— Article —

Pore Formation during Sintering of $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{TiO}_{3+\delta}$ Perovskites ($x = 0, 0.04$) Synthesized by the Pechini Method

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The sintering behavior of $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{Ti}_{1-y}\text{O}_{3+\delta}$ powders ($x, y = 0, 0.04$), synthesized using the Pechini method, has been investigated. Stoichiometric $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ showed a single perovskite phase. For non-stoichiometric samples, secondary TiO_2 and Sr_2TiO_4 phases were observed in the X-ray diffraction patterns of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$, respectively. It was found that during the sintering process, the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ samples expanded anomalously between 1300°C and 1400°C and between 1400°C and 1500°C, respectively, although the powders exhibited good sinterability. Scanning electron microscopy showed that the volume expansion was caused by pore formation within the samples. The release of oxygen from the samples was observed at temperatures at which the samples expanded and is considered to be the likely cause of the expansion.

Key Words : SrTiO_3 , Sintering, Pechini Method, SOFC

1 Introduction

$(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskites have attracted considerable attention as potential solid oxide fuel cell (SOFC) interconnect and anode materials because of their chemical and physical stability under oxidizing and reducing atmospheres.^{1–9)} Previous studies on the $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskite system have reported the oxygen content under oxidizing and reducing atmospheres,^{2,4)} the electrical conductivity across a wide range of oxygen partial pressures^{3,5)} and the thermal expansion in air.^{6,7)}

Recently, it has been reported that La-doped SrTiO_3 perovskites have been used as interconnect materials in segmented-in-series tubular SOFCs.^{10,11)} In order to prevent a decline in anodic performance, the sintering process should ideally be at temperatures of $\leq 1400^\circ\text{C}$. Thus, the synthesis of fine perovskite powders with high sinterability in air is essential in fabricating impervious interconnect layers at low sintering temperatures.

We have previously reported the electrical conductivity of $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskites ($0 \leq x \leq 0.3$) in oxidizing and reducing atmospheres.¹²⁾ In our previous works, the $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskite powders synthesized using the Pechini method exhibited good sintering characteristics. However, a Ruddlesden–Popper phase, such as Sr_2TiO_4 , was more readily formed at temperatures between 1200 and 1500°C during the sintering of these powders compared with powders synthesized by the solid-state mixing method.¹³⁾ This phase, which has low electrical conductivity,¹⁴⁾ remained after the relative density of the perovskite reached $\geq 94\%$ at 1400°C. This is a serious hindrance to the application of $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskites to SOFC interconnects.

SrTiO_3 -based perovskites with A-site or B-site doping

are known to have non-stoichiometry of the A- or B-sites.^{15,16)} We have previously reported that these Sr–La–Ti–O perovskite systems can be either A-site ($(\text{Sr}_{1-x}\text{La}_x)_{1-y}\text{TiO}_{3+\delta}$) or B-site ($(\text{Sr}_{1-x}\text{La}_x)\text{Ti}_{1-y}\text{O}_{3+\delta}$) deficient and that the non-stoichiometry can enhance the sintering characteristics.¹³⁾ In particular, the use of A-site deficient $(\text{Sr}_{1-x}\text{La}_x)_{1-y}\text{TiO}_{3+\delta}$ perovskites is expected to prevent formation of the Ruddlesden–Popper phase during sintering because the Ruddlesden–Popper phase requires an excess of the A-site element.

In this study, we investigated the sintering of $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{Ti}_{1-y}\text{O}_{3+\delta}$ powders ($x, y = 0, 0.04$) synthesized using the Pechini method and the anomalous volume expansion of the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ samples during sintering.

