

# Conductivity and expansion at high temperature in $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$ prepared under reducing atmosphere

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**Abstract**  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimens were prepared in reducing atmosphere, and the structural and electrical properties were studied. The lattice parameter of  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  at room temperature was larger than that expected from Vegard's law between  $\text{SrTiO}_3$  and  $\text{LaTiO}_3$  due to the reductive expansion. The conductivity of this specimen was  $100 \text{ S cm}^{-1}$  at  $1000^\circ\text{C}$ ,  $p_{\text{O}_2} = 10^{-13} \text{ Pa}$ . However, the conductivity was not preserved after an oxidation-reduction cycle. Over  $p_{\text{O}_2} = 10^2 \text{ Pa}$ , the conductivity drastically dropped with increasing  $p_{\text{O}_2}$ . The thermal expansion coefficient of  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  was  $11.8 \times 10^{-6} \text{ K}^{-1}$  in 9%  $\text{H}_2/\text{N}_2$  (room temperature –  $1000^\circ\text{C}$ ). In this  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$ , the chemical expansion on oxidation reached  $\Delta l/l_0 = 0.51\%$ , when changing  $p_{\text{O}_2}$  from  $10^{-11} \text{ Pa}$  to  $2 \times 10^4 \text{ Pa}$  (air) at  $1000^\circ\text{C}$ .

**Keywords** Strontium titanate · Donor doping · Vegard's law · Conductivity · Dilatometry

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## 1. Introduction

Reduced  $\text{SrTiO}_3$  can exhibit a quite high electrical conductivity. The conductivity of single crystalline  $\text{SrTiO}_{2.72}$  was reported as  $1.7 \times 10^3 \text{ S} \cdot \text{cm}^{-1}$  at  $27^\circ\text{C}$  [1]. Such oxygen deficient  $\text{SrTiO}_{3-\delta}$  exhibits a metallic conduction behavior, while stoichiometric  $\text{SrTiO}_3$  is an insulator and the conductivity is only ca.  $1 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  even at  $1000^\circ\text{C}$  [2, 3]. Reduction of Ti introduces electrons into the Ti 3 d orbital involved in the conduction. Donor doping of strontium titanate is also widely studied as a means to improve the conductivity [4–19]. An example is the La doped  $\text{SrTiO}_3$  series. It is expected that the partial substitution of  $\text{La}^{3+}$  for  $\text{Sr}^{2+}$  causes a change of valence from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ , resulting in a high conductivity of  $\text{SrTiO}_3$ . Higuchi et al. reported that the conductivity of a single crystal of  $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_{3-\delta}$  was  $3.0 \times 10^3 \text{ S} \cdot \text{cm}^{-1}$  at  $27^\circ\text{C}$  [4].

The above-mentioned reports on pure and La doped  $\text{SrTiO}_3$  showed metallic conduction behavior, i.e. a conductivity decreasing with increasing temperature. However, Moos et al. reported that La doped  $\text{SrTiO}_3$  could also show a relatively good conductivity even at elevated temperatures [5]: poly-crystalline  $\text{Sr}_{0.6}\text{La}_{0.4}\text{TiO}_{3-\delta}$  showed  $3.0 \times 10^2 \text{ S} \cdot \text{cm}^{-1}$  in a reducing atmosphere at  $1000^\circ\text{C}$ . Such high conductivities have suggested La-doped  $\text{SrTiO}_3$  to be studied as a functional SOFC component under reducing atmosphere. Marina et al. reported a low overpotential for an anode using La-doped  $\text{SrTiO}_3$ , although the performance could only be maintained for 30 min [6]. Pudmich et al., on the other hand, examined La doped  $\text{SrTiO}_3$  as an SOFC interconnect material [7].

