

Effect of calcination temperature on the conductivity of Sm and Cu co-doped ceria

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Abstract. The impact of different calcination temperature (550, 650, 750 and 850 °C) on the structural/electrical properties of sintered Cu/Sm co-doped CeO₂ prepared by sol-gel combustion were studied. Structural properties were studied by X-ray diffraction (XRD), Raman spectroscopy and ultraviolet-visible spectroscopy (UV-VIS). The composition, oxidation state and electrical conductivity of sintered samples were investigated by photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS), respectively. With the increasing calcination temperature, both the oxygen vacancy and Ce³⁺ increase. Therefore, the highest conductivity was obtained for samples calcined at 850 °C.

1. Introduction

The solid oxide fuel cell (SOFC) is one of the renewable energy sources that can produce high electrical power and it can continuously produce electricity as long as the fuel is available. To increase the energy output, an SOFC electrolyte must be dense to allow the fast ionic conduction. The high sintering temperature at around 1500 °C is normally used to attain a dense samarium-doped ceria (SDC). Alternatively, a sintering aid such as copper can be used to lower the sintering temperature down to 950 – 1100 °C [1–3]. The calcination temperature of 600 °C was reported for Cu/Sm – doped ceria (SCDC) synthesized by combustion method using PVA as a complexing agent [1]. Different calcination temperature could lead to difference in structure and conductivity as oxygen vacancy and electronic state may change.

In this work, the impact of calcination temperature toward oxidation state, oxygen vacancy, and electrical conductivity were study. The nano-powder of CeO₂ and SCDC were prepared by combustion method with polyethylene glycol as a complexing agent.

2. Experiment

The Sm_{0.19}Cu_{0.01}Ce_{0.80}O_{2-δ} (SCDC) samples were prepared by sol-gel combustion method from the metal nitrate precursor. The metal nitrates were dissolved in DI-water and then mixed with polyethylene glycol (PEG). The solution was vigorously stirred at 130 °C for 3 h to obtain gel. The gel was combusted at 250 °C for 3 h. Dried powders were calcined at 550, 650, 750, and 850 °C for 3 h which are labeled as SCDC(550), SCDC(650), SCDC(750), and SCDC(850), respectively. The as calcined powders were pressed into pellet under load of 2 tons and then were sintered at 1000 °C for 3 h in air. The calcined powders were characterized by X-rays diffraction (XRD, Panalytical Empyrean), Raman spectroscopy

(JOBIN YVON HORIBA), and Ultraviolet visible spectroscopy (UV-VIS, Agilent Cary 60). The sintered pellets were studied by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD) and Electrochemical impedance spectroscopy (EIS, Princeton Applied Research).

3. Result and discussion

The XRD patterns of calcined SCDC were shown in figure (1a). The XRD patterns signify the fluorite structure, similar to the ceria (JCPDS No. 00-043-1002). The non-cubic Sm_2O_3 peaks are not found. The lattice parameter and crystallite size of each sample were determined from the shifting and broadening of (111) peak, respectively. The crystallite size was calculated by Scherrer's equation following, $\tau = K\lambda / \beta \cos \theta$, where τ is crystallite size, K is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle.

