, sodium, and manganese contents in the manganese oxides were determined by atomic absorption spectrometry, and the aluminum content by ICP spectrometry after dissolving the samples in a mixed solution of HCl and H_2O_2 .

Physical Analysis. An X-ray diffraction (XRD) analysis was carried out using a Rigaku Rotaflex Type X-ray diffractometer (RAD-RC). Infrared spectra were obtained by the KBr method on a Perkin-Elmer infrared spectrometer (1600 Series FTIR). DTA-TG curves were obtained on a Seiko thermal analyzer (SSC5200) at a heating rate of 10 °C/min.

Results and Discussion

Preparations of Layer Manganese Oxide Precursor and Complex Ion Solution. The X-ray diffraction pattern of the birnessite-type sodium manganese oxide (NaBIR) which was used as the precursor is shown in Figure 2a. The manganese oxide has a layered structure, as shown in Figure 3a. It has a basal spacing of 0.72 nm along the c axis, with crystal water and Na⁺ ions between the sheets of the MnO_6 octahedra.^{25,28} Na⁺ ions in the interlayer space are ion exchangeable.

In the preparation of lithium–aluminum hydroxide complex ion solutions, when the LiOH solution was added to the $\text{Al}(\text{NO}_3)_3$ solution, a white precipitate was formed, and the amount of the precipitate increased with increase in the LiOH/ $\text{Al}(\text{NO}_3)_3$ mole ratio. The X-ray diffraction pattern (Figure 2b) of the precipitate indicated that it is a $\text{LiAl}_2(\text{OH})_6\text{NO}_3 \cdot n\text{H}_2\text{O}$ with a layered structure as shown in Figure 3b.^{29,30} The NO_3^-

(24) Feng, Q.; Yanagisawa, K.; Yamasaki, N. *Chem. Commun.* **1996**, 1607.

(25) Feng, Q.; Yanagisawa, K.; Yamasaki, N. *J. Porous Mater.* **1998**, 5, 153.

(26) Feng, Q.; Honbu, C.; Yanagisawa, K.; Yamasaki, N. *Chem. Lett.* **1998**, 757.

(27) Malla, P.; Yamanaka, S.; Komarneni, S. *Solid State Ionics* **1989**, 32/33, 354.

(28) Feng, Q.; Sum, E.-H.; Yanagisawa, K.; Yamasaki, N. *J. Ceram. Soc. Jpn.* **1997**, 105, 564.

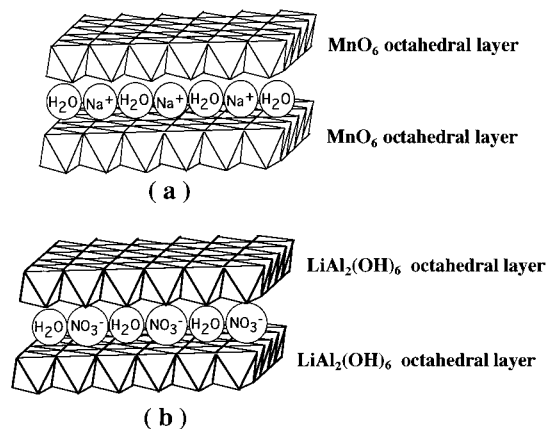


Figure 3. Structures of (a) birnessite-type sodium manganese oxide and (b) LiAl₂(OH)₆NO₃·*n*H₂O.

ions in the interlayer space are ion exchangeable. When excess LiOH is added to the Al(NO₃)₃ solution (Li/Al mole ratio > 3), all the Al³⁺ ions are precipitated into LiAl₂(OH)₆NO₃·*n*H₂O. When Li/Al mole ratio is smaller than 3, however, Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} complex ions can be formed. When NaOH solution was added into the Al(NO₃)₃ solution for the preparation of the Al₁₃O₄(OH)₂₄⁷⁺ solution (Na/Al = 2.0), no precipitate formed. The formation of LiAl₂(OH)₆NO₃·*n*H₂O precipitate when the LiOH solution is used in the preparation of the aluminum hydroxide complex ions suggests that Li⁺ ions preferably combine with aluminum hydroxide complex ions to form Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} complex ions and LiAl₂(OH)₆NO₃·*n*H₂O precipitate. The difference between Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} and Al₁₃O₄(OH)₂₄⁷⁺ complex ions will be discussed in the following sections in detail.

