Synthesis and Characterization of a Novel Misfit-layered Copper Manganese Hydroxide Oxide

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A copper manganese hydroxide oxide, $CuMn_{2.22}O_{5.25}\cdot 2.04H_2O$, which has a novel misfit-layered structure built with pseudohexagonal MnO_2 and orthorhombic $Cu(OH)_2$ sheets, has been hydrothermally synthesized by using the layered birnessite as the precursor. This compound has been investigated by XRD, SEM, TEM, SAED, and TG-DTA. In this compound, manganese oxide sublattice is hexagonal with $a_1 = 0.282$ and $c_1 = 0.942$ nm, and copper hydroxide sublattice is orthorhombic and has a C-center with $a_2 = 0.578$, $b_2 = 0.276$, and $c_2 = 0.942$ nm. The two sublattices in this compound have different symmetry, and they are incommensurate along *a* direction in *ab* plane.

Misfit-layered cobalt oxides $[M_mA_2O_{2+m}]_qCoO_2$ ($m = 1$ or 2; M = Co, Bi, etc.; A = Ca, Sr, etc.), which show good thermoelectric performance, have received considerable attention.[1–8] These oxides are of high thermal and chemical stabilities at high temperature in air, easy manufacture and low cost, so these compounds are considered as potential materials in thermal power generator. Recently, a series of new misfit-layered metal oxides without cobalt, $(Bi_xM_yO_z)_mRhO_2$ (M = Sr and Pb), have been synthesized.[9–11] These rhodium oxides also show good thermoelectric performance. However, the well-known misfit-layered metal oxides with good properties so far are mainly cobalt oxides. Although many means have been tried to improve the thermoelectric performance of these oxides, it is still impossible to use these materials in practice at the present time. Furthermore, because of their unusual properties, the misfit-layered oxides have many potential applications in the field of semiconductors, magnetic materials, ferroelectric materials, and catalysts.

Using the high-temperature solid-state reaction, only cobalt or rhodium oxides with the misfit-layered structure have been prepared.[2,9] In these compounds, the two sublattices are incommensurate only in one direction.[1–11] In contrast with the above method, hydrothermal synthesis is a charming method in the preparation of novel compounds with interesting structures.[12] Using birnessite as the precursor, many manganese oxides, such as layered compounds, cathode material $LiMn_2O_4$, 2 × 4 and 3 × 3 tunnel compounds have been hydrothermally synthesized.[13–16] The distance of the interlayer in birnessite is so easy to be modified that even a large building block such as SiO_2 and TiO_2 can also be induced into the interlayer of birnessite, by which novel compounds were prepared.[17,18] Furthermore, a mixed layered $Ni(OH)_2$–manganese oxide (NMO) with the incommensurate *a* and *b* has been also hydrothermally synthesized by using birnessite as the precursor.[19] This is the first example to prepare a misfit layered oxide in a mild condition. Recently, a novel magnesium hydroxide–manganese oxide (MHMO), which has two incommensurate monoclinic sublattices, has been hydrothermally synthesized by using birnessite as the precursor.[20] However, the two sublattices in the above two misfit-layered manganese oxides have the same symmetry. Here, we present a novel misfit-layered copper manganese hydroxide oxide (CMHO) $CuMn_{2.22}O_{5.25}\cdot 2.04H_2O$, in which the two sublattices have different symmetries.

Firstly, birnessite was synthesized according to the method described in the literature.[14] The powder X-ray diffraction (XRD) pattern (Figure 1A) recorded with a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα ($\lambda = 0.15418$ nm) radiation shows that the product synthesized by this method is a pure Na–birnessite with $d(001) = 0.72$ nm. Then, CMHO was synthesized by using the layered birnessite as a precursor. Na-birnessite (about 1 g of wet sample) was firstly dispersed into a certain $CuCl_2$ solution, after stirring for 20 min, 0.5 M NaOH solution was added into the solution until pH 8–9, then the mixture was filtered and washed with distilled water until pH 7, and autoclaved in distilled water at 120 °C for 1 day. The XRD patterns of the products are shown in Figure 1.

Sample 1 (labeled as A-1) was prepared from the starting mixture with Mn/Cu = 2. Its XRD pattern (Figure 1B) is very similar to that of NMO and MHMO,[19,20] indicating that this sample is a pure copper manganese hydroxide oxide (CMHO) which has a similar structure to that of NMO and MHMO. However, the sample (labeled as A-2) prepared from the starting mixture with Mn/Cu = 1.8 is a mixture of CMHO and CuO (Figure 1C). So the amount of $Cu(OH)_2$ induced into the interlayer of birnessite is limited just like in the case of NMO and MHMO. Furthermore, CMHO synthesized with this method is also in high orientation. In order to investigate the details of the structural of this compound, high-resolution transmission electron microscope (TEM) observations and selected-area electron diffraction (SAED) investigation were carried out on a field emission type TEM (JEOL JEM2010F) operated at 200 kV.

