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Study on Gd³⁺ and Sm³⁺ co-doped ceria-based electrolytes

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Abstract Doped ceria electrolytes of Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}, wherein $a=0.15$ or 0.2 , and $0 \leq y \leq a$, were prepared with the citrate method, and characterized by inductively coupled plasma-atomic emission spectrometry, energy dispersive spectrometry, scanning electron microscopy, powder X-ray diffraction, and AC impedance spectroscopy. The effect of composition on the structure and conductivity was studied. All the samples were fluorite-type ceria-based solid solutions. For the singly doped samples, the optimal composition was Ce_{0.85}Gd_{0.15}O_{1.925} for Gd³⁺-doped ceria (CGO), which showed higher ionic conductivity than the best Sm³⁺-doped ceria (CSO) at 773–973 K. For the co-doped samples, the ionic conductivities were higher than those of the singly doped ones in the temperature range 673–973 K when $a=0.15$, but only better in 673–773 K when $a=0.2$. For the samples of Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}, wherein $0.05 \leq y \leq 0.1$, much higher ionic conductivity was observed than those of the singly doped ceria at 773K~973 K. Therefore, these co-doped samples would be better than CGO and CSO to be the electrolytes of intermediate-temperature solid oxide fuel cells.

Keywords Doped ceria electrolyte · Gd₂O₃ · Sm₂O₃ · Co-doping effect · Conductivity

Introduction

Ceria doped with heterovalent cations, such as alkaline earth and rare earth ions, has been considered one of the most promising electrolyte materials for intermediate temperature solid oxide fuel cells (ITSOFCs). These materials demonstrate much higher ionic conductivity at relatively low temperatures in comparison to that of yttrium-stabilized zirconia (YSZ). Among the various dopants studied, Gd³⁺ and Sm³⁺ singly doped ceria (abbreviated as CGO and CSO) have been reported to have the highest conductivity [1, 2] and to be relatively stable in the reducing environment [3]. The optimal compositions of CGO and CSO, giving the highest conductivities, were Ce_{1-x}Gd_xO_{2-0.5x} ($x=0.1-0.2$) [4] and Ce_{0.8}Sm_{0.2}O_{1.9} [5]. However, there have been some contradictions in the literature concerning which of the two is better. For example, Steele [4] and Van Herle et al. [6, 7] reported that CGO showed higher ionic conductivity than CSO, whereas the reverse was found by other research groups [3, 8, 9]. This disagreement probably results from divergences in sample preparation. Other than the singly doped ceria, many studies [6, 10, 11, 12, 13, 14] have been carried out on co-doped samples. Again, controversial results on the co-doping effect have also been reported. For example, Mori et al. [11] reported that the ionic conductivity of (La_{0.75}Sr_{0.2}Ba_{0.05})_{0.175}Ce_{0.825}O_{1.891} was higher than that of the respective singly doped ceria, and even that of CSO. Similarly, Van Herle et al. [6] found that co-doped ceria with three, five, or ten dopants showed significantly higher conductivity in air (by 10–30%) than the best singly-doped materials with the same oxygen vacancy concentration. These results suggest that co-doping may enhance conductivity. However, Yoshida et al. [12, 14] found that ceria doubly-doped with La³⁺ and Y³⁺, in which the average ionic radii of the dopants were adjusted closely to that of Sm³⁺, did not show any synergistic effects on ionic conductivity, and only gave the average value of the conductivities of the respective singly doped ceria

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samples. Since CGO and CSO are believed the most conductive electrolytes [1, 2] among the singly doped ceria, Gd^{3+} and Sm^{3+} co-doped ceria are probably good and even better electrolytes. However, there is still a lack of systematic studies reported on this kind of material. In this work, Gd^{3+} and Sm^{3+} co-doped ceria-based materials were prepared and characterized. The effect of composition on structure and conductivity was studied in comparison to singly doped ceria.

