Effect of Preparation Techniques of LaFeO₃ Perovskite-Type Oxide on Its Surface Morphologies

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Surface morphology of perovskite-type oxide, LaFeO₃, prepared by thermal decomposition of Fe(III) La(III) heteronuclear coordination polymer, La[Fe(CN)₆] $\cdot$ nH₂O, was compared with those of LaFeO₃ obtained by two conventional preparation methods, solid-state reaction of Fe₂O₃ and La₂O₃ and pyrolysis of a co-precipitated {Fe(OH)₃ + La(OH)₃} precursor. At 1273 K, the first method gave LaFeO₃ with submicrometer-sized pores being highly ordered. At the same temperature, the LaFeO₃ particles with various sizes from nano- to micrometer in diameter and the highly sintered LaFeO₃ were obtained by solid state reaction and co-precipitation method, respectively.

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Perovskite-type oxides, LnMO₃, comprising f-transition (lanthanide, abbreviated hereafter as Ln) and d-transition metal (abbreviated hereafter as M) ions have been one of the most attractive and interesting mixed oxides for the technological applications as functional materials in many fields, including solid oxide fuel cells,^{1,2)} various gas sensors^{3)–11)} and catalysts.¹²⁾ Such peculiar properties of these perovskite-type oxides arise from their nonstoichiometric composition and the mixed conductivity by both ion- and electron-migration. Some of these applications need either the achievement of dense structures or the presence of porosity.

Mixed oxides, including perovskite-type oxides, are conventionally prepared by the following two methods: one is the solid state reaction of oxides, oxalates or carbonates of metal components, and another is the pyrolysis of co-precipitated precursors. Besides these methods, we have proposed the so-called “thermal decomposition technique using d-f heteronuclear coordination polymers”, and found that a series of Ln[M(CN)₆] $\cdot$ nH₂O (M = Fe(III), Co(III)) is one of the most promising precursors of LnMO₃, where the three-dimensional networks are constructed by the Fe–CN–Ln or Co–CN–Ln linkages.^{13)–15)} When these coordination polymers as precursors are thermally decomposed, the formation temperature of perovskite-type oxides is surprisingly lower than that in the solid state reaction of metal oxides. Our next interest is to investigate the microstructures of perovskite-type oxides, because the microstructure is a key factor for the development of functional materials using perovskite-type oxides. However, there is no report on the effect of the kinds of preparation methods of perovskite-type oxides on their microstructures, except for our previous work dealing with LaCoO₃.¹⁶⁾ In the present work, we will compare the surface structures of LaFeO₃ prepared by the above three different methods.

Three kinds of precursors were obtained by solid state reaction, co-precipitation method and thermal decomposition of heteronuclear coordination polymer. In solid state reaction, equimolar amounts of La₂O₃ and Fe₂O₃ powders were ball-

milled for 20 hrs with a small amount of water. In co-precipitation method, an aqueous solution containing equimolar amounts of La(NO₃)₃ and Fe(NO₃)₃ was added to a large excess of concentrated ammoniacal water. After the mixture was stirred at about 353 K for 20 hrs, the precipitates were filtered and dried in the open air. In thermal decomposition method using heteronuclear coordination polymer, La[Fe(CN)₆] $\cdot$ nH₂O was synthesized as a typical precursor by mixing the equimolar amounts of La(NO₃)₃ and K₃[Fe(CN)₆] in water under stirring. The crystals were filtered and dried in the open air. The TG curves were recorded on a thermobalance (Shimadzu DTG 60) in an air stream (50 mL $\cdot$ min^{–1}) from room temperature to 1273 K at the heating rate of 10 K $\cdot$ min^{–1}. Samples for the XRD measurement and the SEM observation were prepared by heating each precursor to the desired temperatures at 10 K $\cdot$ min^{–1} and keeping the respective temperatures for 2 h.

Figure 1 shows the TG curve of La[Fe(CN)₆] $\cdot$ nH₂O as the precursor, which gave a decomposition behavior similar to that previously reported:¹³⁾ the plateau due to the formation of anhydride is observed in the temperature range of 523 and 573 K. Further heating causes an abrupt weight loss by the decomposition of cyanide groups around 623 K. Then, after the gradual weight loss, the last plateau appears above 873 K.

