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Crystal Structure of $LaMnO_{3+\delta}$ Synthesized Using Poly(Acrylic Acid)

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Poly(acrylic acid) (PAA) was used to make a gel from an aqueous solution of lanthanum and manganese nitrates. In the concentration range 3×10^{-2} to 5×10^{-2} *M* of PAA, the single phase of perovskite-type $LaMnO_{3+\delta}$ was synthesized by firing gels at low temperature. The crystal structure of $LaMnO_{3+\delta}$ changes from hexagonal to orthohombic with increasing concentration of PAA. At 5×10^{-2} *M* of PAA, the crystal structure of $LaMnO_{3+\delta}$ changes from orthorhombic to hexagonal with increasing temperature.

Introduction

$LaMnO_3$ has an orthohombic perovskite-type structure with $a = 0.5535$ nm, $b = 0.5758$ nm and $c = 0.7708$ nm (*1*). $LaMnO_3$ is available to be used as an electrode in high temperature solid-state fuel cells or as a catalyst which oxidizes hydrocarbons (*2*, *3*). As $LaMnO_3$ is generally synthesized above 850°C starting from mixtures of metal acetates, the specific surface area is less than 5 m^2/g (*4*). Taguchi *et al.* synthesized $(La_{1-x}Sr_x)MO_3$ through the sol–gel process below 500°C (*5*). If the firing temperature is low, the specific surface area of $(La_{1-x}Sr_x)MnO_3$ is about 17.5–23.5 m^2/g. Recently, we have noticed that the crystal structure of $(La_{1-x}Sr_x)MnO_3$ strongly depends on the concentration of poly(acrylic acid) (PAA) in the gel.

In the present study, we tried to synthesize $LaMnO_{3+\delta}$ at low temperatures using gels with varying concentrations of PAA. Thereafter, the crystal structure and oxygen content of $LaMnO_{3+\delta}$ were examined. These results will provide some information with which to improve the perovskite-type catalysis.

Experimental

The powders of $La(NO_3)_3 \cdot 6H_2O$ (2.9686 g) and $Mn(NO_3)_2 \cdot 6H_2O$ (2.0314 g) were weighed in a chemical equivalent and dissolved in 5 ml of distilled water. Poly(acrylic acid) (PAA) was used to make a gel. Average molecular weight of PAA used is 2000. By dissolving PAA in distilled water, we obtained aqueous solutions of PAA with 1×10^{-2} to 10×10^{-2} *M*. The aqueous solution (10 ml) of PAA was added to the aqueous solutions of metal nitrates; then the pH of the aqueous solution was adjusted to 1.0 by adding nitric acid. The resulting solution was mixed with a magnetic stirrer at room temperature. We obtained a viscous gel after mixing for 5–10 min. The gel was dried at 100°C for 12 hr, then fired at 200 to 1200°C in air for 6 hr. The heating rate was 10°C/min.

The crystal structure of the samples was identified by X-ray powder diffraction

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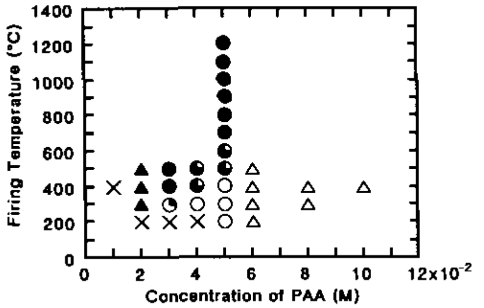

FIG. 1. The relation between the crystal structure of the samples and the synthesis conditions (the concentration of PAA and the firing temperature). The samples were synthesized by firing gels at various temperatures for 6 hr. (○: orthorhombic $LaMnO_{3+\delta}$; ●: hexagonal $LaMnO_{3+\delta}$; ◑: orthorhombic and a trace of hexagonal $LaMnO_{3+\delta}$; ◐: hexagonal and a trace of orthorhombic $LaMnO_{3+\delta}$; △: orthorhombic $LaMnO_{3+\delta}$ and La_2O_3; ▲: hexagonal $LaMnO_{3+\delta}$ and La_2O_3; x: amorphous).

(XRD) using monochromatic Cu$K\alpha$ radiation. The oxygen content in each sample was determined by an oxygen–reduction (redox) method (*6*). After sodium oxalate solution and perchloric acid were added to dissolve the sample in a flask, the solution was titrated with a standard potassium permanganate solution. Differential thermal analysis (DTA) was performed in the temperature range from room temperature to 1100°C.

