Conventional synthesis method for fine polymetallic LaFeO_3 using ethylene glycol solvent addition

Hiromichi AONO,[†] Musashi TOMIDA and Yoshihiko SADAOKA

Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University,
3, Bunkyo-cho, Matsuyama, Ehime 790-8577

The metal nitrates were completely dissolved in a mixed solvent (total 100 ml) of ethylene glycol (EG) (0, 5, 10, 15, 25, and 50 ml) and water, and then dried at 120°C to make precursors for the fine LaFeO_3 (0.05 mol) material. The main product was not LaFeO_3 for the precursor prepared using the nitrate solution containing a small amount of EG (less than 5 ml). The mixed solution of the 10–15 ml EG with water was suitable for the preparation of 0.05 mol LaFeO_3 . In this case, clear XRD peaks of LaFeO_3 single phase were obtained by the calcination even at 350°C using this method. The higher calcination temperature for the formation of the LaFeO_3 phase was needed due to the increased EG amount in the solvent. The particle size was ca. 40 nm for the (EG 10 ml) samples calcined at 350–600°C and it increased with an increase in the calcining temperature.

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Polymetallic oxides containing a lanthanoid (Ln) and transition metal (M), such as a perovskite LnMO_3 , have been investigated for their useful functional properties and used in many applications, such as catalysts,¹⁾ fuel cells,²⁾ solid electrolytes,³⁾ super conductors,⁴⁾ and gas sensors.^{5)–9)} The most conventional method for the heterometallic oxide production is a solid-state reaction of the corresponding single oxides. However, powder materials with a controlled stoichiometry and microstructure are difficult to produce by this method. Chemical processing methods can be used to obtain better control of the powder quality and microstructure. The coprecipitation method is a common chemical method for fine polymetallic materials. However, the homogeneity of metals is affected by the difference in the solubilization and formation speed of the metal hydroxides. We have reported that the thermal decomposition of heteronuclear complexes is a promising method for the preparation of polymetallic oxides.^{10)–15)} In this case, the type of metals is limited for the preparation of the heteronuclear complex. For the chemical method, a polymerization process can be used for all kinds of polymetallic materials, because this method is made in one reaction vessel without filtration. In general, citric acid and ethylene glycol are dissolved in a mixed metal solution, and it polymerized by esterification at 100–200°C.^{16)–18)} For this method, metal ions are homogeneously contained in the polymerized organic material as a precursor. However, this method has problems of particle growth due to the high thermal combustion level of the organic polymer. On the other hand, the amorphous polymetallic complexes as the precursors were synthesized using citric acid without ethylene glycol.¹⁹⁾ For this method, the control of the ratio between the metals and citric acid is difficult, because excessive citric acid also generate the particle growth due to the thermal combustion fever. We considered that the ethylene glycol solution without citric acid for the esterification is effective in order to avoid excessive polymerization. In this case, the mini-

um amount of ethylene glycol polymerizes and acts as a ligand for the cations, because the excessive ethylene glycol evaporates during the precursors preparation process. In this study, we investigated the conventional synthesis method of fine LaFeO_3 powder using ethylene glycol as the solvent.

Metal nitrates of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for making the perovskite LaFeO_3 (0.05 mol) were completely dissolved in a mixed solution (total 100 ml) of ethylene glycol (EG) and water. The EG (0, 5, 10, 15, 25, 50 ml) was mixed using water as the solvent. For the preparation of the precursor, the metal nitrate solution was dried at 120°C for 1 week. The dried powder as the precursor was heat-treated at various temperatures for 1 h in ambient air. Elemental analyses of the C, H, and N in the precursors were carried out at the Central Elemental Analysis Laboratory, Faculty of Science, Kyushu University, Japan. The thermal decomposition behavior of the precursor was examined by simultaneous thermogravimetric and differential thermal analysis (TG/DTA, Seiko Instrument TG/DTA 32), performed at the heating rate of 10°C/min in synthesized air ($\text{CO}_2 < 0.5$ ppm) flow. An X-ray diffraction (XRD, Cu K α radiation, Rint 2000, Rigaku Co., sweep rate 2°/min. 40 kV, 20 mA) analysis was used to study the phases present in the decomposition products. The specific surface area was measured by the one-point BET method. For calculating the particle size, the particle shape was assumed to be spherical.