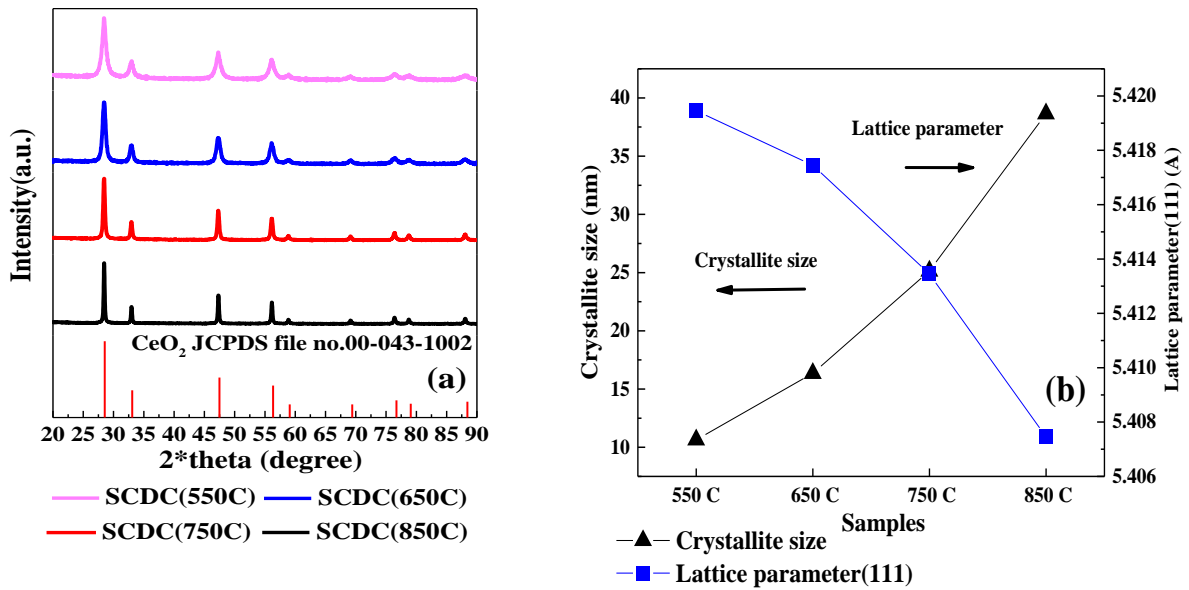


Figure 1. (a) XRD patterns of calcined SCDC and CeO₂ from JCPDS file no. 00-043-1002 and (b) trend of lattice parameter and crystallite size determined from (111) plane.

Increasing calcination temperature results in improvement of the crystallinity and increase of crystallite size as shown in figure 1(b). However, the lattice parameter slightly decreases, which may be due to replacement of Cu^{2+} on the oxygen vacancy sites. Information related to crystallinity, lattice expansion, and oxygen vacancies can be extracted from Raman spectra and plotted in figure 2(a) and 2(b). The Raman spectra of all samples exhibit strong band of Ce–O (F_{2g}) at about 450–460 cm^{-1} , which is known to correspond to a vibration of CeO_8 unit cell. The F_{2g} peak becomes more intense as the temperature increases, meaning the crystallinity are improved. The F_{2g} positions were plotted in figure (3a). The position of F_{2g} slightly shifts to a higher wavenumber with increasing calcination temperature due to the decrease of lattice parameter [4]. These Raman results go well with those of XRD. The oxygen vacancies at around 550 and 600 cm^{-1} are related to α (extrinsic oxygen vacancy) and β (intrinsic oxygen vacancy, respectively [5,6] as shown in figure (3b). The intrinsic oxygen vacancy is produced from Ce^{3+} substitution into Ce^{4+} host sites following Kröger-Vink notations as shown in equation (1) [7];