2 Experimental

2.1 Sample preparation

The starting materials for the synthesis were SrCO_3 pre-dried at 105°C for 48 h (99.9%, Kanto Chem. Co. Inc., Japan), La_2O_3 pre-heated at 1500°C for 1 h (99.9%, High Purity Chem. Co. Ltd., Japan) and an organometallic Ti compound $((\text{NH}_4)_4(\text{Ti}_2(\text{C}_6\text{H}_4\text{O}_7)_2(\text{O}_2)_2) \cdot 4\text{H}_2\text{O}$, Furuuchi Chem. Corp., Japan). The materials were mixed in the required ratios in pure water, and citric acid was added to the solution in an equivalent molar proportion to the total amount of metal cations present. Ethylene glycol was then added to the solution and the mixture was heated to form a viscous gel. The gel was dried and fired at 400°C. Finally the residue was fired at 1000°C for 2 h to remove any remaining organic materials. The resultant powders were homogenized in a rolling ball mill using ethanol and Y_2O_3 -partially stabilized ZrO_2 balls. The

powders were then dried, pressed into tablets at 23 MPa, and fired at the selected temperatures in air at a heating/cooling rate of $200^{\circ}\text{C h}^{-1}$.

2.2 Sample identification

The powder samples were analyzed by powder X-ray diffractometry (XRD; 18 kW, Rigaku, ultraX 18TTR2-300, Japan) using monochromated $\text{CuK}\alpha$ radiation, a scintillation detector and a scanning rate of $0.02^{\circ}\text{s}^{-1}$. These measurements were carried out at room temperature.

Synchrotron XRD (SR-XRD) measurements at room temperature were performed for the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ samples using BL19B2 at SPring-8 (Super Photon ring-8 GeV) under program No. 2009A1797. To obtain good counting statistics, an imaging plate was used as the detector. The SR-XRD data were measured at a wavelength of $0.3500\text{ \AA}$, which was determined by calibration with a National Institute of Standards and Technology (NIST) CeO_2 standard sample, at angles between $2\theta = 5\text{--}70^{\circ}$ for a step interval of 0.01° . The diffraction data, which indicated the space group $Pm\bar{3}m$ (No. 221), were analyzed by the Rietveld refinement technique using RIETAN-FP.¹⁷⁻²⁰⁾ The pseudo Voigt function formulated by Thompson *et al.*²¹⁾ was used for refinement of the SR-XRD measurements. It was assumed that (1) the composition ratio of A-site to B-site elements was limited to being 0.96, (2) the ionic valence of Ti is ≤ 4 , and (3) the oxygen content is equal to be 3 in this refinement.

2.3 Sintering characteristics

The density of the sintered tablets was determined from their size and weight. The relative density was calculated using the theoretical value derived from the experimental lattice parameters and the unit formula. The oxygen content in the perovskite samples after firing in air was assumed to be ≤ 3 , that is, cation-site deficient.⁴⁾ The microstructure of the sintered samples was investigated by scanning electron microscopy (SEM; Hitachi, S-3500H, Japan). The surface-sectional compositions of the tablet samples fired at various temperatures were measured by wavelength dispersive X-ray fluorescence spectroscopy (WDX, Rigaku, ZSX Primus II, Japan).

2.4 Thermogravimetry

Thermogravimetry (TG) was carried out using a thermogravimetric analysis instrument (TG-DTA-5000S, MAC Science Co. Ltd., Japan) at temperatures ranging from room temperature to 1400°C in air. Y_2O_3 stabilized ZrO_2 was used as the reference and the heating/cooling rate was $5^{\circ}\text{C min}^{-1}$.

3 Results and Discussion

3.1 Sample condition

Figure 1 shows the XRD patterns of the samples after calcining at 1000°C for 2 h. For these samples, no exothermic peaks were observed at temperatures $\leq 700^{\circ}\text{C}$ in the differential thermal analysis (DTA) measurement and no peaks for any residual organic materials were observed in the SR-XRD measurement. After calcination, the stoichiometric sample was found to contain minor traces of secondary phases. However, after firing at 1100°C with holding time of 0 h, the XRD pattern shows that only single-phase, cubic perovskite was present, with a

Fig. 1 XRD patterns of the perovskite samples after firing at 1000°C for 2 h; (a) $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$, (b) $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, (c) $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$; ○: SrCO_3 , ▽: TiO_2 , ×: Sr_2TiO_4 .

