Densification and electrical conductivity of Fe and Mndoped $\text{Ce}_{0.83}\text{Sm}_{0.085}\text{Nd}_{0.085}\text{O}_2$ & by solidliquid method

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Densification and Electrical Conductivity of Fe and Mn Doped $\text{Ce}_{0.83}\text{Sm}_{0.085}\text{Nd}_{0.085}\text{O}_{2-\delta}$ by Solid-liquid Method

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Abstract : Fe and Mn doped $\text{Ce}_{0.83}\text{Sm}_{0.085}\text{Nd}_{0.085}\text{O}_{2-\delta}$ (SNDC) powders are successfully synthesized by the simple and efficient solid-liquid method. The crystallinity and morphologies of the powders were characterized by X-ray diffractometer, Raman spectrum, and scanning electron microscopy. The effect of doping on sintering behavior, grain interior, and grain boundary conductivity are studied. The doping of Fe can effectively reduce the sintering temperature from 1450 °C to 1250 °C and keep the same density. Compared with SNDC, 1 mol% Fe-doped SNDC

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(Fe-SNDC) sintered at 1250 °C shows a higher total conductivity of $2.13 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 650 °C. Also, it exhibits that doping of Fe can increase conductivity of grain interior and grain boundary simultaneously. The present work shows that the Fe-SNDC synthesized by solid-liquid method can be used as a potential electrolyte for intermediate-temperature solid oxide fuel cells.

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1. Introduction

In the field of energy conversion, solid oxide fuel cells (SOFC) are considered as one of the most promising devices because of their high energy conversion efficiency and non-polluting advantages¹. In the process of using hydrogen as fuel for power generation, solid electrolyte is an integral part of SOFC. Although yttria-stabilized zirconia (YSZ) is widely used as solid electrolyte in SOFC, the high operating temperature (800-1000 °C) leads to many problems, such as lousy durability of cells, high cost of interconnects and other electrode materials, which limit the development and lifetime of the SOFC^{2, 3}. Therefore, in the past years, a lot of research was used to developing the intermediate-temperature (IT) electrolytes including $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (GDC), $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC), and SNDC⁴⁻⁷. Yahiro et al.⁸ reported Sm^{3+} and Gd^{3+} doped ceria show excellent electrical conductivity, since their ionic radii of Sm^{3+} and Gd^{3+} is so close Ce^{4+} ions that the quite small association enthalpy between oxygen vacancy and other ions. Also, Li et al.⁹ reported that SNDC had been regarded as one of the most excellent electrolytes for IT-SOFC since its high conductivity and chemical compatibility.

There are many synthesis methods for nanometer-sized ceria powders, mainly including solid-state reaction method and liquid-state reaction method^{9, 10}. The solid-state reaction method can synthesize nanopowders efficiently and quickly at a relatively high temperature, but it is difficult to control the purity of the powders due to the impure phase may be introduced at a high

temperature. The citric-acid and sol-gel methods are commonly used in liquid phase synthesis. These methods first dissolve raw materials in a large number of solvents, to achieve molecular level uniformity. It can obtain homogeneous powders at low temperatures, but these methods are time-consuming and polluting the environment. The solid-liquid method (SLM) combines the advantages of the two methods and achieve the molecular level uniformity by ball milling with little complexing agent. Cao et al.⁵ adopted SLM to prepare GDC nanopowder. Zheng et al.¹¹ prepared $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ powder via SLM. In this paper, SNDC has been successfully synthesized by SLM.