However,  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-\alpha}$ , where  $\alpha$  can adopt both positive and negative values, shows a lack of reproducibility of the structure- and conductivity data [4–17]. Howard et al. reported that the lattice parameter increased with increasing

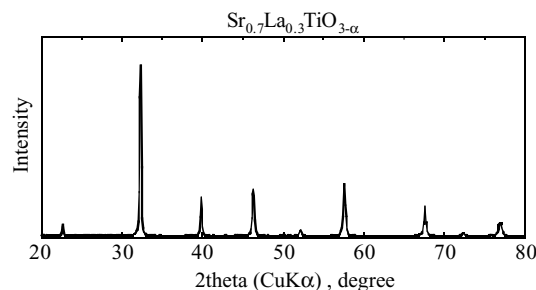
La concentration “ $x$ ” in  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-\alpha}$  [8] while Eror et al. reported that the lattice parameter decreased with increasing “ $x$ ” [9, 10]. Marina et al. stated that the conductivity in  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-\alpha}$  depended on the condition of sample preparation [6]. The conductivities of two  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimens, one prepared in air at  $1650^\circ\text{C}$ , the other prepared in 2%  $\text{H}_2/\text{Ar}$  at  $1650^\circ\text{C}$ , were  $\approx 2 \text{ S} \cdot \text{cm}^{-1}$  and  $2.0 \times 10^2 \text{ S} \cdot \text{cm}^{-1}$  respectively at  $1000^\circ\text{C}$ ,  $p_{\text{O}_2} = 10^{-13} \text{ Pa}$ . Eror et al. suggested the presence of a Ruddlesden-Popper phase [9, 20] in oxidized  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-\alpha}$  materials. La-doped  $\text{SrTiO}_3$  can be overstoichiometric at least up to the limit  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3+x/2}$  as shown by thermogravimetry by Flandermeyer et al. [11] The extra  $x/2$  moles of oxygen/formula unit cannot be accommodated in a normal perovskite structure. Canales-Vázquez et al. [12] suggest that reduced as well as over-stoichiometric doped strontium titanates can be viewed as members of the series  $\text{La}_2\text{Sr}_{n-2}\text{Ti}_n\text{O}_{3n+1-\delta}$ , where “extra” oxygen can be present in special crystallographical directions.  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$ , for instance, would then correspond to the case  $n = 6.66$ .

As above, the valence state of Ti and the oxygen non-stoichiometry seem to cause these differences in La-doped  $\text{SrTiO}_3$ . Therefore, it was expected that reduced La-doped  $\text{SrTiO}_3$ , which has a high conductivity, will be affected by the oxygen partial pressure of the surrounding atmosphere in the high temperature region. This would limit the use of La-doped  $\text{SrTiO}_3$  in high temperature applications. In this study,  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  was prepared in a reducing atmosphere, and the structural and electrical properties were studied. The dependence of the conductivity and expansion on the oxygen partial pressure was measured at  $1000^\circ\text{C}$ , respectively.

## 2. Experimental

A solid-state reaction method was used for the sample preparation.  $\text{Sr}(\text{NO}_3)_2$  solution,  $\text{La}(\text{NO}_3)_3$  solution and  $\text{TiO}_2$  were used as starting materials. The solutions were mixed with the  $\text{TiO}_2$  in an appropriate ratio and dried in a furnace at  $120^\circ\text{C}$ . The resulting white powder was ground and calcined in air at  $1250^\circ\text{C}$  for 12 h. The calcined powder was re-ground by ball milling and re-calcined in air at  $1350^\circ\text{C}$  for 12 h. The powder after the last calcination was ball-milled again, and then pressed into bars and cylinders by uniaxial pressing at 87 MPa, and re-pressed by isostatical pressing at 325 MPa. The bars were sintered in 9%  $\text{H}_2/\text{N}_2$  at  $1500^\circ\text{C}$  (oxygen partial pressure  $p_{\text{O}_2} = 10^{-5} \text{ Pa}$  at  $1500^\circ\text{C}$ ) for 12 h, and quenched to the room temperature in the same atmosphere. The phase characterization and the lattice parameter of the prepared sample were investigated by x-ray diffraction using  $\text{CuK}\alpha$  radiation at room temperature.

The conductivity as a function of oxygen partial pressure ( $p_{\text{O}_2}$ ) at  $1000^\circ\text{C}$  was measured by a dc 4-terminal method.



