IDENTIFICATION OF SECOND PHASE DEPOSITED ON La-DOPED SrT_iO_3 PEROVSKITES SYNTHESIZED BY CITRIC-GEL METHOD

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ABSTRACT: We examined deposition process of the second phase during sintering $Sr_{0.7}La_{0.3}TiO_3$ perovskite at 1400°C and analyzed the detailed composition by means of SEM-EDX technique. The second phase deposited at the corners of the $Sr_{0.7}La_{0.3}TiO_3$ matrix grains was confirmed to be Sr-doped rare-earth B-type La_2O_3.

KEYWORDS: *Citric-Gel Method; Strontium Titanate; Impurity; Rare-Earth B-Type Oxide; A-Site Deficiency*

1.0 INTRODUCTION

Solid oxide fuel cells (SOFCs) are connected electrically in series with the help of an interconnect [1]. La-doped strontium titanates are known to be candidate materials for interconnects of segmented-in-series tubular SOFCs [2-3]. These materials show that their electrical conductivities gradually decrease at the operating temperatures of around 900°C with time [4]. There is a possibility that the decrease behavior of the conductivity is related to a second phase formation in the perovskites. It is reported that second phases generate in $Sr_{0.7}La_{0.3}TiO_3$ perovskite, which was synthesized by the solid-state reaction method, after annealing at 900°C for 2,000 hours [5]. It is also reported for $Sr_{0.8}La_{0.2}TiO_3$ perovskite that second phases generates in at 1100-1500°C even when the sample was prepared by the citric acid method [6-7]. However, compositions, structures, and formation mechanisms of the second phases are still unknown. Meyer et al. [8] reported the influence of high temperature oxygen annealing on (100)-oriented $(La,Sr)TiO_3$ and $Sr(Ti,Nb)O_3$ single crystals. They proposed that the formation of Ruddlesden-Popper intergrowth phases $SrO\cdot(SrTiO_3)n$ [9] by a release of strontium from the perovskite lattice. Wei et al. [10] reported that annealing La-doped $SrTiO_3$ single crystal in air at 1300°C for 120 hours resulted in the formation of insulating islands on the surface which were found to be stoichiometric SrO by means of some X-ray and electron spectroscopic techniques. It seemed certain that Sr-rich phases should be segregated from the perovskite matrix. Our group has been also reported that the second phase observed in $Sr_{1-x}La_xTiO_3$ with $0.2 \leq x \leq 0.4$, when the oxide precursor prepared by a citric-gel method was fired at 1100-1500°C, was confirmed to be Sr-doped La_2O_3 with the rare-earth oxide B-type structure [11]. This impurity phase was the same one as appeared in the La-doped $SrTiO_3$ during the SOFC operation [4].

In this paper, we examined deposition process of the second phase and detailed compositional analysis by means of SEM-EDX technique.

2.0 METHODOLOGY

La_2O_3 (Kojundo Chemical Laboratory Co., LTD, Japan, 99.9%, calcined at 1500°C for 1 hour prior to use), $SrCO_3$ (Kojundo Chemical Laboratory Co., LTD, Japan, 99.9%, dried at 105°C for 48 hours), water-soluble TAS-FINE ($(NH_4)_4[Ti_2(C_6H_4O_7)_2(O_2)_2]$, ammonium citratoperoxo titanate (IV), Furuuchi Chemical Corporation, Japan) were used as starting materials. The Ti content of TAS-FINE was determined quantitatively by thermo gravimetric (TG) measurement. $Sr_{1-x}La_xTiO_3$ samples with x=0.3 were prepared as follows. TAS-FINE was dissolved in a solution mixture of ethylene glycol, citric acid, and distilled water. La_2O_3 and $SrCO_3$ were weighted in a desired ratio and then added to the solution. This solution was heated to 200-300°C for 30 min to form a viscous gel, and this gel was dried at 380°C for 1 hour.

The resulting gel was calcined at 600°C for 12 hours and well ground with an alumina mortar. The obtained powder was fired at 1000°C for 2 hours and was mixed in ethanol for 24 h by a ball milling technique. After drying, the powder was pressed into a pellet, and finally fired at 1400°C for 1 hour up to 1 week.

3.0 RESULTS AND DISCUSSION

Figure 1 shows variation of X-ray diffraction patterns for $Sr_{0.7}La_{0.3}TiO_3$ prepared by citric-gel method as a function of firing duration at 1400°C. All the strong peaks could be assigned to the perovskite-type structure. At an early stage of sintering under 1400°C, the single phase of perovskite-type $Sr_{0.7}La_{0.3}TiO_3$ was formed. However, a very small amount of impurity assigned to the rare-earth B-type La_2O_3 phase appeared and the amount increased with increasing the firing duration. The peak position assigned to the La_2O_3 seemed a slightly lower in 2θ than the reported value in the JCPDS 022-0641 shown in Figure 1, which will be described later.