However, SNDC should be sintered around 1450 °C to obtain good relative density, which high sintering temperature has bad influence on cell production¹². The high temperature accelerates the interfacial reactions between the electrodes and increases the manufacturing cost of the cell^{2, 13}. In recent decades, to reduce the sintering temperature of cerium-based electrolytes and overcome those negative effects, researches on the fabrication technology, the powder properties, and the sintering mechanism of electrolytes have attracted considerable attention. One of the most effective methods is the introduction of transition metal oxides (TMOs) as sintering aids, such as MnO_2 , Fe_2O_3 , and Co_3O_4 ¹⁴⁻¹⁶. Frenkel. J¹⁷ came up with a similar view that a small amount of TMOs could easily migrate to the surface of ceria at low temperatures, forming an amorphous film^{18, 19}. This amorphous film increases the surface tension of ceria and reduces the migration resistance between particles, making CeO_2 easier to rearrange and reduce the sintering temperature. Many researchers have reported Fe and Mn can reduce the sintering temperature of GDC and SDC without damaging the conductivity^{16, 20-24}. In the intermediate-temperature region, the grain boundary (GB) conduction of the cerium-based electrolytes dominates total conduction²⁵. In the sintering process of cerium-based electrolytes, SiO_2 will inevitably be introduced, and a small amount of SiO_2 will seriously damage the GB conductivity²⁶. Ge et al. found that Fe and Mn can react with SiO_2 on the GB and play a role in cleaning impurity²³. SNDC is cerium oxide doped with Sm and Nd at the same time, showing a complex conductive system. The effect of Fe and Mn on the sintering temperature and conductivity of SNDC has little studied.

In this paper, Fe and Mn were doped into SNDC by SLM, and the effect of Fe and Mn on sintering temperature and conductivity were studied. The influence of Fe and Mn on SNDC is further understood by the calculation of grain interior (GI) conductivity, GB conductivity and activation energy of different samples.

2. Experimental

$\text{Ce}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ (99.99% purity, Yutai Qixin China), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99% purity, Yutai Qixin China), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99% purity, Yutai Qixin China), $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity, Sinopharm China), $\text{Mn}(\text{NO}_3)_3$ (99.9% purity, Sinopharm China), and citric acid (CA) were used as raw material. SNDC with 1mol% Fe is labeled as Fe-SNDC, SNDC with 1mol% Mn is labeled as Mn-SNDC, SNDC with 0.5 mol% Fe and 0.5 mol% Mn is labeled as Co-SNDC. According to the molecular formula of all samples, the corresponding amounts of metal salts were added to deionized water, which quality ratio of the total metal salt to the deionized water was 1:1.2. Compared with cerium nitrate, $\text{Ce}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ as a raw material can greatly reduce the emission of nitrogen oxide gas. CA is a commonly used complexing agent, which can form metal complexes in solution and increase solid solubility. Appropriate CA can improve the micromorphology of the synthesized powder. A certain amount of CA was added to the precursor, the mass ratio of CA was 20% of the theoretical mass of SNDC, ball-milled at 300 rpm for 12 h on a planetary ball mill. The precursor was dried at 250 °C for two hours, then calcined at 950 °C for two hours, and ground to finally obtain the powder samples. Fig. 1 shows the main steps in the synthesis of all powders.

To investigate the crystal structure of the powder samples, the phase identification was carried out by using the X-ray diffractometer (XRD, Bruker D8, Germany) in the range of 20° ~ 80° and the Cu K α radiation (1.54056 Å). In the wavelength range of 200 ~ 1000 cm⁻¹, the Raman spectrum of the powder was studied by using Raman spectrometer in (Renishaw in Via Reflex and wavelength is 488 nm). The pellets were made by mold with a diameter of 10 mm under a pressure of 260MPa and then sintered at 1250 °C and 1450 °C for 10 h, respectively. The heating rate of all pellets was 100 °C h⁻¹ in the sintering process, and the samples were cooled in the

furnace after sintering. Microscopic morphology of the powders and pellets were tested using scanning electron microscopy (SEM, Hitachi, S4800, Japan). The actual densities of the sintered pellets were tested by the Archimedes method. Apply silver on the top and bottom of the pellets to collect current. AC impedance spectroscopy (Biologic, VMP3B-20, France) was used for GI and GB conductivities measurement over a frequency range of 0.1 Hz to 1 MHz.

3. Results and discussions

Fig. 2(a) shows the XRD diffraction patterns of all samples. The diffraction peaks of SNDC and doped SNDC can be well matched to cubic fluorite structured ceria (JCPDS card no. 34–0394), and the diffraction peaks of other phases were not observed. The result suggests that Fe and Mn ions form solid solution with CeO₂. Fig. 2(b) shows the peaks of the doped SNDC were shifted slightly relative to that of SNDC, which indicates that larger Sm (Sm³⁺ 1.08 Å), Nd (Nd³⁺ 1.11 Å) and Ce (Ce⁴⁺ 0.97 Å, Ce³⁺ 1.143 Å) in SNDC lattice were replaced by smaller Fe (Fe³⁺ 0.78Å) and Mn (0.96 Å)²⁷⁻²⁹. The crystallite size calculated by Equation 1,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystallite size (nm), λ value of 0.15406 nm is the wavelength of Cu K_{α1}, β is the line broadening at half the maximum intensity (rads), and θ is the Bragg's angle (°). The lattice parameter (a_0) was calculated by the formula below,