**Fig. 1** XRD diffractogram of  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimens prepared in 9%  $\text{H}_2/\text{N}_2$  at  $1500^\circ\text{C}$  ( $p_{\text{O}_2} = 10^{-5} \text{ Pa}$  at  $1500^\circ\text{C}$ )

The  $p_{\text{O}_2}$  was monitored by an YSZ oxygen sensor. First, the specimen was heated to  $1000^\circ\text{C}$  under 9%  $\text{H}_2/\text{N}_2$ , and next, the  $p_{\text{O}_2}$  of the atmosphere was gradually increased using  $\text{N}_2$ , air or  $\text{O}_2$ . After reaching a pure  $\text{O}_2$  atmosphere,  $p_{\text{O}_2} = 10^5 \text{ Pa}$ , the  $p_{\text{O}_2}$  was gradually decreased again to  $p_{\text{O}_2} = 10^{-13} \text{ Pa}$ . The  $p_{\text{O}_2}$  was changed in relatively short steps, and the conductivity was measured at each  $p_{\text{O}_2}$ .

The thermal and isothermal chemical expansions were studied using a high temperature dilatometer (Setaram type 31).  $\text{Al}_2\text{O}_3$  was applied as a standard material for the measurement. The heating rate for this TEC measurement was  $2^\circ\text{C}/\text{min}$ . The isothermal chemical expansion was measured at  $1000^\circ\text{C}$ , and the  $p_{\text{O}_2}$  was controlled and monitored as during the conductivity measurements.

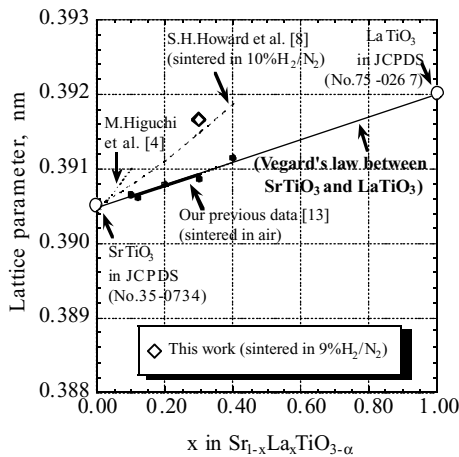
## 3. Results

### 3.1. Crystal structure of the specimen at room temperature

A  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimen, which was sintered in 9%  $\text{H}_2/\text{N}_2$  at  $1500^\circ\text{C}$  and quenched, was densified up to 98% of the theoretical, and the color was black. Figure 1 shows the x-ray diffractogram of the  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3\pm\alpha}$  specimen at room temperature. A single perovskite phase was observed, and indexed as cubic Pm-3m. The lattice parameter of this specimen was calculated from this diffractogram and the value was  $0.39166(7) \text{ nm}$ . It was compared with other literature data including our previous work [4, 8, 13], as shown in Fig. 2, and was larger than that expected from Vegard's law between  $\text{SrTiO}_3$  ( $a = 0.3905 \text{ nm}$ , JCPDS No. 35-0734) and  $\text{LaTiO}_3$  ( $a = 0.3920 \text{ nm}$ , JCPDS No.75-0267).

### 3.2. Electrical conductivity as a function of $p_{\text{O}_2}$ at $1000^\circ\text{C}$

Figure 3 shows the conductivity of the  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimen as a function of  $p_{\text{O}_2}$  at  $1000^\circ\text{C}$ . The conductivity shows a strong dependence on the  $p_{\text{O}_2}$ . The conductivity

