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Syntheses of Doped-LaCrO$_3$ Nanopowders by Hydrothermal Method

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ABSTRACT

The effects of additives and precipitants on the syntheses of doped LaCrO$_3$ (lanthanum chromites) were studied by hydrothermal reaction at temperature ranges of 100°C to 230°C. LaCrO$_3$ nanopowders were synthesized by hydrothermal methods using several types of precipitants such as NaOH, KOH, NH$_4$OH, and NH$_2$CONH$_2$. The influence of Sr, Ca and Co doping on the lanthanum chromites prepared by hydrothermal method were investigated. The synthesized nanopowders were characterized by means of XRD, SEM and densitometer. The electrical conductivity of the doped LaCrO$_3$ was studied at 750°C in air by a DC four point probe method. The particles size of undoped LaCrO$_3$ nanopowder was approximately 100 nm when using KOH as a precipitant. The relative density of lanthanum chromite doped with calcium and cobalt is over 97%. The highest electrical conductivity of La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O$_3$ was 32.75 S/cm at 750°C in air, which is 30 times higher than undoped LaCrO$_3$. The density and electrical conductivity are increased by doping cobalt and calcium on the LaCrO$_3$.

Keywords: Doped LaCrO$_3$; Hydrothermal Reactions; Interconnects for Solid Oxide Fuel Cell

1. Introduction

The interconnect of a SOFC stack electrically and physically is connected to the anode of one unit cell with the cathode of the adjacent unit cell in the stack. The interconnect can be ceramic or metallic materials. The interconnect materials used for SOFC stacks must be electronically conductive, oxidation resistant, impermeable to the diffusion of gases, and chemically stable with fuel cell materials [1]. There are suitable materials, such as ceramics and metals for interconnect in solid oxide fuel cell (SOFC). Each material has advantages, but neither is ideal. Metallic chromium-forming alloys are most commonly used, but the formation of chromium-containing vapor species can lead to poisoning of the cathode after long operation. The resistance to this degradation can be improved through a combination of the two materials by ceramic coating on the metallic interconnect [2].

Ceramic interconnects based upon ceramic oxides with perovskite structure have been subject of intensive study over the past several decades. It was found that only a few such oxides systems can fulfill the rigorous requirements for the interconnect materials in SOFC. Lantha-num chromites (LaCrO$_3$) is the most common candidate material since it demonstrates reasonably high electronic conductivity in both fuel and oxidant atmospheres, moderate stability in the fuel cell environments as well as fairly good compatibility with other cell components in terms of phase, microstructure and thermal expansion. In order to improve the electrical conductivity as well as modify the thermal expansion coefficient (TEC), LaCrO$_3$ is often doped on lanthanum site, chromium site or both sites of the perovskite for practical applications. Due to ionic radius similarity, strontium and calcium tend to replace La ions whereas magnesium, iron, nickel, copper and cobalt prefer to take over the site of Cr ions. As a matter of fact, in SOFC configuration, the doped LaCrO$_3$ is still the most widely used as an interconnect [3].

Nanotechnology is the key for enhancing the performance of fuel cell. It is being used to lower the operating temperature of solid oxide fuel cells (SOFC). Also it can improve durability and increase oxygen-ion conductivity in the low temperature. The interconnect materials prepared using nanopowders in SOFC could be decreased the sintering temperature due to higher surface area. Also, it is advantageous for the formation of the dense film to have high temperature durability [4].

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The nanopowders have been synthesized by several methods such as glycine nitrate process [5], oxalic salt method [6], hydrazine [7], coprecipitation [8], and sol-gel [9]. These chemical processes, however, involve a subsequent calcination at high temperatures beyond 700°C, in order to obtain a stable crystalline phase. The $LaCrO_3$ is suitable for use as an interconnector, due to its high stability at high temperature. However, it has poor sinterability. The advantage of hydrothermal method is easy to control the particle size and shape, and it can be synthesized at low temperatures as a method of synthesis of crystalline nanopowders that depends on the solubility of the material under high pressure.