Ion-Exchange Reaction of Layered Manganese Oxide. NaBIR was treated with the Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} solutions to exchange Na⁺ ions in the birnessite-type manganese oxide with Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} complex ions. X-ray diffraction patterns of the ion-exchanged samples (BIR-LA1.5, BIR-LA2.0, and BIR-LA2.5) revealed that the layered structure remained after the ion-exchange treatments (Figures 4a, 5a, and 6a), but two layered phases with basal spacings of about 0.72 and 0.95 nm were observed in BIR-LA1.5 and BIR-LA2.0, and only one layered phase with a basal spacing of 0.72 nm in BIR-LA2.5. The 0.95 nm basal spacing corresponds to a layered phase with Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} complex ions between the sheets of the MnO₆ octahedra. The 0.72-nm basal spacing corresponds to a layered phase with a single-crystal water sheet between the sheets of the MnO₆ octahedra, which has a similar structure to the birnessite-type sodium manganese oxide. The low crystallinity of the ion-exchanged samples of BIR-LA1.5 and BIR-LA2.0 is due to coexistence of both 0.72- and 0.95-nm phases in one crystal particle.

Transformation of the Layered Structure to the Sandwich Layered Structure. The ion-exchanged birnessite-type manganese oxides were treated under hydrothermal conditions at 100 or 150 °C in distilled water. X-ray diffraction studies indicated that the products were dependent on the Li/Al mole ratio of the

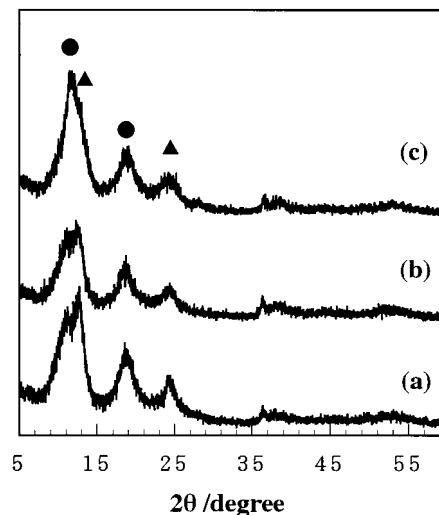


Figure 4. X-ray diffraction patterns of ion-exchange-treated sample with Li/Al = 1.5 solution and hydrothermally treated samples at 100 and 150 °C: (a) BIR-LA1.5; (b) HyLA1.5-100; and (c) HyLA1.5-150. Key: (▲) 0.72-nm layered phase; (●) 0.95-nm layered phase.

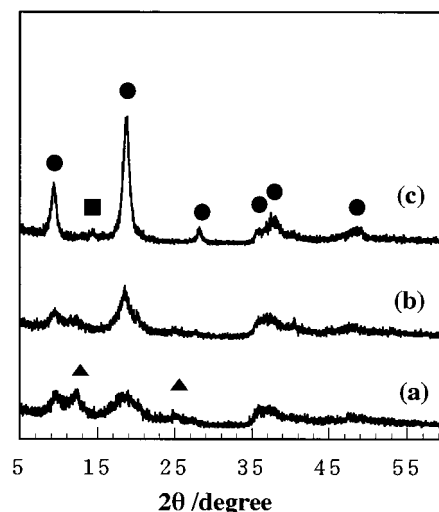


Figure 5. X-ray diffraction patterns of ion-exchange treated sample with Li/Al = 2.0 solution and hydrothermally treated samples at 100 and 150 °C: (a) BIR-LA2.0; (b) HyLA2.0-100; and (c) HyLA2.0-150. Key: (▲) 0.72-nm layered phase; (●) lithiophorite phase; and (■) γ -AlOOH phase.

