

Fabrication processing condition for dense sintered $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ perovskites synthesized by the coprecipitation method (AE = Ca and Sr)

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Abstract

The formation mechanisms of single perovskite phases for 40 mol% alkaline earth metal (AE)-doped lanthanum manganites ($\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$, AE = Ca and Sr), synthesized by the coprecipitation method, have been investigated. After calcining at 600°C for 1 h, X-ray diffraction patterns of both the sample powders showed them to almost be in an amorphous state, and small peaks, related to the perovskite phase, were observed. The second phases were small amounts of $\text{Ca}_2\text{Mn}_3\text{O}_8$, La_2O_3 , La_2CO_5 and MnO_2 for the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, and SrMnO_3 , La_2O_3 , La_2CO_5 and MnO_2 for the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. With increasing temperature, the second phases gradually disappeared, and both powders changed into an almost single perovskite phase after calcining at 1100°C for 1 h. Using these perovskite powders, the fabricating conditions for the dense sintered specimens have been clarified. The powders showed the best sintering characteristics after calcining at 1100°C for 1 h for $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and at 1100°C for 5 h for $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. The relative densities of the specimens reached $\geq 95\%$ at 1500°C for 5 h for the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and 1580°C for 5 h for the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Alkaline earth metal (AE = Ca and Sr)-doped lanthanum manganite perovskites are quite useful as cathode materials in high-temperature solid oxide fuel cells (SOFC) using an Y_2O_3 -stabilized ZrO_2 (YSZ) electrolyte [1]. The cathode material on the YSZ electrolyte plays an important role in the catalysis of the oxygen reduction reaction ($\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$) under oxidizing atmospheres at an operating temperature of approximately 1000°C. On the other hand, the sintered cathode ceramic body, with some porosity, is being used as a cell component having good mechanical strength, for use as a cathode-supported tube in a tubular-type SOFC [2], for example. Fully sintered cell components of the cathode material are also adapted as an electrical current collector between the cathode and lanthanum chromite separator in the planar-type SOFC [3]. In this case, the single cells and separators should be con-

nected electrically and mechanically in series with the help of the electric current collectors.

D'Souza and Sammes [4] reported the mechanical properties of the $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_{3+\delta}$ perovskite, which was synthesized using the Pechini method. The test specimens had a density of approximately 96% of the theoretical density. They measured the three-point bending strength between room temperature and 1000°C and discussed a relationship between the mechanical strength and the evolution of the perovskite cell unit. Although fundamental data of mechanical properties of the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$, such as mechanical strength and Young's modulus, are indispensable to establish the reliability of the SOFC modules and stacks when used as cell components, few papers have been published on the mechanical properties of these materials.

Quite recently, Hiei et al. [5] observed that sintered $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ perovskites, with an AE-content of $0 \leq x \leq 0.3$, showed a shrinkage during thermal cycling measurements between 600 and 1100°C under oxidizing atmospheres. Because the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ perovskites with an AE-content of $0 \leq x < 0.4$ release and absorb oxygen be-

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tween 600 and 1100°C, the shrinkage phenomena should be related to a relationship between the microstructure of the sintered specimen and the release and absorption of oxygen. Since no shrinkage behavior of the $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$, which shows a stoichiometry of A-site, B-site and O-site, was observed during thermal cycling measurement, their mechanical data, for use as an SOFC cathode material and other cell components would be quite important.

For mechanical properties to be assured, an appropriate way of fabricating a dense sintered body with relative densities $\geq 95\%$ must be found. Recently, researchers [6–8] have reported the preparation and characteristics of dense samples of $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ perovskites with a low AE-content of $0 \leq x \leq 0.3$. However, for the heavily AE-doped lanthanum manganites with 40 mol% AE-content, synthesis of the single perovskite phase by the solid-state technique is required to undergo an unavoidable high-temperature heat treatment of approximately 1400°C for 20–40 h during the synthesizing process [9]. The coarse perovskite powders impose unavoidable porosity on the specimens and thus $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ perovskites are difficult to fully sinter.

