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# $LaFeO_3$ perovskite-type oxide prepared by oxide-mixing, co-precipitation and complex synthesis methods

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The perovskite oxide, $LaFeO_3$, was synthesized by three different preparation methods i.e., the calcination of a mixture of $La_2O_3$ and $Fe_2O_3$ (La-Fe-O), a co-precipitated precursor (La-Fe-OH), $La(OH)_3$ and $Fe(OH)_3$, and a heteronuclear complex (La-Fe-CN), $La[Fe(CN)_6] \cdot 5H_2O$. The obtained powders were characterized by thermogravimetric analysis, powder X-ray diffraction, electron microprobe analysis, specific surface area measurement and scanning electron microscopy. The formation of $LaFeO_3$ is clearly recognized for La-Fe-O, La-Fe-OH and La-Fe-CN at calcining temperatures above 1000, 800 and 600°C, respectively. The mean particle diameter of La-Fe-CN calcined at 600°C for 2 hours was 30 nm. The $LaFeO_3$ perovskite oxide powder obtained by the thermal decomposition of La-Fe-CN was most uniform on an atomic level and the nanosized $LaFeO_3$ powder was obtained at low temperatures. Furthermore, the sinterability was good.

## 1. Introduction

Functional ceramics related to rare-earth (RE) transition metal (Me) perovskite oxides, $REMeO_3$, are very promising materials for use in advanced technologies such as solid oxide fuel cells [1, 2], catalysts [3] and chemical sensors [4]. The functional properties of the $REMeO_3$ powders are enhanced by the homogeneity and high surface area. Mixed oxides, like $REMeO_3$, are conventionally prepared by the solid-state reaction at high temperatures of the corresponding single oxides. By using these methods, it is difficult to obtain single phase materials, since residual amounts of the starting oxides are likely to remain in the final product, unless the repeated cycling of milling and heating are performed. Moreover, because of the synthesis at high temperatures, the obtained powders have a low specific surface area. To lower the preparation temperature and to obtain an ultrafine and chemically pure powder of the mixed oxides, much effort has been recently spend on the development of chemical methods. Several methods have been attempted for the preparation of $REMeO_3$, which include sol-gel or hydrothermal treatment techniques and the thermal decomposition of wet chemically co-precipitated precursors [5–7]. Recently, we proposed a new method based on the thermal decomposition of a cyanide-bridged hetronuclear complex, $La[Fe(CN)_6] \cdot 5H_2O$, and found that a perovskite oxide $LaFeO_3$ powder with ultrafine and homogeneous particles, having an La/Fe atomic ratio, of unity (1.0) was formed at low temperature [8, 9]. However, a series of investigations of the various preparation techniques of the $REMeO_3$ powders carried out by same research group has been slightly reported.

In the present work, we examined the difference in the preparation of the perovskite oxide, $LaFeO_3$, by the calcination of a mixture of $La_2O_3$ and $Fe_2O_3$, the thermal decomposition of a co-precipitated precursor, $La(OH)_3$ and $Fe(OH)_3$, and the thermal decomposition of a hetronuclear complex, $La[Fe(CN)_6] \cdot 5H_2O$.

## 2. Experimental

### 2.1. Sample preparation

The precursors prepared by the oxide-mixing, co-precipitation and complex synthesis methods were labeled La-Fe-O, La-Fe-OH and La-Fe-CN, respectively. The 1 : 1 mixture of $La_2O_3$ and $Fe_2O_3$ (La-Fe-O) was prepared by ball-milling for 24 hours. A co-precipitate of the hydrate (La-Fe-OH) was obtained by the titration of ammonia water into a 1 : 1 solution of La and Fe in which $La_2O_3$ and $Fe_2O_3$ were dissolved by nitric acid. The $La[Fe(CN)_6] \cdot 5H_2O$ (La-Fe-CN) complex was synthesized by mixing aqueous solutions of equal molar amounts of lanthanium (III) nitrate hydrate and potassium hexacyanoferrate (III) with continuous stirring. The elemental analysis results for the obtained La-Fe-OH and La-Fe-CN are summarized in Table I.

### 2.2. Measurement

The thermal decomposition behaviors of La-Fe-OH and La-Fe-CN were examined by thermogravimetric

TABLE I Analytical results

| | La (wt%) | Fe (wt%) | C (wt%) | H (wt%) | N (wt%) |
|---|---|---|---|---|---|
| | $La_2O_3$ | $Fe_2O_3$ | | | |
| La-Fe-OH | 67.25[a] | 32.75[a] | – | – | – |
| | (67.11)[b] | (32.89)[b] | | | |
| La-Fe-CN | 30.38 | 12.14 | 16.30 | 2.19 | 19.96 |
| | (31.50)[c] | (12.67)[c] | (16.34)[c] | (2.29)[c] | (19.06)[c] |

[a] The values for $La_2O_3$ and $Fe_2O_3$ are those measured for the sample calcined at 1000°C.

