

Short communication

## Polyvinyl alcohol-induced low temperature synthesis of CeO<sub>2</sub>-based powders

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### Abstract

Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) powders have been synthesized by a combustion method with polyvinyl alcohol (PVA) as the fuel and nitrate as oxidizer. A calcination temperature of 350 °C was found to be sufficient for the formation of pure SDC powders. The cell parameters were calculated using the peak positions determined from the XRD patterns, and it was found that stoichiometric SDC powder could be obtained only when stoichiometric PVA fuel contents were used. The as-prepared SDC pellets exhibited 98% of the theoretical density sintered at 1300 °C. This shows that the SDC powders obtained by this combustion method have excellent sintering properties, which can densified at a relatively low sintering temperature. The powders made by this method, due to its high conductivity of 0.033 S cm<sup>-1</sup> at 700 °C, are suitable for intermediate temperature solid oxide fuel cells (IT-SOFCs).

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**Keywords:** Combustion synthesis; Conductivity; Solid oxide fuel cells; Polyvinyl alcohol; Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> powders

### 1. Introduction

Ceria doped with rare earth elements has attracted extensive attention by researchers due to the high oxygen ion conductivity [1] and excellent oxygen storage capacity [2], which gives rise to various applications such as an electrolyte for solid oxide fuel cells (SOFCs) at intermediate temperature [3] and a catalyst for synthetic gas production [4].

The synthesis of ceria-based powders with controlled powder characteristics such as a high stoichiometric proportion and structural homogeneity is important for practical applications. To obtain the desired powders, numerous synthetic routes including solid-state reactions [5], sol–gel [6], hydrothermal [7], coprecipitation [8] methods have been developed. Recently, many interests have been focused on propellant combustion synthesis, which can produce nanopowders with a high surface area, a homogeneous structure and fewer impurities in a short time at a lower temperature [9,10]. Especially, this method shows

advantages in the synthesis of the doped compound powders, which makes the dopant incorporate into the lattice by instant combustion and the compound avoids deviating from stoichiometry [11]. The success of this process is dependent on the use of a suitable fuel. So far, besides the common fuel glycine and citric acid [12–15], other kinds of fuel have been used such as urea [16], alanine [17], hexamethylenetetramine [18,19], oxalylhydrazide [20], carbonylhydrazide [21], ethylene glycol [22], etc. These substances in the combustion synthesis are used not only as the fuel but also as a complexing agent due to their special functional group properties.

Having all the properties desired by combustion, polyvinyl alcohol (PVA) has been used in the chemical process for the nanopowders. For example, Rocha and Muccillo [23] have prepared gadolinia doped ceria powders by the combustion synthesis process, however, no detailed sintering and conductivity information on this material for the IT-SOFC application was reported.

The target of this work is to synthesize SDC powders by the PVA combustion method. The crystal structure and particle size of the as-prepared powders were characterized by XRD, FESEM and TEM. In particular, the sintering and conductivity

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properties are presented in this paper to test the performance of these powders for the intermediate temperature solid oxide fuel cells (IT-SOFCs) electrolyte application.

## 2. Experimental and characterization

The PVA-induced synthetic process for a CeO<sub>2</sub>-based powder is very easy and simple. To prepare the PVA solution blended with cerium and samarium nitrates, cerium and samarium nitrates mixed solution with a concentration of 0.5 M of cations were first obtained by dissolving Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.95%) and Sm<sub>2</sub>O<sub>3</sub> (99.99%) in the correct stoichiometric proportions in distilled water and dilute nitric acid, respectively. Subsequently, a stock aqueous PVA (1750 ± 50, 5 wt.%) was added to the solution of cerium and samarium nitrates with various ratios of PVA to cations called P:C. After homogenization of this solution, the temperature was raised to 80 °C, and maintained to remove excess water. The initial thermal decomposition of the precursor was carried out at about 150 °C for 1 h. The resulting ash-like material was afterwards calcined at different temperatures for 2 h.