Li_{*x*}Al_{*n*}(OH)_{*m*}^{*z+*} solution used in the ion-exchange treatment and hydrothermal treatment temperature. The fraction of the 0.72-nm layered phase decreased, and that of the 0.95-nm layered phase increased for the BIR-LA2.0, after the hydrothermal treatment (Figure 5). Only the 0.95-nm layered phase was observed after the hydrothermal treatment at 150 °C. The X-ray diffraction pattern of the hydrothermally treated sample at 150 °C corresponds to that of natural lithiophorite (JCPDS 41-1378), except that a small diffraction peak with a *d* value of 0.62 nm is observed in the hydrothermally treated sample. The small diffraction peak with a *d* value of 0.62 nm corresponds to γ -AlOOH (boehmite, JCPDS 21-1307). The formation of lithiophorite by the hydrothermal treatment at 150 °C can be also confirmed by IR and DTA-TG studies, which will be described later. The lithiophorite obtained by the hydrothermal treatment has a sandwich layered structure, as shown in Figure 1, which belongs to the hexagonal system

(29) Serna, C. J.; Rendon, J. L.; Iglesias, J. E. *Clay Clay Miner.* **1982**, *30*, 180.

(30) Dutta, P. K.; Puri, M. *J. Phys. Chem.* **1989**, *93*, 376.

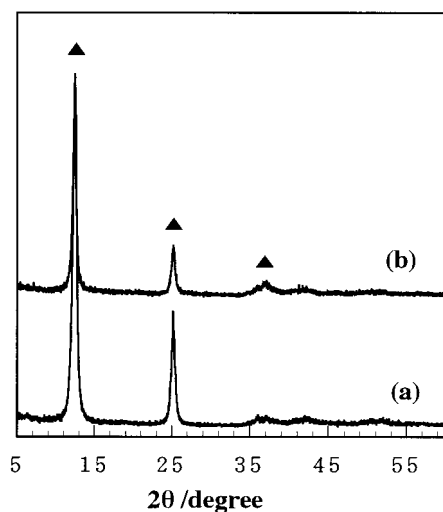


Figure 6. X-ray diffraction patterns of ion-exchange treated sample with Li/Al = 2.5 solution and hydrothermally treated sample at 150 °C: (a) BIR-LA2.5; (b) HyLA2.5-150. (▲) 0.72-nm layered phase.

(*R3m*) with lattice constants of $a = 0.292$ nm and $c = 2.85$ nm.

In the case of BIR-LA1.5, only a slight increase of the 0.95-nm layered phase and a slight decrease of the 0.72-nm layered phase were observed after the hydrothermal treatment at 100 and 150 °C (Figure 4). A pure 0.95-nm layered phase, however, was not obtained from BIR-LA1.5. For the BIR-LA2.5; almost no structural change was observed after the hydrothermal treatment at 150 °C (Figure 6). These results suggest that the lithium–aluminum complex ion solution, with Li/Al mole ratio = 2.0, is best for the preparation of lithio-phorite.

To compare $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ complex ions with Keggin ions ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$), the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ solution was used in the ion-exchange treatment, and the ion-exchanged sample was hydrothermally treated at 150 °C. BIR-NA2.0 which was obtained by treating NaBIR with the $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ solution showed similar ion exchange and hydrothermal behavior to BIR-LA1.5. The two layered phases with basal spacing of about 0.95 and 0.72 nm were formed after the ion exchange, and the fraction of the 0.95-nm phase increased slightly after the hydrothermal treatment (Figure 7). However, a pure sandwich phase could not be obtained by hydrothermal treatment. These facts reveal that $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ behaves differently from $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, and the $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ is suitable for the formation of sandwich layered structures.