In this study, we synthesized doped $LaCrO_3$ nanopowder without secondary phase at low temperatures of 100°C - 230°C using hydrothermal method for interconnect materials in solid oxide fuel cell (SOFC). In order to improve its poor sinterability and electrical properties, Ca, Sr and Co were doped on lanthanum chromites, the sintering and electrical properties behaviors were investigated.

2. Experimental

2.1. Hydrothermal Synthesis and Sintering

The doped $LaCrO_3$ nanopowders were synthesized by hydrothermal method. All the raw materials were used reagent grade without purification. The starting materials were used $La(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich Co., USA), $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich Co., USA) and $Ca(NO_3)_2 \cdot xH_2O$ (>98%, Sigma-Aldrich Co., USA), $Co(NO_3)_2 \cdot 6H_2O$ (>98%, Sigma-Aldrich Co.), $Sr(NO_3)_2$ (>99%, Sigma-AldrichCo., USA) as dopants. The highly crystalline $LaCrO_3$ nanopowders were prepared under hydrothermal conditions using several species of precipitants such as urea (NH_2CONH_2, Junsei, Chemical Co., Tokyo, Japan), ammonia (NH4OH, GR, Dae Jung Chemical, Korea), potassium hydroxide (KOH, GR, Dae Jung Chemical, Korea) and sodium hydroxide (NaOH, GR, Kanto Chemical Co., Tokyo, Japan). Aqueous solutions with 0.05 M of $La(NO_3)_3$ to $Cr(NO_3)_3$ and dopants (Ca, Sr, Co) were prepared with deionized water. The several precipitant aqueous solutions of KOH (0.35 M), NaOH (0.5 M), NH_2CONH (0.25 M), and NH4OH (0.3 M) were prepared. The nitrate salts was added slowly in deionized water with precipitants. The mixture was poured into a teflon–liner in autoclave after ultrasonic treatment for 30min. The autoclave was heated at various temperature of 100°C - 230°C for a reaction time between 8 - 30 h. After the hydrothermal reaction, the nanopowder was washed with distilled water using centrifuge (FLETA5, Hanil), and then, dried in an oven at 260°C - 280°C for 7 h. The undoped lanthanum chromite ($LaCrO_3$) and doped lanthanum chromite ($La_{1-x}M_xCr_{1-y}Co_yO_3$) with M ($La_{1-x}M_xCrO_3$,

M = Ca, Sr) were synthesized by hydrothermal methods at low temperature (100°C - 230°C). In the present study, x is from 0 to 0.4 and y is from 0 to 0.2.

The sintering of the nanopowders was conducted by a conventional firing in air. The nanopowders was mixed with poly vinyl alcohol as a binder and pressed into quadrilateral sheet with a diameter of 10 mm at 10 MPa, and then compressed by press (CARVER, 385L-0) at 1 psi for 5 min. The pellets were sintered in a covered alumina crucible at 1200°C - 1500°C for 1 to 5 h in air. The pellet was heated at a constant heating rate of 5°C/min up to the sintering temperature.
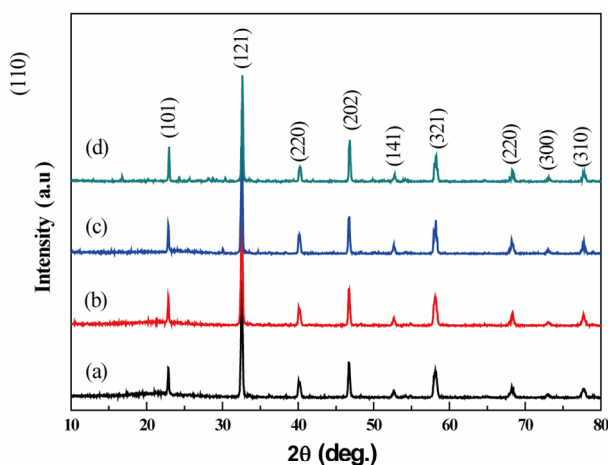
2.2. Characterizations

