Electrical Properties of La and Sm Co-Doped SrTiO₃ for Mixed Ionic-Electronic Conductor

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Abstract. The mixed conductor materials La₀.₃Sr₀.₇SmₓTi₁₋ₓO₃₋δ was prepared via sol-gel method. The influence of Sm content on the electrical properties of La, Sm co-doping SrTiO₃ was investigated. Sm-doping increased the sinterability of La₀.₃Sr₀.₇SmₓTi₁₋ₓO₃₋δ. With the Sm-doping increasing, the total electrical conductivity and the ionic conductivity of La₀.₃Sr₀.₇SmₓTi₁₋ₓO₃₋δ increased. The optimized La₀.₃Sr₀.₇Sm₀.₀₈Ti₀.₉₂O₃₋δ sample exhibits the total electrical conductivity in the order of 0.132-0.315 S·cm⁻¹ at 500-900 °C. The ionic conductivity for La₀.₃Sr₀.₇Sm₀.₀₈Ti₀.₉₂O₃₋δ was 9.22×10⁻³ S·cm⁻¹ and increased about 266% compared with La₀.₃Sr₀.₇Sm₀.₀₄Ti₀.₉₆O₃₋δ at 950 °C. The possible charge compensation mechanism in La₀.₃Sr₀.₇SmₓTi₁₋ₓO₃₋δ was discussed.

1. Introduction
The mixed oxygen ionic and electronic conductors with perovskite structure had received much attention due to their controllable electrical properties, the microstructural stability to improve reliability and long-term performance and high melting and decomposition temperatures, thus they can be used as electrodes of solid oxide fuel cells, oxygen sensors, membrane reactors and oxygen separator, and so on [1-4].

Among the perovskite materials for mixed conductor, La-doped SrTiO₃ has been widely investigated due to its high electronic conductivity and good dimensional and chemical stability [5-7]. However, all La-substituted SrTiO₃ materials show very poor electro-catalytic performance [8]. Substituting the titanium on the B-site with other dopants has the possibility to improve the catalytic and the electrical properties [9]. Iron, scandium, manganese, nickel, cobalt and chromium as dopants on Ti-site of SrTiO₃ were investigated, and the electrical conductivity of the compounds are strongly influenced by the choice of dopants [2, 10-17].

Considering Sm³⁺ ion has a similar ionic radius with Ti⁴⁺ ion, in this study, the Sm element was selected to partially substitute for Ti⁴⁺ ions with the aim of improving the electrical properties. Therefore, the effects of Sm-doping content on the structural characteristics, electrical properties, such as electronic and ionic conductivities of La₀.₃Sr₀.₇SmₓTi₁₋ₓO₃₋δ, were investigated. The charge compensation mechanism in La₀.₃Sr₀.₇SmₓTi₁₋ₓO₃₋δ was discussed.
2. Experiments

La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ ($x=0.04$, 0.06, 0.08) powders were prepared via sol-gel method by using high purity Sr(CH$_3$COO)$_2$·2H$_2$O(AR), Ti(CH$_3$CH$_2$CH$_2$O)$_4$(AR), Sm$_2$O$_3$(AR) and Y$_2$O$_3$(AR) as raw materials. The powder mixtures were calcined at 1100°C for 10h in air. The calcined powders were uniaxially pressed into pellets (diameter 8 mm, thickness 1.2 mm), followed by sintering at 1400°C for 5h in air to get dense samples. The phase composition and crystal structure of the samples was identified by X-ray diffraction (XRD, Rigaku D/ max-A X-ray diffractometer, using Cu K$_\alpha$ radiation). The scanning electron microscope (SEM, HITACHI-SU8010) was used to observe the microstructure of the sintered pellets.

The total electrical conductivity of the samples was measured with AC impedance method in air in the temperature range of 500–900 °C. The ionic conductivity was determined by electron-blocking method within 700-900°C. All the conductivity data were measured every 50 °C after holding at each temperature to equilibrate until no change was observed. The AC impedance spectra were obtained over the frequency range of 1 MHz to 0.01 Hz by an electrochemical workstation (CHI660B). Details of the electron-blocking and electrode-fabricated methods can be found in the literature [10].

3. Results and discuss

3.1. Crystal structure and microstructure

All the sintered samples La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ ($x=0.04$, 0.06, 0.08) were white in color. The XRD patterns of dense samples after sintered at 1400 °C for 5h are shown in Figure 1. The sample with $x=0.04$ shows a single cubic perovskite structure, while a trace amount of impurity phase appears when $x=0.06$ and 0.08. The peak intensity of the second phase increases with Sm-doping amount increasing, which indicated that Sm-doping is unfavorable for the formation of single cubic perovskite phase.