[b] The values for $La_2O_3$ and $Fe_2O_3$ in parentheses are those calculated for La : Fe = 1 : 1.

[c] The values for La, Fe, C, H and N in parentheses are those calculated for $La[Fe(CN)_6] \cdot 5H_2O$.

analysis (TG) and high temperature X-ray diffraction. The calcining samples were prepared by holding for 2 hours at several temperatures in ambient air after raising the temperature at 5°C $min^{-1}$. The crystal phases were examined using a powder X-ray diffractometer (XRD). The elemental distribution analysis of the powders was carried out with an electron microprobe analyzer (EPMA). Specific surface areas were determined by the BET method using nitrogen as the adsorbate. The sinterabilities were determined with a scanning electron microscope (SEM) after sintering at 1300°C.

## 3. Results and discussion

### 3.1. Thermal decomposition behavior

The TG curves for La-Fe-OH and La-Fe-CN are shown in Fig. 1.

For La-Fe-OH, an abrupt weight loss is observed below 100°C and the weight loss proceeds slowly in the temperature range of 100 to 700°C. The formation of the perovskite oxide, $LaFeO_3$, can be recognized in the last plateau above 700°C by XRD. At the × position, the formation of $La(OH)_3 \cdot Fe(OH)_3$ is assumed by calculating the weight loss percent of the last plateau.

On the other hand, the TG curve for La-Fe-CN shows that the weight loss started slowly at about 80°C, followed by a faster loss which was completed at about 300°C. At 280°C, the weight loss was 20%, which was similar to that (20.43%) calculated by assuming the formation of the anhydrate from $La[Fe(CN)_6] \cdot 5H_2O$. A weight loss step, start abruptly at 300°C, was observed in the TG curve above 300°C. Further heating in the temperature range of 350–600°C induced a further gradual decrease in the weight. At temperatures above 600°C, the weight loss remained constant. The total weight loss was 44.6%, which agreed very well with the theoretical loss (44.95%) calculated for the formation of $LaFeO_3$.

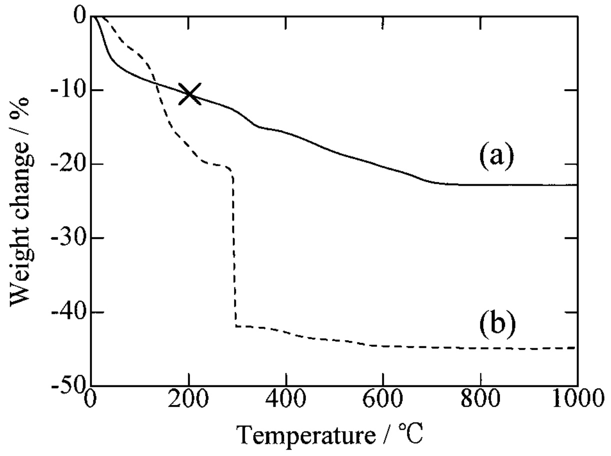

*Figure 1* TG curves of La-Fe-OH (a) and La-Fe-CN (b).

### 3.2. XRD

The powder XRD results of the products of La-Fe-O, La-Fe-OH and La-Fe-CN calcined at several temperatures for 2 hours are shown in Figs 2, 3 and 4, respectively.

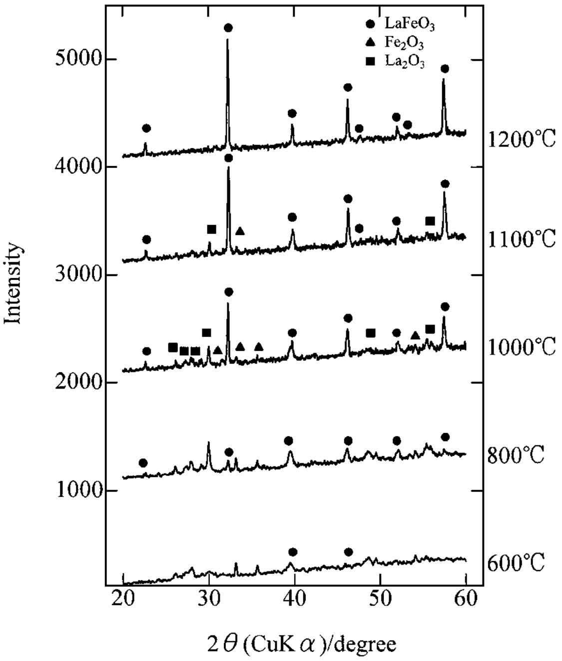

*Figure 2* XRD results of La-Fe-O calcined at several temperature.