X-ray powder diffraction (XRD) patterns were carried out on a Philips X'Pert Pro Super Diffractometer with Cu Kα radiation (λ = 1.5418 Å) for phase analysis and crystal size calculation. Data were recorded at a scanning rate of 1° min<sup>-1</sup> with a scanning step size of 0.02° in the 2θ ranges 10–80°. The crystal size was determined by Scherrer equation using the XRD data of the (1 1 1), (3 1 1), (2 2 2) peaks. UnitCell software was used for the calculation of the lattice parameter values using the XRD pattern of all prominent lines. The particle size and morphology of SDC powder were obtained from scanning electron microscopy (SEM, KYKY 1010B) and field emission scanning electron microscopy (FESEM, JSM-6700F) and transmission electron microscopy (TEM, JEOL-2010). The as-obtained powders were prepared pellets by uniaxial pressing at 200 MPa. The pellets were then sintered at 1200–1400 °C for 5 h. The densities were measured by the Archimedes' method and the microstructure was characterized by scanning electron microscopy (SEM, KYKY-EM3200).

ac impedance spectroscopy measurements were conducted on electrochemical impedance spectrum analyzer (CHI 600A, Chenhua Inc., Shanghai) over the range of 0.1–100 kHz. The pellets were coated with silver paste and fired at 800 °C for 1 h before measurements, and then were put into the tube furnace and heated at a heating rate of 2 °C min<sup>-1</sup> in air. To determine the activation energy of conduction, measurements were made in 50 °C steps between 500 and 800 °C. In all measurements, the lead resistance was subtracted by measuring the impedance of a blank cell. The value of conductivity at different temperatures were calculated by Eq. (1):

$$\sigma = \frac{L}{RS} \quad (1)$$

where *L* is the thickness of the pellets, *S* the area of the pellets (*S* = 1/4π*D*<sup>2</sup>, *D* is diameter) and *R* is the resistance of the pellets at different temperatures.

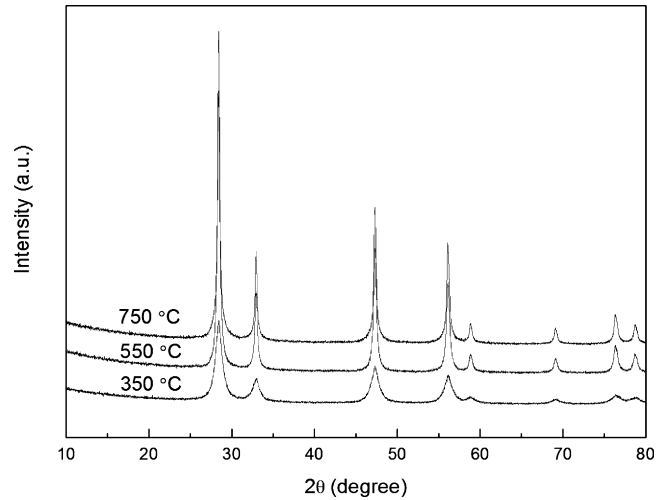


Fig. 1. XRD patterns for the samples synthesized at different temperatures.

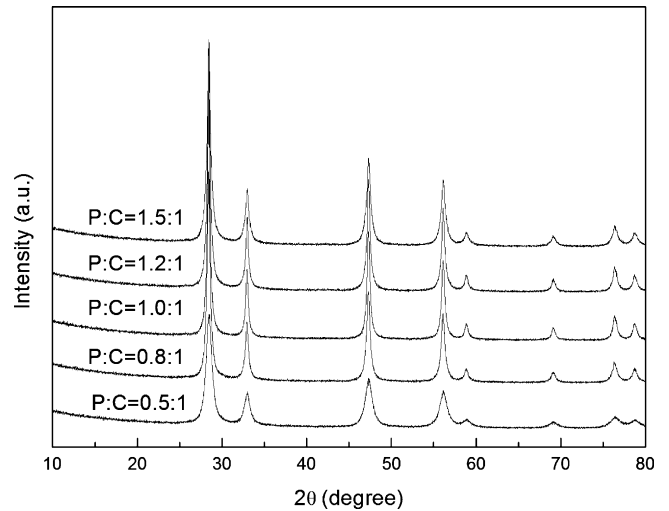


Fig. 2. XRD patterns of synthetic samples with different P:C ratios.