$$a_0 = \frac{\lambda \sqrt{(h^2 + k^2 + l^2)}}{2 \sin\theta} \quad (2)$$

where h , k , and l are the Miller indices. The theoretical density (ρ_{th} , g·cm⁻³) of ceria-based material was calculated by the formula below,

$$\rho_{th} = \frac{4[xM_d + (1-x)M_{ce} + (2-0.5x)M_O]}{N_A[a_0]^3} \quad (3)$$

where M_d , M_{ce} , and M_O are the relative atomic mass of doping elements, Ce, and O (amu) respectively, N_A value of 6.023×10^{23} mole⁻¹ is the Avogadro's number. Relative density can be obtained by dividing the actual density to the theoretical density.

The crystallite sizes and the relative densities of all samples are listed in Table 1. The crystallite size of SNDC is 40.9 nm, and that of doped SNDC is about 30 nm, smaller than that of

SNDC. Nano-sized powders offer the possibility to obtain high relative density sintered at lower temperature. It is well known that the relative density is highly correlated with conductivity. Apparently, the relative densities of doped SNDC are greater than that of SNDC. In particular, the relative density of Fe-SNDC sintered at 1250 °C can exceed 95%, but the SNDC pellet needs to be sintered at 1450 °C to obtain similar densification, which demonstrate a greatly enhanced sinterability in the doped SNDC samples. Moreover, the relative densities of Mn-SNDC and Co-SNDC sintered at 1250 °C are 92.8% and 94.1%, respectively. The relative densities of all pellets sintered at 1450 °C are all above 95%. Obviously, doping 1 mol% transition metal into SNDC can greatly reduce the sintering temperature with good relative densities, which has a great positive effect on improving the sintering performance of SNDC.

Raman spectroscopy was used to further analyze the structural characteristics of the powder. Mandal et al.³⁰ reported that the band in the Raman spectrum of CeO₂ was located near 465 cm⁻¹, which give rise to F_{2g} vibration peak of face-centered cubic fluorite structured. Moreover, it is mainly the symmetric vibration of oxygen vacancy around Ce⁴⁺. Fig. 3 shows that the main Raman bands of the four powders were observed at about 465 cm⁻¹, which are consistent with the Raman band of pure CeO₂. The results suggest that the doped ions are successfully introduced into the cerium oxide lattice. In addition, a less obvious band is seen at 550 ~ 600 cm⁻¹, because the tetravalent cerium ions are replaced by trivalent ions to form oxygen vacancies³¹.

The morphologies of powders and pellets were investigated by SEM. It can be seen from the Fig. 4 that the morphologies of SNDC and doped SNDC powders are similar, which are uniform in shape, approximately spherical, with little agglomeration, and the particle size is less than 100 nm. The doping of Fe and Mn has almost no influence on the morphologies of the powders.

The surface morphologies of all pellets sintered at 1250 °C are shown in Fig. 5. While SNDC shows vague GB and poor density, the GBs of doped SNDC are clear and GI size and shape are similar. The result shows that the sintering of SNDC is not enough, and the doped SNDC has been fully sintered. Fig. 5(a) shows that many open pores were found in the SNDC and it is showed that the sample had very low relative densities. The result is consistent with the measured SNDC

relative density of 83.5% listed in Table 1. With the same sintering temperature, few pores were found in the doped SNDC and the relative densities of doped SNDC were higher than that of SNDC. The result is in accordance with the measured relative density of above 92% for doped SNDC as listed in Table 1. Especially, pores were hardly found in the pellets of Fe-SNDC. Only a few pores were found in the Mn-SNDC and Co-SNDC samples. It can be preliminarily inferred that Fe and Mn can accelerate the densification of SNDC, and the effect of Fe is more obvious than that of Mn. This is because, during the sintering process, the transition metal forms a liquid phase, which increases the shrinkage area between the particles and promotes the diffusion of particles²¹. Fig. 6 shows the EDX spectra of SNDC and Fe-SNDC samples. The results show that Fe-SNDC is composed of O, Ce, Sm, Nd and Fe elements. A little amount of Fe was found on the surface of the sample, which may be due to the dissolution of iron in ceria with the increase of sintering temperature¹⁶.

