Synthesis of a Misfit-layered Magnesium Manganese Hydroxide Oxide

Yaohua Xu,[†,††] Noriaki Nakayama,* Keiko Fujiwara, Tadato Mizota, and Seishi Goto
Department of Advanced Materials Science and Engineering, Faculty of Engineering,
Yamaguchi University, Ube 755-8611
[†]*The Venture Business Laboratory (VBL), Yamaguchi University, Ube 755-8611*
[††]*Department of Chemistry, Jilin University, Changchun 130010, P. R. China*

(Received January 5, 2005; CL-050012)

A new magnesium manganese hydroxide oxide, $[Mg(OH)_2]_{10}[MnO_{1.86}(OH)_{0.07}]_{14}\cdot 2.34H_2O$, which has a novel incommensurate misfit-layered structure built from two pseudohexagonal MnO_2 and $Mg(OH)_2$ sheets, has been hydrothermally synthesized by using the layered birnessite as the precursor. This compound has been investigated by TEM, XRD, TG-DTA. The lattice parameters are $a_1 = 0.496(2)$, $b_1 = 0.292(5)$, $c_1 = 0.957(2)$ nm, and $\beta_1 = 94.1(9)°$ for manganese oxide sublattice, and $a_2 = 0.534(6)$, $b_2 = 0.313(6)$, $c_2 = 0.958(1)$ nm, and $\beta_2 = 94.8(4)°$ for magnesium hydroxide sublattice.

Misfit-layered compounds are very interesting because of their unusual structures as well as their properties.[1–3] Typical examples are ternary transition metal chalcogenides $(MX)_nTX_2$ (M = rare earth metal, Sn, Pb, Sb, Bi; T = Ti, V, Cr, Nb, Ta, and X = S, Se) and mixed cobalt oxides $[M_mA_2O_{2+m}]_qCoO_2$ ($m = 1$ or 2; M = Co, Bi, etc.; and A = Ca, Sr, etc.)[4,5] The structures of these compounds are built from two substructures; CdI_2-type hexagonal TX_2 or CoO_2 sheets and NaCl-type square-planar MX or $M_mA_2O_{2+m}$ sheets are stacked alternately. The two sheets have the same lattice period along the one of the in-plane crystallographic axes. However, along another axis they show lattice mismatch leading to the one dimensionally incommensurate lattice. Besides above compounds, some of the mixed layered minerals have the misfit-layered structures.[6] However, there have been less attention paid to them so far, probably because the misfit-layered crystals grown in the natural condition are always disordered in the layers stacking with poor crystallinity.

It is an attractive method to prepare some novel compounds by using the layered compounds as a precursor.[7–9] The layered sodium manganese oxides $Na_xMnO_2\cdot yH_2O$ with birnessite-type structure have been used to prepare several compounds with layered or tunnel structures, such as so called 7 and 10 Å manganates.[10–12] However, to our knowledge, there has been no report about a misfit-layered hydroxide oxide with a monoclinic structure built from two kinds of sheets with the same in-plane symmetry. We present here a new magnesium manganese hydroxide oxide with such a structure built from the noncommensurate sheets of MnO_2 and $Mg(OH)_2$.

At first, we synthesized birnessite (Bir-A) according to the method described in the literature.[13] The powder X-ray diffraction (XRD) pattern of the sample shows that the crystallinity of the compound is very low despite the aged time of more than 20 days (Figure 1, Bir-A). In order to increase the crystallinity of birnessite, Bir-A was further hydrothermally treated in 2 mol·dm^{-3} NaOH solution at 200 °C for 10 h. This sample was labeled as Bir-B. Figure 1 shows that the crystallinity of Bir-B is very high. 0.86 g of Bir-B (wet) was dispersed into 0.023 mol·dm^{-3} $MgCl_2$ solution (30 cm^3). After stirring for 1 day, 0.5 mol·dm^{-3} NaOH solution was added until the pH value in the range from 11 to 12. After filtration and washing, the precipitate was autoclaved in water at 200 °C for 3 days. The XRD pattern of this magnesium manganese hydroxide oxide (MMHO) shows an intense peak indicating the lattice spacing of about 0.954 nm with high preferred orientation (Figure 1). As the manganese minerals having such a long lattice spacing as about 1 nm, todorokite with a tunnel structure and buserite with a layered structure are known.[10] However, because of the strong preferred orientation, the intensity of the higher angle peaks in the XRD pattern of MMHO were too weak to identify the structure. Therefore we have used transmission electron microscopy (TEM) for the characterization of the MMHO.

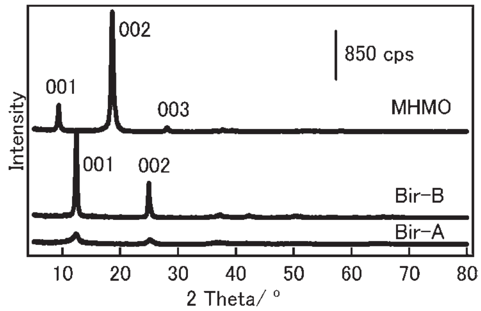

Figure 1. XRD patterns of the samples.

