SINTERING AND ELECTRICAL PROPERTIES IN AIR FOR A-SITE DEFICIENT $(\text{Sr}_{0.7}\text{La}_{0.3})_{1-y}\text{TiO}_3$ PEROVSKITE SAMPLES WITH AND WITHOUT TiO_2 PHASE

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The sintering and electrical properties of A-site-deficient perovskites, namely, $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ with TiO_2 and $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ with a single perovskite phase, were investigated in air using powders synthesized by solid-state mixing. $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ showed much higher sintering characteristics than $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$. The relative density of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ reached 96% at 1500 °C with zero holding time, but decreased with increasing holding time, owing to pore formation inside the sample. The resistivity of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ was lower than that of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ at measurement temperatures ≤ 600 °C, although the reverse was observed at temperatures ≥ 700 °C. Because the total resistivity of $(\text{Sr},\text{La})\text{TiO}_3$ perovskites should be governed primarily by grain boundary resistivity at low temperatures, $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ with many grain boundaries showed higher resistivity, compared to that of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$.

Keywords: Perovskite; A-site deficiency; sintering characteristics.

1. Introduction

$(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$ perovskites are promising segmented-in-series tubular solid oxide fuel cell (SOFC) interconnect materials because of their chemical and physical stability under oxidizing and reducing atmospheres¹. During the fabrication of these materials, green multilayers of anodes, electrolytes and interconnects on a porous tube should be cofired at high temperature. To prevent a decline in anodic performance, the sintering should ideally be performed at temperatures ≤ 1400 °C, and the electrolytes and interconnects should be fully densified. Thus, the synthesis of fine $(\text{Sr},\text{La})\text{TiO}_3$ perovskite powders with high sintering characteristics in air is essential in fabricating impervious interconnects at low sintering temperatures.

In our previous works, we found that $(\text{Sr},\text{La})\text{TiO}_3$ powders synthesized by the Pechini method exhibit good sintering characteristics². However, Ruddlesden–Popper phases (i.e., $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$) are more readily formed between 1200 °C and 1500 °C during the sintering of these powders than during the sintering of powders synthesized by solid-state

mixing³. These phases, which have low electrical conductivity⁴, remain when the relative density of the perovskite becomes $\geq 94\%$ at 1400 °C. This is a serious problem in the application of $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$ perovskites in SOFC interconnects.

A-site-deficient $(\text{Sr}_{1-x}\text{La}_x)_{1-y}\text{TiO}_3$ perovskites are expected to prevent the formation of Ruddlesden–Popper phases during SOFC fabrication because such phases require an excess of the A-site element. We previously reported that the A-site deficiency in $(\text{Sr},\text{La})_{1-y}\text{TiO}_3$ systems increases with increasing La content and reaches $y = 0.12$ for $(\text{Sr}_{0.7}\text{La}_{0.3})_{1-y}\text{TiO}_3$ ³. In the present study, the effects of TiO_2 as the second phase on the sintering and electrical properties of $(\text{Sr}_{0.7}\text{La}_{0.3})_{1-y}\text{TiO}_3$ have been investigated using $(\text{Sr},\text{La})\text{TiO}_3$ perovskite powders synthesized by solid-state mixing.

2. Experimental

Sample powders were prepared in air by solid-state mixing³. $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ and $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ perovskites have an orthorhombic structure. The peak at approximately $2\theta = 38^\circ$ is very small, and thus the 031, 112, 211 reflections are difficult to index. The difference in cell volume between the orthorhombic and cubic units is small⁵; therefore, the samples were assumed to crystallize as a cubic unit.

Table I Nominal and calculated compositions, cell volumes, theoretical densities and a second phase of the samples. $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$: 1600 °C for 5 h, $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$: 1500 °C with zero holding time

Nominal composition	Calculated composition used for molecular weight ⁶	Symmetry	Cell volume	Theoretical density
$(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_{3.012}$	$\text{Sr}_{0.614}\text{La}_{0.263}\text{Ti}_{0.996}\text{O}_3$	Ortho	$59.174 \text{ \AA}^3$	5.22 g cm^{-3}
$(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_{2.978}$	$\text{Sr}_{0.614}\text{La}_{0.263}\text{Ti}_{0.996}\text{O}_3 + \text{TiO}_2$	Ortho	$59.123 \text{ \AA}^3$	5.19 g cm^{-3}

Sintering characteristics were evaluated by the density of the sintered pellet³. The composition of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ was estimated to be 98 mol % $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ and 2 mol% TiO_2 . The samples were confirmed by powder X-ray diffractometry (XRD; 18 kW, Rigaku, UltraX 18TTR2-300, Japan). The microstructure of the sintered samples was investigated by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis (Hitachi, S-3500H, Japan). To evaluate the resistivity of $(\text{Sr},\text{La})\text{TiO}_3$, sample pellets were tested in air by AC impedance measurement³.

3. Results and Discussion

From the results of XRD analysis, after firing at 1400 °C for 5 h, the $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ powder showed a single perovskite phase and the $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ powder included TiO_2 as a second phase, as shown in Fig. 1.

Figs. 2 show the relative densities of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ and $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$. In general, the density of ordinary ceramics increases with both firing temperature and holding time. The sintering behavior of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ is the same as that of ordinary ceramics. An acceptable relative density of SOFC interconnects is $\geq 94\%$. The density of

this material reached 95% upon firing at 1600 °C for 1 h. For $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$, the density increased markedly compared with that of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$. The density of this material was 97% upon firing at 1400 °C for 3 h, and 96% upon firing at 1500 °C with zero holding time. These results suggest that TiO_2 enhances perovskite densification.