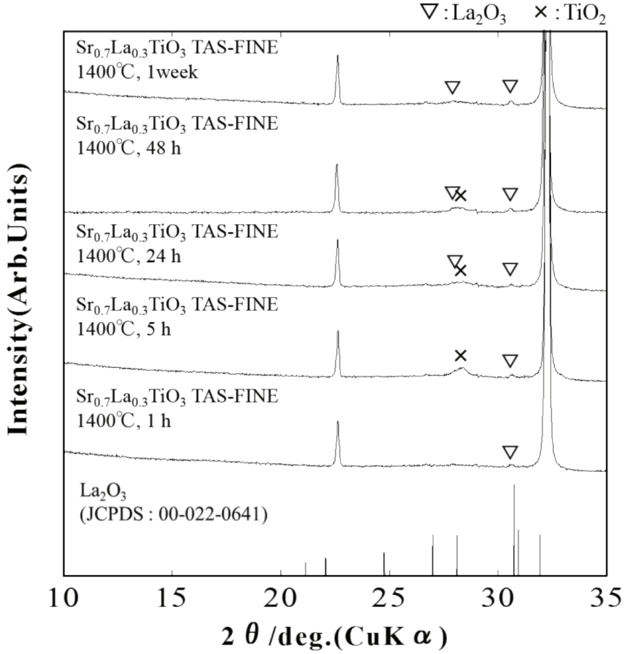
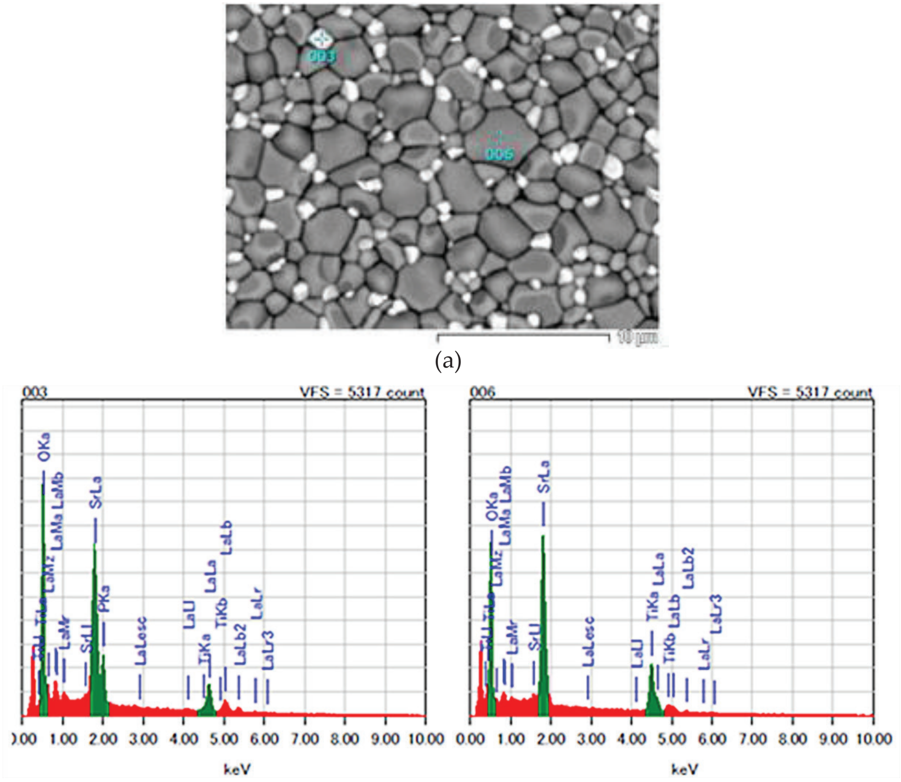


Figure 1: Variation of X-ray diffraction for $Sr_{0.7}La_{0.3}TiO_3$ fired at 1400°C as a function of firing duration

In the middle of sintering, a small but broad peak at around 2θ=27.8° also appeared, which would correspond to the strongest peak of the rutile-type TiO_2. It seems that TiO_2 was released from the perovskite matrix at the same timing of exudence of La_2O_3. Finally, the released TiO_2 seemed to be incorporated again to the perovskite matrix but the exuded La_2O_3 still existed as an impurity phase. That means, the perovskite matrix should possess A-site deficiency, where the A-site means the site that the larger cation A should occupy when the perovskite-type oxide can be expressed as ABO_3. In the previous papers, such an A-site deficiency is preferable for perovskite-type structure [7, 12]. The sintering characteristics were highly improved in the A-site deficient perovskites [7]. In other words, the progress in sintering of the perovskite matrix may promote the A-site deficiency. Thus the B-type La_2O_3 was dispersively deposited on the perovskite $Sr_{0.7}La_{0.3}TiO_3$ matrix with a slight A-site deficiency probably.