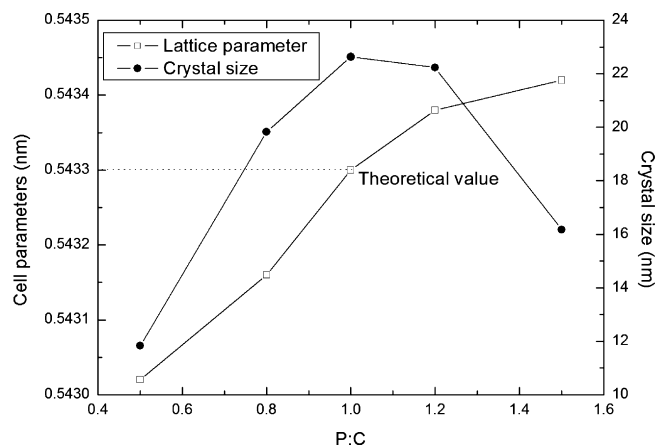


Fig. 3. Cell parameters and crystal size vs. the fuel contents.

### 3. Results and discussion

#### 3.1. XRD pattern

Fig. 1 shows XRD patterns of the samples synthesized at different temperatures. The results showed that a calcination temperature of 350 °C was sufficient for the formation of pure SDC powders. Low synthesis temperature was attributed to the assistance of PVA, which was an efficient fuel and reducer for

the combustion synthesis. High temperature will lead to increasing of crystal size. Therefore, in our experiments, 550 °C was applied to the following synthesis process to remove all the residual organics. The XRD patterns of the as-prepared powders synthesized with different PVA as fuel are shown in Fig. 2. In addition, the advantage of this method is also shown by cell parameter calculations. The results of cell parameters and crystal size calculated from Fig. 2 are presented in Fig. 3. From Fig. 3, it can be seen, when fuel-deficient PVA contents were used in the

