Synthesis, structural and morphological studies of Sr$^{2+}$ and Gd$^{3+}$ co-doped Ceria electrolyte system for LT-SOFC

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Abstract. This paper reports the effect of Sr$^{2+}$ addition on the structural, microstructural properties of Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ (GDC) electrolyte for low temperature solid oxide fuel cell application. The Sr$^{2+}$ (0, 0.5, 1 and 2 mol %) doped GDC solid electrolytes have been prepared by solid state method. The sintered densities of the samples are around 95%. XRD study reveals the cubic fluorite structure. The microstructure of the samples resulted into grain sizes in the range of 4.3 to 0.868 $\mu$m. Raman spectra also confirms the presence of GDC single phase.

1. Introduction

Ceria-based materials have found potential application as electrolyte materials for the intermediate temperature (500-750°C) solid oxide fuel cell application (IT-SOFC). Several trivalent rare-earth oxides form solid solutions with ceria. Among several trivalent rare earth substituted ceria electrolytes, Ce$_{1-x}$Gd$_x$O$_{2-\delta}$ (CGO) and Ce$_{1-x}$Sm$_x$O$_{2-\delta}$ (SDC) exhibit conductivity exceeding that of YSZ at 1073 K (>0.1 S cm$^{-1}$) [1]. Kim et. al. [2] reported that the dopant ion has a ‘critical radius’ (0.104 nm) for trivalent cations, which cause neither expansion nor contraction in the ceria lattice. According to Kim’s expression $r_c$ = 0.1106nm for divalent ions (alkaline earth oxides) and 0.1038 nm for trivalent ions (Rare earth oxides). The alkaline earth ions like Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ are more environmental friendly and naturally more abundant than the rare earth ions, resulting in a significantly lowered production cost. As a consequence, recently it has been observed that an increasing interest has been shown in alkaline earth doped ceria [3]. Other than singly doped ceria, many studies have been reported on co-doped samples and results suggest that co-doping may enhance conductivity even at moderate or intermediate temperatures [4]. Ionic conductivity of ceria influenced by two factors one dopant concentration, binding energy (the energy to pull the crystal apart into a set of free atoms). Oxygen ions easily migrate when average binding energy of ceria based electrolytes should be lower and also depends on ionic radius of the dopant. If the ionic radius of the dopant is too large then much strain is induced in the lattice of the electrolyte and the ionic conductivity decreases [5]. Table-1 shows the ionic radii and lattice binding energies of divalent cations.
Table 1 Ionic radii of divalent cations and lattice binding energy values of divalent oxides

| Ionic Radius (Å) | Be$^{2+}$ | Mg$^{2+}$ | Ca$^{2+}$ | Sr$^{2+}$ | Ba$^{2+}$ |
|------------------|-----------|-----------|-----------|-----------|-----------|
| Lattice binding  | 44.57     | 39.40     | 35.44     | 33.40     | 31.44     |
| energy (eV)      |           |           |           |           |           |

For example, 20 mol% of dopants produces sufficient concentration of oxygen vacancies in samarium doped ceria (SDC) [6] and gadolinium doped ceria (GDC) [7] systems. If the content of the trivalent dopant exceeds 20 mol% then the ionic conductivity of ceria reduces due to defect association and/or oxygen vacancy clustering. Besides, the lattice strain and the association energies of SDC and GDC are lower than CeO$_2$ doped with other rare earth cations. Zhang et al. [8] reported that when alumina is added, the grain conductivity of 20GDC (20 mol% Gd-doped CeO$_2$) increased by ~60% and grain boundary conductivity rapidly decreased. A similar phenomenon has also been reported on systems of GDC20 doped with transition metal ions such as Co, Fe, and Cu [9]. Lienigol and Gauckler have used cobalt as the sintering aid for gadolinium-doped CeO$_2$ (GDC) and found that GDC (Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$,δ) with density higher than 99% could be obtained even when sintering at 900$^\circ$C with 1 mol% CeO$_2$O$_4$ addition [10]. Size match of the dopant with the host has been a main criterion in selecting the dopant for ceria. The ionic radius of Sr$^{2+}$ (1.26 Å) is close to that of Ce$^{4+}$. Hence, Sr$^{2+}$ can be a good divalent dopant for ceria from the alkaline earth series [11]. Sr$^{2+}$ suppresses the ordering of oxygen vacancies to decrease the activation energy for migration of O$_2$ ions leading to increase conductivity. Partial substitution of Sr$^{2+}$ lowers the binding energy of O$_2$ as compared to that of CeO$_2$. This decreases the activation energy for diffusion of oxygen ion leading to increase in the conductivity [12]. Kim et al. [13] studied the scavenging effect of SrO and observed that Sr$^{2+}$ acts as grain growth inhibitor. Sr$^{2+}$ reacts with SiO$_2$ and resultant material gathers at triple phase junction as a result reduces the grain boundary resistance. Solubility limit of Sr$^{2+}$ in ceria ranges between 5 and 10 mol%. Although many co-doped ceria materials have been investigated, such as Ce$_{1-x-y}$Gd$_x$Pr$_y$O$_{2+$δ}, Ce$_{1-x-y}$Sm$_x$La$_y$O$_{2+$δ} [15], Ce$_{1-x-y}$Y$_x$La$_y$O$_{2+$δ} [16], and Ce$_{1-x-y}$Gd$_x$Sm$_y$Y$_2$O$_{12+$δ} [17], etc., no systematic studies were done. Here we present the effect of (Sr$^{2+}$), (Gd$^{3+}$) co-doping in ceria. We have selected divalent (Sr$^{2+}$) and trivalent (Gd$^{3+}$) as co-dopants because average radii of the do-pants will become close to the critical radii and average binding energy will be lowered as proposed for multiple doping. Ce$_{0.8}$-Gd$_{0.2}$O$_{1.9}$Sr$_x$ (x = 0, 0.005, 0.01, 0.02) which were prepared by solid state method. The results of the properties such as structural, morphological and electrical properties of Sr$^{2+}$-doped GDC system are discussed.