Materials and methods

Sample preparation The starting materials were reagent grade nitrate salts (Acros), which were used as purchased. Aqueous solutions of Ce^{3+} , Gd^{3+} , and Sm^{3+} ions were prepared by dissolving the nitrate salts in distilled water and diluting them to the desired concentrations. An aqueous solution of citric acid (CA) and polyethylene glycol (PEG) in a weight ratio of CA/PEG = 60 was also prepared and was termed CP solution. According to the composition ($\text{Ce}_{1-a}\text{Gd}_{a-y}\text{Sm}_y\text{O}_{2-0.5a}$, wherein $a=0.15$ or 0.2 , $0 \leq y \leq a$) of the electrolyte samples, different volumes of metal ion solutions were taken and mixed in a beaker. CP solution was then added into the beaker until the molar number of citric acid was equal to the total number of the metal ions in the beaker. The mixed solution was evaporated under stirring at 353 K until it gelled. The gel was dried at 378 K, ground and calcined in air at 973 K for 4 h, and then ground again to form calcined powder. The powder was uniaxially pressed under 750 MPa into green pellet using a stainless steel die of 13 mm diameter. The green pellet was further sintered at 1,773 K for 14 h with a heating rate of 1 K/min to form a dense pellet (simplified as pellet hereafter).

Sample characterization The relative densities of all the pellet samples were measured by Archimedes' method and were found to be greater than 90%. Scanning electron microscopy (SEM) analysis of the cross section of the pellets was conducted on a Hitachi S-2400 electron microscope. The crystal phases of the powder and the pellet (ground to powder again for measurement) samples were identified at room temperature using a PANalytical X-ray diffractometer (XRD) (45 kV, 40 mA, Cu $K\alpha$ radiation). The compositions of the pellet samples were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Jarrell-Ash, ICAP9000) and an energy dispersive spectrometer

(EDS) (Hitachi S-2400 Scanning Electron Microscope, Kevex Delta class 80000 EDS).

Conductivity measurement For conductivity (σ) measurement, Ag paste was brushed onto both sides of the pellet, then sintered at 1,073 K for 30 min to form Ag electrodes. Pt leads were attached to the electrodes using Ag paste and were sintered again at 1,073 K for 30 min. Impedance was measured using the two-probe method with an Autolab Impedance Analyzer (30 mV, 1 MHz–0.01 Hz). The measurements were taken at constant temperature within 473–973 K and in air (25sccm). Prior to data collection at each temperature, the system was kept at the constant temperature and in given gas flow for 30 min. The conductivity data were obtained from the impedance plots by using the same method as that described in details in the literature [15]. In the following context, the word “conductivity” is used to represent the total conductivity of grain and grain boundary.

It has been documented that the main contribution of the conductivity of ceria-based compounds in air is oxide ionic conductivity (> 99.5%) and that from electronic conductivity is negligible [8, 15]. In this study, the conductivity measured in air was treated as the oxide ionic conductivity only.

Results and discussion

Compositions

The compositions of the pellet samples were analyzed with an EDS and an ICP-AES. For the ICP-AES analysis, the samples were ground to powder form and dissolved in a mixed solution of hydrofluoric acid and nitric acid. Three typical results are listed in Table 1. The compositions analyzed by both techniques are close to the designed values, indicating that the effect of multi-step preparation, which includes the high temperature sintering, on the compositions of the pellet samples is negligible. Therefore, it is reliable to use designed composition data of the pellet samples directly.

Crystal structures

All the electrolyte samples prepared in this work showed XRD patterns similar to that of pure ceria. The XRD patterns of three typical samples are given in Fig. 1. Those of pure CeO_2 , Gd_2O_3 , and Sm_2O_3 in powder form

Table 1 Chemical compositions of the pellet samples

Sample	Ce: Gd: Sm atomic ratio		
	Designed	EDS	ICP
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$	0.90:0.10:0	0.907:0.093:0	0.908:0.093:0
$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$	0.80:0:0.20	0.819:0:0.181	-
$\text{Ce}_{0.85}\text{Gd}_{0.05}\text{Sm}_{0.1}\text{O}_{1.925}$	0.85:0.05:0.10	0.842:0.047:0.111	0.847:0.053:0.100