Figure 1 shows the typical TG/DTA curves for the precursors prepared without (0 ml) and with 10 ml ethylene glycol (EG). The sample without EG (EG 0 ml) showed endothermic DTA peaks due to decomposition of the metal nitrates. The weight decreased with an increase in the temperature, and then remained constant at 55.0 wt% around 600°C and higher for the formation of the metal oxides. The nitrate (NO_3^-) ratio estimated using this TG result was 3.68 which was lower than 6.00 when anhydrous metal nitrates ($\text{La}^{3+} : \text{Fe}^{3+} : \text{NO}_3^- = 1 : 1 : 6$) decompose to metal oxides. The metal nitrates partially decomposed to the oxide during the drying at 120°C in the precursor preparation. On the other hand, the precursor with 10 ml EG showed two exothermic DTA

[†] Corresponding author: H. Aono; E-mail: haono@eng.ehime-u.ac.jp

Fig. 1. TG/DTA curves for the precursor prepared without EG (EG 0 ml) and with 10 ml EG (EG 10 ml) containing solution (10°C/min).

Table 1. TG/DTA Results for the Precursors Prepared by the EG Addition

EG (ml)	0	5	10	15	25	50
EG (mol)	0	0.09	0.18	0.27	0.45	0.90
Final Weight (%)	55.0	58.3	58.2	53.9	49.5	41.4
DTA peak 1 (°C)	115(endo)	220	238	238	231	214
DTA peak 2 (°C)	400(endo)	272	294	320	333	337

Table 2. Elemental Contents (wt% of H, C, and N) in Precursors PREPARED by the EG Addition

EG (ml)	0	5	10	15	25	50
H/wt%	0	0.76	1.28	1.88	2.49	2.55
C/wt%	0	6.03	8.40	12.15	14.26	16.02
N/wt%	14.26	4.79	4.06	3.91	3.27	2.69

peaks. The endothermal peaks for the decomposition of the nitrate were not observed in the DTA result. The TG curve showed two regions of abrupt weight loss around 230–240°C and 290–300°C followed by a slower loss that ended at about 700°C, accompanied by exothermic effects, as shown by the DTA peaks. The final weight was 58.2% for the formation of the oxide material. **Table 1** lists the final decomposition weight and decomposition temperature estimated from the TG results and two DTA peaks, respectively. The precursor showed two exothermic peaks in the DTA measurement for all the EG added samples. Although the first DTA peak around 230°C was not shifted by changing the amount of EG for the preparation, the second peak around 270–340°C was shifted with an increase in the added EG content. These exothermal peaks would be ascribed to the combustion of the organic ligand.

Table 2 shows the results of the elemental analysis for the precursors. The elemental wt% for H and C increased and that for N decreased with the increase in the added EG amount. The decomposition of nitrates during the precursor preparation easily proceeded for the EG added samples. The elemental mole ratio in the precursors was estimated using the TG value and elemental analysis value. **Figure 2** and **Table 3** show these mole ratios for the precursors. The elemental ratio calculated using the start-

Fig. 2. Elemental mole ratio for La, Fe, H, C and N for precursors vs. the amount of EG.

Table 3. Elemental Mole Ratio in Precursors Prepared by EG Addition. The Values Calculated from the Starting Materials are Shown in () in this Table

EG(ml)	La	Fe	H	C	N
0	1	1	0	0	3.68(6.0)
5	1	1	3.14 (10.8)	2.09 (3.6)	1.43 (6.0)
10	1	1	5.28 (21.6)	2.91 (7.2)	1.21 (6.0)
15	1	1	8.38 (31.5)	4.56 (10.8)	1.26 (6.0)
25	1	1	12.09 (54.0)	5.82 (18.0)	1.14 (6.0)
50	1	1	14.77 (108.0)	7.80 (36.0)	1.12 (6.0)

ing material is also shown in the table. The H, C, and N contents were lower than those of the starting materials. The large amount of EG and nitrates evaporated and decomposed during the preparation process of the precursors.