The coprecipitation method is one of the most appropriate ways of synthesizing a fine powder with a single perovskite phase at low-temperatures. The fine perovskite powders give a large selection of conditions during the fabricating process. This paper details the characteristics of the $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ (AE = Ca and Sr) powders synthesized by the coprecipitation method, and the fabrication processing conditions of the dense sintered $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ specimens using the fine powders.

2. Experimental

$\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ perovskite sample powders were prepared by the co-precipitation method: Concentration of aqueous solutions of $\text{La}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ were confirmed by inductively couple plasma (ICP) analysis. They were mixed in a selected proportion of $\text{La}/\text{AE}/\text{Mn} = 0.6/0.4/1$ and were then poured into an ethanolic solution of oxalic acid. Since oxidation from Mn^{3+} to Mn^{4+} was sometimes observed, hydrogen peroxide, which was a reducing agent for Mn^{4+} to Mn^{3+} , was used. After the organic compounds were burnt out at 600°C for 1 h in air, the sample powders were calcined at selected temperatures in air with heating and cooling rates of 6°C/min. X-ray diffraction (XRD) patterns of the powdered samples were obtained using a Philips X'Pert MPD diffractometer system using monochromatic $\text{CuK}\alpha$ radiation and a scintillation detector; a scanning rate of 0.02°/s was used.

The calcined sample powders were used after milling with ethanol in a ball mill, where the inner wall material of the mill was polypropylene and the balls were Y_2O_3 -par-

tially stabilized ZrO_2 . After drying, the powders were pressed into pellets of 14 mm in diameter and approximately 2 mm thickness under a pressure of 100 MPa. The pellets were isostatically pressed at a pressure of 200 MPa and then sintered at selected temperatures with a heating rate of 2°C/min in air. It should be noted that no organic additives were added to the powder before sintering because they are not usually required when a high-pressure process is undertaken. The organic additives also require a slow burn-out time, which is considered inconvenient when estimations of the sintering characteristics are to be realised. The holding time at the selected temperatures was varied from between 0 to 10 h. Zero hours means no holding time in this paper. A cooling rate of 6°C/min was used. Relative density was derived using the theoretical value determined from the experimental lattice parameters and unit formula. In this study, the compositions of the perovskite samples after heating were confirmed by ICP analysis again, and were in good agreement with the starting compositions within experimental error $\leq 2\%$.

Microanalysis and compositional analysis of the $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ powders and dense specimens were carried out using a Hitachi S4000 scanning electron microscope (SEM). Energy dispersive X-ray analysis (EDX) was obtained using a Kevex microanalyzer attachment.

3. Results and discussion

3.1. Perovskite sample powder preparation by the coprecipitation method

Figs. 1 and 2 show the XRD patterns of the $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ powders after calcining at the selected tem-

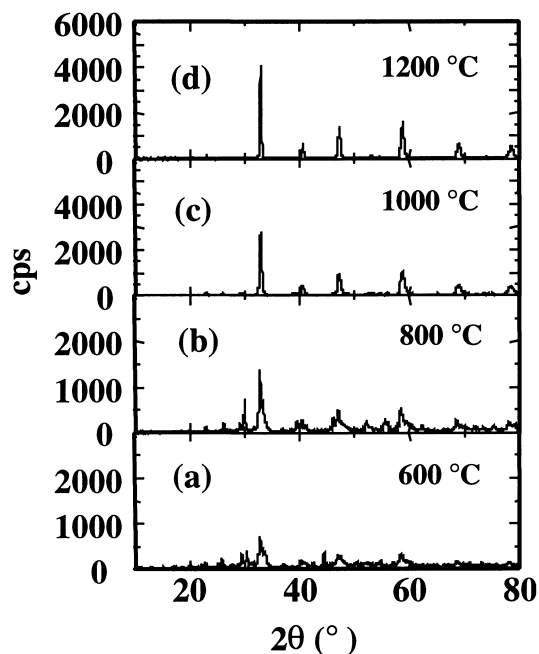


Fig. 1. XRD patterns of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ powders after calcining at selected temperatures between 600 and 1200°C for 1 h in air.