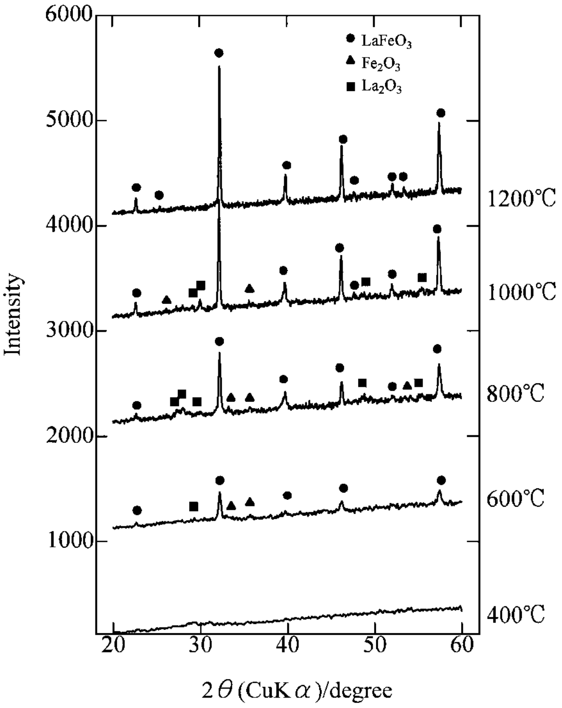

*Figure 3* XRD results of La-Fe-OH calcined at several temperature.

As seen in Fig. 2, the XRD pattern of La-Fe-O calcined at 800°C showed many peaks attributed to $La_2O_3$ and $Fe_2O_3$ as the major products, together with some peaks attributed to the perovskite oxide, $LaFeO_3$, as a minor product, though the formation of the $LaFeO_3$ perovskite oxide was observed above 600°C. On the other hand, the XRD patterns of La-Fe-O calcined at temperatures above 1000°C showed an increase in the intensity of the $LaFeO_3$ perovskite oxide peaks with increasing calcining temperature and a corresponding decrease in the intensity of the $La_2O_3$ and $Fe_2O_3$ peaks. However, some weak peaks attributed to $La_2O_3$ and $Fe_2O_3$ were detected for La-Fe-O calcined even at 1200°C.

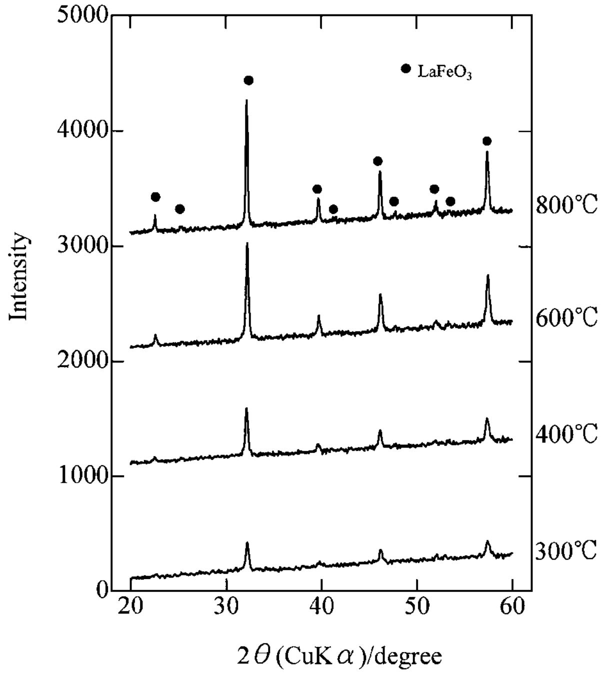

*Figure 4* XRD results of La-Fe-CN calcined at several temperature.

For La-Fe-OH calcined at 400°C, the main peaks were attributed to $La_2O_3$ and $Fe_2O_3$, together with a broad band centered at about 30° in $2\theta$, though weak peaks attributed to the $LaFeO_3$ perovskite oxide were observed as shown in Fig. 3. The formation of the $LaFeO_3$ perovskite oxide was clearly recognized at the calcining temperature above 800°C. The intensity of the $La_2O_3$ and $Fe_2O_3$ peaks decreased with the increasing calcining temperature.