Result and Discussion

Figure 1 shows the relation between the crystal structure of the samples and synthesis conditions (the concentration of PAA and the firing temperature). Below 2×10^{-2} or above 6×10^{-2} *M* of PAA, we could not obtain a single phase of $LaMnO_{3+\delta}$. From XRD patterns, it is obvious that the samples are amorphous or a mixture of $LaMnO_{3+\delta}$ and La_2O_3. In the concentration range 3×10^{-2} to 5×10^{-2} *M* of PAA, we could obtain perovskite-type $LaMnO_{3+\delta}$. The crystal structure of $LaMnO_{3+\delta}$ is strongly influenced by the concentration of PAA or the firing temperature. At a certain firing temperature, the crystal structure of $LaMnO_{3+\delta}$ changes from hexagonal to orthohombic with increasing the concentration of PAA.

At 5×10^{-2} M of PAA, we fired the gel at 200 to 1200°C for 6 hr. The relation between the crystal structure of $LaMnO_{3+\delta}$ and the firing temperature is also shown in Fig. 1. The crystal structure of $LaMnO_{3+\delta}$ is orthohombic below 400°C. At 500 and 600°C, both hexagonal and a trace of orthorhombic $LaMnO_{3+\delta}$ coexist. Above 700°C, the crystal structure of $LaMnO_{3+\delta}$ is hexagonal. Figure 2 shows the DTA curve of La $MnO_{3+\delta}$. This sample is synthesized by firing the gel with 5×10^{-2} *M* of PAA at 200°C for 6 hr. $LaMnO_{3+\delta}$ gave an endothermic peak at ca. 475°C on heating. From the results of Figure 1, the endothermic peak in the DTA curve corresponds to the phase transition of $LaMnO_{3+\delta}$.

Figure 3A shows the oxygen content of $LaMnO_{3+\delta}$. These samples were synthesized by firing gels with 5×10^{-2} *M* of PAA at 200 to 800°C for 6 hr. The oxygen content abruptly increases at 400 to 600°C. The oxygen content of the $LaMnO_{3+\delta}$ samples which were synthesized by firing gels with 3×10^{-2} to 5×10^{-2} *M* of PAA at 400°C for 6 hr is also shown in Fig. 3B. With increasing concentration of PAA, the oxygen content abruptly decreases to 3.00. In Fig. 3, the crystal structure of $LaMnO_{3+\delta}$ is also shown. From this result, it is obvious there is a close relation between the oxygen con-

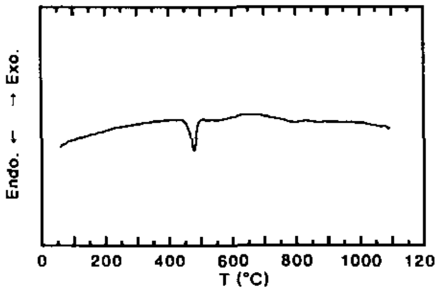

FIG. 2. DTA curve of $LaMnO_{3+\delta}$. The sample was synthesized by firing the gel with 5×10^{-2} *M* of PAA at 200°C for 6 hr. Heating rate is 10°C/min.

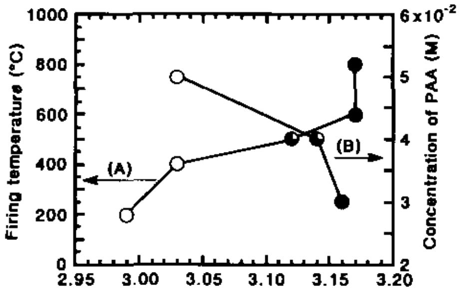

FIG. 3. (A) The oxygen content of $LaMnO_{3+\delta}$. The samples were synthesized by firing gels with 5×10^{-2} *M* of PAA at 200, 400, 500, 600, and 800°C for 6 hr. (B) The oxygen content of $LaMnO_{3+\delta}$. The samples were synthesized by firing gels with 3×10^{-2} to 5×10^{-2} *M* of PAA at 400°C for 6 hr. (○: orthorhombic $LaMnO_{3+\delta}$, ●: hexagonal $LaMnO_{3+\delta}$, ◐: hexagonal and a trace of orthorhombic $LaMnO_{3+\delta}$).

tent and the crystal structure of $LaMnO_{3+\delta}$. In case that $3 + \delta$ is nearly 3.00, the crystal structure of $LaMnO_{3+\delta}$ is orthorhombic. But, in the range ca. $3.12 \leq 3 + \delta \leq 3.17$, the crystal structure of $LaMnO_{3+\delta}$ is hexagonal. According to the data of the Joint Committee on Powder Diffraction Standards, $LaMnO_{3.00}$ is orthorhombic and $LaMnO_{3.15}$ is hexagonal (*7*). Takeda *et al.* reported the crystal structure and the oxygen content of $LaMnO_{3+\delta}$ ($-0.01 \leq \delta \leq 0.09$) after annealing at various temperatures (*8*). The crystal structure of $LaMnO_{3+\delta}$ changes from orthorhombic to hexagonal at ca. $\delta = 0.05$. This agrees with our present results.