2. Experimental

GDC (99.9% pure, 40nm particle size, Cotter International, India) and SrCO$_3$ (AR grade Sigma Aldrich USA, 99.9% purity) were used as starting materials. The powders of GDC and SrCO$_3$ were mixed in required stoichiometric proportion (0.5, 1 and 2 mol% of SrCO$_3$). The mixture was ground in agate and mortar for 2 hours and calcined at 800$^\circ$C for 2 hours. 2 wt% of polyvinylpyridine was added to the powder as binder and was mixed thoroughly. All the samples were uniaxially pressed to obtain a disc shaped pellets and sintered at 1400$^\circ$C for 2 hours in air at ramp of 2$^\circ$C/minute and cool down to room temperature by the same ramp. The synthesized pellets were characterized using X-ray diffraction (Philips X-ray diffractometer), Scanning Electron Microscopy (ZEISS EVO® series SEM) and Raman Spectroscopy.
3. Results and discussion
3.1. XRD analysis

The XRD patterns of Sr\(^{2+}\) doped GDC and pure GDC sintered at 1400°C for 2h are shown Fig 1. The XRD patterns of Sr\(^{2+}\) doped GDC samples are similar to that of pure GDC structure. These patterns confirm that all the compositions show single phase cubic fluorite structure with space group Fm\(3m\) (JCPDS No 81-0792).

![XRD patterns of Sr\(^{2+}\) doped GDC and pure GDC](image)

**Fig. 1** XRD patterns of (a) GDC and (b) 0.5, (c) 1, and (d) 2 mol % Sr\(^{2+}\) doped GDC pellets sintered at 1400°C for 2h.

All the samples show the presence of highly intense (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (3 3 1) diffraction peaks in the scanning range 20 to 80°. No other phases were detected in the Sr\(^{2+}\) doped GDC samples. With doping of Sr\(^{2+}\) the peaks are shifted towards higher angle side compared to pure GDC.

**Table 2** Structural parameters of Sr\(^{2+}\) doped GDC samples

| Composition         | Crystalline size (nm) | Lattice Constant (Å) | Structure | Density% |
|---------------------|-----------------------|----------------------|-----------|----------|
| GDC 1400            | 23.24                 | 5.401                | Cubic     | 95       |
| 0.5 mol% Sr\(^{2+}\) doped GDC | 32.88                | 5.425                | Cubic     | 94       |
| 1 mol% Sr\(^{2+}\) doped GDC | 44.31                | 5.427                | Cubic     | 91       |
| 2 mol% Sr\(^{2+}\) doped GDC | 46.58                | 5.429                | Cubic     | 91       |

The variation of lattice constant with composition values are placed in Table 2. The substitution of Sr\(^{2+}\) in GDC results in the increase of lattice parameters when compared with pure GDC. However, the addition Sr\(^{2+}\) concentration in pure GDC results into a slight change in lattice parameter due to larger radius of Sr\(^{2+}\) (1.26 Å) than Ce\(^{4+}\) (0.97 Å) and the bond length of the ceria matrix (Ce-O/Ce Cations) was stretched by substitution of strontium whose binding energy of lattice with oxygen ion is lower than the ceria matrix. Doping of Sr\(^{2+}\) in ceria lattice will induce a
homogeneous strain in the lattice as the material is elastically deformed. There is no indication of presence of secondary phase formation as a result of Sr$^{2+}$ addition, suggesting its dissolution in the ceria lattice [18]. It is pragmatic that crystalline size increased with increasing Sr$^{2+}$ concentration when comparing with pure GDC range from 23-46 nm due to effect of co-doping of Sr$^{2+}$ in GDC. The densities of all these samples were measured by Archimedes principle and found density range 90-95% of the theoretical density.