unit cell parameter $a = 3.9035(2)\text{ \AA}$, and $Z = 1$ (space group $Pm\bar{3}m$, No.221).²²⁾ For the non-stoichiometric samples, the secondary phases seen after calcination were SrCO_3 (○) and rutile TiO_2 phases (▽), and SrCO_3 and Ruddlesden-Popper (Sr_2TiO_4) phases (×) for $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$, respectively. Although the SrCO_3 phase disappeared at temperatures $\geq 1100^{\circ}\text{C}$, even after firing at 1500°C , TiO_2 and Sr_2TiO_4 remained as the secondary phases of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$, respectively. From the results of XRD analysis, (1) $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ showed a single perovskite phase, (2) A-site deficient $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and B-site deficient $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$ included TiO_2 and Ruddlesden-Popper phases, respectively, and (3) the linearity of the decreased lattice parameter as a function of Ti content in the perovskite structure was observed in the $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{Ti}_{1-y}\text{O}_{3+\delta}$ system. Thus, it was determined that the chemical compositions of the prepared samples were comparable with those of the starting materials.

For perovskites synthesized by the solid-state mixing method, the amount of A-site and B-site vacancy formation depended on the La content; in the case of $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{Ti}_{1-y}\text{O}_{3+\delta}$, the limits of cation vacancy formation were $x < 0.07$ for the A-site and $y < 0.06$ for the B-site vacancies.¹³⁾ The cation vacancy ranges of the perovskite samples prepared by the solid-state mixing method and the Pechini method were different. The nominal and calculated compositions, lattice parameters and theoretical densities of the samples that were synthesized by the Pechini method are summarized in Table 1. These results were obtained from the samples fired at 1500°C for 5 h.

Figures 2(a), (b) and (c) show the SEM micrographs of ball-milled perovskite powders after firing at 1000°C for 2 h. The average primary particle in the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ powder was $\sim 0.2\text{ }\mu\text{m}$ in diameter. These particles partially sintered and large particles of $1\text{--}2\text{ }\mu\text{m}$ in diameter were formed. However, the $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$ powders showed small particle sizes of $0.1\text{--}0.2\text{ }\mu\text{m}$ and $0.05\text{--}0.1\text{ }\mu\text{m}$, respectively, although it was observed that these particles strongly aggregated

Table 1 Nominal and calculated compositions, lattice parameters, theoretical densities and second phases of the samples fired at 1500 °C for 5 h.

Nominal composition	Calculated composition used for molecular weight	Lattice parameter after firing at 1500 °C	Theoretical density	Second phase
$(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3.01}$	$\text{Sr}_{0.862}\text{La}_{0.096}\text{Ti}_{0.997}\text{O}_3$	3.9042(2) Å	5.15 g cm ⁻³	TiO ₂
$(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3.05}$	$\text{Sr}_{0.885}\text{La}_{0.098}\text{Ti}_{0.984}\text{O}_3$	3.9046(1) Å	5.20 g cm ⁻³	–
$(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{2.97}$	$\text{Sr}_{0.900}\text{La}_{0.100}\text{Ti}_{0.960}\text{O}_{2.97}$	3.9073(1) Å	5.18 g cm ⁻³	Sr ₂ TiO ₄

(a) $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ (b) $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ (c) $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$ **Fig. 2** SEM micrographs of $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{Ti}_{1-y}\text{O}_{3+\delta}$ after firing at 1000 °C for 2 h.

into secondary particles of various sizes greater than 2 μm.