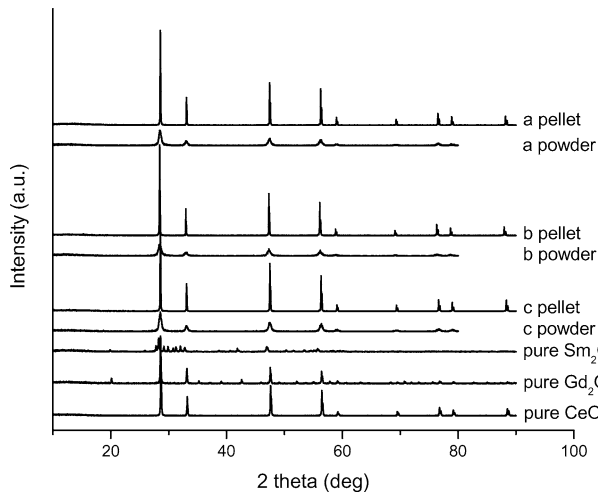


Fig. 1 X-ray diffraction patterns of CeO_2 , Gd_2O_3 , Sm_2O_3 and ceria-based samples with nominal composition of $\text{Ce}_{0.85}\text{Gd}_{0.05}\text{Sm}_{0.1}\text{O}_{1.925}$ (a), $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (b), and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (c). Powder samples were calcined at 973 K. Pellet samples were sintered at 1,773 K

are also given for comparison. It can be seen that the doped ceria pellet samples (sintered at 1,773 K) showed the same XRD patterns as the powder samples (just calcined at 973 K) of the same compositions, except that the XRD peaks were much sharper for the former. Furthermore, the XRD patterns of the doped ceria samples were different from those of pure Gd_2O_3 and Sm_2O_3 , but similar to that of pure CeO_2 . These results indicate that the doped ceria samples are all ceria-based solid solutions of fluorite-type structures, which are formed in the calcination process and crystallized better in the sintering process.

More accurate XRD measurements with quartz as inner standard showed that the 2 theta values of the doped ceria shift slightly towards lower angles in comparison to that of pure CeO_2 . This is because the ionic radius decreases in the order $\text{Sm}^{3+} > \text{Gd}^{3+} > \text{Ce}^{4+}$, so that the substitution of Ce^{4+} with Sm^{3+} and Gd^{3+} in the lattice of CeO_2 would enlarge the crystal lattice. As shown in Fig. 2, the lattice constant of $\text{Ce}_{1-y}\text{Gd}_y\text{O}_{2-0.5y}$ and $\text{Ce}_{1-y}\text{Sm}_y\text{O}_{2-0.5y}$ increased linearly with the dopant content (y), but the slope for the former (0.081) was lower than that for the latter (0.134) because Gd^{3+} is smaller than Sm^{3+} . Similarly, the lattice constants of $\text{Ce}_{0.85}\text{Gd}_{0.15-y}\text{Sm}_y\text{O}_{1.925}$ and $\text{Ce}_{0.8}\text{Gd}_{0.2-y}\text{Sm}_y\text{O}_{1.9}$ increased linearly with y . For the same y , the lattice constant was smaller for $\text{Ce}_{0.85}\text{Gd}_{0.15-y}\text{Sm}_y\text{O}_{1.925}$ than for $\text{Ce}_{0.8}\text{Gd}_{0.2-y}\text{Sm}_y\text{O}_{1.9}$. The results in Fig. 2 follow Vegard's rule [16] and further confirm that all the doped ceria samples of this work are ceria-based solid solutions.