With increasing Sm-doping amount, the porosity of samples decreases, as evidenced by SEM observation, as shown in Figure 2, indicating that Sm-doping can increase the sintering activity of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ and thus facilitate the densification process. Bulk density measurement indicates that the relative densities for samples with $x=0.04$ and 0.08 are 92.54% and 98.31%, respectively.

![Figure 1. XRD patterns of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ ($x=0.04$, 0.06, 0.08) after sintering at 1400 °C for 5h.](image)
Figure 2. SEM micrographs of fracture surfaces of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$: (a) $x=0.04$ and (b) $x=0.08$.

Figure 3. Temperature dependences of the total electrical conductivities of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ ($x=0.04$, $0.06$, $0.08$) in 500-900°C in air.
3.2. Electrical characteristic of La, Sm-doped strontium titanate

The total electrical conductivity and the ionic conductivity of samples La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3+\delta}$ ($x=0.04$, $0.06$, $0.08$) were measured in air in the temperature range of 500-900°C and 700-950°C, respectively. Samples of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3+\delta}$ show a mixed conduction behavior in the investigated temperature range, as presented in Figure 3 and Figure 4.

As shown in Figure 3, the total electrical conductivity increases with increasing temperature, indicating p-type conduction mechanism, which was attributed to electron-hole generation, tending to increase the conductivity as the temperature increases [17]. In addition, Sm-doping improves the electrical conductivity of La and Sm co-doped SrTiO$_3$. It appears that the higher charge carrier (electron–hole) concentration is responsible for the observed high conductivity in La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3+\delta}$ since La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3+\delta}$ has the electrons generated by the donor (La$^{3+}$) and the electron holes by the acceptor (Sm$^{3+}$). The optimized La$_{0.3}$Sr$_{0.7}$Sm$_{0.08}$Ti$_{0.92}$O$_{3+\delta}$ sample exhibits an electrical conductivity in the order of $0.315 \text{ S \cdot cm}^{-1}$ at 900°C. Compared with La$_{0.3}$Sr$_{0.7}$Sm$_{0.04}$Ti$_{0.96}$O$_{3+\delta}$, the total electrical conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_{0.08}$Ti$_{0.92}$O$_{3+\delta}$ increased. The value at 900°C is approximately 1.47 times higher than La$_{0.3}$Sr$_{0.7}$Sm$_{0.04}$Ti$_{0.96}$O$_{3+\delta}$.

![Temperature dependences of the ionic conductivities of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3+\delta}$ ($x=0.04$, $0.06$, $0.08$) in 700-950°C in air.](image-url)
On the other hand, the ionic conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ increased with Sm-doping amount increasing remarkably (Figure 4 (a)). The ionic conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_{0.08}$Ti$_{0.92}$O$_{3-\delta}$ was $9.22 \times 10^{-3}$ S·cm$^{-1}$ at 950°C. Compared with La$_{0.3}$Sr$_{0.7}$Sm$_{0.04}$Ti$_{0.96}$O$_{3-\delta}$, the ionic conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_{0.08}$Ti$_{0.92}$O$_{3-\delta}$ increased about 266%. It is well known that the ionic conductivity is primarily dependent on the oxygen vacancy concentration and the migration energy of oxygen ion at certain temperature. However, according to the activation energy for oxygen ion migration ($E_a$) calculated by Arrhenius rule, as shown in Figure 4 (b), $E_a$ of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ increased with Sm-doping increasing. Therefore, the oxygen vacancy concentration should be responsible for the increasing ionic conductivity with Sm-doping increasing. According to the Eq. (2), the substitution of Sm$^{3+}$ for Ti$^{4+}$ will result in the appearance of the oxygen vacancy. The oxygen vacancy concentration increases with Sm-doping amount increasing. In a word, the higher oxygen vacancy concentration results in the increase of ionic conductivity.