Chemical Composition of Manganese Oxides.

The composition analysis results for the precursor, ion-exchanged, and hydrothermally treated samples are given in Table 1. Almost all Na^+ was removed from NaBIR by the ion-exchange treatments with $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ complex ion solutions. In the ion-exchanged sample of BIR-LA1.5, the Li content is very low, suggesting that most of Na^+ ions were exchanged with aluminum hydroxide complex ions ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$). This means that $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ is easily formed in the solution of Li/Al = 1.5. This is the reason BIR-LA1.5 shows the similar ion exchange and hydrothermal behavior to BIR-NA2.0. On the other

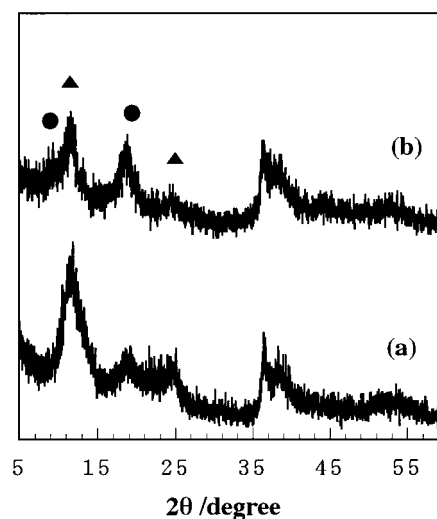


Figure 7. X-ray diffraction patterns of ion-exchange treated sample with Keggin ion (Na/Al = 2.0) solution and hydrothermally treated sample at 150 °C: (a) BIR-NA2.0 and (b) HyNA2.0-150. Key: (▲) 0.72-nm layered phase; (●) 0.95-nm layered phase.

Table 1. Composition of Manganese Oxides

sample	Na/Mn	Li/Mn	Al/Mn	Li/Al
precursor				
NaBIR	0.31			
ion-exchanged				
BIR-LA1.5	0.002	0.049	0.44	0.11
BIR-LA2.0	0.005	0.30	0.90	0.33
BIR-LA2.5	0.001	0.29	0.013	22
BIR-NA2.0	0.010	—	0.39	—
hydrothermally treated				
HyLA1.5-150	—	0.051	0.45	0.11
HyLA2.0-150	—	0.28	0.84	0.33
HyLA2.5-150	—	0.26	0.011	24
HyNA2.0-150	0.001	—	0.38	—

hand, in the BIR-LA2.5 sample, there is almost no Al in the ion-exchanged sample, since most of the Al^{3+} is precipitated to $\text{LiAl}_2(\text{OH})_6\text{NO}_3 \cdot n\text{H}_2\text{O}$ in the solution with Li/Al mole ratio = 2.5, and the Na^+ ions were exchanged with Li^+ ions remaining in the solution. In BIR-LA2.0, however, the contents of both Li and Al are high, and the Li content (Li/Mn = 0.30) is close to the ion-exchange capacity of NaBIR (Na/Mn = 0.31). By considering the charge balance (ion-exchange capacity) of the birnessite, this suggests that Li and Al are inserted into the interlayer space of birnessite structure as a complex ion form of lithium–aluminum hydroxide, and not as isolated Li^+ ion and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ion. If Li^+ ions and aluminum hydroxide ions exist as individual ions in the interlayer space, the charge density of the ions will be 0.78/Mn by assuming the aluminum hydroxide complex ion as $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$. This is much larger than the charge density of NaBIR. The lithium–aluminum hydroxide complex ion can be expressed as $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$, although the parameters x , n , m , and z , and the structure of this complex ion are unclear at the present stage.