In order to determine the crystalline phase and the lattice parameter constants of the synthesized nanopowder, X-ray diffraction analyses were carried out. The crystal structures of the sintered specimens were examined using an X-ray diffractometer (XRD, D/MAX 2500-V/PC, Rigaku, Japan) with graphite-monochromatized Cu Ka radiation at 40 kV and 100 mA. Diffraction patterns were taken from 10 to 80° at a scanning speed of 4°/min. Morphological aspects of the nanopowders were examined by scanning electron microscope (FE-SEM, Supra 40, Zeiss) equipped with an energy dispersive X-ray spectroscopy (EDX). The particle size was measured by particle size analyzer (PSA, Beckman Coulter LS 13 320). Moreover, the relative densities of the hydrothermally synthesized nanopowders were calculated from the densitometer. The electrical conductivity of the samples was studied at 750°C in air by a standard DC four point probe method.

3. Result and Discussion

The highly crystalline $LaCrO_3$ nanopowders were prepared by hydrothermal method using several species of precipitants such as urea, ammonia, potassium hydroxide and sodium hydroxide. Aqueous solutions with 0.05 M of $La(NO_3)_3$ to $Cr(NO_3)_3$ and dopants (Ca, Sr, Co) were prepared with deionized water. The aqueous solutions of precipitants which are KOH of 0.35 M, NaOH of 0.5 M, NH_2CONH_2 of 0.25 M and NH_4OH of 0.3 M were prepared. **Table 1** shows the optimal hydrothermal synthesis condition of $LaCrO_3$, according to the species of precipitants. **Figure 1** shows X-ray diffraction patterns of the reaction product after hydrothermal reaction at the several conditions. $LaCrO_3$ phase formed when it treated hydrothermally in the autoclave at 250°C for 30 h using urea and ammonia as the precipitant. However, precipitants such as KOH and NaOH result in the complete transformation to the perovskite structure of ABO_3 type at the low temperature, which is the reaction temperature of 220°C to 230°C. The XRD pattern of the specimen

Table 1. The optimal hydrothermal syntheses conditions of LaCrO₃.

Precipitants	Mole ratio (La: Cr: Precipitant)	Reaction Time (h)	Reaction Temperature (℃)	Identified Phase
		Reaction conditions		
NH_2CONH_2	1 : 1 : 5	30	250	$LaCrO_3$, $La(OH)_3$, $La(CO_3)OH$
NH_4OH	1 : 1 : 6	30	250	$LaCrO_3$
KOH	1 : 1 : 7	24	220	$LaCrO_3$
NaOH	1 : 1 : 10	24	230	$LaCrO_3$

Figure 1. X-ray diffraction patterns of synthesized LaCrO₃ nanopowder using several precipitants by hydrothermal method; (a) 0.5 M NaOH, at 230°C for 24 h; (b) 0.35 M KOH, at 220°C for 24 h; (c) 0.25 M Urea, at 250°C for 30 h; (d) 0.3 M Ammonia, at 250°C for 30 h.

prepared from the different ratio of KOH with nitrate precursor shows that it occurs small amounts of secondary phases, such as $La(OH)_3$ and $La(CO_3)OH$. Small amounts of secondary phases were only observed when the NH_2CONH_2 of 0.25 M was used as a precipitant. The preferential formation of $La(CO_3)OH$ phase might be attributed to CO_2 absorption in alkaline media [10]. The presence of a small amount of $La(OH)_3$ might be due to an incongruent dissolution behavior of La^{3+} in alkaline solvents [11].

Figure 2 shows the morphology of hydrothermally synthesized LaCrO₃ nanopowders observed by SEM and the particle size measured by PSA. It shows some differences on particle shape and size when various precipitants were used. When NaOH of 0.5 M as a precipitant was used, the particle size was approximately 230 nm and it exhibits clusters of round-shaped particles as shown in Figure 2(a). The LaCrO₃ nanopowder using KOH of 0.35 M has a regular morphology, which is oval shape and homogeneous size distribution as shown in Figure 2(b), the average particle size was less than 100

nm. The LaCrO₃ nanopowder, using NH_2CONH_2 of 0.25 M had irregular morphology and wide particle size distribution in which particle size was about 380 nm, as shown in Figure 2(c). In contrast, the LaCrO₃ nanopowders, using NH4OH of 0.3 M formed plate type and small particle agglomerated together with larger cluster. The particle size was about 280 nm as shown in Figure 2(d). The shape of the nanoparticles seems to be affected by species of the precipitants.