3.2 Sintering characteristics

Figure 3(a) shows the relative densities of the perovskite samples after firing at selected temperatures with holding time of 0 h. The broken line represents the density of the $(\text{Sr}_{0.8}\text{La}_{0.2})\text{TiO}_{3+\delta}$ sample.¹²⁾ In general, the density of ceramics increases with both firing temperature and holding time. For $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ powders synthesized by the solid-state mixing method, the sintering behaviors were the same as those of general ceramics. For $(\text{Sr}_{0.8}\text{La}_{0.2})\text{TiO}_{3+\delta}$ powder synthesized by the Pechini method, the densification of the samples started at around 1100 °C and the sintering characteristics in the temperature region of 1100–1400 °C were ordinary and similar to those of $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$.¹²⁾ The relative density of the $(\text{Sr}_{0.8}\text{La}_{0.2})\text{TiO}_{3+\delta}$ powder increased with the temperature and reached ≥ 94 % at 1400 °C.

For the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ samples synthesized by the Pechini method, their densities initially increased with temperature but then decreased when fired at higher temperatures. The decrease in density was first detected at 1300 °C for $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$

and 1400 °C for $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$. In contrast, the density for $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$ increased monotonically with the firing temperature. Figure 3(b) shows the volume changes of the samples after firing at selected temperatures with holding time of 0 h. The relative density of the tablets is represented by the function $\rho_{re} = 100(M_{ob}/V_{ob} \rho_{th})$, where ρ_{re} , M_{ob} , V_{ob} and ρ_{th} are the relative density, the observed weight, the observed volume and the calculated theoretical density for the sample, respectively. This equation indicates that a decrease in volume leads to an increase in density. The holding time dependence of density showed a trend opposite to that of volume. Since no significant weight change in the samples was observed, the lowering of the density was caused by increases in the diameter and thickness of the samples; the samples expanded.

Figures 4(a) and (b) show the relative densities of the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ perovskites as a function of holding time at different firing temperatures. With holding time of 0 h, the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ samples reached ≥ 90 % relative density at 1300 °C and at 1400 °C, respectively. The $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ samples showed a small increase in their relative

Fig. 3 Relative densities and volume of the perovskite samples after firing at selected temperatures with zero holding time. $\circ$: $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$, $\triangle$: $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, $\square$: $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$, ----: $(\text{Sr}_{0.8}\text{La}_{0.2})\text{TiO}_{3+\delta}$.

Fig. 4 Relative densities of the perovskite samples as a function of holding time with a parameter of firing temperatures.

densities as a function of holding time at 1400°C and 1500°C. On the other hand, for $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, the density at 1300°C increased dramatically with a holding time of up to 1 h and then remained constant. It was found that the densities of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ at 1300°C and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ at 1400°C and 1500°C decreased with an increase in the holding time. After sintering, it was observed that the sample volumes increased with the holding time at these temperatures, despite the XRD patterns showing no discernible changes. For the B-site deficient $(\text{Sr}_{0.9}\text{La}_{0.1})\text{Ti}_{0.96}\text{O}_{3+\delta}$ sample, the density increased with the holding time.

3.3 Sample observation

The microstructures of the samples were analyzed by SEM in order to clarify the mechanism causing the expansion during sintering. Figures 5(a) and (b) are cross-sectional SEM micrographs of $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ after fir-

ing at 1400°C. It is clear that some small pores remain inside the sample sintered at 1400°C with holding time of 0 h. This sample had a relative density of 90%, indicating that some small and closed pores remained in the sample. The pore sizes were observed to be in the range 0.5–2 μm . However, many large pores were observed in the interior of the $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ sample sintered at 1400°C for 5 h. The pore sizes increased to >10 μm , although small pores of approximately 1 μm were also observed. The relative density of the $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ sample fired at 1400°C for 5 h was 64%. These results suggest that during sintering, pores formed and enlarged in the interior of the sample, while the grains grew. It is thus concluded that the anomalous expansion of the sample is related to pore formation in the interior of the $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ sample. The pore formation was also confirmed by SEM for the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ sample

(a) With zero holding time (b) For 5 h
Fig. 5 Cross-sectional SEM micrographs of $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ after firing at 1400°C .

(a) With zero holding time (b) For 5 h
Fig. 6 Surface-sectional SEM micrographs of $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ after firing at 1400°C .

during sintering at 1300°C .²³⁾ It should be noted that, in the case of $(\text{Sr}_{0.8}\text{La}_{0.2})\text{TiO}_{3+\delta}$, no pore formation and no secondary phases within the sample were observed.