Conductivities

For the Gd^{3+} -doped ceria, CGO electrolytes, there are some controversial reports on the best composition. For example, Tianshu et al. [5] reported that the best com-

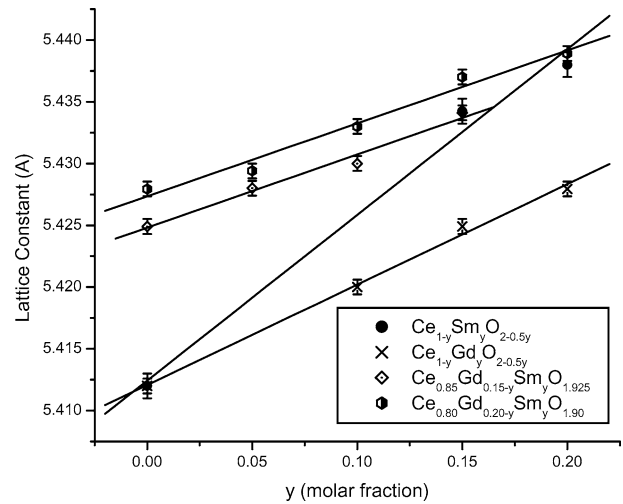


Fig. 2 Dependence of lattice constant on the composition (y) of different doped ceria electrolytes (sintered at 1,773 K for 14 h)

position was $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, whereas Steele et al. [4] claimed that the best composition was $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$. This disagreement most probably results from the difference in preparation and purity of the starting materials. In this work, a set of samples were designed and prepared with the nominal composition of $\text{Ce}_{1-y}\text{Gd}_y\text{O}_{2-0.5y}$, wherein $0.1 \leq y \leq 0.2$. The conductivities of these samples in air and at 473–973 K are shown in Fig. 3 in the form of $\ln(\sigma T)$ versus $1,000/T$. It can be seen that the activation energy of conduction increases with y . The maximum conductivity appeared at $y=0.15$ when temperature ≥ 773 K, but at $y=0.1$ when temperature < 773 K. Since the operating temperature range of ITSOFCs is at 773–973 K, the samples with $y=0.15$ and 0.2 (total dopant of 15–20 mol%), which showed higher conductivities than that with $y=0.1$, became the main object of this study.

In order to investigate any co-doping effect and at the same time avoid the effect of oxygen vacancy concen-

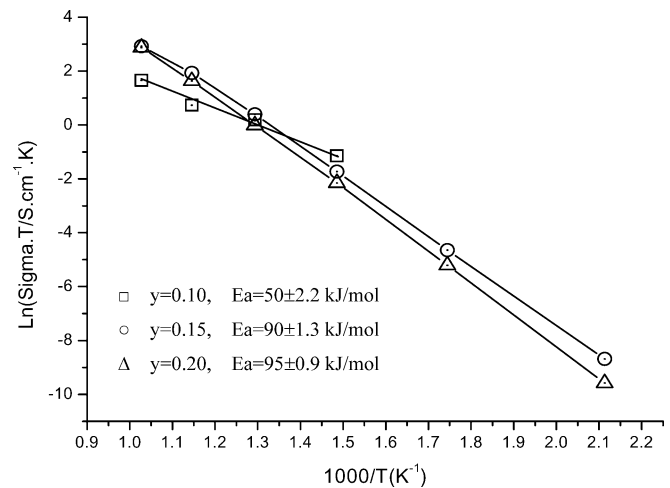


Fig. 3 Effect of temperature (T) on the conductivity (σ) of the pellet samples in air with nominal composition of $\text{Ce}_{1-y}\text{Gd}_y\text{O}_{2-0.5y}$