On the other hand, some peaks attributed to the $LaFeO_3$ perovskite oxide were observed for the XRD pattern of La-Fe-CN calcined at 300°C (Fig. 4). The situation did not change for sintering temperatures lower than 600°C. When La-Fe-CN was calcined at temperatures higher than 600°C, the XRD analysis showed only the pattern corresponding to the $LaFeO_3$ perovskite oxide and no peaks attributable to $La_2O_3$ and $Fe_2O_3$ were observed.

In agreement with the literature data (JCPDS File No.37-1493), the crystallographic data for the $LaFeO_3$ perovskite oxide obtained by the sintering of La-Fe-O, La-Fe-OH and La-Fe-CN were evaluated as follows: $a = 0.556$ nm, $b = 0.785$ nm, $c = 0.555$ nm, and an orthorhombic system. The crystallographic data did not significantly change based on the preparation method of the starting materials.

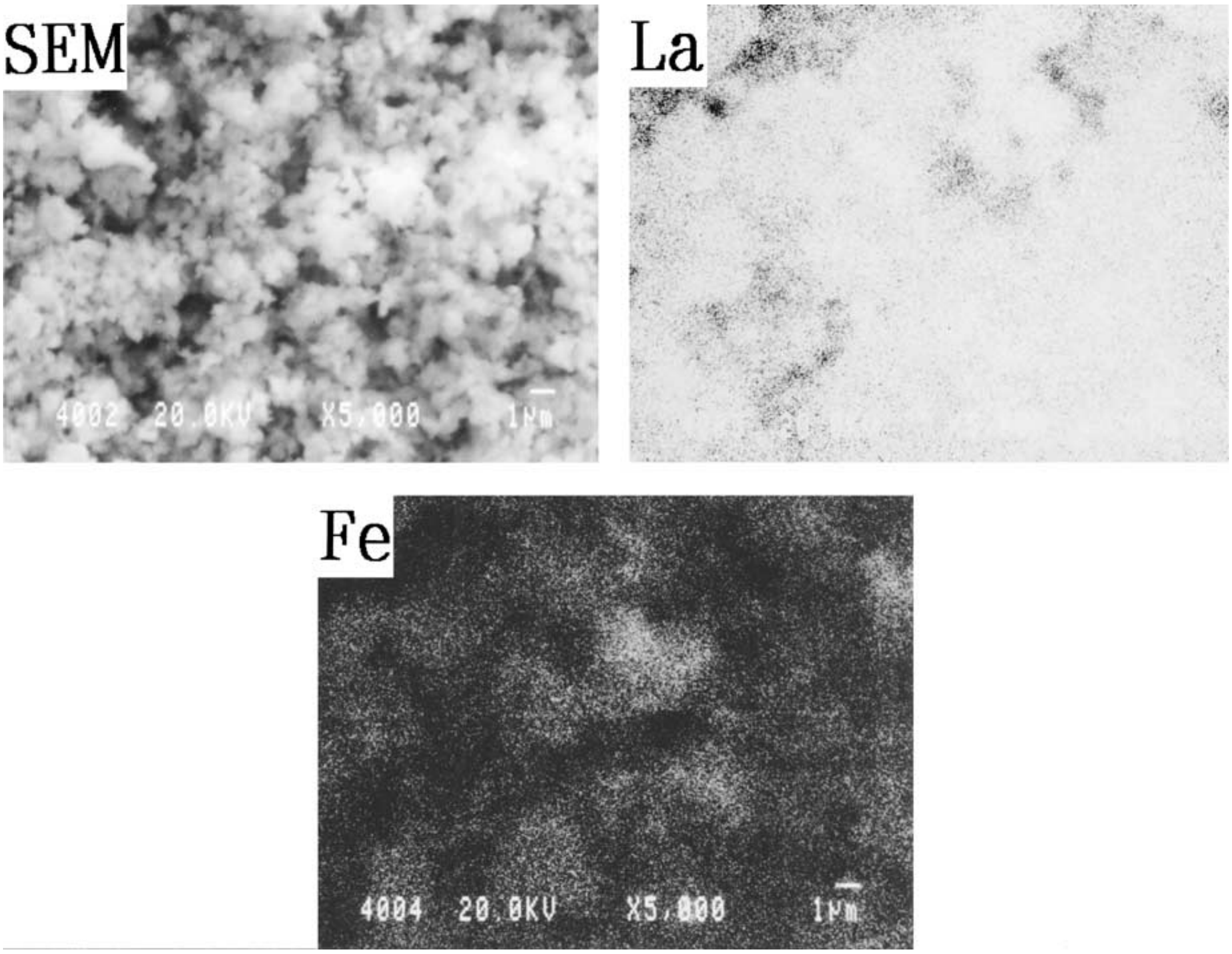

*Figure 5* EPMA results for La-Fe-O calcined at 1000°C.