We also synthesized the doped lanthanum chromites ($La_{1-x}M_xCr_{1-y}Co_yO_3$, M = Ca, Sr) by hydrothermal reaction at 220°C. Potassium hydroxide was used as a precipitant, and then the mole ratio of KOH to nitrates precursor was 7:1 in all composition. The prepared specimens were $La_{1-x}M_xCr_{1-y}Co_yO_3$ with x = 0 to 0.4 and y = 0 to 0.2. The nitrate precursor was mixed in distilled water. Figure 3 shows the X-ray diffraction patterns of doped LaCrO₃ nanopowders. Figure 3(a) shows X-ray diffraction patterns of the Ca-doped LaCrO₃ nanopowders. Most of Ca-doped LaCrO₃ nanopowders were obtained crystalline phase, but the $La_{0.85}Ca_{0.15}CrO_3$ was observed a small amount of secondary phase, $CaCrO_4$. Generally, the X-ray diffraction pattern peaks is shifted to higher angle with increasing calcium concentration. It could be decreased the lattice constants of perovskite structure because the Ca ions is substituted to La ions, due to the Ca ionic radius (0.99Å) smaller than La (1.15Å) [12]. Figure 3(b) shows the X-ray diffraction patterns of Co-doped LaCrO₃ nanopowders. The cobalt is added to improve the sintering process. It is observed a slight increase of the peak intensity by increasing the amount of Co. It indicates that Co is substituted to Cr in solid solution [13]. Figures 3(c) and (d) show X-ray diffraction patterns of (Sr,Co)-doped LaCrO₃, which de-
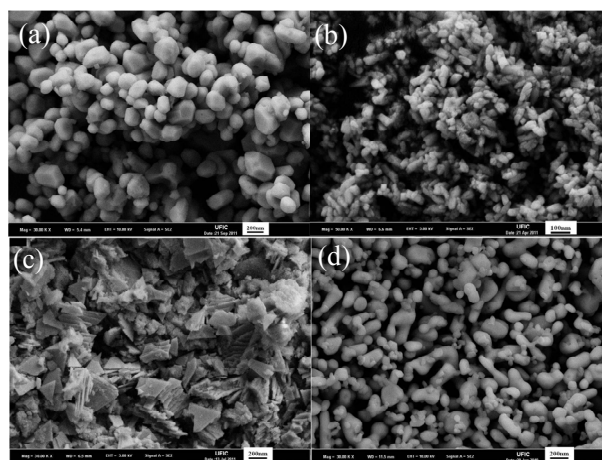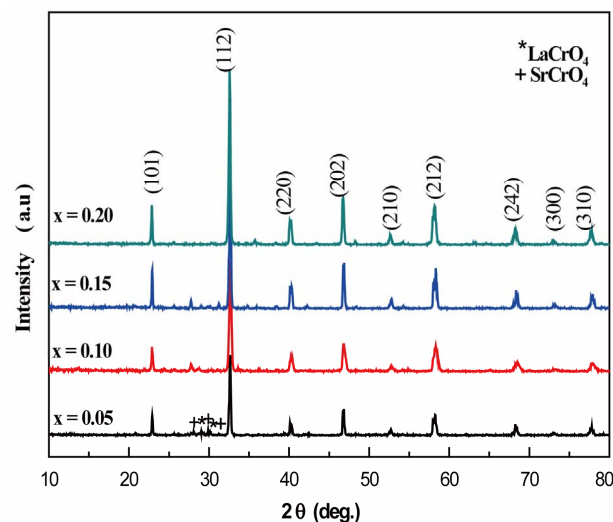