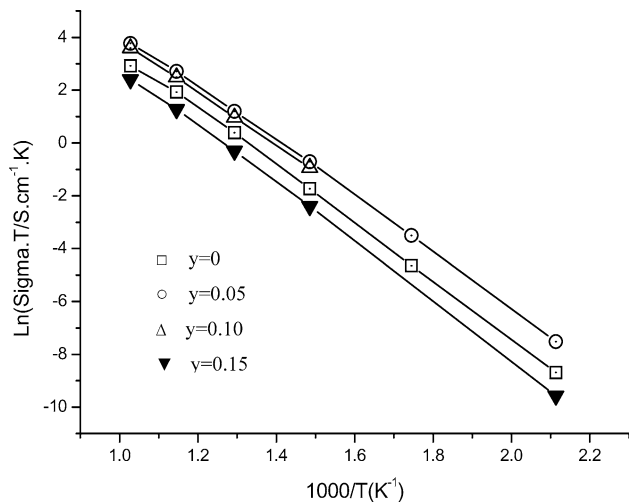


Fig. 4 Effect of temperature (T) on the conductivity (σ) of the pellet samples in air with nominal composition of $\text{Ce}_{0.85}\text{Gd}_{0.15-y}\text{Sm}_y\text{O}_{1.925}$

tration, a set of samples with the nominal composition $\text{Ce}_{0.85}\text{Gd}_{0.15-y}\text{Sm}_y\text{O}_{1.925}$, wherein $0 \leq y \leq 0.15$, were prepared and characterized. The conductivities of these samples in air at 473–973 K are shown in Fig. 4 in the form of $\ln(\sigma T)$ versus $1,000/T$. It can be seen that co-doped samples showed conductivities higher than those of singly doped samples. At 973 K and $y=0.05$, the conductivity of the co-doped samples reached 0.046 S cm^{-1} , higher than the best results in the literatures for CGO (0.0316 S cm^{-1}) [5] and CSO (0.041 S cm^{-1}) [17]. The activation energies of conduction of the samples, calculated from the line slopes in Fig. 4, are given in Fig. 5 as a function of y . The activation energy was lower for the co-doped samples than for the singly doped samples, and reached its minimum at y of about 0.07.

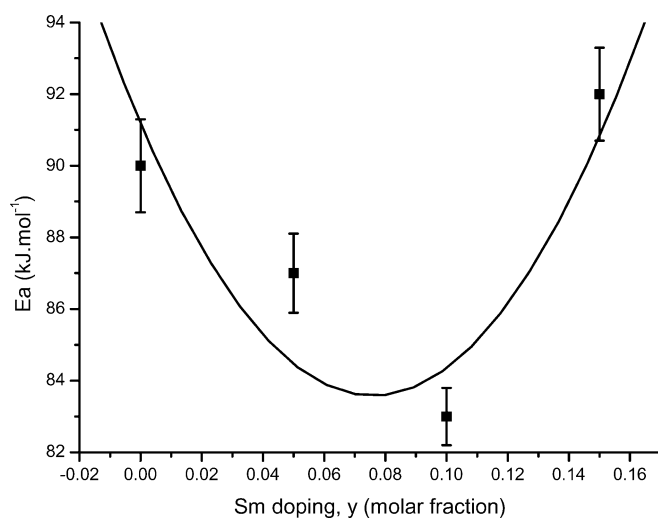


Fig. 5 Effect of Sm doping concentration (y) on the activation energy (E_a) of conduction of the pellet samples with nominal composition of $\text{Ce}_{0.85}\text{Gd}_{0.15-y}\text{Sm}_y\text{O}_{1.925}$

Similarly, another set of samples with the nominal composition $\text{Ce}_{0.8}\text{Gd}_{0.2-y}\text{Sm}_y\text{O}_{1.9}$, wherein $0 \leq y \leq 0.2$, were prepared and characterized. The conductivities of these samples in air and at 473–973 K are shown in Fig. 6 in the form of $\ln(\sigma T)$ versus $1,000/T$. It can be seen that the conductivities of the co-doped ceria were higher than those of the singly doped ceria when temperature $\leq 773 \text{ K}$, but between those of the singly doped ceria when temperature $> 773 \text{ K}$. Similarly, the changes of co-doping effect in different temperature ranges were also observed on $\text{Ce}_{0.82}\text{Gd}_{0.06}\text{Sm}_{0.06}\text{Y}_{0.06}\text{O}_x$, $\text{Ce}_{0.9}\text{Sm}_{0.03}\text{Y}_{0.03}\text{O}_x$, and ceria doped with La^{3+} and Y^{3+} [6, 11, 12, 13, 14].