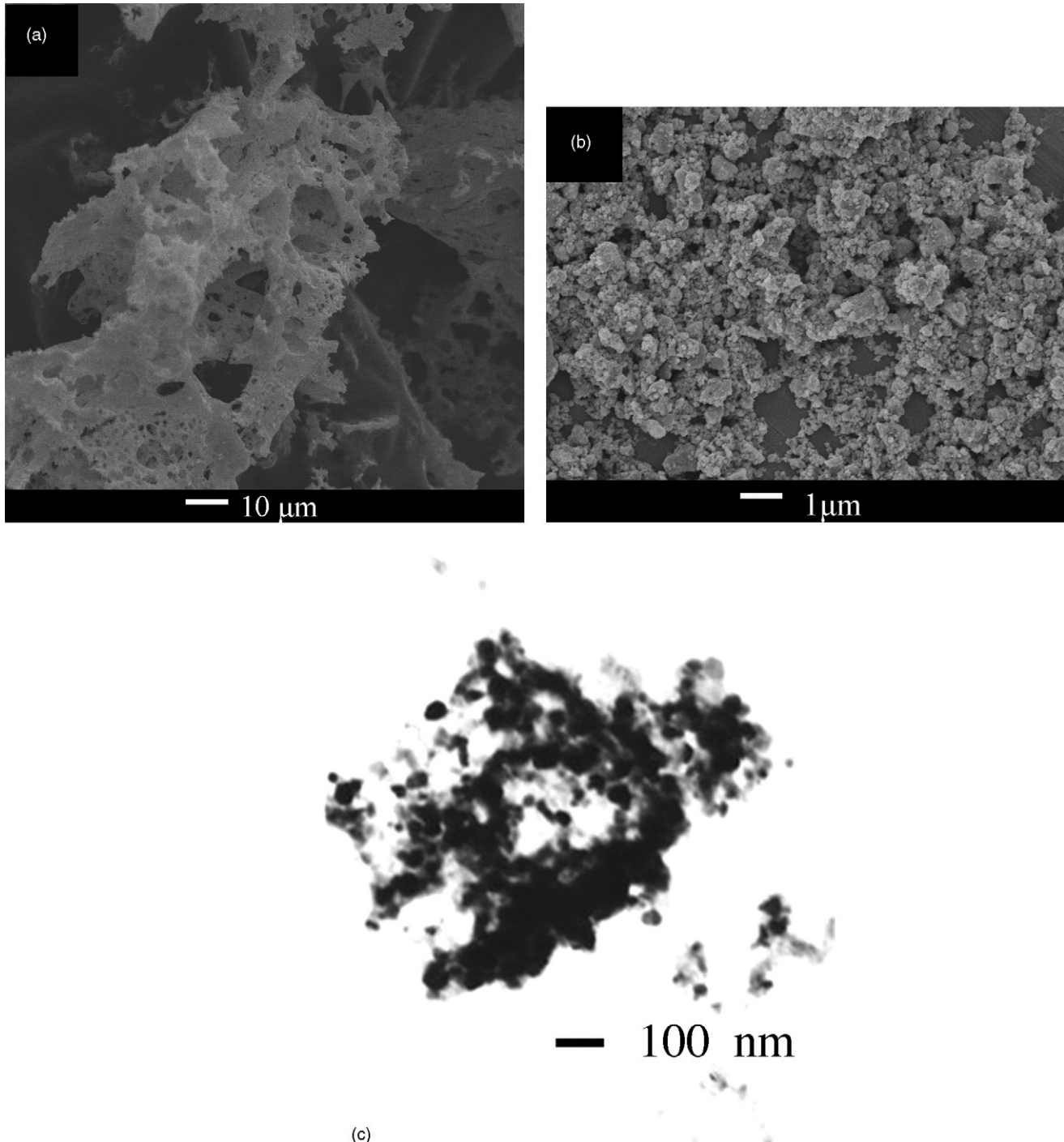


Fig. 4. (a) SEM of as-prepared powder; (b) FESEM image of milled powder; (c) TEM micrograph of as-prepared SDC powder.

synthesis process, the cell parameters of the as-prepared powder were smaller than the theoretical values of  $Ce_{0.8}Sm_{0.2}O_{1.9}$ . The possible reason was that little samarium incorporated into the lattice of ceria, which led to a small change in cell parameters. While, when a stoichiometric proportion or fuel-rich PVA content was applied in the combustion synthesis, the cell parameters were nearly in agreement with the literature value (JCPDS Card Number 75-0158). These results and interpretations can be verified by the following experimental phenomena. When fuel-deficient PVA contents were used, no obvious combustion reaction was observed. Even though the value of P:C was 0.8, which was nearly equal to the stoichiometric proportion, combustion reaction was not as violent as when a stoichiometric proportion of fuel was used.

Interestingly, the trend in crystal size with the ratio of P:C is not the same as the trend in the cell parameters which increase with the content of PVA. Firstly, the crystal size increased with the ratio of P:C before it reached 1.0, and then the crystal size became smaller with further increase in fuel content. Calculation with the Scherrer equation indicates that the crystal size of the as-prepared powder was about 22.6 nm when P:C was 1.0. The special phenomenon of our experimental is not completely consistent with the results that the crystal size and particle size

increased with the content of fuel reported by Mokkelbost et al. [24] The complex changes are probably related to the variation of the Sm-doped contents as well as the combustion temperature due to the different ratios of P:C.

### 3.2. SEM and TEM images

Fig. 4(a) is the SEM image of the as-prepared powder. These agglomerates consisted of porous particles of the as-prepared material. This porous structure was typical for powders prepared by the combustion technique [15,17]. Fig. 4(b) shows the picture of the milled powder where a drastic reduction of the agglomerate size can be observed. These characteristics (porous structure and friability) probably result from gases released by the redox reaction of PVA and metal nitrates. Typical TEM measurements shown in Fig. 4(c) confirm the XRD calculations of crystal size. Some agglomerates are about 100 nm are observed.

