

PHYSICAL PROPERTIES OF $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($X = 0-0.6$) SYNTHESIZED VIA CITRATE GEL COMBUSTION[†]

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Abstract

$\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_{3-\delta}$ has been selected as base material for fuel cell interconnect. The effects of Ni substitution on the B site of lanthanum strontium chromite ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$) have been investigated on phase, microstructure and electrical conductivity. All compositions were synthesized by citrate gel combustion method. The suitable calcination temperature of these compositions to obtain a perovskite phase was 1100°C with a soaking period for 4 h. The sample bars were formed by cold isostatic press and sintered at 1,400°C for 5 h in air. The phase, microstructure, thermal expansion coefficient (TEC) and electrical conductivity were determined by XRD, SEM, Dilatometer and dc four-probe as a function of temperature. For the compositions with $x \leq 0.5$, the results show a single phase after sintering and the conductivity of Ni-doped composition increases as Ni content increases. The maximum conductivity of 72.76 S cm⁻¹ at 800°C in air was obtained from $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.5}\text{Ni}_{0.5}\text{O}_{3-\delta}$ and its activation energy in the range of 100-800°C was 0.15 eV. The thermal expansion coefficient in a temperature range of 200 - 800°C for this composition was 12.5×10^{-6} K⁻¹.

Keywords: Solid oxide fuel cell, LaCrO_3 , citrate gel, interconnect

Introduction

Lanthanum chromite-based perovskite oxides have been investigated as interconnect for SOFCs due to the high stability in oxidizing and reducing environment and good electrical conductivity. In order to enhance the performance of LaCrO_3 , an increasing electronic conductivity at low temperature of LaCrO_3 is required. The partial substitutions of alkaline earth metal ions into La-site (Mori *et al.*, 1999) and transitional metal ions into Cr-sites have been studied on mechanical stability, thermal expansion and

electrical conductivity (Mori and Sammes, 2002; Ding *et al.*, 2006; Zhong, 2006; Ghosh *et al.*, 2007). An addition of Ba performed the lower electrical conductivity than that of Sr and Ca (Ong and Wu, 2007).

Ghosh *et al.* (2007) synthesized nanocrystalline powders of $\text{La}_{0.9}\text{Ca}_{0.1}\text{Cr}_{1-x}\text{M}_x\text{O}_{3-\delta}$ (M=Al, Co, and Mg). Substitution with Co improved the electrical properties but simultaneously increased the thermal expansion coefficient. In contrast, substitution with Al deteriorated its electrical

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property but enhanced the densification. Zhong (2006) studied the mechanical stability of $\text{La}_{0.75}\text{Ca}_{0.25}\text{Cr}_{0.92-x}\text{Co}_{0.08}\text{Al}_x\text{O}_{3-\delta}$ in reducing atmosphere. The mechanical stability decreased with an increasing Al content; however, their electrical conductivity increased.

Ding *et al.* (2006) reported the substitution effect of Ca, Mg, and Sr into A site and Ni, Cu, and Co into B site on sinterability, electrical property, and TEC behavior of LaCrO_3 . The Co- and Ni-doped samples exhibited higher conductivity values than Cu-doped composition. $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{Ni}_{0.02}\text{Co}_{0.02}\text{O}_3$ showed higher conductivity at high temperature than $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{Co}_{0.05}\text{O}_3$. The sintering temperature is a critical parameter for electrical conductivity of $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{Ni}_{0.02}\text{Co}_{0.02}\text{O}_3$. The conductivity of samples sintered at 1300°C is higher than that sintered at 1350°C . The activation energy of this composition sintered at 1300°C is 0.104 eV, which is lower than the value of LaCrO_3 (0.18 eV) (Koc and Anderson, 1992). Sr-doped LaCrO_3 perovskites were preferable to Ca-doped LaCrO_3 as interconnects, because the TEC of Sr-doped LaCrO_3 is more compatible with that of 8YSZ electrolyte (Ding *et al.*, 2006; Mori *et al.*, 1999)

In this study, the effects of both Sr and Ni doped into La and Cr site on phase and conductivity are investigated.

Materials and Methods

The starting materials were metal nitrate hydrate: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The compositions of LaCrO_3 , $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0-0.6$) were prepared by citrate gel combustion method. Stoichiometric amounts of metal nitrate were dissolved in minimal amount of deionized water. After mixing, aqueous solution of citric acid (2 mol of citric acid per 1 mol of total cations) was added to the mixture. The mixed solution was heated on a hot plate until it turned into a gel. The gel slowly foamed, swelled and finally burnt to obtain dark residue. After grinding, powder was calcined at 1100°C with a soaking time for 4 h and the calcined phase was analyzed by

X-ray diffraction (XRD, Bruker D5005). The calcined powders were pressed into pellets with cold isostatic press under a pressure of 200 MPa and sintered in air at 1400°C for 5 h. The microstructure of the sintered specimens was characterized by scanning electron microscope (SEM, Jeol JSM-6400). The electrical conductivity was determined by dc four-probe as a function of temperature. The data were collected from room temperature to 800°C with a heating rate of $4^\circ\text{C}/\text{min}$. Thermal expansion coefficient was measured by a dilatometer (NETZSCH DIL 402EP) from 50 - 800°C with a heating rate of $3^\circ\text{C}/\text{min}$.