Figures 6(a) and (b) show SEM micrographs of the $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ surface after firing at 1400°C . The surface of the sample fired at 1400°C with holding time of 0 h consists of densely packed particles with a grain size of $\leq 1\ \mu\text{m}$. Although some small pores remain on the surface of $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, the sample has undergone densification. After sintering for 5 h, the surface displays remarkable grain growth, with the grain size increasing to 2–3 μm . These vastly different microstructures suggest that different sintering mechanisms operating on the surface and in the interior of the sample.

3.4 Weight decrease at high temperature

We have previously reported that the expansion and shrinkage of spinel and perovskite oxides and their phenomena are related to a phase change caused by oxygen release.^{24–26)} Figure 7 shows the TG curves of the 10 mol % La-doped perovskite samples. The perovskite powders synthesized by the solid-state mixing method were annealed at 1000°C after firing at 1600°C .¹²⁾ The open and closed symbols indicate the results for samples synthesized by the Pechini method and by the solid-state mixing method, respectively. It was found that all the samples showed weight changes in the TG measurement and that the weight decrease tended to increase with a lower Ti content. The sample weight showed (i) a decrease between room temperature and 700°C for all samples, (ii) a decrease at temperatures greater than approximately 1200°C for the samples synthesized by the

Fig. 7 TG curves of the 10 mol % La-doped SrTiO_3 perovskite powders in air. The open and closed symbols represent the results synthesized by the Pechini method and solid-state mixing one, respectively.

Pechini method. The weight decreases (i) at low temperatures should correspond to the release of adsorbed oxygen and/or water from the sample powders. On the other hand, the weight decrease (ii) at high temperatures should correspond to the release of oxygen from the perovskites because WDX analysis reveals no compositional changes in Sr, La and Ti at the surface of the samples fired between 1200°C and 1500°C . No decrease in the weight of the perovskites synthesized by the solid-state mixing method was observed at temperatures $\geq$

1200°C.

Figure 8 shows the weight changes of the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ powder at 1200°C and 1300°C as a function of holding time. The samples synthesized by the Pechini method were used. The weight change of these samples at 1200°C and 1300°C with holding time of 0 h is assumed to be zero. A decrease in weight was observed at 1300°C although no change in weight was observed at 1200°C. This indicates that the oxygen release from the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ sample continues during the expansion of the sample at 1300°C. The release of oxygen during sintering should be a factor in pore formation in the interior of the sample. As seen in Fig. 6(a), the surface of the sample was first densified at approximately 1300°C. Since at temperatures $\geq 1300^\circ\text{C}$, oxygen gas is released from the perovskite particles and cannot escape from the surface of the sample, the pores might form in the interior of the sample. This could be explained by the fact that the samples with high sintering characteristics, namely, $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, expand-

Fig. 8 Weight changes of the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ samples at 1200°C and 1300°C as a function of holding time.

(a) $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$

(b) $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$

Fig. 9 Lattice parameters of the perovskite samples after firing at selected temperatures with zero holding time and for 5 h.

ed in volume, whereas all the samples used in the present study released oxygen, which is a likely cause of the anomalous sample expansion.

3.5 Effect of oxygen release on lattice parameter

To clarify the effect of oxygen release on the lattice parameters of the perovskite samples, the lattice parameters of the perovskite samples after firing at selected temperatures with holding time of 0 h or 5 h were examined (Figs. 9(a) and (b)). At temperatures $\geq 1200^\circ\text{C}$ where the release of oxygen from the perovskite samples started, the lattice parameters of the samples fired for 5 h were much larger than those of the samples fired with holding time of 0 h. These results are related to the oxygen release shown in the TG measurement. Since the La-doped SrTiO_3 perovskites do not undergo a change in the ionic valence of A-site and B-site ions, the Ti^{4+} ions must be reduced to Ti^{3+} by oxygen release at temperatures $\geq 1200^\circ\text{C}$; the ionic radius are 81 pm for Ti^{3+} and 74.5 pm for Ti^{4+} .²⁷⁾ Because the XRD measurements were carried out at room temperature, the results suggest that Ti^{3+} ions in the perovskites exist stably until room temperature. On the other hand, the release of oxygen implies the formation of oxygen vacancy in the perovskite. For doped LaCrO_3 perovskites, there has been a report that generation of space in the crystal lattice reduces the Columbic interactions among cations or anions, causing the crystal lattice to expand accordingly.²⁸⁾