Now, we consider the reason the crystal structure or the oxygen content of $LaMnO_{3+\delta}$ changes with the concentration of PAA or the firing temperature. At 400°C (in Fig. 1), for example, the crystal structure changes from amorphous to the mixture of hexagonal $LaMnO_{3+\delta}$ and La_2O_3, hexagonal $LaMnO_{3+\delta}$, orthorhombic $LaMnO_{3+\delta}$ and the mixture of orthorhombic $LaMnO_{3+\delta}$ and La_2O_3 with increasing concentration of PAA. According to Taguchi *et al.* (*5*), the DTA curve of the gel ($x = 0.3$) gave both a large and a small exothermic peak at 170°C and 250°C, respectively. These exothermic peaks correspond to the combustion of PAA. In the present method, PAA burns below 300°C and the combustion heat of PAA is used to synthesize $LaMnO_{3+\delta}$. As the combustion heat is insufficient to yield $LaMnO_{3+\delta}$ below 2×10^{-2} *M* of PAA, the sample is amorphous or includes La_2O_3. Above 3×10^{-2} *M* of PAA, the combustion heat is high enough to yield $LaMnO_{3+\delta}$. Kamata *et al.* reported that the oxygen content of $LaMnO_{3+\delta}$ depends on the partial pressure of oxygen (*1*). At a low partial pressure of oxygen, $LaMnO_{3+\delta}$ decomposes into La_2O_3 and MnO. Though, in the present study, the gel is fired in air, the partial oxygen pressure extremely near $LaMnO_{3+\delta}$ is considered to decrease with increasing concentration of PAA. The decrease of partial pressure of oxygen results from CO or CO_2 by the decomposition of PAA. It is impossible to know the generated partial pressure of oxygen extremely near $LaMnO_{3+\delta}$, but both the decrease of the oxygen content of $LaMnO_{3+\delta}$ at high concentrations of PAA (Fig. 3B) and the presence of La_2O_3 above 6×10^{-2} *M* of PAA suggest that the partial pressure of oxygen is low. At 5×10^{-2} *M* of PAA, the oxygen content of $LaMnO_{3+\delta}$ increases with increasing firing temperature (Fig. 3A). As CO is easily oxidized on the surface of $LaMnO_{3+\delta}$ at high temperatures (*3*, *4*), the partial pressure of oxygen extremely near $LaMnO_{3+\delta}$ is considered to increase with increasing temperature. Consequently, a part of the manganese ions in $LaMnO_{3+\delta}$ oxidize to Mn^{4+}ions and the crystal structure changes from orthorhombic to hexagonal (*8*).

It is concluded that we have defined the conditions to synthesize $LaMnO_{3+\delta}$ by using PAA. In the concentration range 3×10^{-2} to 5×10^{-2} *M* of PAA, hexagonal or orthorhombic perovskite-type $LaMnO_{3+\delta}$ was synthesized by firing gels at low temperature. The crystal structure of $LaMnO_{3+\delta}$ is strongly influenced by the concentration of PAA or the firing temperature. This phase transition depends on the partial pressure of oxygen extremely near of $LaMnO_{3+\delta}$.

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References

1. K. Kamata, T. Nakajima, T. Hayashi, and T. Nakamura, *Mater. Res. Bull.* **13,** 49 (1978).
2. J. H. Kuo, H. U. Anderson, and D. M. Sprain, *J. Solid State Chem.* **87,** 55 (1990).
3. T. Arakawa, A. Yoshida, and J. Shiokawa, *Mater. Res. Bull.* **15,** 269 (1980).
4. T. Nitadori, S. Kurihara, and M. Misono, *J. Catal.* **98,** 221 (1986).
5. H. Taguchi, D. Matsuda, M. Nagao, K. Tanihata, and Y. Miyamoto, *J. Am. Ceram. Soc.* **75,** 201 (1992).
6. N. Mizutani, A. Kitazawa, N. Okuma, and M. Kato, *Kogyo Kagaku Zasshi* **73,** 1097 (1970). [in Japanese]
7. Joint Committee on Powder Diffraction Standards 35-1353 and 32-484.
8. Y. Takeda, S. Nakai, T. Kojima, R. Kanno, N. Imanishi, G. Q. Shen, O. Yamamoto, M. Mori, C. Asakawa, and T. Abe, *Mater. Res. Bull.* **26,** 153 (1991).