Results and Discussion

Figure 1 shows the XRD patterns of all compositions after calcinations at 1100°C . The result shows a single phase of perovskite similar to LaCrO_3 (JCPDS: 89-8770). This indicates that the substitution of 60 atom% Ni into Cr can form a solid solution with $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$. Further addition of Ni affects an appearance of other phases.

Figure 2 shows the XRD patterns of all compositions after sintering at 1400°C . The results show a single phase for the compositions of $x = 0-0.5$. In contrast, with $x = 0.6$ the appearance of secondary phases, can be observed from the addition peaks at $2\theta = 30.6, 31.5, 42.8,$ and 43.9° as indicated by the arrows. The possible phases are Sr_2CrO_4 and either $(\text{La}_{1.4}\text{Sr}_{0.6})\text{NiO}_4$ or $(\text{La}_{1.6}\text{Sr}_{0.4})\text{NiO}_4$. Therefore, the composition of $x = 0.6$ is beyond the solubility limit of $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$.

Figure 3 shows the linear relationship between $\ln \sigma T$ and $1000/T$. The electrical conductivity of LaCrO_3 is 0.1 Scm^{-1} at 800°C which is lower than Ong and Wu's (2007) report, 0.34 Scm^{-1} . Doping Sr into La site, the electrical conductivity is much higher than that of LaCrO_3 . With an addition of Ni into $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$, this composition exhibits higher electrical conductivity. In contrast, doping with $x = 0.6$ into $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$, the electrical conductivity is lower than that of $x = 0.5$. This is possibly due to the presence of secondary phase as appeared

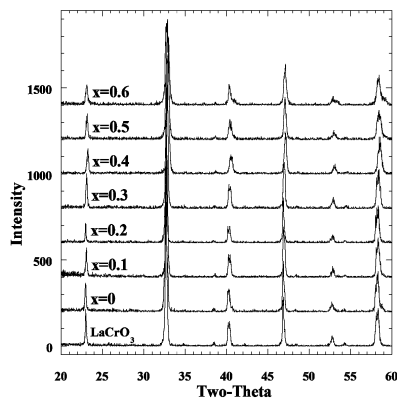


Figure 1. XRD patterns of LaCrO_3 and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0-0.6$) after calcination at 1100°C

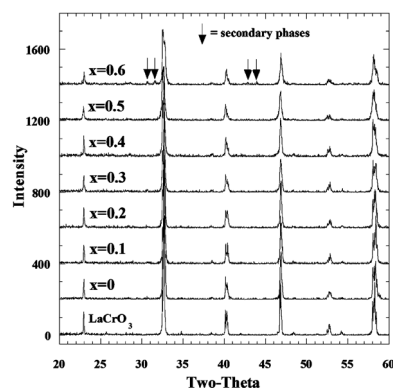


Figure 2. XRD patterns of LaCrO_3 and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0-0.6$) after sintering at 1400°C

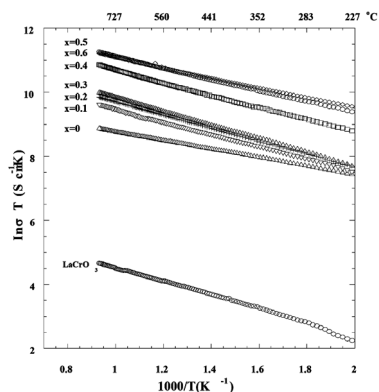


Figure 3. Arrhenius plots of the electrical conductivity for compositions of LaCrO_3 and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0-0.6$)