3.3. Charge compensation mechanism of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$

Based on the defect chemistry, oxygen vacancies [$V'_{O^{**}}$], free electrons ($e^-$) and holes ($h^+$) are prevalent in La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ as a result of the substitution of Sm$^{3+}$ on Ti$^{4+}$ and La$^{3+}$ on Sr$^{2+}$ due to the $p$-type conduction of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$. The defects produced in La$^{3+}$ donor doping and Sm$^{3+}$ acceptor doping SrTiO$_3$ can be expressed respectively as:

$$La_2O_3 \xrightarrow{\text{SrTiO}_3 \text{Sm}_{x}O} 2La^{*} + 2O^{*} + \frac{1}{2}O_2 + 2e^- \quad (1)$$

$$Sm_2O_3 \xrightarrow{\text{La}_0.3\text{Sr}_{0.7}\text{Ti}_{1-x}O_3} 2Sm^{*} + V'_{O^{**}} + 3O^{*}_O \quad (2)$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \quad (3)$$

Based on equation (2), oxygen vacancies are also equilibrium with oxygen gas and electron holes at high $P_{O_2}$:

$$V'_{O^{**}} + \frac{1}{2}O_2 \xrightarrow{} O^{*}_{O} + 2h^+ \quad (4)$$

There are three possible charge compensation mechanisms. The first possible mechanism is Sm$^{3+}$ ions in place of Ti$^{4+}$ ions, which can be expressed as $La_{0.3}Sr_{0.7}Sm_{x}Ti^{4+}_{0.7-2\delta-x}Ti^{3+}_{0.3+2\delta-x}O_{3-(\delta+x/2)}$. The defects produced in La, Sm co-doping SrTiO$_3$ can be expressed as Eq. (2). In this case, the ionic conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ may increase due to the increased oxygen vacancy concentration with Sm-doping amount increasing. However, the electronic conductivity will keep unchanged because of the unchanged concentration of Ti$^{3+}$ ions. In fact, the experimental results show that the total electrical conductivity of $p$-type conduction increases. Therefore, this is inconsistent with the experimental results.

The second possibility can be described that Sm$^{3+}$ only takes the place of Ti$^{3+}$ site. The defects produced by Sm-doping can be expressed as:

$$Sm_{2}O_3 \rightarrow 2Sm_{p^{3+}}^{*} + 3O^{*}_O \quad (5)$$

In this case, the electronic conductivity may increase and oxygen vacancy concentration will keep unchanged. This conflicts with the experimental results.

The third charge compensation mechanism can be expressed as

$$La_{0.3}Sr_{0.7}Sm_{x}^{3+}Ti^{4+}_{0.7-2\delta-x}Ti^{3+}_{x}O_{3-(\delta+x/2)} \quad (x = x_1 + x_2)$$

(Eq. (2) and (5)). In other word, Sm ions replace both Ti$^{4+}$ and Ti$^{3+}$ sites simultaneously. With Sm-doping amount increasing, the Sm$^{3+}$ ion may tend to replace Ti$^{4+}$ to produce more oxygen vacancy,
hole and electron, therefore, the ionic conductivity and electronic conductivity (p-type conduction) increase with Sm-doping amount increasing. Therefore, this agrees with the experimental results.

4. Conclusions

La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ ($x=0.04$, 0.06, 0.08) exhibits a single cubic phase perovskite structure when the $x$ value is 0.04. Sm-doping is unfavorable for the formation of single cubic perovskite phase due to the increasing peak intensity of the second phase. Partial oxygen ionic conductivity La$_{0.3}$Sr$_{0.7}$Sm$_x$Ti$_{1-x}$O$_{3-\delta}$ ($x=0.04$, 0.06, 0.08) increases with Sm-doping increasing, which may be attributed to the increases of oxygen vacancy concentration. The total electrical conductivity increases with Sm-doping amount, corresponding to the high charge carrier (electron-hole). The total electrical conductivity and ionic conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_{0.08}$Ti$_{0.92}$O$_{3-\delta}$ is 0.315 S · cm$^{-1}$ at 900°C and 9.22×10$^{-3}$ S · cm$^{-1}$ at 950°C, respectively. Compared with La$_{0.3}$Sr$_{0.7}$Sm$_{0.04}$Ti$_{0.96}$O$_{3-\delta}$, the total electrical conductivity and ionic conductivity of La$_{0.3}$Sr$_{0.7}$Sm$_{0.08}$Ti$_{0.92}$O$_{3-\delta}$ increased about 147% at 900°C and 266% at 950°C, respectively. The possible charge compensation mechanism of La and Sm co-doping SrTiO$_3$ can be described as

\[ \text{La}^{3+}\text{Sr}^{2+}\text{Ti}^{4+}_{0.7-2\delta-x_1}\text{Ti}^{3+}_{0.3+2\delta-x_2}\text{O}_{3-(\delta+x_1/2)}(x = x_1 + x_2). \]

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