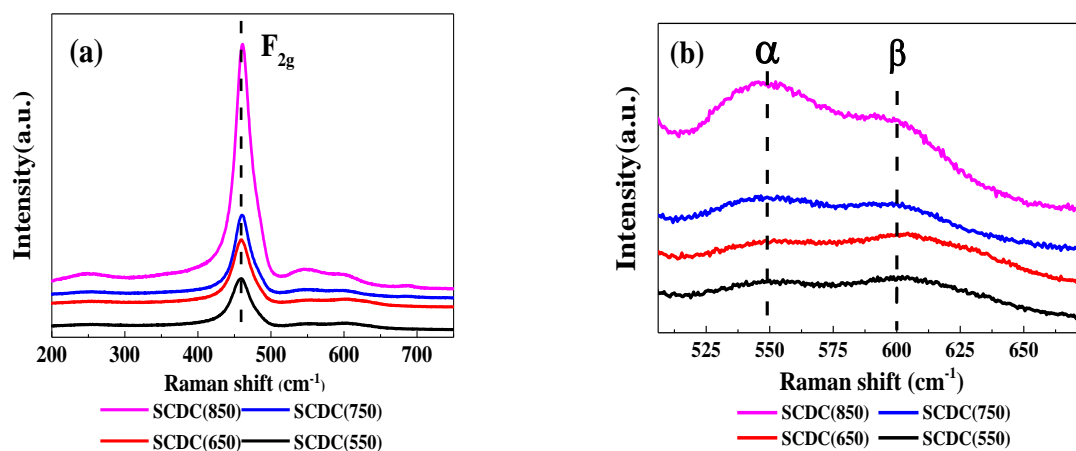


Figure 2. (a) Raman spectra of calcined SCDC and (b) oxygen vacancy peaks at 550 and 600 cm^{-1}

The area under the peak (figure 3(b)) of intrinsic oxygen vacancy (A_{600}) is slightly increased with the increasing temperature because more Ce^{3+} are generated from Ce^{4+} reduction. Also, the area underneath extrinsic (A_{550}) peak significantly increases, indicating that defect clusters associated with dopants are more prevalent.

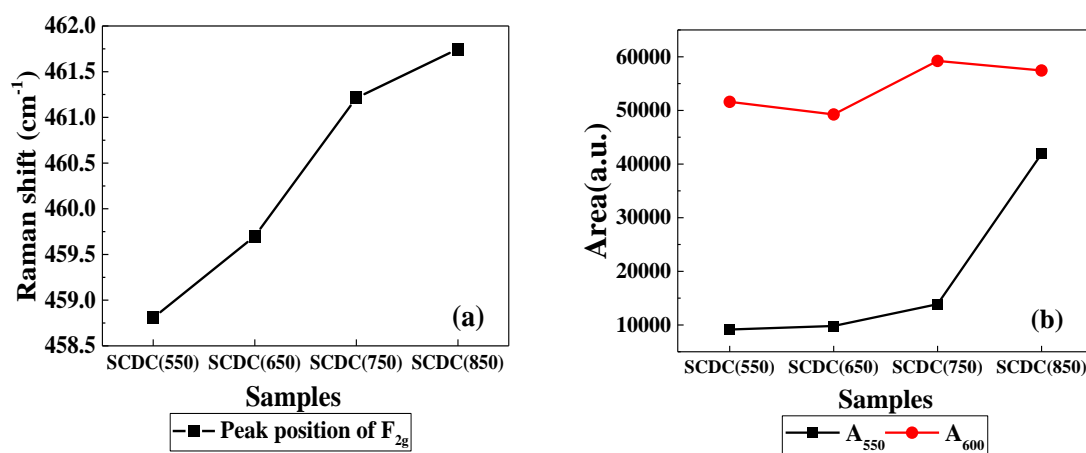


Figure 3. (a) Raman shift of F_{2g} of calcined SCDC and (b) peak area at 550 and 600 cm^{-1} of calcined SCDC.

The UV VIS spectra of calcined SCDC were shown in figure 4. The strong absorption band at about 380 nm is related to change in charge transfer between $\text{O}(2p)$ and $\text{Ce}(4f)$ orbitals. The absorption spectra exhibit blue shift due to the valence change from Ce^{4+} to Ce^{3+} [4] when the temperature was increased from 550 to 650 $^{\circ}\text{C}$. However, there was no significant change when the temperature was further increased. The subtle transformation of Ce^{4+} to Ce^{3+} at the surface may be more stable with the larger crystallite size. XPS spectra of all samples (figure 5(a)) show both oxidation states of Ce^{4+} and Ce^{3+} [8], which coexist on a surface of sintered SCDC samples. The amount of Ce^{4+} and Ce^{3+} from XPS spectra were summarized in Table 1. Increasing calcination temperature results in the increase of the Ce^{3+} in sintered SCDC. This infers the transformation of Ce^{4+} to Ce^{3+} at the higher temperature. Moreover, from figure 5(b), the lattice oxygen peak is shift to higher binding energy and its intensity decreases with

increasing calcination temperature. This may be due to nanoscale segregation of Sm and/or Cu at high temperature during sintering process [9].