From the line slopes in Fig. 6, we found that the activation energies of conduction of the co-doped ceria are lower than those of the singly doped ceria. This is consistent with the results in Fig. 5.

Comparing Fig. 6 with Fig. 4, it can be seen that for the same y , the samples of $\text{Ce}_{1-a}\text{Gd}_{a-y}\text{Sm}_y\text{O}_{2-0.5a}$, wherein $0 \leq y \leq a$, showed higher ionic conductivity at 773–973 K for $a=0.15$ than for $a=0.2$, and that the best CGO sample ($\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$) showed higher ionic conductivity than the CSO samples of $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$.

It has been proved that the ionic conductivity of doped ceria electrolytes is affected by not only the concentration and the distribution of oxygen vacancy [8, 12, 18] but also the lattice strain [19]. Yamamura et al. [18] had studied the co-doping effect on the ionic conductivity in the $(\text{Ce}_{(1-x-y)}\text{La}_x\text{M}_y)\text{O}_{2-\text{delt}_a}$ ($M = \text{Ca}, \text{Sr}$) system, and found that co-doping might suppress the ordering of oxygen vacancy, and therefore lower the activation energy of conduction and improve the ionic conductivity. Kim [19] had studied the relationship between the lattice parameter and the ionic conductivity of the doped ceria, and found that the reduction of the lattice deviation of the doped ceria from the pure ceria

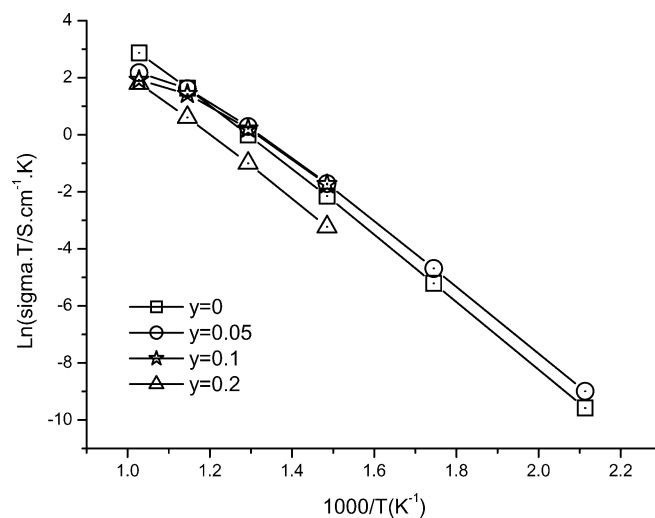


Fig. 6 Effect of temperature (T) on the conductivity (σ) of the pellet samples in air with nominal composition of $\text{Ce}_{0.8}\text{Gd}_{0.2-y}\text{Sm}_y\text{O}_{1.9}$

would lead to the reduction of the lattice strain of the doped ceria, and, as a result, lead to the decrease of the activation energy of conduction and the increase of the ionic conductivity of the doped ceria. In the present work, for the samples of constant dopant concentration $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$, the partial substitution of Gd with Sm might cause two opposite effects. On the one hand, similar to the results of Yamamura et al. [18], the ordering of the oxygen vacancy might be suppressed, which led to the decrease in activation energy of conduction and the increase in ionic conductivity. On the other hand, the deviation of the lattice parameter from pure CeO_2 was enlarged (as shown in Fig. 2), which, according to Kim's results [19], led to the increase in activation energy of conduction and the decrease in ionic conductivity [8, 19]. When the Sm content (y) was low, the first effect might be stronger than the second. Therefore, with the increase in Sm content (y), the activation energy of conduction decreased and the ionic conductivity increased, especially in the lower temperature range (≤ 773 K). However, when the Sm content (y) was too high, the second effect might become stronger than the first. Therefore, with the increase of Sm content (y), the activation energy of conduction increased and the ionic conductivity decreased.