In order to characterize the products formed by thermal treatment of each precursor, powder XRD patterns were measured at various temperatures. **Figure 2** shows the XRD results for the precursor prepared by solid state reaction of La₂O₃ and Fe₂O₃. Almost all of the XRD signals are due to each metal oxide component at temperatures lower than 873 K, at which very weak signals due to LaFeO₃ appear. At 1173 K, some signals due to La₂O₃ and Fe₂O₃ are still observed, and LaFeO₃ is almost completely formed at 1273 K. The XRD results for the co-precipitated precursor are given in **Fig. 3**, which shows that LaFeO₃ is also formed at 873 K. At 1273 K, signals due to LaFeO₃ are mainly observed, in addition to some weak signals attributable to La(OH)₃, La₂O₃ and Fe₂O₃ around 15° and in the range of 25 to 30° in 2 θ . The for-

Fig. 1. TG curve of coordination polymer, $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

Fig. 2. Powder XRD results of products obtained at various temperatures by solid state reaction.

mation of $\text{La}(\text{OH})_3$ was recognized on long standing in the open air after the thermal treatment at 1273 K. **Figure 4** shows the XRD results for the heteronuclear coordination polymer, $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$. At 623 K, which is the temperature just after the abrupt decomposition of cyanide groups, XRD pattern shows a broad signal centered around 30° in 2θ . At this temperature, some very weak signals due to LaFeO_3 are also recognized, indicating that the formation temperature of LaFeO_3 is surprisingly low beyond imagination for the solid state reaction and the co-precipitation method. The XRD profiles of decomposition products in the range of 873 to 1273 K showed only the pattern of LaFeO_3 . From these results given in Figs. 2–4, it was confirmed that, in the formation of pure LaFeO_3 phase, our method based on the thermal decomposition of coordination polymer, $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, is superior to those based on the solid state reaction and the co-precipitation.

In order to investigate how the different preparation

Fig. 3. Powder XRD results of products obtained at various temperatures by co-precipitation method.

Fig. 4. Powder XRD results of products obtained at various temperatures by thermal decomposition of $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

methods affect the microstructure of LaFeO_3 , SEM analyses of samples obtained at 1273 K were made. **Figures 5 and 6** show SEM photographs of samples prepared by the solid state reaction and by the co-precipitation method, respectively. Both of these samples have rough surfaces and there is no regularity in their surface structure. Difference between these two methods is that the solid state reaction gives the LaFeO_3 particles with various sizes from nano- to micrometer in

Fig. 5. SEM Photographs of product obtained at 1273 K by solid state reaction.

Fig. 6. SEM Photographs of product obtained at 1273 K by co-precipitation method.

Fig. 7. SEM Photographs of product obtained at 1273 K by thermal decomposition of $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

diameter, whereas the co-precipitation method gives the highly sintered LaFeO_3 . The SEM photographs of LaFeO_3 prepared by the decomposition of $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ are shown in Fig. 7. This LaFeO_3 is very porous and the highly ordered submicrometer-sized pores with 100–200 nm in diameter are clearly observed. According to our previous studies,^{17),18)} as the decomposition temperature was increased from 623 to 1273 K, sintering gradually proceeded to increase the particle size of LaFeO_3 . Moreover, during thermal decomposition, the crystal shape of $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ precursor was maintained, even though the decomposition temperature was 1273 K. Similar situation can be seen in Figure 7. From these observation, it may be concluded that the formation of the highly ordered pores is the result of a coordinated movement

of component atoms and an isotropic sintering between LaFeO_3 particles with the shape of $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ precursor being kept. Similar porous LaFeO_3 was obtained by thermal-treatment of the mixture of $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ and glass resin at 1273 K.⁵⁾ The present result shows that only the coordination polymer, $\text{La}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, without glass resin is adequate for the formation of porous LaFeO_3 . The catalytic activity of this porous LaFeO_3 for the methane combustion is under investigation, and the results will be reported in the near future, together with the activities of LaFeO_3 prepared from the solid state reaction and the co-precipitation method.

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