Fig. 1 XRD patterns of the samples: (a) $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$, (b) $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$

Fig. 2 Relative densities of the samples as a function of holding time with a parameter of firing temperature: (a) $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$, (b) $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$

Although a TiO_2 phase was observed in the XRD pattern of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$, no TiO_2 particles were observed for the sample fired at 1500 °C with zero holding time in its SEM image or EDX profile. Thus, the TiO_2 component is thought to be distributed homogeneously throughout grains of the perovskite. However, as shown in Fig. 3, after firing at 1500 °C for 5 h, the layers were observed at grain boundaries, which were

identified to be TiO_2 by EDX. This suggests that the layers are deposited at boundaries between perovskite grains during sintering. Thus, the migration of TiO_2 throughout the grains should enhance the densification of the perovskite grains.

Fig. 3 SEM image of the $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ sample after firing at 1500 °C for 5 h

In Fig. 2(b), a slight decrease in relative density was observed for the $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ samples fired at 1500 °C and 1600 °C although the density of the same sample fired at 1400 °C increased with increasing holding time. Quite recently, we found that $(\text{Sr},\text{La})\text{TiO}_3$ perovskites synthesized by the Pechini method gradually release oxygen in air at temperatures greater than approximately 1200 °C through Ti^{3+} formation⁷. Thus, when the surface of the sample is densified first, oxygen gas cannot escape from the surface of the sample, and pores are generated inside the sample. Since $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ showed good sintering characteristics, it is clear that pores were formed inside the sample by the same mechanism.

Fig. 4 Cross-sectional SEM images of the samples after firing at 1600 °C for 5 h: (a) $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$, (b) $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$

As shown in Figs. 4, for $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$, a densified cross section is observed although very small pores remain. On the other hand, for $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$, large pores inside the sample are observed despite its densified cross section.

For the resistivity measurement, the following dense samples with relative densities $\geq 95\%$ were used: $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ fired at 1500°C with zero holding time and $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ fired at 1600°C for 5 h. The resistivities of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ and $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ at 900°C were $23.8\ \Omega\text{ cm}$ and $7.94\ \Omega\text{ cm}$, respectively. The resistivity of 30 mol % La-doped SrTiO_3 with stoichiometric composition is approximately $1\text{--}10\ \Omega\text{ cm}^{1,2,8}$, and thus the A-site deficient $(\text{Sr},\text{La})_{1-y}\text{TiO}_3$ perovskites showed higher resistivity than perovskites of stoichiometric composition. This trend is in good agreement with the results reported by Li *et al.*⁹.

Fig. 5 Resistivity of the samples as a function of temperature

Fig. 5 shows that the resistivity of both samples tends to decrease with increasing temperature. At temperatures $\geq 700^\circ\text{C}$, the resistivity of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ was higher than that of $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$. On the other hand, at temperatures $\leq 600^\circ\text{C}$, the reverse results for resistivity were obtained. Since TiO_2 is an insulator, it increases the resistivity of the composite¹⁰. Rodewald *et al.*¹¹ have separated the bulk and grain-boundary resistivities from total resistivity at temperatures less than approximately 400°C through the use of SrTiO_3 -based perovskites, thus showing that grain-boundary resistivity is much higher than bulk resistivity. In addition, Abrantes *et al.*¹² have reported that grain-boundary resistivity increases markedly with decreasing temperature. Thus, the total resistivity of $(\text{Sr},\text{La})\text{TiO}_3$ perovskites should be governed primarily by grain-boundary resistivity at low temperatures.

For $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$, since the TiO_2 component is thought to be distributed homogeneously throughout grains of the perovskite, it should affect the bulk resistivity. As shown in Figs. 6, $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ shows small grain sizes of $5\text{--}15\ \mu\text{m}$, whereas $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.88}\text{TiO}_3$ shows large grain sizes of $10\text{--}35\ \mu\text{m}$, owing to its high-temperature heat treatment. This indicates that $(\text{Sr}_{0.7}\text{La}_{0.3})_{0.85}\text{TiO}_3$ has many grain boundaries with high resistivity. Thus, the discrepancy between the observed and theoretical resistivity at

temperatures ≤ 600 °C is observed. Further investigation of the resistivity of La-doped SrTiO₃ is currently in progress.

Fig. 6 Surface-sectional SEM images of the samples: (a) (Sr_{0.7}La_{0.3})_{0.88}TiO₃ sample fired at 1600 °C for 5 h, (b) (Sr_{0.7}La_{0.3})_{0.85}TiO₃ sample fired at 1500 °C with zero holding time

4. Conclusion

The effects of TiO₂ in (Sr_{0.7}La_{0.3})_{0.85}TiO₃ on the sintering and electrical properties of perovskite were investigated in air using (Sr_{0.7}La_{0.3})_{0.85}TiO₃ perovskite powder synthesized by solid-state mixing. The presence of TiO₂ enhanced the sintering characteristics of the perovskite, with the density of (Sr_{0.7}La_{0.3})_{0.85}TiO₃ reaching 96% at 1500 °C with zero holding time. The relative density at 1500 °C and 1600 °C decreased with holding time because pores formed inside the sample through the release of oxygen. The presence of TiO₂ in the sample increased resistivity at temperatures ≥ 700 °C.

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