### 3.3. Sintering and electrical properties

The relative densities of the pellets are represented in Table 1. When the pellet was sintered at 1300 °C, the relative density has reached 98%, while a slight decrease of the relative density

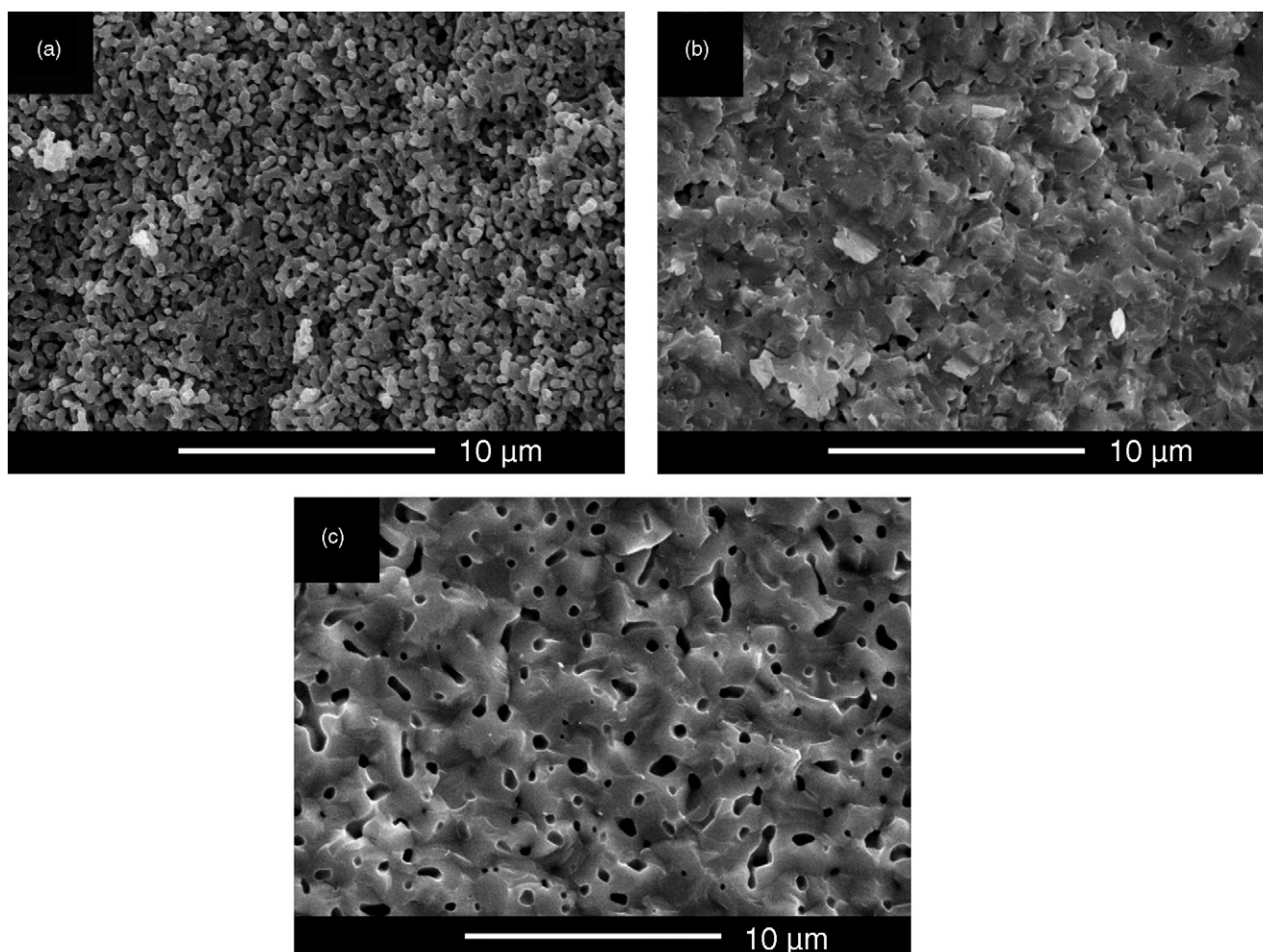


Fig. 5. SDC pellets sintered at: (a) 1200 °C; (b) 1300 °C; (c) 1400 °C.