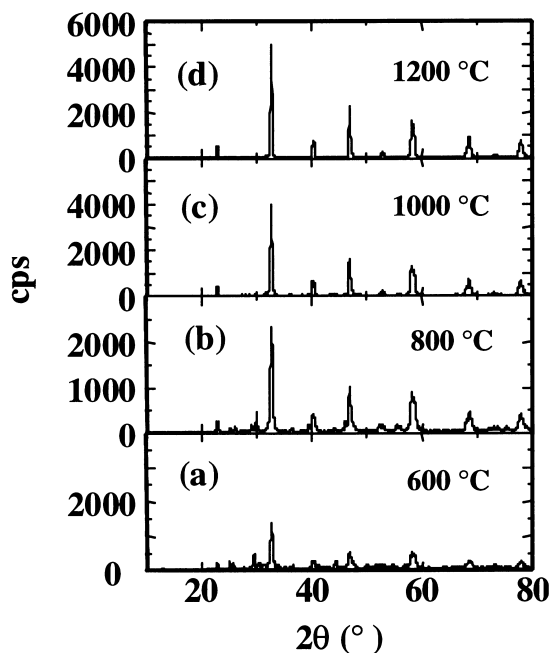
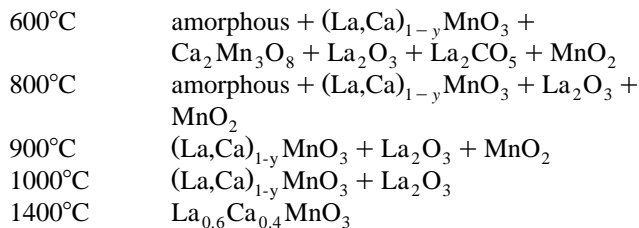


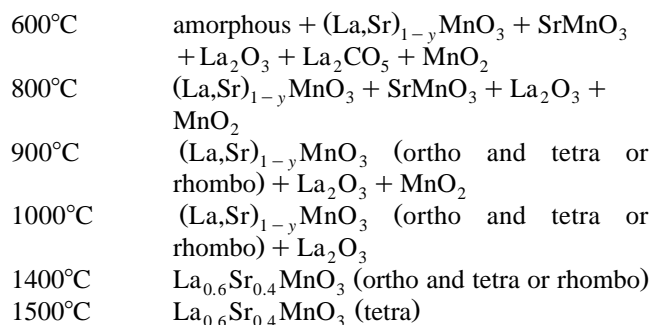
Fig. 2. XRD patterns of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powders after calcining at selected temperatures between 600 and 1200°C for 1 h in air.

peratures between 600 and 1200°C for 1 h in air. It can be seen that both the sample powders heated at 600°C for 1 h to dehydrate were in a nearly amorphous state (Fig. 1(a) and Fig. 2(a)). The XRD pattern of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ showed some second phases, which included small amounts of La_2O_3 , La_2CO_5 , $\text{Ca}_2\text{Mn}_3\text{O}_6$ and MnO_2 . With increasing temperature, the peaks of the second phases gradually disappeared, and the XRD pattern of the powders showed almost a single perovskite phase after heating at temperatures $\geq 1100^\circ\text{C}$. However, the very small peaks of La_2O_3 remained at 1300°C for 1 h. Since the perovskite phase of $(\text{La}_{1-x}\text{AE}_x)_{1-y}\text{MnO}_3$ with A-site defects should be more stable, its formation was observed at the lower temperatures $\leq 1300^\circ\text{C}$, after which the two phases changed into $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ at 1400°C for 1 h. The formation process of a single $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ perovskite phase could be postulated using the following sequence:



The single perovskite phase formation, and the observed second phases, for the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powder were almost similar to those of the Ca-doped one. We observed that the GdFeO_3 -type perovskite with orthorhombic symmetry (space group Pbnm) [10] appeared at temperatures $\geq 900^\circ\text{C}$. Some researchers [11,12] reported that the