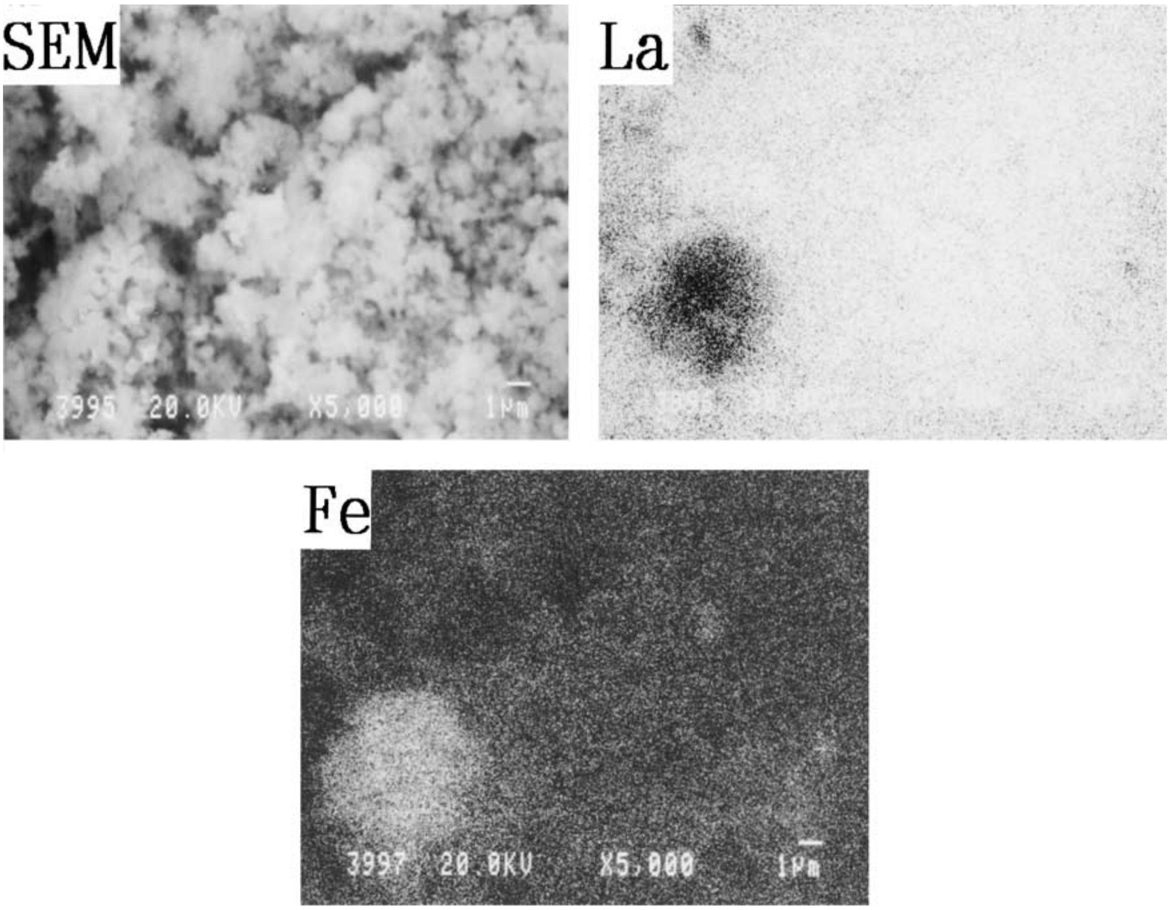

*Figure 6* EPMA results for La-Fe-OH calcined at 1000°C.