Fig. 7 shows the surface morphologies of all pellets sintered at 1450 °C. The GBs of all samples are clear, and the grain size of doped SNDC is slightly larger than that of SNDC. Fig. 7(a) shows that only closed pores were found in the SNDC, and Fig. 7(b) to (d) show that surfaces of doped SNDC are completely dense without any pore. These results are consistent with the measured density data listed in Table 1, in which the SNDC and doped SNDC pellets achieved high relative densities of more than 95% when sintered at 1450 °C. In addition, Fig. 7 also shows that the grain size of the doped SNDC electrolytes increases for the SNDC, which can be explained as the TMOs formed an amorphous film at CeO₂ surface, which reduces surface friction to enhance the grain size²⁰. These microtopographies provide a prerequisite for discussing conductivity.

The AC impedance spectra of all pellets tested in air at 350 °C shown in Fig. 8. Generally speaking, the typical impedance spectra of the sample has three semicircles, which corresponding respectively to the conduction of the GI, GB and electrode-specimen interface from left to right in the lateral axis. However, as the measured temperature rises to the operating temperature of IT-SOFC, the arcs will gradually move toward high frequency area, which leads to the

disappearance of arcs corresponding to the GI and GB will disappear. Therefore, the GI and GB conductivity at the operating temperature cannot be calculated directly from the impedance spectra. In the report of Li et al.³² and Pérez-Coll et al.³³, the GB conductivity is almost linear in the Arrhenius plot. The GI resistance (R_{gi}) can be calculated by subtracting the GB resistance (R_{gb}) from the total resistance ($R_{tot}=R_{gi}+R_{gb}$) as proposed elsewhere. The Arrhenius representation of conductivity is as following:

$$\sigma_t = \sigma_0 \exp \left(-\frac{E_a}{kT} \right) \quad (4)$$

where T is the Kelvin temperature (K), σ_0 is the pre-exponential factor being a constant in a certain temperature range, E_a denotes the activation energy (eV), and k value of 8.617×10^{-5} eVK⁻¹ is Boltzmann constant. Usually, the resistance (R_i) and conductivity (σ_i) can be converted by Equation 5:

$$\sigma_i = \frac{l}{R_i S} \quad (5)$$

where l , S and R_i are pellets thickness (cm), electrode surface area (cm²), and resistance value (Ω), respectively.

Fig. 8(a) shows EIS results of all samples sintered at 1250 °C. R_{tot} , R_{gi} and R_{gb} were extracted from the impedance spectra according to the indications shown in the spectra of SNDC. The insert in Fig. 8(a) presents the equivalent circuit used to fit the Nyquist plot. Generally, the equivalent circuit diagram can reflect the conduction mechanism of the material. In this equivalent circuit diagram, R represents resistance and CPE represents capacitance. A remarkable decrease in total resistance for doped SNDC versus SNDC is seen in Fig. 8(a). About the total resistance, the order from the smallest to the largest is Fe-SNDC, Co-SNDC, Mn-SNDC, SNDC. As high density is a prerequisite for high ionic conductivity, this result is consistent with the SEM results. The impedance spectra of samples sintered at 1450 °C shown in Fig. 8(b). Taking the Mn-SNDC as an example, semicircular arcs corresponding to R_{tot} , R_{gi} and R_{gb} are marked in Fig. 8(b). It can be seen that Fe-SNDC has the smallest total resistance, which is the same trend as for samples sintered at 1250 °C. Unexpectedly, Fig. 8(b) shows that the total resistance of Mn-SNDC is very

close and slightly larger than the total resistance of SNDC. In the doped samples, compared with the total resistance of SNDC, the decrease of Fe-SNDC total resistance is the largest. Therefore, the results from Fig. 8 indicate that among these different doping components, doping 1 mol% of Fe is very effective in terms of reducing the total resistance of SNDC.