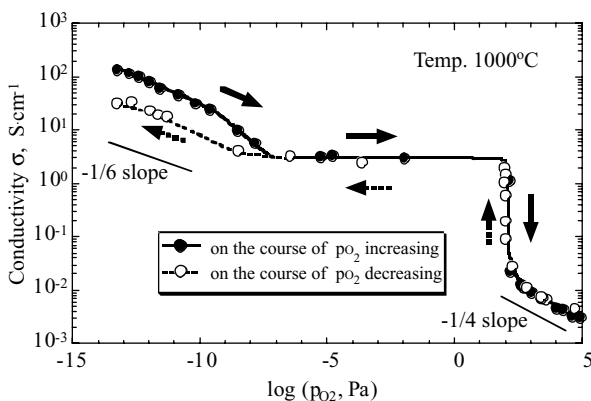


**Fig. 2** Lattice parameter at room temperature as a function of  $x$  in  $Sr_{1-x}La_xTiO_{3-\alpha}$

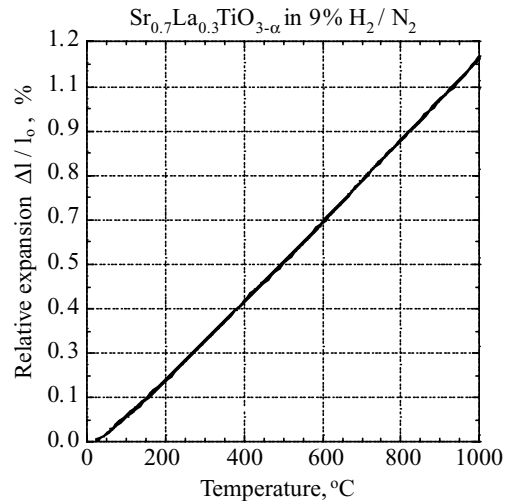
of  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  at  $p_{O_2} = 10^{-14}$  Pa was high,  $\sim 100$  S  $\cdot$   $cm^{-1}$ . It decreased with increasing  $p_{O_2}$  in the low  $p_{O_2}$  region. In the range of  $p_{O_2} = 10^{-7}$  Pa to  $10^2$  Pa, the conductivity remained almost constant with  $p_{O_2}$ . Over  $p_{O_2} = 10^2$  Pa, the conductivity drastically dropped with increasing  $p_{O_2}$ . The  $p_{O_2}$  was gradually decreased again from  $p_{O_2} = 10^5$  Pa to  $p_{O_2} = 10^{-13}$  Pa. During the stepping down in  $p_{O_2}$ , the conductivity traced previous values until  $p_{O_2} \approx 10^{-7}$  Pa, i.e. the end of the plateau region. However, in the region of  $p_{O_2} < 10^{-7}$  Pa, the conductivity did not recover to the initial value, and it was 30 S  $cm^{-1}$  at  $p_{O_2} = 10^{-13}$  Pa compared to the initial value of 100 S  $cm^{-1}$  under the same  $p_{O_2}$ . The slope of  $\log \sigma$  versus  $\log p_{O_2}$  approaches  $-1/6$  in the boundary region  $p_{O_2} < 10^{-10}$  Pa and  $-1/4$  at  $p_{O_2} > 10^3$  Pa.

### 3.3. Thermal and chemical expansion at high temperature

The  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  specimen was then subjected to a dilatometric study. Figure 4 shows the linear thermal ex-



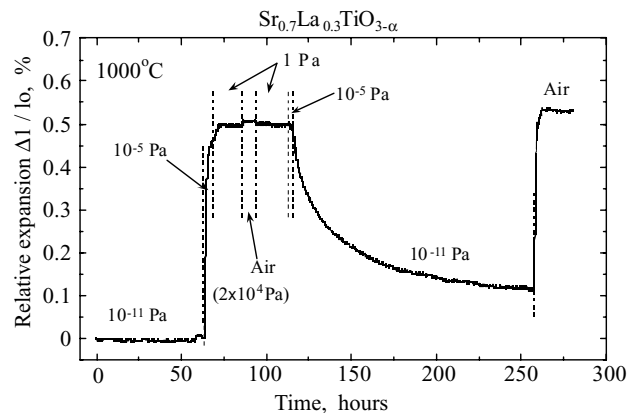
**Fig. 3** Dependence of conductivity of  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  on  $p_{O_2}$  at  $1000^\circ C$