Only slight changes occur in the Li/Mn and Al/Mn mole ratios for all samples after the hydrothermal treatments (Table 1), indicating that there is almost no dissolution of Li and Al under hydrothermal conditions. The compositional analysis and the X-ray diffraction results reveal that both Li and Al are necessary for the formation of the sandwich layer structure. The ideal

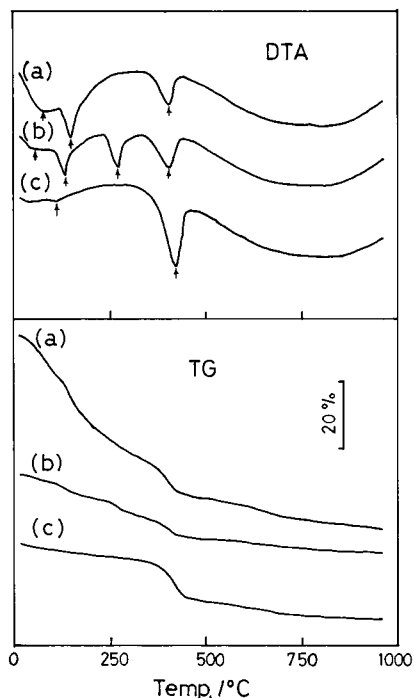


Figure 8. DTA (top) and TG (bottom) curves for ion-exchanged and hydrothermally treated samples: (a) BIR-LA2.0; (b) HyLA2.0-100; and (c) HyLA2.0-150.

formula for lithiophorite is $\text{LiAl}_2(\text{OH})_6\text{Mn}_3\text{O}_6$.^{3,20,23,31} The Li/Mn mole ratio in HyLA2.0-150 (=0.28) is slightly smaller than the theoretical value (=0.33). This may be due to the presence of a small amount of Li^+ ion vacancies in the $\text{LiAl}_2(\text{OH})_6$ octahedral sheet. The Al/Mn mole ratio (=0.84) is larger than the theoretical value (=0.67), due to the γ - AlOOH impurity in the sample. The formation of γ - AlOOH under the hydrothermal conditions is due to the excess Al from the lithiophorite which is ejected from the interlayer space of the birnessite structure during the polymerization reaction of $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ to the $\text{LiAl}_2(\text{OH})_6$ octahedral sheet.

DTA-TG Analysis of Manganese Oxides. DTA-TG analyses were carried out for the ion-exchanged sample BIR-LA2.0, and the hydrothermally treated samples HyLA2.0-100 and HyLA2.0-150. These three samples show different DTA-TG curves (Figure 8). BIR-LA2.0 showed endothermic peaks around 60, 150, and 400 °C. Each was accompanied by a weight loss. An X-ray diffraction study indicated that the layered structure remained after heat treatment in air at 330 °C, but was destroyed at 550 °C (Figure 9). Therefore, the endothermic peaks around 60 and 150 °C can be assigned to evaporation of absorbed water and dehydration of crystal water from the interlayer space. The peak around 400 °C corresponds to dehydration of an -OH group of Li-Al-OH in the interlayer space, accompanying the destruction of the layered phase to form a Li-Al-Mn-O spinel phase. After heat treatment below 330 °C, the proportion of 0.72-nm layered phase decreased, and the proportion of 0.95-nm layered phase increased (Figures 5a and 9a). A good crystalline 0.95-nm layered phase like that produced by hydrothermal treatment cannot, however, be obtained by heat treatment in air.

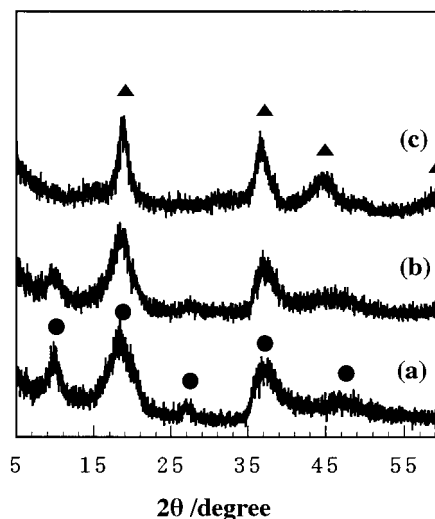


Figure 9. X-ray diffraction patterns of heat-treated BIR-LA2.0 at (a) 230, (b) 330, and (c) 550 °C for 1 h in air. Key: (●) 0.95-nm layered phase; (▲) Li-Al-Mn-O spinel phase.