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite with an AE-content of $0.1 \leq x \leq 0.4$ shows rhombohedral symmetry. As having been indicated in the literature [13], the rhombohedral cell was isostructural with LaAlO_3 structure (space group $R\bar{3}C$). On the other hand, it has been reported that the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite with an AE-content of $0.1 \leq x \leq 0.3$ has been shown to have a tetragonal symmetry using Raman spectra measurement [14]. It is not an easy task to distinguish the difference between the tetragonal and rhombohedral perovskites from the XRD data between 900 and 1400°C. At 1500°C, the peaks of the orthorhombic perovskite phase disappeared, and the single perovskite phase with tetragonal symmetry was formed. The formation process of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite could be explained as follows:



ortho: orthorhombic, tetra: tetragonal, rhombo: rhombohedral

After heating at 1500°C, the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ crystallized in an orthorhombic perovskite unit $a = 5.432 \text{ \AA}$, $b = 5.484 \text{ \AA}$ and $c = 7.683 \text{ \AA}$ and $z = 4$, and the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ crystallized in a tetragonal perovskite unit $a = 5.492 \text{ \AA}$ and $c = 7.714 \text{ \AA}$ and $z = 4$, respectively.

3.2. Characteristics of the perovskite powders

Fig. 3 shows the relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ specimens as a function of calcined temperature, where the holding time at the calcined temperature was 1 h. The circles represent the specimens prepared using a ball milling process for 20 h, and the triangles represent the specimens prepared without the milling process. When the powders using the milling process were compared to those without milling, the relative densities of both the green bodies were almost the same. However, after heating, the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ sample powders, using the milling process, showed higher sintering characteristics. Although the particle size of the powders was independent of the calcination temperature, the relative density of the green body increased with the calcination temperature of the powder. The discrepancy between the particle size of the powder and the relative density of the green body should be explained by specific surface area difference of the powders.

SEM examination of both the powders after calcination, showed that the effect of milling was not significant,

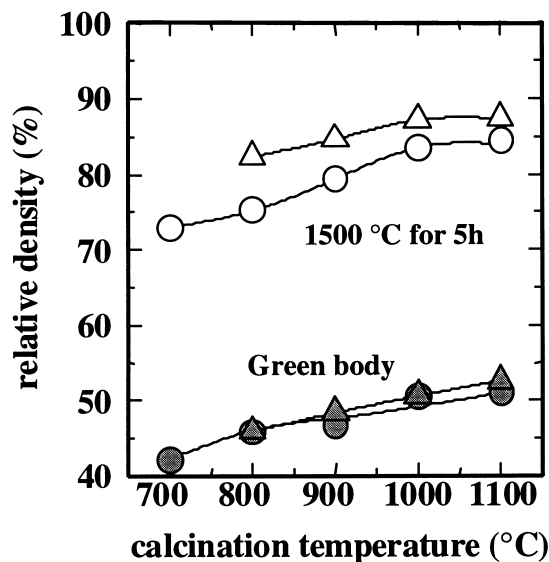


Fig. 3. Relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ specimens as a function of calcination temperature, where the holding time at the calcination temperature was 1 h. \circ \bullet : before the milling process; \triangle \blacktriangle : after the milling process.

although milling did allow for the agglomerates to be removed. The particle size of both the perovskite powders was approximately $0.04\text{--}0.08\ \mu\text{m}$ in diameter on average for milled and unmilled material.

In order to clarify the effect of the ball milling process on the sintering characteristics, the particle size of the powders was measured using a laser diffraction particle size analyzer (Lasersizer, Malvern, UK). The average particle sizes of both the $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ perovskite powders were in the region of $0.08\text{--}0.12\ \mu\text{m}$. No significant change of the particle size before and after the ball milling process was observed, although the particle size distribution had reduced after the milling process. Two peaks were observed for the particle size distribution of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powder, before and after the milling. SEM and EDX analysis showed that the small particles contained a higher concentration of Sr when compared to the larger particles.