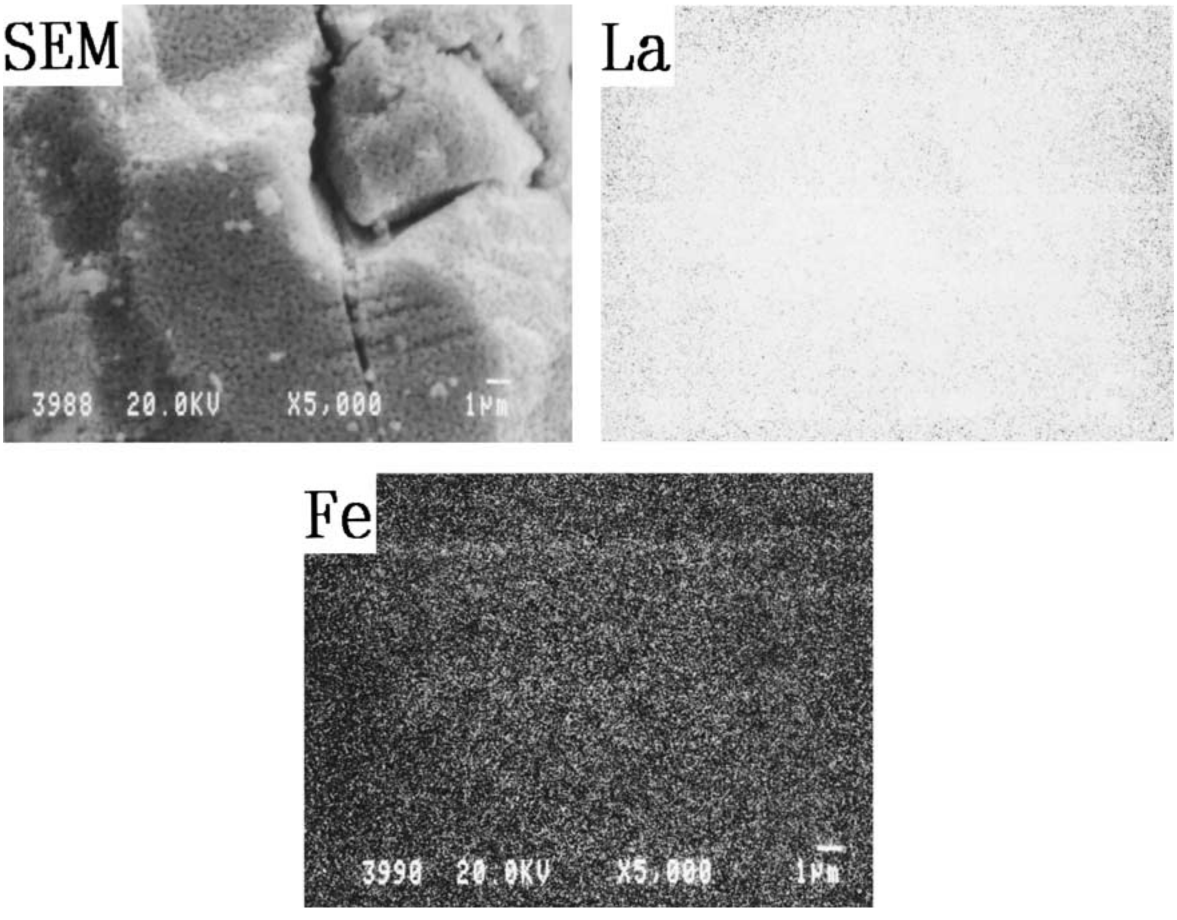

*Figure 7* EPMA results for La-Fe-CN calcined at 1000°C.

## 3.3. EPMA

Figs 5, 6 and 7 show the elemental analysis results by EPMA for La-Fe-O, La-Fe-OH and La-Fe-CN calcined at 1000°C, respectively. For La-Fe-CN, the distribution of the La and Fe species was very homogeneous, while for La-Fe-OH and La-Fe-O, the La-rich phase and Fe-rich phase were clearly separated. Similar distributions of La and Fe were also detected in the samples calcined at 1100 and 1200°C. Thus it is concluded as expected that La-Fe-CN is a preferable process to prepare the single oxide-free the $LaFeO_3$ perovskite-type oxide. The homogeneity increased in the order of La-Fe-O < La-Fe-OH ≪ La-Fe-CN. The heterogeneity of the calcined La-Fe-OH powder may be attributed to the difference in pH region when precipitated as $La(OH)_3$ and $Fe(OH)_3$ by the reaction of $La^{3+}$ or $Fe^{3+}$ and $OH^-$ ions.

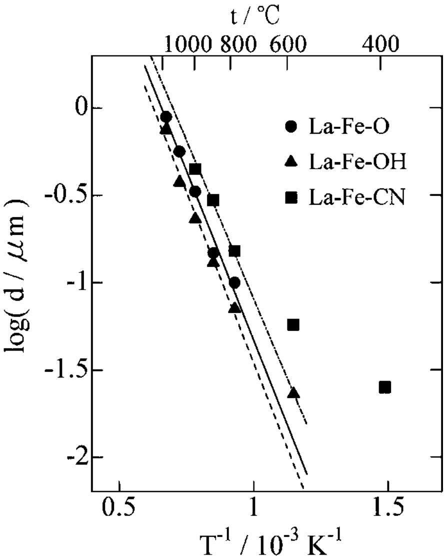

*Figure 8* Correlation between mean particle diameter and calcining temperature.

