$LaMnO_3$ Fine Powder Prepared by the Thermal Decomposition of a Heteronuclear Complex, $LaMn(dhbaen)(OH)(NO_3)(H_2O)_4$

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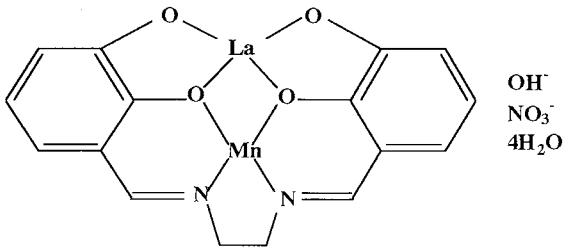
(Received July 29, 1999; CL-990669)

The heteronuclear $LaMn(dhbaen)(OH)(NO_3)(H_2O)_4$ complex was synthesized and perovskite-type hexagonal $LaMnO_3$ was obtained by its thermal decomposition at 700 °C. Particle size of the samples decomposed at 600 °C and 700 °C is ca. 20 nm and 50 nm, respectively.

Perovskite-type oxides such as $LaMnO_3$ are the most promising material as electrodes of fuel cells and chemical sensors.[1] Solid state reaction using oxides has been applied as the conventional synthesis method. Chemical processing might be used to obtain fine powders such as the sol-gel method.[2] Recently, we proposed the thermal decomposition of heteronuclear complexes as a new method for the preparation of di- or tri-metallic oxides. We found that heterometallic oxides with relatively high specific surface area were formed at low temperatures when heteronuclear hexacyano-complexes were used as precursors.[3,4] The decomposition of the heteronuclear complexes is a promising method for the preparation of homogeneous mixed oxides at an atomic level.[5]

In this study, we synthesized a $LaMn(dhbaen)(OH)(NO_3)(H_2O)_n$ complex, where dhbaen is N,N'-bis(3-hydroxysalicylidene)-ethylenediamine for the first time, and the decomposition products were characterized by thermogravimetry analysis (TGA), X-ray diffraction (XRD) using Cu-Kα radiation, fourier transform infrared (FT-IR) spectroscopy, and transmission electron microscopy (TEM). Selected area diffraction pattern (SADP) measurements were also performed during TEM analysis.

A mononuclear Mn(III) complex, $[Mn(H_2dhbaen)Cl]_3 \cdot H_2O$, was synthesized in advance as follows: $Mn(CH_3COO)_2 \cdot 4H_2O$ was added to a suspension of prepared $H_4dhbaen$ (6 mmol) in methanol (220 cm^3) and filtrated as deep brown crystals. A heteronuclear Mn(III)-La(III) complex, $MnLa(dhbaen)(OH)(NO_3)(H_2O)_n$, was obtained in the following manner: a methanolic solution (3 cm^3) of $LiOH \cdot H_2O$ (4 mmol) was added to a suspension of the mononuclear Mn(III) complex (2 mmol) in methanol (80 cm^3). A methanolic solution (3.5 cm^3) of $La(NO_3)_3$ (2 mmol) was added to the resulting transparent solution. After the mixture was warmed with stirring for 2 h, crystals were collected by suction filtration, washed successively with distilled water, methanol and diethyl ether, and then dried in the open air. The heteronuclear Mn(III)-La(III) complex thus obtained was used without purification. Elemental analyses of C, H, and N in the complex were carried out at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University, Japan. From results of elemental analysis, the complex was estimated to be $LaMn(dhbaen)(OH)(NO_3)(H_2O)_4$ will the following structure:



The thermal decomposition behavior was examined by TGA analysis, performed with a heating rate of 5 °C/min in syn-air. The heat-treated samples were prepared by holding the complex at various temperatures in ambient air for 30 min. In order to characterize the decomposition products, X-ray diffraction patterns were recorded (Rint 2000, Rigaku, scanning rate 2°/min 40 kV, 20 mA). Surface area was determined by BET method.

Figure 1 shows the results of TGA and XRD for the decomposed samples. Dehydration by the loss of water of crystallization started at about 150 °C. Further heating caused a weight loss due to the exothermal decomposition of the ligand (confirmed

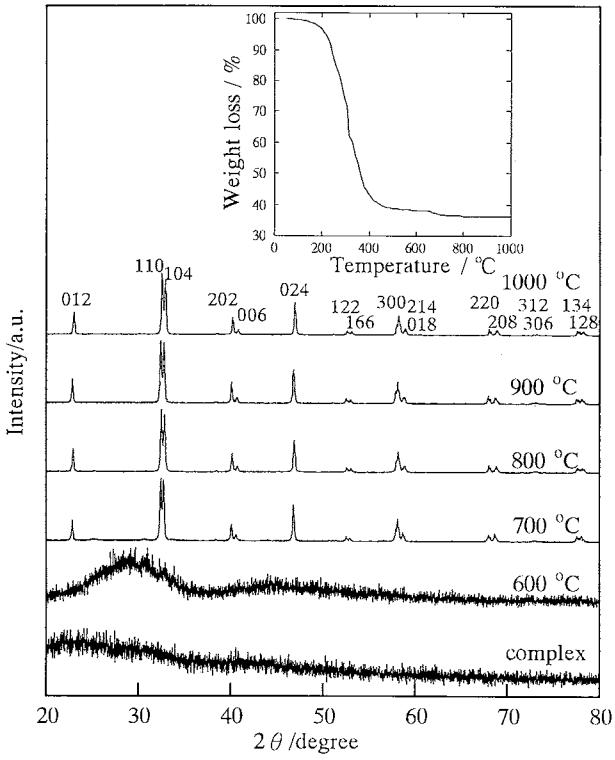


Figure 1. TGA and XRD results of LaMn-complex in air. The TGA was measured by heating rate 5 °C/min in air. Decomposition temperature for XRD in °C are shown in the figure.