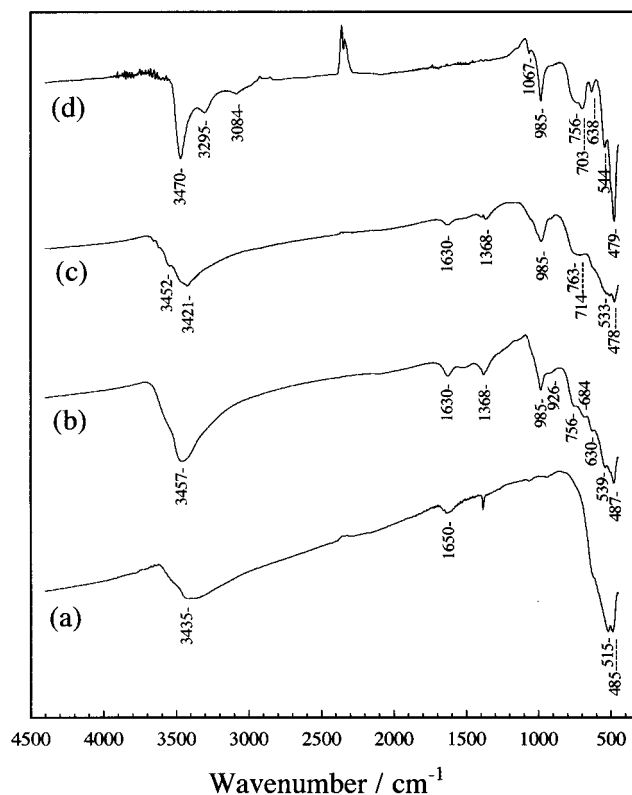


Figure 10. IR spectra of starting, ion-exchanged, and hydrothermally treated samples: (a) NaBir; (b) BIR-LA2.0; (c) HyLA2.0-100; and (d) HyLA2.0-150.

This fact reveals that the hydrothermal reaction is more suitable for the preparation of sandwich layered compound than the solid-state reaction in air.

For HyLA2.0-100, endothermic peaks around 50, 140, and 410 °C, which correspond to those of the ion-exchange sample BIR-LA2.0, were observed (Figure 8b). Another endothermic peak around 273 °C with a weight loss was also observed. The heat-treated HyLA2.0-100 at 230, 330, and 550 °C in air showed similar XRD patterns to those of BIR-LA2.0 (Figure 9), respectively. These results suggest that an intermediate of the sandwich layered compound can be formed under the