It can also be seen from Fig. 8 that the GI resistance of the four samples is relatively close. After 1250 °C sintering, the GB resistance of Fe-SNDC is much smaller than that of SNDC. After 1450 °C sintering, the GB resistance of Fe-SNDC and Co-SNDC is similar and smaller than that of SNDC. To further study the effect of Fe and Mn on the GI and GB conductivities, the results calculated by Equation 5 are summarized in Table 2. When sintered at 1250 °C, the GI and GB conductivity of Fe-SNDC are 4.5 times and 5 times higher than that of SNDC, respectively. As compared to the SNDC sintered at 1250 °C, the GB conductivity has been increased by a factor of four for Co-SNDC. At the same sintering temperature, when doped with Mn, the GB conductivity of Mn-SNDC has increased, but the GI conductivity has little increased. Table 2 also shows that, when sintered at 1450°C, the GI conductivity and GB conductivity of Fe-SNDB are 1.1 times and 2.8 times higher than that of SNDC, respectively. The GB conductivity of Co-SNDC is increased by about twice. The GB conductivity of Mn-SNDC has increased slightly. From the above results, a critical conclusion can be drawn that doping of Fe can increase GI and GB conductivity simultaneously, while doping of Mn increases GB conductivity only. As described by Li et al.³⁴, generally, few additives have been found that can have a positive effect on the conductivity of GI and GB simultaneously, like Fe₂O₃.

Fig. 9 presents Arrhenius plots of total conductivity of all pellets sintered at 1250 °C for 10h. It can be seen that the total conductivity of SNDC is the smallest, and it is much lower than that of doped SNDC. Among the doped SNDC samples, the total conductivity of Fe-SNDC is the highest, Mn-SNDC is the lowest, and Co-SNDC is in-between. Distinctly, the doping of Fe and Mn can improve the total conductivity of SNDC electrolytes, especially Fe. Moreover, the activation energy of total conductivity was calculated from the slopes of the linear plots between $\ln(\sigma_{\text{tot}}T)$ and $(1000/T)$ according to Equation 4. SNDC shows the highest activation energy of 1.09 eV, and

higher than that of doped SNDC. Among doped SNDC, the activation energy of Fe-SNDC is the lowest with a value of 0.96 eV.

The Arrhenius plots of total conductivity of all samples sintered at 1450 °C for 10h shown in Fig. 10. It can be seen that the total conductivity of SNDC is close to that of Mn-SNDC, and much lower than of Fe-SNDC and Co-SNDC. Among the doped SNDC samples, the trend of Fe-SNDC total conductivity sintered at 1450 °C is the same as that at 1250 °C, which is the highest. Among all samples, the activation energy of SNDC is the highest with a value of 0.97 eV and the activation energy of Fe-SNDC is the lowest with a value of 0.89 eV.

The results obtained from Fig. 9 and Fig. 10 show that the total conductivity and relative density listed in Table 1 agree with each other. The total conductivities of the sample at 650 °C are summarized in Table 3. It suggests that total conductivity of doped SNDC is apparently higher than that of SNDC, notably, the conductivity of Fe-SNDC increased the most, followed by Co-SNDC, and finally Mn-SNDC. However, it can be seen that at 1450 °C sintering temperature, the increase of conductivity for doped SNDC is less than that at 1250 °C sintering temperature, as the density of pure SNDC has reached 95.3% at 1450 °C. Table 3 shows that Fe-SNDC sintered at 1250 °C exhibits excellent conductivity with the value of $2.13 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 650 °C, about 2.6 times higher than that of SNDC. It also can be concluded that the Fe doping has the best effect on the improvement of the conductivity and the relative density, and the beneficial effect of Mn doping effect is less than that of the Fe doping and co-doping.

4. Conclusions

Fe and Mn doped SNDC powders are successfully synthesized by the simple and efficient solid-liquid method at temperature of 950 °C. It can be seen from the results of XRD and Raman spectroscopy that the average crystallite size of powders is less than 41 nm and the doped ions are successfully introduced into the cerium oxide lattice. The increase of relative density is achieved by doping of Fe and Mn. The relative density of Fe-SNDC sintered at 1250 °C can exceed 96%, but the SNDC pellet needs to be sintered at 1450 °C to obtain similar densification, which shows that the sintering performance of SNDC can be greatly improved by doping Fe. The AC

impedance spectra of all pellets measured in air at 350 °C shows Fe can simultaneously increase GI and GB conductivity, but doping of Mn increases GB conductivity only. In terms of total conductivity, Fe-SNDC sintered at 1250 °C exhibits excellent conductivity and lowest activation energy, with a measured conductivity value of $2.13 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 650 °C, about 2.6 times higher than that of SNDC. Therefore, these advantages make Fe-SNDC a potential electrolyte material for IT-SNDC.