Figure 2 shows SEM image of $Sr_{0.7}La_{0.3}TiO_3$ fired at 1400°C for 48 hours and its EDX spectra from selected areas of the bright impurity grain and the dark matrix grain. The impurity grain was bright because the constituent atoms would be those with the heavier atomic number in average, which is consistent with the fact that the phase of the impurity grain would be the rare-earth B-type La_2O_3. According to the EDX analysis, Ti was hardly detected whereas Sr and La was rich in the bright, impurity phase, the peaks of which can be seen in an energy region around 4.5keV. From the results of XRD and EDX analyses, the second phase should be Sr-doped La_2O_3 phase with the rare-earth B-type structure. Peak shift toward the lower 2θ-side compared with the JCPDS data would be due to the larger ionic size of Sr^{2+} than La^{3+} [13].



(a)

(b)

(c)

Figure 2: (a) SEM image of $Sr_{0.7}La_{0.3}TiO_3$ fired at 1400°C for 48 hours and its EDX spectra from selected areas: (b) bright impurity and (c) dark matrix

Figure 3 shows SEM images of $Sr_{0.7}La_{0.3}TiO_3$ fired at 1400°C for the given firing durations from 1 hour to 1 week. As the firing period got longer, the average grain sizes increased. Firing for 1 hour made the grain size still fine and homogenous, probably due to adopting citric-gel technique in preparation. Soft chemical techniques such as a citric-gel method will be effective for obtaining homogeneous fine powders in a short duration fired at a low temperature [6-7, 11, 14-15]. Even in the sample fired for 5 hours, there were some small bright grains, which would be Sr-doped La_2O_3. This fact is in consistent with the X-ray results. Once the segregation of Sr-doped La_2O_3 from the perovskite matrix occurred, the grain growth of the perovskite matrix was accelerated and the sintering proceeded so that some macro-pores between grains disappeared. Long-term firing at 1400°C led to further sintering of the grains, seen from change in the surface morphology from round grains to angulated, flat grains but to anew creation of macro-pores between grains.

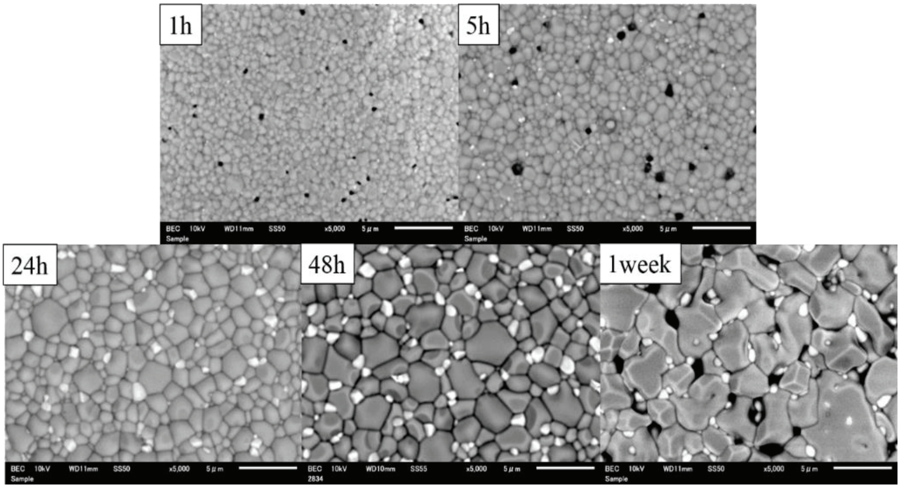


Figure 3: SEM images of $Sr_{0.7}La_{0.3}TiO_3$ fired at 1400℃ for the given firing durations from 1 hour to 1 week

4.0 CONCLUSION

The second phase deposited on the perovskite-type $Sr_{0.7}La_{0.3}TiO_3$ matrix after firing at 1400°C was found to be the rare-earth B-type La_2O_3 containing Sr. This impurity should be identical with that appears at an operating temperature of SOFC around 900°C. The deposition of Sr-doped La_2O_3 would proceed so that the A-site site deficiency was created in $Sr_{0.7}La_{0.3}TiO_3$.

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