by DTA) followed by a gradual weight loss up to ca. 700 °C. The weight loss percentage 36.2% in the last plateau range is slightly lower than 37.7% calculated by assuming the formation of $LaMnO_3$. The XRD patterns for the samples fired below 600 °C did not shows any peaks. For the complex decomposed at 700 °C, hexagonal $LaMnO_3$ was observed and no other compounds were detected by XRD.[6,7] This result shows that the heterometallic oxide was directly formed from the complex by its decomposition.

Figure 2 shows TEM photographs with SADP for the samples fired at 600 °C and 700 °C. The particle size was estimated in the order 20 nm (surface area : 27.9 m^2g^{-1}) and 50 nm (surface area : 15.6 m^2g^{-1}) for the samples decomposed at 600 °C and 700 °C, respectively. Although XRD analysis did not show the peaks of $LaMnO_3$ for the sample fired at 600 °C (Figure 1), SADP confirmed the formation of polycrystalline materials. Figure 3 shows FT-IR results for both samples. The bands attributable to carbonate, nitrate and hydroxy groups were observed at the 1400, 1500, and 3500 cm^{-1} for the sample fired at 600 °C, and disappeared for the sample decomposed at 700 °C. Therefore, one can conclude that the carbonate, nitrate and hydroxy groups formed by the thermal decomposition of the complex remained on the surface of the polyclystalline grains for the sample of 600 °C.

In conclusion, perovskites of $LaMnO_3$ single phase having fine particle size were formed by the thermal decomposition of the synthesized heteronuclear complex at low temperature. The proposed synthesis method is very promising for the preparation of electroceramics materials. Further work will include the synthesis of comlexes in the LnMn-system using other rare earths (Ln), and their application as electrode materials.

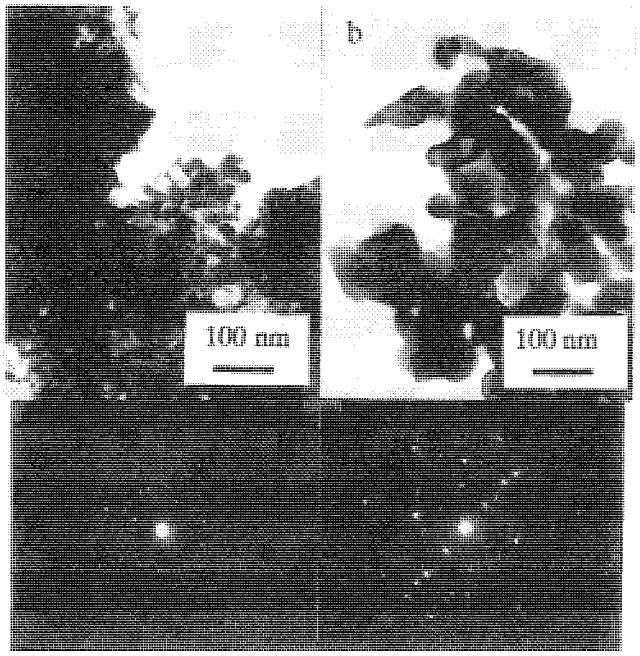


Figure 2. TEM micrographes with SADP for the samples decomposed at 600 °C (a) and 700 °C (b).

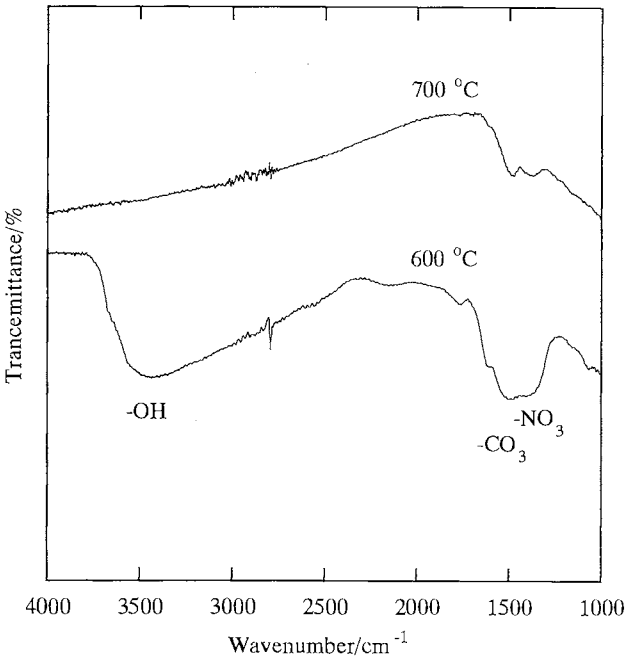


Figure 3. FT-IR spectra of LaMn-complex decomposed at 600 °C and 700 °C.

References and Notes

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