Table 1  
Relative densities of the sample sintered at various temperatures

Sintering temperature (°C)	Relative density (%)
1200	90
1300	98
1400	97

was found when sintering temperature was increased to 1400 °C. This result shows that the as-prepared powders in this work have a high sintering activity. Therefore, near theoretical density can be obtained at a low sintering temperature. Fig. 5(a), (b) and (c) are SEM images of the SDC pellets sintered at 1200 °C, 1300 °C and 1400 °C, respectively. For lower sintering temperatures at 1200 °C, the SEM image reflects the porous microstructure with grain sizes of only about 500 nm. Relatively dense microstructures with a few closed pores could be obtained when the sintering temperature was 1300 °C (SEM image is shown in Fig. 5(b)). However, too high a temperature (1400 °C) led to the appearance of closed pores at the tri-junctions of the grain boundaries. In addition, the relative density decreased slightly for the pellets sintered at 1400 °C, which further confirmed that high temperature sintering was not favorable.

The electrical properties of SDC powder are important for IT-SOFC applications. The conductivity data are parameterized by the Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

where  $\sigma$ ,  $\sigma_0$ ,  $E_a$ ,  $k$  and  $T$  are the conductivity, pre-exponential factor, activation energy, Boltzmann constant and absolute temperature, respectively.

Fig. 6 shows the Arrhenius plots of  $\ln(\sigma T)$  versus  $1/T$  for as-obtained SDC powders sintered at 1300 and 1400 °C. The conductivities of as-prepared powders sintered at 1300 °C and 1400 °C were 0.033 S cm<sup>-1</sup>, 0.017 S cm<sup>-1</sup> at 700 °C, respectively. These results are in agreement with those obtained by Li

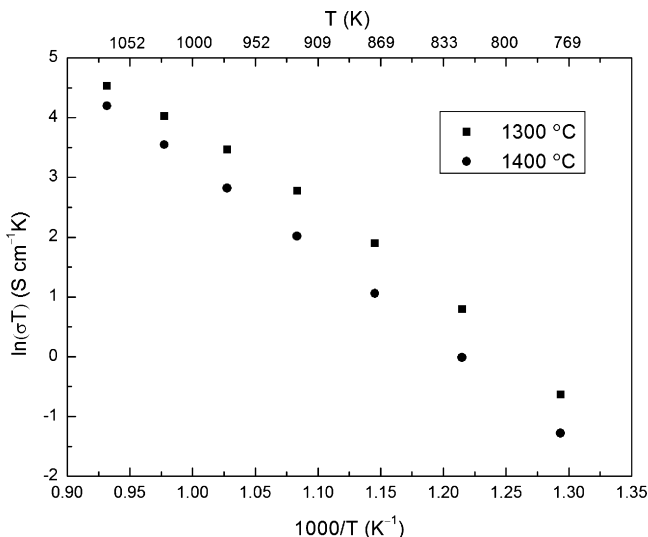


Fig. 6. The relationship between the conductivity and temperature.

et al. [25]. These conductivity measurements show that the PVA combustion synthesis is an effective method to prepare doped ceria powder having excellent electrical performance. As we know, ceramic sintering bodies consist of grain, grain boundary and gas pores, which are the main factors that directly affect the conductivity of the pellets. The densities only showed a weak decrease when the temperature changed from 1300 to 1400 °C. It seems that the conductivities of the pellets sintered at 1300 and 1400 °C should have the same values. However, the conductivity of the SDC pellet sintered at 1400 °C was lower than that of SDC pellet sintered at 1300 °C. From the SEM images shown in Fig. 5, a possible reason was that the formation and growth of closed pores led to the reduced conductivity. The sample sintered at 1300 °C had only 8% closed porosity, while a 14% closed porosity was in the pellets sintered at 1400 °C.

#### 4. Conclusions

Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) powders can be prepared by a combustion method with PVA as the fuel. The route is easy to perform, and yields nearly phase-pure SDC powders at a relatively low calcination temperature. The influence of different fuel contents on the cell parameters and crystal sizes were investigated. It was found that the cell parameters increased with increasing fuel content. Interestingly, the crystal size increased with the ratio of P:C before it reached 1.0, and then the crystal size became smaller with further increase in fuel content. High sintering activity made the compacted bodies achieve almost theoretical density for the samples sintered at 1300 °C. The conductivity of the samples prepared by this method was 0.033 S cm<sup>-1</sup> at 700 °C.