As a function of firing temperature, the $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ lattice parameters tended to increase whereas those of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ tended to maintain a constant value at temperatures $\geq 1200^\circ\text{C}$ (Figs. 9). No significant change in lattice parameter was observed at temperatures between 1300°C and 1400°C for $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ or between 1400°C and 1500°C for $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, although the oxygen release continues in this temperature range. This can be attributed to the different rates of oxygen release from the samples in each measurement; the samples used in the sintering measurement were the tablets, and those used in the TG measurement were powder.

Generally, the ionic valence of titanium ion in the Ti-based perovskite oxides tends to be +4 at 1000°C in air. When the perovskites fired at 1500°C for 5 h were annealed at 1000°C for 5 h in air, it was observed that the lattice parameters decreased; $a = 3.9042(2)\text{Å} \rightarrow a = 3.9009(2)\text{Å}$ for $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $a = 3.9046(1)\text{Å} \rightarrow a = 3.9018(2)\text{Å}$ for $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ (Fig. 10). Although the $(\text{Sr},\text{La})\text{TiO}_{3+\delta}$ samples were light yellow or light gray, despite the fact that most materials containing Ti^{3+} ions are black, the results of XRD analysis were in good agreement with the TG measurements.

Hashimoto *et al.*²⁹⁾ reported that, from consideration of electronic conduction and thermal expansion properties, La-doped SrTiO_3 perovskites are in the $(\text{Sr}_{1-x}\text{La}_x)(\text{Ti}^{4+}_{1-x}\text{Ti}^{3+}_x)\text{O}_{3+\delta}$ state without cation and anion vacancies under oxygen partial pressures in the range from 10^2 down

Fig. 10 Lattice parameters of the perovskites fired and annealed as a function of Ti content. These Ti contents used are the calculated compositions used for molecular weight when the oxygen content in the perovskite samples is assumed to be ≤ 3 .

Fig. 11 Observed, calculated, and differential patterns of Rietveld refinements of SR-XRD for $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ at 1300°C with zero holding time. The plus symbols and the solid line denote the observed and calculated intensities, respectively.

to 10^{-7} Pa at 1000°C. Our experimental results from XRD diffraction and thermal expansion analysis⁷⁾ also support the conclusion by Hashimoto *et al.*²⁹⁾ Thus, the oxygen vacancies, which are formed by the release of oxygen, join with the cation vacancies and the cation vacancies might disappear at high temperatures $\geq 1200^\circ\text{C}$ in reducing atmospheres.

Since the effect of vacancies on the perovskite structure is quite complex,^{24,30,31)} it is not an easy task to clarify the effect of the disappearance and formation of vacancies in the crystal lattice by XRD analysis. However, it should be noted that this issue is not yet settled. The lattice parameters of La-doped SrTiO_3 samples have been reported to decrease after heat treatment in a reducing atmosphere.⁷⁾ On the other hand, in the present study, the lattice parameters of the $(\text{Sr}_{0.9}\text{La}_{0.1})_{1-x}\text{TiO}_{3+\delta}$ samples increased after the heat treatment in air. Thus, there is a possibility that the mechanisms of Ti^{3+} formation are different.