**Fig. 4** Linear thermal expansion rate of  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  in 9%  $H_2/N_2$  ( $p_{O_2} = 10^{-11}$  Pa at  $1000^\circ C$ ). (temperature range :  $27^\circ C$ – $1000^\circ C$ , reference material:  $Al_2O_3$ , heating rate:  $2^\circ C/min$ , base line : length  $l_0$  at  $27^\circ C$ )

pansion ratio of a  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  bar in 9%  $H_2/N_2$  ( $p_{O_2} = 10^{-11}$  Pa at  $1000^\circ C$ ) from room temperature to  $1000^\circ C$ . The thermal expansion was almost linear, as no phase transitions are expected for a cubic perovskite, and the average thermal expansion coefficient (TEC) in 9%  $H_2/N_2$  was  $11.8 \times 10^{-6}$   $K^{-1}$  from room temperature to  $1000^\circ C$ .

The relative expansion of the  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  with time, caused by  $p_{O_2}$  changes at  $1000^\circ C$  is shown in Fig. 5. Before the measurement, the specimen was heated up to  $1000^\circ C$  under 9%  $H_2/N_2$  ( $p_{O_2} = 10^{-11}$  Pa at  $1000^\circ C$ ) in the dilatometer. The length of the specimen after reaching  $1000^\circ C$  was used as basis. The sample was first held at  $1000^\circ C$  under 9%  $H_2/N_2$  for 63 h. During the holding, the length was constant within a small background noise. Next,  $p_{O_2}$  was stepwise changed from  $10^{-11}$  Pa to  $2 \times 10^4$  Pa (air) by using gas mix-



**Fig. 5** Relative expansion of  $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$  specimen with time, caused by  $p_{O_2}$  change at  $1000^\circ C$ . The initial length  $l_0$  at  $1000^\circ C$  is used as a base line

tures of  $\text{H}_2 + \text{N}_2 + \text{H}_2\text{O}$ ,  $\text{N}_2$  or air. In the step from  $10^{-11}$  to  $10^{-5}$  Pa, the  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimen expanded rapidly in length by 0.46%. The relative expansion upon oxidation finally reached 0.51% after exposure to air. Afterwards, the sample was returned to  $p_{\text{O}_2} = 10^{-11}$  Pa after passing 2 steps. However, the contraction was very slow, and did not come back to the original length even after 140 h. Finally,  $p_{\text{O}_2}$  was changed abruptly from  $10^{-11}$  to  $2 \times 10^4$  Pa (air) and the specimen responded by a rapid expansion again.

#### 4. Discussion

The lattice parameter of the  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimen that was sintered in 9%  $\text{H}_2/\text{N}_2$  at  $1500^\circ\text{C}$  and quenched to room temperature, was compared with other literature data [4, 8, 13], as shown in Fig. 2. In our previous work [13], the lattice parameters of  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-\alpha}$  specimens, which were sintered in air at  $1450\text{--}1650^\circ\text{C}$ , all lie on the Vegard's line between  $\text{SrTiO}_3$  ( $a = 0.3905$  nm, JCPDS No. 35-0734) and  $\text{LaTiO}_3$  ( $a = 0.3920$  nm, JCPDS No. 75-0267). We concluded that they were close to being stoichiometric  $\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3.0}$ , since all of the Ti in  $\text{LaTiO}_3$ , which is known as a typical Mott-Hubbard insulator [21], should be  $\text{Ti}^{3+}$ . In this study, the lattice parameter of the  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimen sintered in 9%  $\text{H}_2/\text{N}_2$  was larger than predicted from Vegard's law. The value (0.39166(7) nm) nearly agreed with the data (0.39148 nm) by S.A. Howard et al. (sintering condition: 10%  $\text{H}_2/\text{N}_2$  ( $p_{\text{O}_2} = 10^{-12}$  Pa), at  $1400^\circ\text{C}$  for 17 h) [8]. The Vegard's slope determined by M. Higuchi et al. [4] was even steeper. Their samples were single crystals, grown in a  $\text{N}_2$  atmosphere at very high temperatures, e.g.  $1900^\circ\text{C}$ . Such reducing atmospheres at elevated temperatures are considered to lead to further reduction of Ti in these specimens, leading to oxygen deficiency  $-\text{Sr}_{1-x}\text{La}_x\text{TiO}_{3-\alpha}$  ( $\alpha > 0$ ). As a consequence, their lattice parameters will also be larger than those predicted by Vegard's law. This is a combined action of the larger radius of  $\text{Ti}^{3+}$  and the introduction of oxygen vacancies.