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#### References

- [1] G.M. Christie, F.P.F. van Berkel, *Solid State Ionics* 83 (1996) 17–27.
- [2] R. Si, Y.-W. Zhang, S.-J. Li, B.-X. Lin, C.-H. Yan, *J. Phys. Chem. B* 108 (2004) 12481–12488.
- [3] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, *Solid State Ionics* 52 (1992) 165–172.
- [4] B.M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loidant, J.-C. Volta, *J. Phys. Chem. B* 107 (2003) 5162–5167.
- [5] G.-B. Jung, T.-J. Huang, *J. Mater. Sci.* 38 (2003) 2461–2468.
- [6] C. Laberty-Robert, J.W. Long, E.M. Lucas, K.A. Pettigrew, R.M. Stroud, M.S. Doescher, D.R. Rolison, *Chem. Mater.* 18 (2006) 50–58.
- [7] W. Huang, P. Shuk, M. Greenblatt, *Chem. Mater.* 9 (1997) 2240–2245.
- [8] T.S. Zhang, J. Ma, Y.J. Leng, Z.M. He, *J. Crystal Growth* 274 (2005) 603–611.
- [9] B. Murugan, A.V. Ramaswamy, D. Srinivas, C.S. Gopinath, V. Ramaswamy, *Chem. Mater.* 17 (2005) 3983–3993.
- [10] S. Polizzi, S. Bucella, A. Speghini, F. Vetrone, R. Naccache, J.C. Boyer, J.A. Capobianco, *Chem. Mater.* 16 (2004) 1330–1335.
- [11] C.-C. Hwang, T.-Y. Wu, J. Wan, J.-S. Tsai, *Mater. Sci. Eng. B* 111 (2004) 49–56.
- [12] R. Peng, C. Xia, Q. Fu, G. Meng, D. Peng, *Mater. Lett.* 56 (2002) 1043–1047.

- [13] R.D. Purohit, B.P. Sharma, K.T. Pillai, A.K. Tyagi, *Mater. Res. Bull.* 36 (2001) 2711–2721.
- [14] C. Peng, Y. Zhang, Z.W. Cheng, X. Cheng, J. Meng, *J. Mater. Sci.: Mater. Electron.* 13 (2002) 757–762.
- [15] M. Alifanti, B. Baps, N. Blangenois, J. Naud, P. Grange, B. Delmon, *Chem. Mater.* 15 (2003) 395–403.
- [16] Y.-P. Fu, C.-H. Lin, C.-W. Liu, K.-W. Tay, S.-B. Wen, *J. Power Sources*, in press.
- [17] D.Y. Chung, E.H. Lee, *J. Alloy Compd.* 374 (2004) 69–73.
- [18] A.S. Prakash, A.M.A. Khadar, K.C. Patil, M.S. Hegde, *J. Mater. Synth. Process.* 10 (2002) 135–141.
- [19] K. Nagaveni, M.S. Hegde, N. Ravishankar, G.N. Subbanna, G. Madras, *Langmuir* 20 (2004) 2900–2907.
- [20] T. Mimani, *J. Alloy Compd.* 311 (2001) 123–128.
- [21] S.T. Aruna, K.C. Patil, *Nanostruct. Mater.* 10 (1998) 955–964.
- [22] W. Chen, F. Li, J. Yu, *Mater. Lett.* 60 (2006) 57–62.
- [23] R.A. Rocha, E.N.S. Muccillo, *Brit. Ceram. Trans.* 102 (2003) 216–218.
- [24] T. Mokkelbost, I. Kaus, T. Grande, M.-A. Einarsrud, *Chem. Mater.* 16 (2004) 5489–5494.
- [25] H. Li, C. Xia, M. Zhu, Z. Zhou, G. Meng, *Acta Mater.* 54 (2006) 721–727.