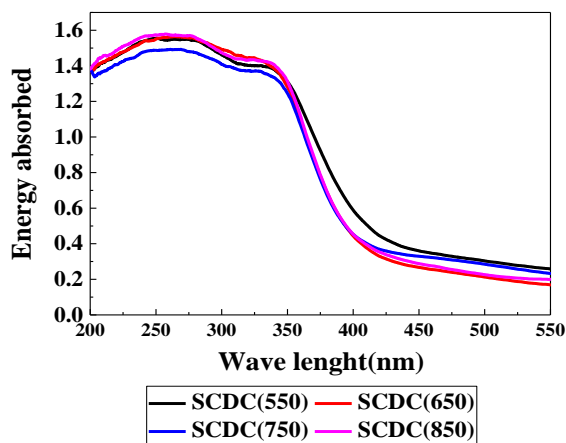


Figure 4. UV-VIS spectra of calcined SCDC.

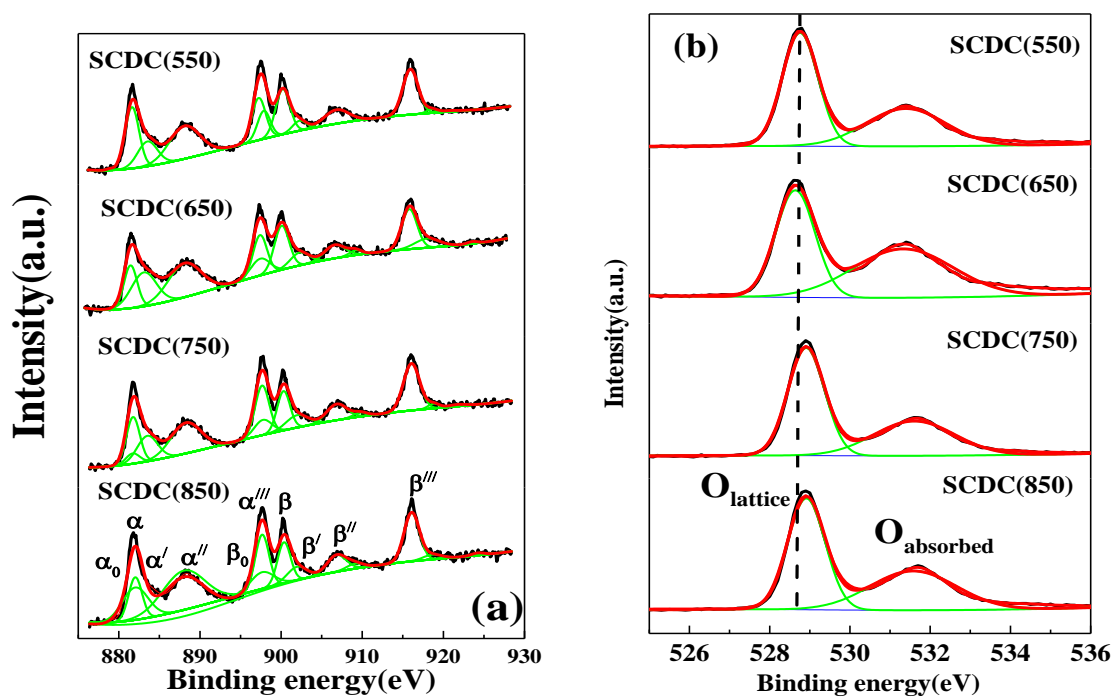
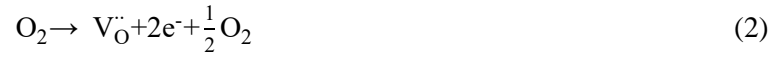


Figure 5. XPS spectra of (a) Ce(3d) and (b) O(1s) core level spectra of sintered SCDC.