For samples of the same Sm content (y), the co-doped ceria of $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$ showed higher ionic conductivities at 773~973 K for $a=0.15$ than for $a=0.2$. It

is probably because the former has lattice parameters much closer to that of pure CeO_2 than the latter (as shown in Fig. 2).

In Fig 7a–c are three typical SEM micrographs of the side-view of the broken pellet samples with nominal compositions of $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.8}Sm_{0.2}O_{1.9}$, and $Ce_{0.85}Gd_{0.05}Sm_{0.1}O_{1.925}$ respectively. It can be seen that some micro-pores were present on these samples. This is consistent with the relative density values being less than 100%. It also implies that the conductivity may be further improved by increasing the density.

Conclusions

Samples of co-doped ceria with nominal composition of $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$, wherein $a=0.15$ or 0.2 , $0 \leq y \leq a$, were prepared and studied in comparison to singly doped ceria on the structure and conductivity. All the electrolyte samples were found to be fluorite-type ceria-based solid solutions, which were formed in the calcining process at 973 K and crystallized better in the sintering process at 1,773 K. After sintering, the crystal structures and chemical compositions of the calcined samples did not change, but the relative densities of the pellet samples increased to more than 90%. For the singly doped samples, the best Gd^{3+} -doped ceria was $Ce_{0.85}Gd_{0.15}O_{1.925}$, which showed higher ionic conductivity at 773–973 K than the best Sm^{3+} -doped ceria. For the co-doped samples, ionic conductivities were found to be higher than the singly doped ones in the temperature range of 673–973 K when the total dopant concentration was 15%, but only better in 673–773 K when the total dopant concentration was 20%. Therefore, the co-doped ceria of the composition $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$, wherein $0.05 \leq y \leq 0.1$, would be better than singly doped CGO and CSO to be used as the electrolytes of ITSOFCs.

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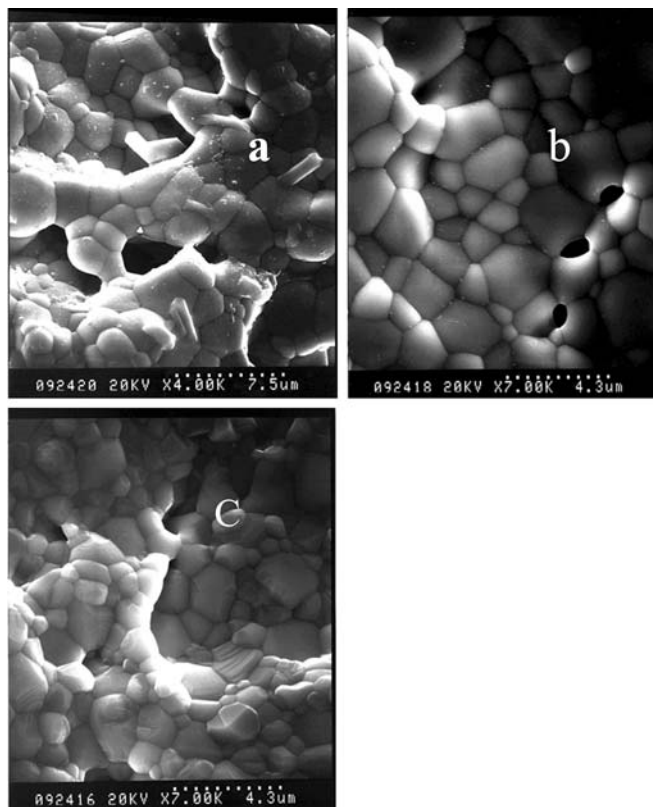


Fig. 7a–c Scanning electron microscope photographs of the side-view of **a** $Ce_{0.9}Gd_{0.1}O_{1.95}$, **b** $Ce_{0.8}Sm_{0.2}O_{1.9}$, and **c** $Ce_{0.85}Gd_{0.05}Sm_{0.1}O_{1.925}$ pellets

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