Scanning electron microscope (SEM) observation (not shown here) performed on a JEOL JSM–6700F cold field emission scanning electron microscope shows that the crystals of CMHO (sample A-1) are sheet-like with different dimensions.

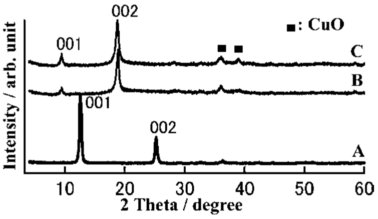

Figure 1. The XRD patterns of (A) Na–birnessite, (B) sample A-1 and (C) sample A-2.

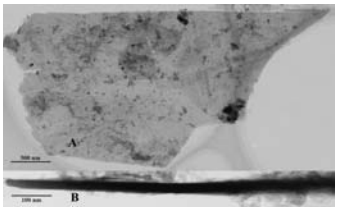

Figure 2. TEM images of sample A-1. (A) big sheet, (B) long bar.

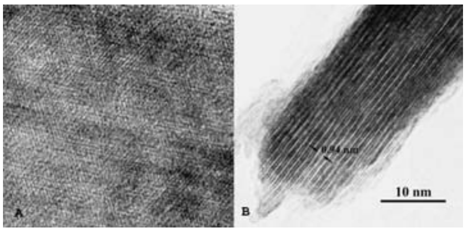

Figure 3. High-resolution TEM images of CMHO (observed from the same crystals shown in Figure 2).

The maximum plane area of the big sheet-like crystal is about 2 × 1.5 μm. However, the thickness of the crystals is smaller than 0.2 μm. The TEM observations show that the appearance of most CMHO crystals is thin and sheet-like (Figure 2A) and that a few of them show small long-bar aspect (Figure 2B). These results confirm that the crystals of CMHO are in high orientation, which is in well agreement with the result of the XRD analysis.

The high-resolution TEM observations indicate that the arrangement of the atoms is pseudohexagonal in the *ab* plane of the CMHO crystal (Figure 3A), while the arrangement of the atoms is line-like along the *a* direction in the *ac* plane (Figure 3B). The distance between the two strong lines is about 0.9 nm (Figure 3B), which is agreed with the distance of $d(001) = 0.94$ nm in the XRD pattern of CMHO (Figure 1B). This result confirms that CMHO has a layered structure rather than 3 × 3 tunnel structure (todorokite-type structure) although their XRD patterns are very similar.

Figure 4 shows the SAED patterns obtained from the same two crystals shown in Figure 2. There are two set of diffraction dots with different symmetry in Figure 4A. One set of the dots with pseudohexagonal symmetry is attributed to MnO_2 sublattice and the other set of dots with orthorhombic symmetry is ascribed to $Cu(OH)_2$ sublattice. The $Cu(OH)_2$ sublattice has a *C*-center. In the previous misfit-layered manganese oxides NMO and MHMO, the two sublattices have the same symmetry.[19,20] For example, the two sublattices in MHMO are monoclinic, and they are incommensurate in both of the *a* and *b* directions. However, the two sublattices in CMHO have different symmetry, and the sublattices are incommensurate only in one direction (i.e., in *a* direction) in the *ab* plane (Figure 3A). This result implies that misfit-layered compounds with different type of sublattices can be synthesized by using a layered precursor.

The lattice parameters of CMHO are calculated from the SEAD and XRD data. The manganese oxide sublattice is hexagonal with $a_1 = 0.282$, and $c_1 = 0.942$ nm, and the copper hydroxide sublattice is orthorhombic with $a_2 = 0.578$, $b_2 = 0.276$, and $c_2 = 0.942$ nm.

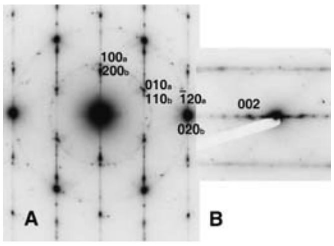

Figure 4. SAED patterns of the sample A-1 observed (A) along (001) direction and (B) along (010) direction.

The theoretical formula of this compound can be written as $[Cu(OH)_2H_m][MnO_2]_{1.16}$. The experimental formula of the sample A-1 is $CuMn_{2.22}O_{5.25}\cdot 2.04H_2O$, which is determined from the thermogravimetric (TG) analysis data and composition analysis data. This compound can be stable up to 200 °C. More details will be published elsewhere.

This work is supported by the NSFC through the Creative Research Team Fund (No. 20121103), the Youth Foundation of Jilin University and the Creative Foundation of Jilin University. Dr. Yaohua Xu also thank Prof. Qifeng Zhou for his grand support to this research.

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