3.6 Rietveld refinements

To obtain further information about the vacancies in $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskite, the Rietveld refinements for the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ samples, which were fired at 1300°C with holding time of 0 h, 1 h or 5 h, were carried out using the SR-XRD results. Figure 11 shows a typical result for the Rietveld refinement of the observed and calculated profiles for $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ at 1300°C with holding time of 0 h. The crystal structure of this sample belongs to the space group $Pm\bar{3}m$. Tables 2, entries (a), (b) and (c), show the structural parameters and reliability factors of each sample. The reliability factors after the Rietveld refinements are acceptably small. The cation site occupancy increased as the annealing time increased. It is deduced that $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ is more stable at 1300°C without the cation deficiency than with one. We intend to further investigate this phenomenon using alternative methods such as first-principle calculations.

It has been reported that under oxidizing conditions, charge compensation due to La-doping occurs via the formation of SrO vacancies in the lattice, coupled with the formation of SrO layers within the structure.^{2,32)} This suggests that the excess of oxygen in $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_{3+\delta}$ perovskites is characterized by cation vacancies rather than by interstitial oxygen. The $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ perovskites synthesized by the Pechini method show oxygen release at temperatures $\geq 1200^\circ\text{C}$. At these temperatures, Ti^{4+} ions are reduced to Ti^{3+} by charge compensation and oxygen vacancies should be formed. Because the number of cation vacancies also decreases at 1300°C, the results suggest that oxygen vacancies join simultaneously with the cation vacancies and that cation rearrangement occurs in the perovskite structure.

4 Conclusion

The sintering characteristics of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$, $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$, and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{0.96}\text{O}_{3+\delta}$ powders synthesized using the Pechini method have been investigated. It was found that the $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ and $(\text{Sr}_{0.9}\text{La}_{0.1})\text{TiO}_{3+\delta}$ samples expanded during sintering because large

Table 2(a) Crystal structure parameters of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ with with space group $Pm\bar{3}m$ after firing at 1300°C with zero holding time.

Atom	Site	g	x	y	z	$U_{\text{iso}}(\text{\AA})$
Sr, La	1a	0.958(2)	0	0	0	0.00626(7)
Ti	1b	0.998(3)	1/2	1/2	1/2	0.0045(1)
O	3c	1.000(3)	0	1/2	1/2	0.0097(3)

Unit cell parameters: $a=b=c=3.90202$ (1) $\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$, g : Occupancy, x, y, z : Fractional coordinates, U_{iso} : isotropic atomic displacement parameters, the reliability weighted pattern factor: $R_{\text{wp}}=0.0220$, the goodness of fit factor: $S=1.07$, the reliability Bragg factor: $R_{\text{B}}=0.0174$.

Table 2(b) Crystal structure parameters of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ with with space group $Pm\bar{3}m$ after firing at 1300°C for 1 h.

Atom	Site	g	x	y	z	$U_{\text{iso}}(\text{\AA})$
Sr, La	1a	0.958(2)	0	0	0	0.00627(9)
Ti	1b	0.998(3)	1/2	1/2	1/2	0.0044(2)
O	3c	1.000(3)	0	1/2	1/2	0.0078(4)

$a=b=c=3.90262$ (1) $\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{wp}}=0.0226$, $S=1.10$, $R_{\text{B}}=0.0232$.

Table 2(c) Crystal structure parameters of $(\text{Sr}_{0.9}\text{La}_{0.1})_{0.96}\text{TiO}_{3+\delta}$ with with space group $Pm\bar{3}m$ after firing at 1300°C for 5 h.

Atom	Site	g	x	y	z	$U_{\text{iso}}(\text{\AA})$
Sr, La	1a	0.960(2)	0	0	0	0.00608(6)
Ti	1b	1.000(3)	1/2	1/2	1/2	0.0043(1)
O	3c	1.000(3)	0	1/2	1/2	0.0076(3)

$a=b=c=3.90300$ (1) $\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$, $R_{\text{wp}}=0.0245$, $S=1.21$, $R_{\text{B}}=0.0255$.

pores were formed inside the samples. TG measurements suggest that at the temperature where expansion occurs, oxygen was released from the perovskites, and SR-XRD analysis indicates that the number of cation vacancies decreased. The release of oxygen during the grain-growth process is likely to be related to pore formation.

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