The effect of AE-content in the perovskites on the sintering was estimated using the shrinkage, which is represented by the function form as $100(L_0 - L)/L_0$ (L_0 : initial length, L : final length). Fig. 4 shows the shrinkage curves for the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ samples after heating at 1300°C for 20 h in air, where the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ powders were prepared using the solid state technique, milled twice and heated to 1200°C for 10 h. It is clear that the sintering characteristics of the Sr-doped lanthanum manganites have a tendency to decrease with increasing Sr-substitution. This leads to a discussion relating to the difference of the Sr-content in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ particles. It could be postulated that this difference causes the appearance of the two peaks in the particle size distribution. On the other hand, the shrinkage of the Ca-doped

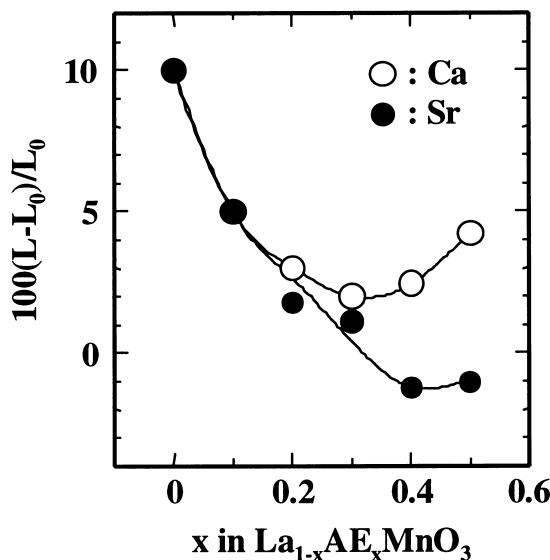


Fig. 4. Shrinkage curves for the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ specimens after heating at 1300°C for 20 h in air, where the $\text{La}_{1-x}\text{AE}_x\text{MnO}_3$ powders were prepared at 1200°C for 10 h and milling twice by the solid-state technique.

lanthanum manganites decreases with increasing Ca-content up to 30 mol%, and then increased.

4. Fabrication condition for dense sintered perovskite samples

4.1. $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$

Fig. 5 shows the relative density of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, after heating at 1400°C for 5 h in air, as a function of

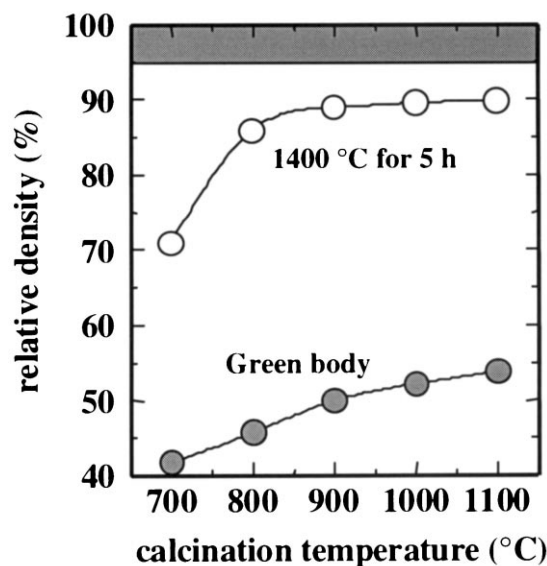


Fig. 5. Relative density of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ after heating at 1400°C for 5 h in air as a function of calcination temperature of the perovskite powders, where the holding time at the calcination temperature was 1 h.

calcination temperature of the perovskite powders, where the holding time at the calcination temperature was 1 h. Generally, an acceptable relative density for the ceramic samples for measuring the mechanical properties is $\geq 95\%$, as giving in the shaded region in Fig. 5. The closed circles represent the relative density of the green bodies. The theoretical density used was 5.874 g/cm^3 . The relative densities of the green and sintered bodies had a tendency to increase with the calcination temperature of the sample powder. The $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ powders, which were calcined at 1200°C for 1 h and 1100°C for 5 h, could not be pressed into pellets without a binder. The $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ powder, which was calcined at 1100°C for 1 h, showed the best sintering characteristics, as well as showing its sintered body with high precision after the high-temperature heat-treatment. It can be seen in Fig. 5 that the relative density of the green body is quite important when fabrication to a dense sintered body is required.