## 3.4. Surface area

Table II summarizes the specific surface areas of La-Fe-O, La-Fe-OH and La-Fe-CN calcined for 2 hours at several temperatures with the confirmed formation of the $LaFeO_3$ perovskite oxide. Fig. 8 shows the relationship between the reciprocal of the absolute calcining temperature, $1/T$, and the logarithm of the mean particle diameter, $\log d$, calculated from the specific surface area shown in Table II and the perovskite oxide $LaFeO_3$ density (6.64 g $cm^{-3}$). For example, the mean particle diameter, $d$, of La-Fe-CN calcined at 600°C for 2 hours is 30 nm. It is well known that metallic oxides may be prepared by the thermal decomposition of carbonates or hydroxides, and that their physicochemical properties are determined by the temperature at which they are formed and by the duration of the calcination. For

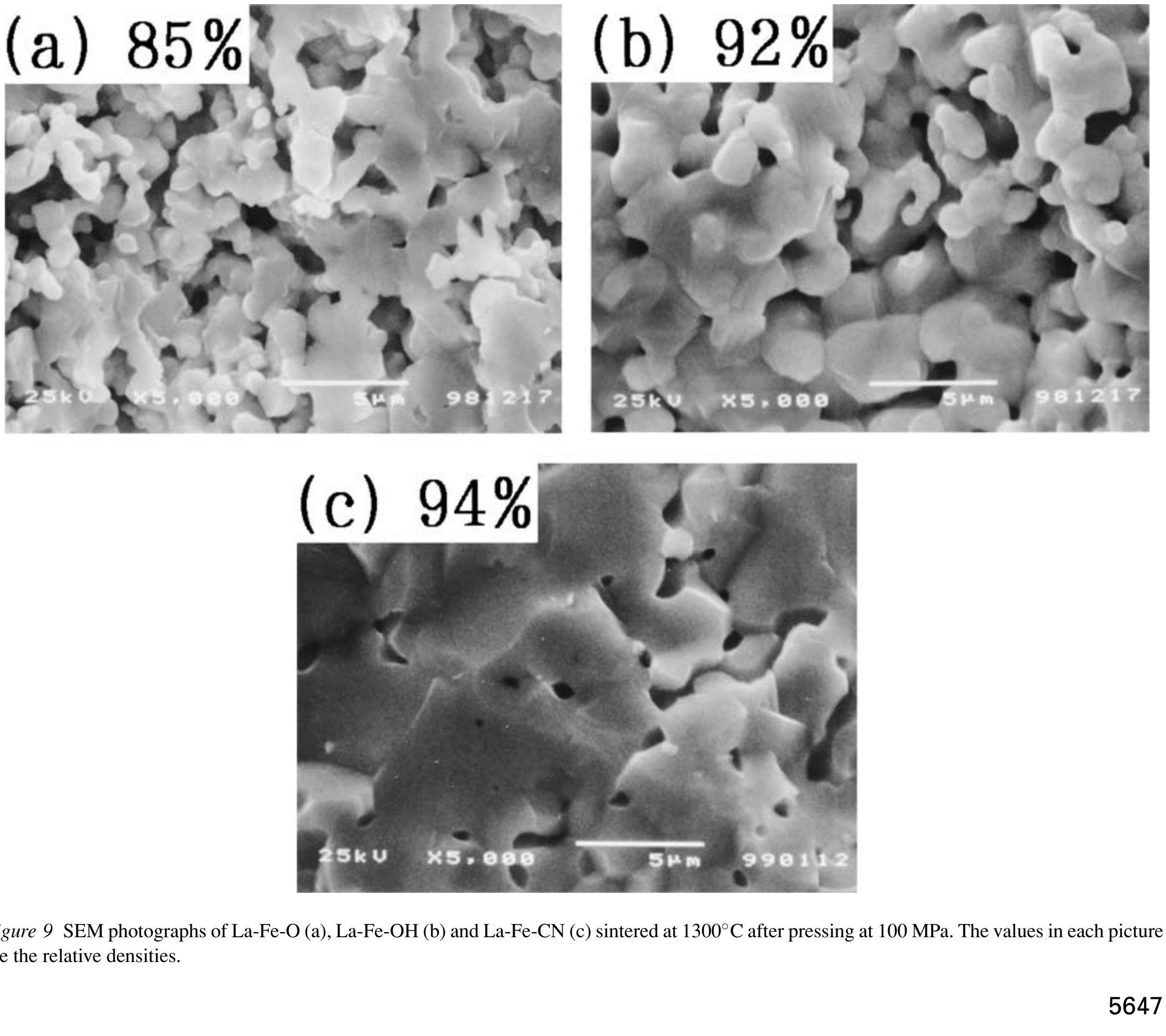

*Figure 9* SEM photographs of La-Fe-O (a), La-Fe-OH (b) and La-Fe-CN (c) sintered at 1300°C after pressing at 100 MPa. The values in each picture are the relative densities.