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Conflict of interest

The authors declare no conflict of interest.

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Table 1 Crystallite size and relative density at different sintered temperature of all compositions

Composition	Crystallite size	Relative density at 1250 °C	Relative density at 1450 °C
	/nm	/%	/%
SNDC	40.9	83.5	95.3
Fe-SNDC	32.8	96.3	97.3
Mn-SNDC	28.1	92.8	95.8
Co-SNDC	28.3	94.1	96.9

Table 2 Total (σ_{tot}), GI (σ_{gi}) and GB (σ_{gb}) conductivities of all compositions (sintered at 1250 °C and 1450 °C) measured at 350 °C in air

Sintering temperature	Sample	$\sigma_{\text{gi}}/\text{S}\cdot\text{cm}^{-1}$	$\sigma_{\text{gb}}/\text{S}\cdot\text{cm}^{-1}$	$\sigma_{\text{tot}}/\text{S}\cdot\text{cm}^{-1}$
1250 °C	SNDC	3.56×10^{-4}	1.85×10^{-5}	1.76×10^{-5}
	Fe-SNDC	1.47×10^{-3}	1.05×10^{-4}	9.82×10^{-5}
	Mn-SNDC	3.98×10^{-4}	3.74×10^{-5}	3.42×10^{-5}
	Co-SNDC	3.92×10^{-4}	7.09×10^{-5}	6.00×10^{-5}
1450 °C	SNDC	4.66×10^{-4}	9.45×10^{-5}	7.85×10^{-5}
	Fe-SNDC	5.24×10^{-4}	2.61×10^{-4}	1.74×10^{-4}
	Mn-SNDC	4.44×10^{-4}	1.04×10^{-4}	8.41×10^{-5}
	Co-SNDC	5.16×10^{-4}	2.14×10^{-4}	1.51×10^{-4}

Table 3 The total conductivity of all compositions (sintered at 1250 °C and 1450 °C) measured at 650 °C in air

Sintering temperature	Conductivity/ $\text{S}\cdot\text{cm}^{-1}$			
	SNDC	Fe-SNDC	Mn-SNDC	Co-SNDC
1250 °C	0.82×10^{-2}	2.13×10^{-2}	1.38×10^{-2}	1.94×10^{-2}
1450 °C	1.91×10^{-2}	2.51×10^{-2}	1.76×10^{-2}	2.44×10^{-2}

Figure Captions

Fig. 1 Steps used during the synthesis of all powders using solid-liquid method.

Fig. 2 (a) XRD patterns of SNDC, Fe-SNDC, Mn-SNDC and Co-SNDC calcined at 950 °C, (b) enlarged XRD pattern of (a) around 28°.

Fig. 3 Raman spectra of SNDC, Fe-SNDC, Mn-SNDC and Co-SNDC powders.

Fig. 4 SEM images of the (a) SNDC, (b) Fe-SNDC, (c) Mn-SNDC and (d) Co-SNDC powders

Fig. 5 SEM surface images of all pellets sintered at 1250 °C. (a) SNDC; (b) Fe-SNDC; (c) Mn-SNDC; (d) Co-SNDC.

Fig. 6 EDX spectra of SNDC and Fe-SNDC samples.

Fig. 7 SEM surface images of all pellets sintered at 1450 °C. (a) SNDC; (b) Fe-SNDC; (c) Mn-SNDC; (d) Co-SNDC.

Fig. 8 The AC impedance spectra of all samples measured at 350 °C in air. (a) sintered at 1250 °C; (b) sintered at 1450 °C.

Fig. 9 Arrhenius plot of total conductivity of all samples sintered at 1250 °C for 10 h.

Fig. 10 Arrhenius plot of total conductivity of all samples sintered at 1450 °C for 10 h.

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