Using the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ powder with the best sintering characteristics, fabricating conditions for the dense sintered specimens were clarified. In order to clarify the effect of the heating temperature on sintering, the relative densities of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample can be studied as a function of heating temperature. The densification of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample started at around 1200°C . The density gradually increased with increasing heating temperature, and the main shrinkage took place in the temperature region of $1300\text{--}1500^\circ\text{C}$.

In general, sintering of ceramics depends on heating temperature and holding time [15]. The sintering of LaMnO_3 -based perovskites should proceed by a bulk ionic diffusion mechanism [16]. In this case, the materials show the most important sintering behavior within 10 h. Fig. 6 shows the relative density of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ as a

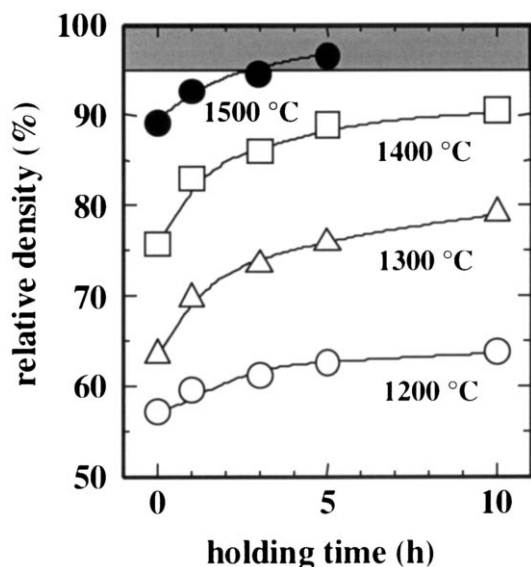


Fig. 6. Relative densities of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ sample after calcining at 1100°C for 1 h as a function of heating temperature.

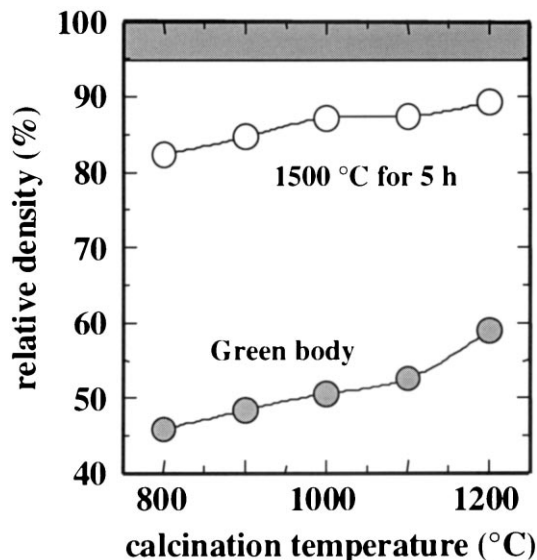


Fig. 7. Relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ after heating at 1500°C for 5 h as a function of calcination temperature, where the holding time at the calcination temperature was 1 h.

function of holding time with a parameter of heating temperature. The relative density of 96.6% was attained after heating at 1500°C for 5 h.

4.2. $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$

Fig. 7 shows the relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ after heating at 1500°C for 5 h as a function of calcination temperature, where the holding time at the calcination temperature was 1 h. The theoretical density used was 6.321 g/cm^3 . The relative densities of both the green and sintered bodies had a tendency to increase with calcination