The electronic conduction in  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  is considered to be n-type in this study, even in air because of the negative  $p_{\text{O}_2}$  dependence in Fig. 3. The amount of  $\text{Ti}^{3+}$  is thus controlling the conductivity since the electrons conduct through a conduction band involving the Ti 3d orbital [14, 21, 22]. The conductivity of  $p_{\text{O}_2}$  dependence in Fig. 3 are as outlined in the paper by Moos and Härdtl, cf. their Fig. 1 [14]. Therefore, plateau region likely reflect  $n \approx [\text{La}^\bullet]$ , i.e. the status of “ $\text{Sr}_{0.7}\text{La}_{0.3}\text{Ti}^{4+}_{0.7}\text{Ti}^{3+}_{0.3}\text{O}_{3.0}$ .”

Around  $p_{\text{O}_2} = 10^2$  Pa, the abrupt change of a factor of 100 in conductivity was observed. It is known that La doped  $\text{SrTiO}_3$  can take Ruddlesden-Popper phases in high  $p_{\text{O}_2}$  region and extra oxygen is placed in rock salt structure in-

tergrowth layers [11, 12]. This change in conductivity was expected to be caused by the formation of such a high  $p_{\text{O}_2}$  phase or the formation of a secondary phase, for an example,  $\text{Sr}_2\text{TiO}_4$ .

In Fig. 5, the expansion of  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  upon oxidation was observed. It is considered that new unit cells are created as in overstoichiometric  $\text{LaMnO}_{3+\delta}$  [23]. However, the  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  expanded very fast compared with that of  $\text{LaMnO}_{3+\delta}$ . And furthermore, the expansion with oxidation occurred around  $p_{\text{O}_2} = 10^{-5}$  Pa while the conductivity drop in Fig. 3, which should be also caused by new phase formation, occurred around  $p_{\text{O}_2} = 10^{-2}$  Pa. To explain these contradictions, supplementary experiments and phase observations using high temperature and atmosphere controlled XRD, TEM and so on are needed.

We observe that neither the conductivity nor the relative expansion come back to their initial value after an oxidation-reduction cycle. This is due to the fact that the as-fabricated specimen (at  $1500^\circ\text{C}$ ) must initially contain more oxygen vacancies and  $\text{Ti}^{3+}$  than at thermo-dynamical equilibrium at  $1000^\circ\text{C}$ ,  $p_{\text{O}_2} = 10^{-13}$  Pa. It is also considered that the large oxidative expansion as shown in Fig. 5 introduces considerable stress into the specimen. These facts mean that strongly reduced La-doped  $\text{SrTiO}_3$  demand careful handling and stress-proof microstructure in practical use at high temperature.

#### 5. Conclusion

$\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$  specimens, prepared in a reducing atmosphere, show  $100 \text{ S cm}^{-1}$  at  $1000^\circ\text{C}$ ,  $p_{\text{O}_2} = 10^{-13}$  Pa. However, the conductivity is not preserved after an oxidation-reduction cycle, although the initial high conductivity is very attractive for high temperature applications, e.g. in SOFC components. The conductivity drastically drops on increasing  $p_{\text{O}_2}$  over  $p_{\text{O}_2} = 10^2$  Pa. In  $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_{3-\alpha}$ , the chemical expansion on oxidation reaches  $\Delta l/l_0 = 0.51\%$ , when changing  $p_{\text{O}_2}$  from  $10^{-11}$  Pa to  $2 \times 10^4$  Pa (air) at  $1000^\circ\text{C}$ .

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