TABLE II Specific surface areas

| Calcining temperature/°C | La-Fe-O ($m^2\ g^{-1}$) | La-Fe-OH ($m^2\ g^{-1}$) | La-Fe-CN ($m^2\ g^{-1}$) |
|---|---|---|---|
| 400 | – | – | 35.5 |
| 600 | – | 38.7 | 15.5 |
| 800 | 9.1 | 12.6 | 6.2 |
| 900 | 6.1 | 6.9 | 3.0 |
| 1000 | 2.7 | 3.9 | 2.0 |
| 1100 | 1.6 | 2.4 | – |
| 1200 | 0.8 | 1.2 | – |

TABLE III Activation energies for the crystal growth of perovskite oxide, $LaFeO_3$

| | |
|---|---|
| La-Fe-O | 94.1 (kJ $mol^{-1}$) |
| La-Fe-OH | 75.0 (kJ $mol^{-1}$) |
| La-Fe-CN | 45.8 (kJ $mol^{-1}$) |

example, the equation of the growth of the mean crystal diameter, $d$, of magnesium oxide from $Mg(OH)_2$ is reported by Kotera *et al.* [10] as follows;

$$d = Kt^{1/n} \exp(-E/kT)$$

where $K$ is a constant, $t$ is the calcining time, and $E$ is the activation energy for the crystal growth. As seen in Fig. 8, the relation between log $d$ and $1/T$ for La-Fe-O, La-Fe-OH and La-Fe-CN is linear above 900, 800 and 600°C, respectively. The activation energy for the crystal growth estimated from the relation between log $d$ and $1/T$ decreased in the order of La-Fe-O > La-Fe-OH > La-Fe-CN (Table III). The activation energy (71 kJ $mol^{-1}$) for La-Fe-OH agreed with that (71 kJ $mol^{-1}$) of MgO prepared from $Mg(OH)_2$.

## 3.5. Sinterability

The sinterabilities of La-Fe-O, La-Fe-OH and La-Fe-CN were examined as follows: after calcining La-Fe-O, La-Fe-OH and La-Fe-CN at 1000°C for 2 hours, these calcining powders were ball-millied with deionized water into fine powders and dried. The fine powders thus obtained were pressed at 100 MPa and sintered in air at 1300°C for 2 hours. The fracture surfaces of the sintering samples are shown in Fig. 9. As can be seen from the SEM photographs and the relative densities calculated by Archimedes method, the sinterabilities increased in the order of La-Fe-O ≪ La-Fe-OH < La-Fe-CN.

## 4. Conclusions

The difference in the preparation of the $LaFeO_3$ perovskite oxide by the calcination of a mixture of $La_2O_3$ and $Fe_2O_3$ (La-Fe-O), the thermal decomposition of a co-precipitated precursor (La-Fe-OH), $La(OH)_3$ and $Fe(OH)_3$, and the thermal decomposition of a hetronuclear complex (La-Fe-CN), $La[Fe(CN)_6] \cdot 5H_2O$, was investigated. The formation of the $LaFeO_3$ perovskite oxide is clearly recognized for La-Fe-O, La-Fe-OH and La-Fe-CN at calcining temperatures above 1000, 800 and 600°C, respectively. The homogeneity of the powders calcined at 1000°C increased in the order of La-Fe-O < La-Fe-OH ≪ La-Fe-CN. The estimated activation energy for the crystal growth of the $LaFeO_3$ perovskite oxide decreased in the order of La-Fe-O > La-Fe-OH > La-Fe-CN. Furthermore, the sinterabilities at 1300°C increased in the order of La-Fe-O ≪ La-Fe-OH < La-Fe-CN. Based on these results, it is found that the $LaFeO_3$ perovskite oxide powder synthesized by the thermal decomposition of the $La[Fe(CN)_6] \cdot 5H_2O$ hetronuclear complex is the most uniform on an atomic level and the formation of pure and the nanosized $LaFeO_3$ powder is obtained at low temperatures. This preparation method is rather simple and the obtained powder is expected for applications as functional ceramics (sensors, SOFCs, electrodes, or even magnetic and ferroelectric properties).

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