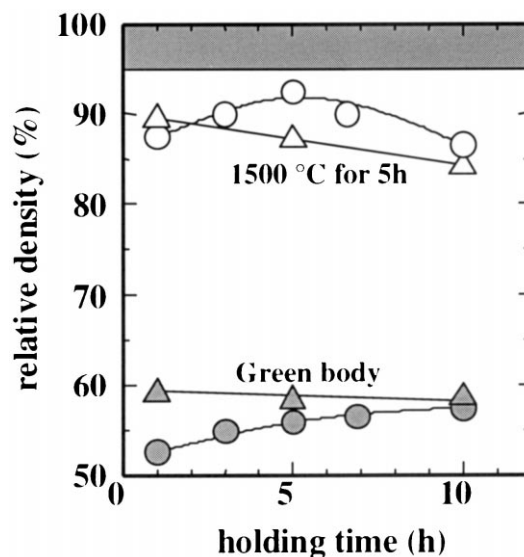


Fig. 8. Effect of holding time at the calcination temperatures of 1100 and 1200°C on the relative density of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$.

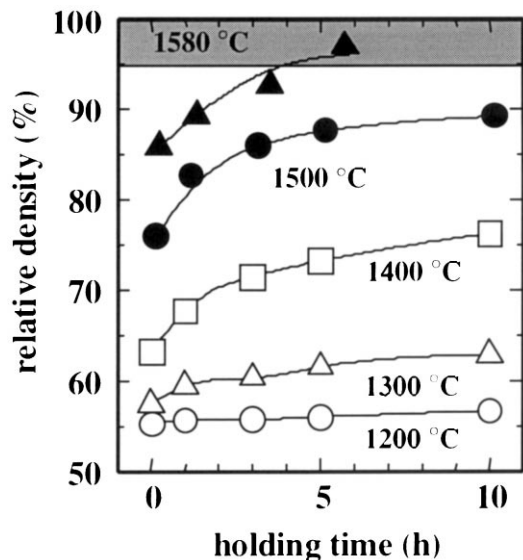


Fig. 9. Relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ as a function of holding time with a parameter of heating temperatures. ○ ●: 1100°C; △ ▲: 1200°C.

temperature. The maximum relative density of the samples obtained was approximately 87.7% even at 1500°C for 5 h. The sintering characteristics of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ were lower than those of $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$.

Fig. 8 shows the effect of holding time at the calcination temperatures of 1100°C and 1200°C on the relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ specimens. The circles and triangles represent the specimens calcined at 1100°C and at 1200°C, respectively. When the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powder, calcined at 1200°C for 1 h, was compared to that calcined at 1100°C for 1 h, it showed the higher sintering characteristics (87.4% for 1100°C vs. 89.3% for 1200°C at holding time of 1 h). However, at the calcination temperature of 1200°C, the relative densities of the green and sintered bodies decreased with increasing the holding time. On the other hand, at a calcination temperature of 1100°C, the relative density of the green body had a tendency to increase with holding time. After heating at 1500°C for 5 h, the relative densities of the sintered specimens increased with increasing holding time up to 5 h, and then decreased. A maximum relative density of 92% was observed. It can be seen that the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powder, which was calcined at 1100°C for 5 h, showed the best sintering characteristics.

Using the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ powder with the best sintering characteristics, we attempted to fabricate dense sintered samples. Fig. 9 shows the relative density of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ as a function of holding time with a parameter of heating temperature. The relative density of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ specimen reached 96.3% at 1580°C for 5 h.

SEM examination of the dense $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ specimens showed the grain size to be in the range of 2–6 μm for $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and in the range of 0.5–3 μm for $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$.

5. Conclusion

The mechanism of lanthanum manganite perovskite powders with a high content of 40 mol% Ca and Sr synthesized using the coprecipitation method has been investigated. The single perovskite phase of $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ was obtained after heating at 1100°C for 1 h. In addition, using $\text{La}_{0.6}\text{AE}_{0.4}\text{MnO}_3$ powders, the fabricating conditions to produce dense sintered bodies have been clarified. When using the $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ powder calcined at 1100°C for 1 h, the relative density reached 96.6% when fired at 1500°C for 5 h. On the other hand, the relative density of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ reached 96.3% at 1580°C for 5 h when using the powder calcined at 1100°C for 5 h. These results will be useful when evaluating the mechanical properties of the material with different dopants, and also in optimizing the microstructure of the cathode, which can be used to attain both excellent cathodic performance and good mechanical strength.

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