Figure 2. SEM micrographs of synthesized LaCrO₃ nanopowders using several precipitants by hydrothermal method. (a) 0.5 M NaOH, at 230°C for 30 h; (b) 0.35 M KOH, at 220°C for 24 h; (c) 0.25 M Urea, at 250°C for 30 h; (d) 0.3 M Ammonia, at 250°C for 30 h.
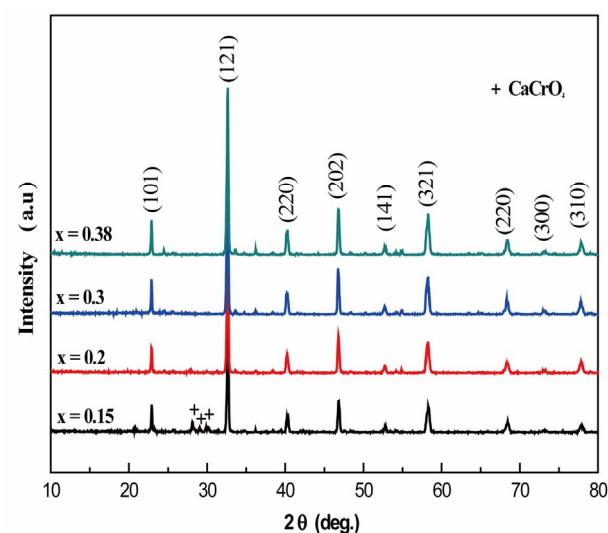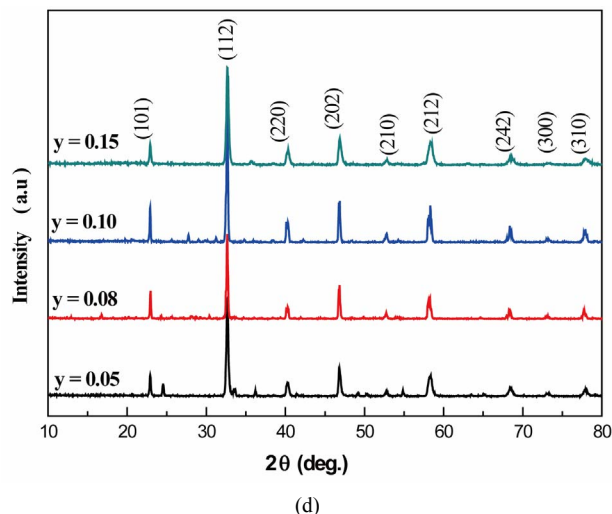
(a)
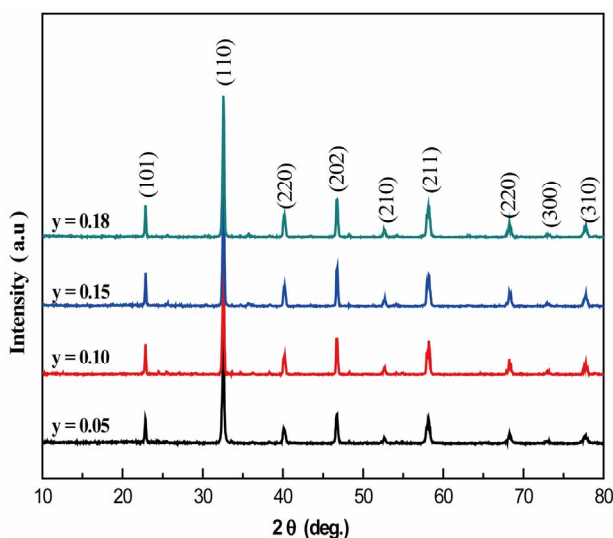
(b)

(c)

(d)

Figure 3. X-ray diffraction patterns of doped LaCrO₃ nanopowders; (a) La$_{1-x}$Ca$_x$CrO$_3$ (0 ≤ x ≤ 0.4); (b): La$_{1-x}$Ca$_x$Cr$_{1-y}$Co$_y$O$_3$ (x = 0.38, 0 ≤ y ≤ 0.2); (c): La$_{1-x}$Sr$_x$CrO$_3$ (0 ≤ x ≤ 0.2); and (d) La$_{1-x}$Sr$_x$Cr$_{1-y}$Co$_y$O$_3$ (x = 0.2, 0 ≤ y ≤ 0.2).

pends on the amount of doping precursor. Sr-doped La-CrO₃ can synthesize homogeneous nanopowders at relatively low temperature. Additionally, secondary phases such as LaCrO₄, SrCrO₄ and Sr(NO₃)₂ was observed. It is possible to the solubility limits of Sr in the LaCrO₃. La-CrO₄ can be considered as an intermediate phase in the lanthanum chromites [14,15].