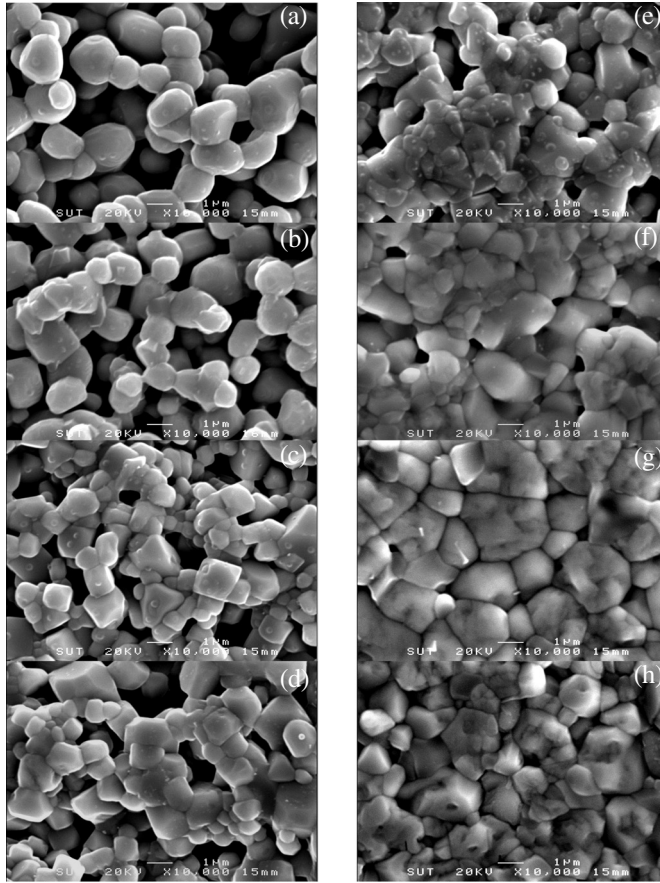


Figure 4. SEM micrographs of the sintered compositions of (a) LaCrO_3 , (b) $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$, (c) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$, (d) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.8}\text{Ni}_{0.2}\text{O}_3$, (e) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{O}_3$, (f) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.6}\text{Ni}_{0.4}\text{O}_3$, (g) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.5}\text{Ni}_{0.5}\text{O}_3$, (h) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.4}\text{Ni}_{0.6}\text{O}_3$

Table 1. Electrical conductivity (σ) at 800°C , thermal expansion coefficient ($200 - 800^\circ\text{C}$) and activation energy (E_A) of sintered compositions

Compositions	σ at 800°C (S cm^{-1})	$\text{TEC}_{200-800^\circ\text{C}}$ ($\times 10^{-6}\text{K}^{-1}$)	E_A (eV) 100 - 800°C
LaCrO_3	0.10	8.81	0.21
$\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$	6.73	9.82	0.12
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$	13.63	9.11	0.17
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.8}\text{Ni}_{0.2}\text{O}_3$	17.54	10.48	0.18
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.7}\text{Ni}_{0.3}\text{O}_3$	20.68	10.52	0.18
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.6}\text{Ni}_{0.4}\text{O}_3$	48.40	11.98	0.16
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.5}\text{Ni}_{0.5}\text{O}_3$	72.76	12.51	0.15
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.4}\text{Ni}_{0.6}\text{O}_3$	69.20	12.86	0.13

in the XRD result from Figure 2

In this study, the highest electrical conductivity of 72.76 S.cm^{-1} can be obtained from $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.5}\text{Ni}_{0.5}\text{O}_{3-d}$ at a measuring temperature of 800°C . The conductivity, activation energy determined from the slope and TEC for all compositions are given in Table 1. The activation energy represents the temperature dependence of conductivity and depends on the type of dopant. From the result, Sr reduces the activation energy of LaCrO_3 from 0.21 to 0.12 eV. However, it is independent of the concentration of dopant. The TEC of pure LaCrO_3 of $8.8 \times 10^{-6} / ^\circ\text{C}$ is similar to Zhong's work (2006). With Sr and Ni dopants, the TEC of LaCrO_3 increases. In addition, it increases with Ni content.

Figure 4(a-h) represents the SEM micrographs of the sintered compositions after polished and thermally etched. The result shows the microstructure of LaCrO_3 is porous and its average grain size is approximately 2 μm as illustrated in Figure 4(a). As interconnect of SOFC, the high density of this material is required to prevent the gas leakage between the cathode and anode during the operation. Therefore the higher sintering temperature should employ for this composition. With 10 atom% Sr substitution into La site, the grain size tends to reduce (Figure 4(B)). An addition of Ni enhances the connection between the grains resulting in an increase of densification as revealed in Figure 4(C)-(H). This higher density of samples performs the higher conductivity as shown in Figure 3.

Conclusions

The compositions of LaCrO_3 , $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{1-x}\text{Ni}_x\text{O}_{3-d}$ ($x = 0-0.6$) were prepared by citrate gel combustion method. The powders show a single perovskite phase after calcination at 1100°C . The substitution of Sr increases the conductivity and thermal expansion of LaCrO_3 . The densification of sintered samples increases with Ni content, which results in the higher electrical conductivity and thermal expansion. The maximum electrical conductivity is limited to the Ni content of $x = 0.5$.

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