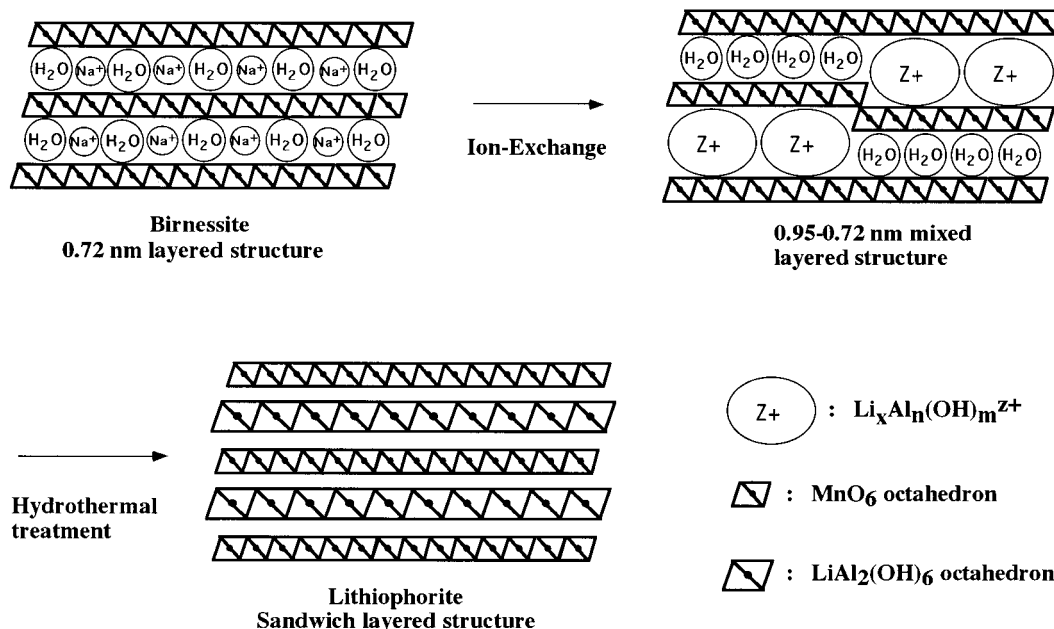


Figure 11. A model of the formation reaction of the sandwich layered structure of lithiophorite.

hydrothermal conditions. The endothermic peak around 273 °C can be assigned to a dehydration of the crystal water in the intermediate. Therefore, there are two types of crystal water in the intermediate.

HyLA2.0-150 showed similar DTA and TG curves to natural lithiophorite (Figure 8c).²⁰ A small endothermic peak around 120 °C and a large endothermic peak around 430 °C, which correspond to the dehydrations of the crystal water and an -OH group of $\text{LiAl}_2(\text{OH})_6$ layer, respectively, were observed. An X-ray diffraction study indicated that the dehydration of the -OH group of $\text{LiAl}_2(\text{OH})_6$ layer accompanies the destruction of the sandwich layered structure of lithiophorite. The crystal water content decreases with increasing temperature of the hydrothermal treatment, and there is almost no crystal water in HyLA2.0-150. These facts reveal that the formation of the $\text{LiAl}_2(\text{OH})_6$ sheet in the interlayer space of the birnessite structure accompanies the dehydration of the crystal water from the interlayer space.

IR Spectra of Manganese Oxides. The formation of the lithiophorite can be confirmed also by a FT-IR spectrum study. The IR spectra of NaBIR, BIR-LA2.0, HyLA2.0-100, and HyLA2.0-150 are shown in Figure 10. In the IR spectrum of Na-BIR (Figure 10a), the bands at 3435 and 1650 cm^{-1} can be assigned to stretching and bending vibrations of -OH groups of crystal and adsorbed water molecules, respectively. The bands in the region from 450 to 800 cm^{-1} can be assigned to Mn-O stretching vibrations. After the ion exchange with $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$, the bands of Mn-O stretching vibrations shifted and new bands were observed in the region from 450 to 1500 cm^{-1} (Figure 10b). The IR spectrum of the ion-exchanged sample changes after the hydrothermal treatment. This fact suggests that a reaction occurs under the hydrothermal conditions. The spectrum of HyLA2.0-150 (Figure 10d) corresponds to natural lithiophorite,³² which suggests that lithiophorite is formed after the hydrothermal treatment at 150 °C. The absence of the -OH bending

mode of water near 1600 cm^{-1} in the spectrum of the lithiophorite prepared here indicates that there is almost no crystal water in this sample. The bands at 3470, 3295, and 3084 cm^{-1} can be assigned to the stretching vibrations of -OH groups of the $\text{LiAl}_2(\text{OH})_6$ sheet. The presence of the bands at 3295 and 3084 cm^{-1} suggest that the lithiophorite prepared here has a good crystallinity, since these two bands are observed only at liquid nitrogen temperature even for well-crystallized natural lithiophorite.³²