We studied the influence of additives, which are calcium, strontium and cobalt, for the densification behavior of the doped LaCrO₃ nanopowders. The relative densities of doped LaCrO₃ sintered at temperature ranges of 1200°C to 1500°C are shown in **Figure 4**. The relative density of the undoped LaCrO₃ is 74.9% at 1400°C. The densities of doped LaCrO₃ were increased with increasing the sintering temperature. The density of all the A-site doped LaCrO₃ was increased at all the temperature ranges. The density of (Ca,Co)-doped LaCrO₃ was higher than (Sr,Co)-doped LaCrO₃. The La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O$_3$ sintered at 1200°C for 4 h exhibits the highest density. When the sintering temperature increased over 1500°C, the relative density was hardly change because the doped LaCrO₃ was fully sintered at 1400°C for 4 h. The sintering temperature of La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O$_3$ is approximately 200°C lower than undoped LaCrO₃ samples, due to enhanced sinterability by doping Ca and Co [16-18].

Figure 5 shows the microstructures of the nanopowders and sintered doped LaCrO₃ nanopowders at the several conditions. **Figure 5(a)** shows micrograph of La-CrO₃ nanopowder and the particle size was ~100 nm. **Figure 4(b)** shows the fracture surface of the LaCrO₃ sintered at 1400°C for 4 h. **Figure 5(c)** shows the microstructure of the La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O$_3$ nanopowder which is the optimum composition, and the particle size
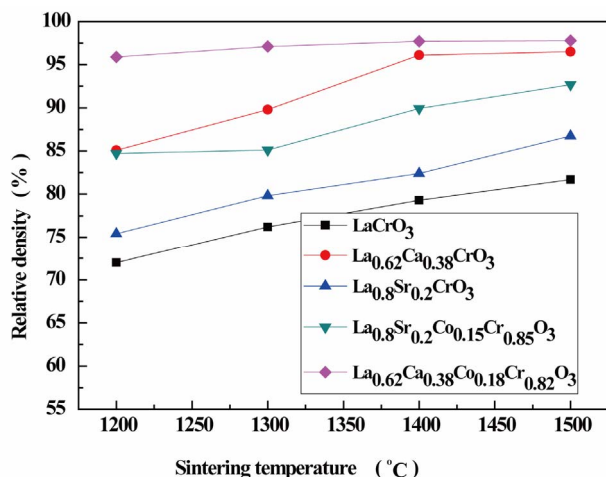
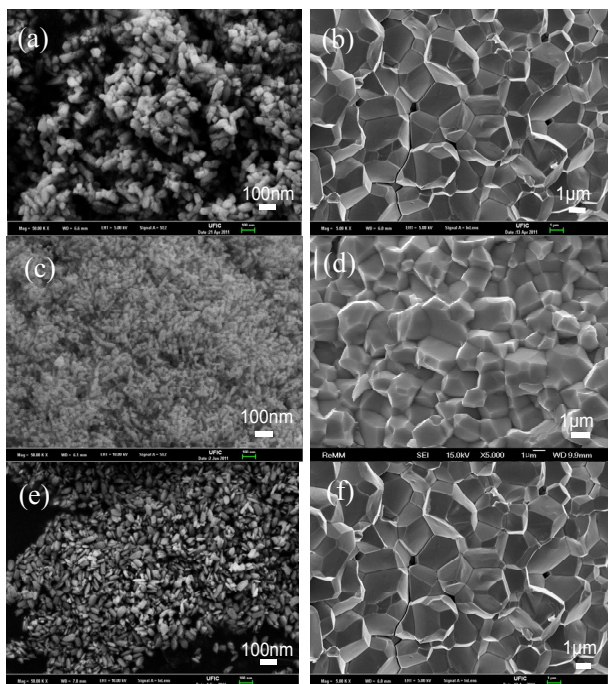**Figure 4. Relative density of doped LaCrO₃ at the several sintering temperature.**