Table 1. Oxidation state of cerium ion in sintered SCDC samples

oxidation state (%Ce)	Temperature (°C)			
	550	650	750	850
%Ce ³⁺	30.1721	35.9131	37.1658	39.9702
%Ce ⁴⁺	69.8279	64.0869	62.8342	60.0298

The Arrhenius plot of SCDC in figure 6(a) shows that the SCDC(850) has highest conductivity. The conductivity value increases with increasing oxygen vacancies. Extrinsic oxygen vacancy comes from Sm³⁺ doping effect whilst intrinsic oxygen vacancy formation (e.g.1) is dominated by the availability of Ce³⁺ ions as more Ce³⁺ ions should give rise in intrinsic oxygen vacancy. The Ce³⁺ ions come from the reduction of Ce⁴⁺ ions by electrons which are generated following equation (2) [7]. Note that (e.g.2) itself is related to oxygen released from lattice site at high temperature or low oxygen partial pressure.



The SCDC(850) conductivity is 0.0202 S/cm which is rather high as compared to other's (figure 6(b)). Our result is close to that of Yingchao Dong *et al.* [1] whose works is Cu_{0.01}Sm_{0.2}Ce_{0.8}O_{2-x} which was calcined at 600 °C and sintered at 950 °C.

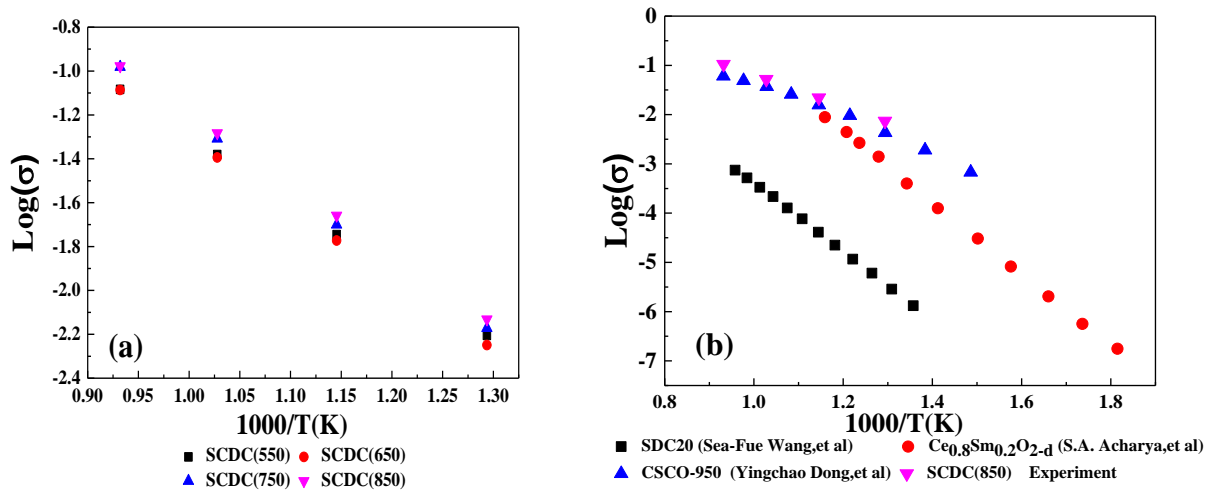


Figure 6. The comparison of Arrhenius plot of the total conductivity of (a) calcined SCDC after sintered at 1000 °C for 3 h and (b) comparison of SCDC(850) and other works.

4. Conclusion

The increase of calcination temperature leads to slight shrinkage of lattice parameter as well as increase of both extrinsic defects and a crystallite size. Additionally, transformation of oxidation state from Ce⁴⁺ to Ce³⁺ becomes more prominent with increasing calcination temperature. The highest total conductivities were achieved for SCDC (850) samples.

References

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