The selected area electron diffraction (SAED) patterns, TEM images and energy-dispersive X-ray (EDX) spectroscopy were obtained with a field emission type TEM (JEOL JEM2010F) operated at 200 kV. TEM images show that the most of MMHO are large sheet-like crystals with two kinds of appearances; ones are the smaller pseudohexagonal sheet crystals with the diameters ranging from 800 to 200 nm, and the others are rectangular sheet crystals with the dimensions ranging from 7000 × 3000 to 1000 × 150 nm, the appearance of which is similar to that of the precursor Bir-B. However, all of the sheet-like crystals show the same SAED pattern as shown in Figure 2a and the similar EDX spectra, suggesting that they have the same composition and crystal structure. Besides the sheet-like crystals, a few of the MMHO crystals are thin and stick-like with the typical dimension of 600 × 30 nm and give the SAED patterns similar to either Figures 2b or 2c. The EDX spectra show that these stick-like crystals have the same composition as that of the sheet-like crystals. The observed longest lattice spacing in the SAED patterns in Figures 2b and 2c, $d = 0.97$ nm, agrees with the lattice spacing of the first peak in the XRD pattern, $d = 0.954$ nm. The d spacings observed in Figure 2a are in agreement with those of

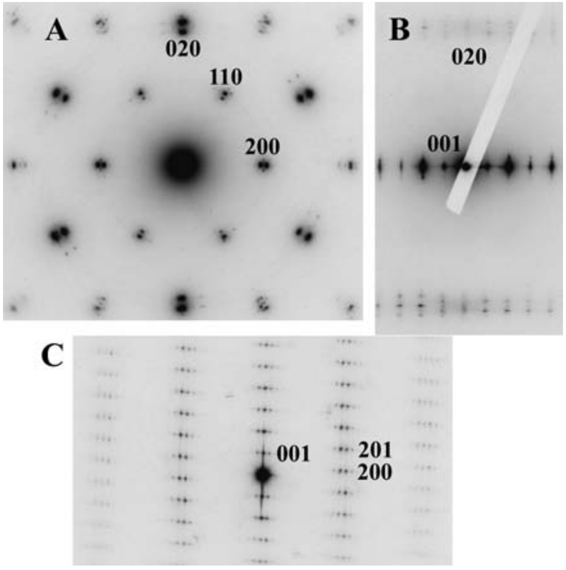

Figure 2. SAED patterns of the sample. (A) sheet-like crystals, (B) and (C) stick-like crystals.

the very weak peaks found in the XRD pattern. The high-resolution transmission electron microscopy images also show almost regular lattice fringes of about 0.95 nm.

The SAED pattern in Figure 2a shows the pseudohexagonal symmetry and is similar to the [001] zone SAED pattern of the monoclinic birnessite-type structure ($C2/m$) as indexed in the figure.[14] However, each diffraction spot splits into two or more spots; for example, $d_1 = 0.148$ nm and $d_2 = 0.159$ nm for two intense spots corresponding to the 020 reflection. The shorter d_1 almost agrees with the 020 lattice spacing (0.142 nm) of the birnessite.[14] The longer d_2 almost agrees with the $d(110) = 0.153$ nm of hexagonal ($P\bar{3}m$) $Mg(OH)_2$.[15] The SAED patterns in Figures 2b and 2c can be indexed as [100] and [010] zone diffraction patterns of $C2/m$ lattice, respectively. They also show the splitting for most of the diffraction spots along a^* and b^*. However, they show no splitting along c^* axis, indicating the regular stacking of the layer units.

The above features of SAED patterns indicate that the present MMHO has a misfit structure built with noncommensurate sheets of MnO_2 and $Mg(OH)_2$ as shown in Figure 3. The model structure is based on the commensurate structure reported for lithiophorite $[(Al,Li)MnO_2(OH)_2]$ in which the octahedral (or CdI_2 type) MnO_2 and $(Al,Li)(OH)_2$ sheets are stacked alternately.[16] Assuming the space group $C2/m$ for both MnO_2 and $Mg(OH)_2$ sublattices, the lattice parameters of two sublattices deduced from SAED and XRD patterns are as follows: $a_1 = 0.496(2)$, $b_1 = 0.292(5)$, $c_1 = 0.957(2)$ nm, and $\beta_1 = 94.1(9)^\circ$ for manganese oxide sublattice, and $a_2 = 0.534(6)$, $b_2 = 0.313(6)$, $c_2 = 0.958(1)$ nm, and $\beta_2 = 94.8(4)^\circ$ for magnesium hydroxide sublattice. The mutual relationship of the two sublattices is that $c_1{}^* = c_2{}^*$, and $b_1{}^* \,//\, b_2{}^*$ in the reciprocal space. In the real space, $d_{(001)} = c_1 \sin\beta_1 = c_2 \sin\beta_2$, $a_1 \,//\, a_2$ and $b_1 \,//\, b_2$. The two sublattices are noncommensurate both along the lateral a and b axes, and the β angles are also different. The most of the reported misfit layered structure is noncommensurate only along the one direction and the two sublattices have different in-plane symmetry.