Figure 3 shows the XRD powder diffraction patterns for the products of the decomposition of the precursor at various temperatures for EG 0 ml (a), EG 10 ml (b), and EG 25 ml (c) samples. For the samples without EG (a), the peaks of the perovskite type material could not be observed even at 600°C. In the case of EG 10 ml (b), the sample calcined at 300°C showed very weak peaks of LaFeO_3 with a broad halo at around 30°. The broad halo disappeared and only the LaFeO_3 peaks were observed for samples decomposed at 350°C. It was confirmed that the full-width-at-half-maximum (FWHM) of all the LaFeO_3 peaks decreases with an increase in decomposition temperature because of crystallite growth. The XRD peaks for the LaFeO_3 was observed at 500°C and 600°C for the EG 25 ml (c) sample and EG 50 ml sample, respectively. **Table 4** shows the main phase for the sample calcined at various temperature. The perovskite phase was clearly observed for the EG 10 ml and 15 ml samples by the calcination at 350°C. These results suggest that the La^{3+} and Fe^{3+} ions are homogeneously distributed in the precursors. The suitable ligand for the metal coordination would be synthesized by the heating of the metal nitrates and EG in the precursor preparation when the added EG content was greater than 10 ml. The ligand would be a quasi-polymerized EG with NO_3^- and metal cations. The cations would be coordinated to the oxygen molecules in the ligand. The molecular weight for the quasi-polymerized materials seems to increase with amount of EG, because the

Fig. 3. XRD powder diffraction patterns of the calcined samples for the precursors prepared using (a) EG 0 ml, (b) 10 ml, and (c) 50 ml containing solutions. The decomposition temperatures in °C are shown in the figure.

final decomposition weight decreased and the decomposition temperature increased as shown in Table 1. The most suitable ratio of metal ions and ligand was EG 10 ml and 15 ml for the preparation of the LaFeO₃ (0.05 mol) at a low temperature.

Table 4. Main Phase for the Calcined Precursors Prepared by the EG Addition

EG (ml)	0	5	10	15	25	50
600°C	La ₂ O ₃	LaFeO ₃	LaFeO ₃	LaFeO ₃	LaFeO ₃	LaFeO ₃
500°C	?	La ₂ O ₂ CO ₃	LaFeO ₃	LaFeO ₃	LaFeO ₃	Amorphous
400°C	?	La ₂ O ₂ CO ₃	LaFeO ₃	LaFeO ₃	Amorphous	Amorphous
350°C	?	Amorphous	LaFeO ₃	LaFeO ₃		
300°C			Amorphous	Amorphous

Fig. 4. Particle size of the calcined samples for the precursors prepared using EG 10 ml and EG 25 ml.

Figure 4 shows the particle size for the calcined samples estimated using the BET surface area for the EG 10 ml and EG 25 ml samples. The particle diameter was 30 nm–50 nm for the samples calcined below 700°C for both samples. The larger particle size for the EG 25 ml sample calcined at 400°C would be ascribed to be the amorphous phase formation as shown in Fig. 3. The particle size increased with an increase in the calcining temperature.

Conclusions

We studied the conventional synthesis method for fine LaFeO₃ particles using the precursors obtained from the EG solution. The single LaFeO₃ phase having a 30–50 nm particle size was obtained for the sample decomposed at 350–700°C. In general, the polymerization method is very difficult for preparing fine particles at low temperature due to the particle growing due to the high thermal combustion level of the organic polymer. However, our method in this study was very suitable for obtaining a homogeneous particle, because the excessive organic solvent evaporated during the preparation of the precursor. Further work will be performed for the preparation of another combination of Ln₂M- and LnM₂- complexes, their decomposition products, and their applications.

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