Formation Reaction of the Sandwich Layered Structure. The formation reaction of the sandwich layered structure of lithiophorite can be described by a reaction model as shown in Figure 11. In the first step, Na^+ ions in the birnessite-type manganese oxide are exchanged with $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ ions, and a 0.95/0.72-nm mixed layered phase is formed. In the second step, $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ ions become unstable under the hydrothermal conditions, and polymerize to form the $\text{LiAl}_2(\text{OH})_6$ octahedral sheet between the manganese oxide layers by hydrolysis of $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ and dehydration of crystal water from the interlayer space of the layered structure. The layered structure of the birnessite-type manganese oxide acts as a template for the two-dimensional polymerization of $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ ions to the $\text{LiAl}_2(\text{OH})_6$ octahedral layer.

Two types of model have been proposed for the mixed layered compounds prepared by intercalation reactions.³³ Rudorff³⁴ has proposed that the mixed layer consists of stacked two types of layers with different basal spacings. On the other hand, Daumas et al.³⁵ have proposed a model of the coexistence of two different basal spacing regions in the same layer. We think that the Daumas model is reasonable for the mixed layer in the ion-exchanged sample here, because the transformation reaction from the 0.95/0.72-nm mixed layered

(33) Fogg, A. M.; Dunn, J. S.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 356.

(34) Rudorff, W. Z. *Phys. Chem.* **1940**, *45*, 42.

(35) Daumas, N.; Herold, A. C. R. *Acad. Sci. Paris C* **1969**, *268*, 373.

(32) Potter, R. M.; Rossman, G. R. *Am. Miner.* **1979**, *64*, 1199.

phase to the sandwich layer phase proceeds continuously, with the increase of hydrothermal treatment temperature (Figure 5) and is also possible by low-temperature heat treatment in air (Figure 9). For the Rudorff model, $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ complex ions have to dissolve from the 0.95-nm layered phase to the solution phase, and then reinsert into the 0.72-nm layered phase in the hydrothermal formation reaction of the sandwich layered structure. The dissolution–reinsertion reaction, however, is impossible in the solid-phase reaction by low-temperature heat treatment in air.

The hydrothermal treatment of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ exchanged birnessite-type manganese oxide also causes the increase of 0.95-nm layered phase (Figure 7), suggesting that the polymerization of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ in the interlayer space also occurs under the hydrothermal conditions. The pure 0.95-nm layered phase, however, cannot be obtained by using $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ as the insertion ion. It is preferable to use $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ as the insertion ion for the sandwich layered structure. Li^+ ions play an important role in the formation reaction of the sandwich layered structure, because Li^+ ions can locate at vacant sites of $\text{Al}(\text{OH})_6$ octahedral sheets for

formation of the uniform $\text{LiAl}_2(\text{OH})_6$ layer sheets, and balance the charge between the $\text{LiAl}_2(\text{OH})_6$ layer and the MnO_6 octahedral layer. In the case of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, the formation of a uniform layer sheet between the MnO_6 octahedral layers may be difficult under the hydrothermal conditions.

Conclusion

$\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ complex ions can be formed by reacting an $\text{Al}(\text{NO}_3)_3$ solution with a LiOH solution. Na^+ ions in the birnessite-type manganese oxide can be exchanged with $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ complex ions. Lithiophorite, with a sandwich layered structure, can be obtained by hydrothermal treatment of the $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ ion-exchanged birnessite-type manganese oxide. The layered structure of the birnessite-type manganese oxide acts as a template for the two-dimensional polymerization of $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ to the $\text{LiAl}_2(\text{OH})_6$ layer in the formation reaction of the sandwich layered structure. Li^+ ions play an important role in the formation reaction of the $\text{LiAl}_2(\text{OH})_6$ octahedral layer.

CM990133N