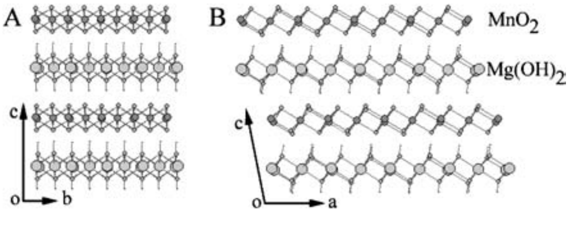

Figure 3. The proposed structure of MMHO.

The Mn, Mg, and Na compositions of MMHO are 34.5, 10.8 and 0.009%, respectively, in mass (Mn/Mg = 1.41 in mole), which were analyzed by a Hitach-Z-5310 atomic absorption spectrophotometer. The EDX analysis in TEM also shows the Mn/Mg molar ratio in the range from 1.3 to 1.4. TG and XRD results indicate that this misfit-layer MMHO decomposes above 300 °C. Above 700 °C, it transforms to a Mn_3O_4-like compound. The TG curve shows a stepwise weight loss; (a) a gradual loss up to 300 °C (2.3%), (b) the steeper loss up to 500 °C (10.3%), and (c) an abrupt loss at around 650 °C (4.9%). We assumed them as (a) the loss of interlayer water, (b) the water loss from hydroxide component, and (c) the O_2 evolution from manganese oxide, respectively. Accordingly, a chemical formula $[Mg(OH)_2]_{10}$-$[MnO_{1.86}(OH)_{0.07}]_{14}\cdot 2.34H_2O$ was obtained. The mole ratio of Mn/Mg = 1.16 calculated according to the ideal model structure in Figure 3 is smaller than that obtained from the EDX and AAS analyses (Mn/Mg = 1.41). Some vacancies and/or the incorporation of Mn atoms in the $Mg(OH)_2$ sublattices are well assumed as the origin of the discrepancy. For example, without vacancies, 10 atom % Mn in the $Mg(OH)_2$ sublattice gives the Mn/Mg molar ratio of 1.4.

References

1 I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B*, **56**, R12685 (1997).
2 S. Hebert, S. Lambert, D. Pelloquin, and A. Maignan, *Phys. Rev. B*, **64**, 172101 (2001).
3 O. Pena, P. Rabu, and A. Meerschaut, *J. Phys.: Condens. Matter*, **3**, 9929 (1991).
4 J. Morales, J. Santos, J. Baas, G. A. Wiegers, and J. L. Martinez, *Chem. Mater.*, **11**, 2737 (1999).
5 S. Li, R. Funahashi, I. Matsubara, K. Ueno, and H. Yamada, *J. Mater. Chem.*, **9**, 1659 (1999).
6 F. V. Chukhrov, B. A. Sakharov, A. I. Gorshkov, V. A. Drits, and Y. P. Dikov, *Int. Geo. Rev.*, **27**, 1082 (1985).
7 D. Mochizuki, A. Shimojima, and K. Kuroda, *J. Am. Chem. Soc.*, **124**, 12082 (2002).
8 R. E. Schaak and T. E. Mallouk, *Chem. Commun.*, **2002**, 706.
9 Y. Xu, Q. Feng, K. Kajiyoshi, and K. Yanagisawa, *Chem. Mater.*, **14**, 697 (2002).
10 D. C. Golden, C. C. Chen, and J. B. Dixon, *Science*, **231**, 717 (1986).
11 Z. Liu and K. Ooi, *Chem. Mater.*, **15**, 3696 (2003).
12 Q. Feng, Y. Xu, K. Kajiyoshi, and K. Yanagisawa, *Chem. Lett.*, **2001**, 1036.
13 Q. Feng, K. Yanagisawa, and N. Yamasaki, *J. Porous. Mater.*, **5**, 154 (1998).
14 V. A. Drits, E. Silvester, A. I. Gorshkov, and A. Manceau, *Am. Mineral.*, **82**, 946 (1997).
15 L. Desgranges, G. Calvarin, and G. Chevrier, *Acta Crystallogr., Sect. B*, **52**, 82 (1996).
16 L. Pauling and B. Kamb, *Am. Mineral.*, **67**, 817 (1982).

Published on the web (Advance View) February 23, 2005; DOI 10.1246/cl.2005.448