Figure 5. SEM micrographs of doped LaCrO₃; (a) LaCrO₃ nanopowder; (b) Fracture surface of (a) sintered at 1400°C for 4 h; (c) La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O₃ nanopowder; (d) Fracture surface of (c) sintered at 1200°C for 4 h; (e) La$_{0.8}$Sr$_{0.2}$Co$_{0.15}$Cr$_{0.85}$O₃ nanopowder; and (f) Fracture surface of (e) sintered at 1500°C for 4 h.

was about 80 nm. **Figure 5(d)** shows the fracture surface of La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O₃ sintered at 1200°C for 4 h. **Figure 5(e)** shows microstructure of the La$_{0.8}$Sr$_{0.2}$Co$_{0.15}$Cr$_{0.85}$O₃ nanopowder and the particle size was ~200 nm. **Figure 5(f)** shows the fracture surface of the La$_{0.8}$Sr$_{0.2}$Co$_{0.15}$Cr$_{0.85}$O₃ sintered at 1500°C for 4 h. When sintered at over 1200°C, the doped LaCrO₃ were densely sintered. It indicated that sintering density is dependent on the

additives and sintering temperature.

Figure 6 shows the electrical conductivity of doped LaCrO₃ measured at 750°C in air. The electrical conductivity increased in all the doped LaCrO₃. The La$_{0.62}$Ca$_{0.38}$-Co$_{0.18}$Cr$_{0.82}$O₃ sintered at 1200°C had maximum conductivity of 32.73 S/cm at 750°C in air, which is about 30 times as high as that of undoped LaCrO₃.

4. Conclusion

LaCrO₃ nanopowders were synthesized by hydrothermal method at temperature ranges of 100°C to 230°C for 8 - 30 hrs. The average particle size of undoped LaCrO₃ was approximately 80 nm when the KOH was used as a precipitant. The particles size of (Sr, Co)-doped LaCrO₃ nanopowder was approximately 200 nm. The (Ca,Co)-doped LaCrO₃ nanopowders exhibit improved crystalline compared with the undoped LaCrO₃ nanopowders. The undoped LaCrO₃ nanopowder has a poor sinterability in air, but a highly dense La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O₃ was obtained by doping Ca and Co. The sintering temperature of La$_{0.62}$Ca$_{0.38}$Co$_{0.18}$Cr$_{0.82}$O₃ is about 200°C lower than undoped LaCrO₃. The relative density increased over 97% by doping Ca on perovskite A site and Co on perovskite B site. The electrical conductivity of La$_{0.62}$Ca$_{0.38}$-Co$_{0.18}$Cr$_{0.82}$O₃ was 32.73 S/cm. However, Sr- doped lanthanum chromite nanopowders were observed the secondary phases of LaCrO₄ and SrCrO₄ for all the compositions. The electrical conductivity of La$_{0.8}$Sr$_{0.2}$Co$_{0.15}$-Cr$_{0.85}$O₃ was 29.4 S/Cm at 750°C. The density and electrical conductivity were increased by doping calcium and cobalt on the LaCrO₃. The (Ca, Co)-doped LaCrO₃ is adequate for applications as an interconnector in SOFC.
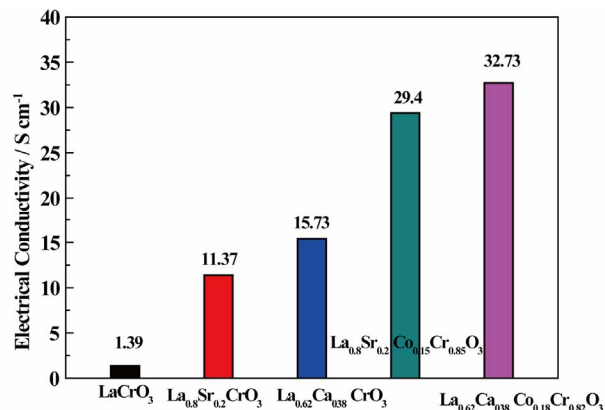
5. Acknowledgements

Figure 6. Electrical conductivity of doped LaCrO₃ measured at 750°C in air.

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