3.2. Morphological studies

Micro structural morphologies of the specimens of GDC and Sr$^{2+}$-GDC (0.5 mol%, 1mol%, 2 mol%) studied by SEM as shown in Fig. 2(a-d). All the grains are almost uniformly homogeneous, with very less pores within, which indicate the suppression of inter-particle porosity and inter-agglomerate porosity was observed, by increasing concentration of Sr$^{2+}$. These results in all the samples are consistent with measured densities of the sintered pellets [19].

![Fig. 2 Surface morphologies of (a) GDC, (b) 0.5, (c) 1 (d) 2 mol % Sr$^{2+}$ doped GDC pellets sintered at 1400°C for 2h](image)

The grain size of the specimens of 0.5 mol% Sr$^{2+}$ doped GDC has highest value of (4.3 μm. Further increase of Sr content, the grain size decreases (1.421 for 1 mol% of Sr$^{2+}$ and 0.868 for 2 mol% of Sr$^{2+}$). This result implies that there is a correlation between the characteristics of oxygen vacancy and grain size in the specimens. Doping strontium into ceria increases the number of oxygen vacancies and decreases the amount of grain boundary, hence we can expect enhancing of the ionic conductivity of the co-doping ceria system [20]. The gradual decrease of grain size by increasing concentration of Sr$^{2+}$ is due to Sr$^{2+}$ as it controls the grain growth and acts as a grain growth inhibitor (Decreased grain size more grains as well as grain boundaries in unit area ) [21].

3.3. EDAX

The EDAX spectra shown in Fig 3(a-d) gives the distribution of elements in the composition, and the presence of Ce$^{4+}$, Gd$^{3+}$, O and Sr$^{2+}$ in all the compositions. Ce$^{4+}$, Gd$^{3+}$, O$^2$ and Sr$^{2+}$ ions were almost fully dissolved into the CeO$_2$ matrix, which was confirmed by EDS.
3.4. Raman Analysis

Fig. 3 EDX spectra of (a) GDC and (b) 0.5, (c) 1, and (d) 2 mol % Sr$^{2+}$ doped GDC pellets sintered at 1400 °C for 2h.

Fig. 4. Raman spectra of (a) GDC powder and (b) 0.5, (c) 1, and (d) 2 mol % Sr$^{2+}$ doped GDC pellets sintered at 1400 °C for 2h.

Raman spectra of GDC and Sr$^{2+}$-GDC (0.5 mol%, 1 mol%, 2 mol %) samples are shown in Fig. 4. All the sintered pellets (0.5, 1, 2 mol% Sr$^{2+}$) exhibited typical structure of ceria. There is a clear vibrational mode at the main peak at 462-474 cm$^{-1}$ attributed to the raman mode (F2g) of the fluorite-type structure [22]. The Raman spectra pertaining to the fluorite-type structures is dominated mainly
by oxygen lattice vibrations which are sensitive to the crystalline symmetry. The O- vacancies mode is shown at 559.3 cm$^{-1}$ representing the same compensating defects as for rare earth doped ceria [23].

**4. Conclusions:** Sr$^{2+}$ doped GDC solid electrolytes are successfully synthesized by solid state reaction method. The XRD study reveals cubic structure lattice parameter as well as crystallite size increases with increasing Sr$^{2+}$ content. The grain size is 1.72 $\mu$m for pure GDC and for 0.5mol% Sr is 4.300 $\mu$m. Further addition of Sr$^{2+}$, the grain size decreased to 1.42 $\mu$m for 1mol% Sr$^{2+}$ and 0.868 $\mu$m for 2mol% Sr. Raman spectra show the presence of band at 471 cm$^{-1}$ corresponding to CeO$_2$ and SrO were absent.

**References**

[1] Sammes N M and Cai Z Ionic, 1997*Solid State Ionics* **100**: 29-39-44
[2] Kim D J, 1989 *J. Am. Ceram. Soc.* **72** 1415–1421
[3] Moure A, Moure C, Tartaj J, 2011 *J. Power Sources* **196** 10543-10549.
[4] H. Yoshida, H. Deguchi, K. Miura, M. Horiuchi, 2001 *Solid State Ionics* **140** 191
[5] Minervini L, Zacate M O and Grimes R W 1999 *Solid State Ion* 116- 339
[6] Yahiroy H, Eguchi K and Arai H1989 *Solid State Ion* **36** 71
[7] Kim D J 1989 *J. Am. Ceram. Soc.* **72** 1415
[8] Zhang T, Zeng Z, Huang H, Hing P and Kilner 2002 *J Mater Lett* **57** 124
[9] Tianshu Z, Hing P, Huang H and Kilner 2001 *J Mat Sci Eng B* **83** 235
[10] Kleinlogel C, Gauckler L J 2000 *Solid State Ionics* **135** 567
[11] T.H. Yeh, C.C. Chou, 2007 *Phys. Scr.* T **129** 303-307
[12] D.-J. Kim, 1989J. Am. Ceram. Soc. **72** 1415–1421
[13] Y.H. Cho, P.S. Cho, D.K. Kim, J.H. Lee, D.Y. Kim, et al.2007 *Acta Mater.* **55** 4807
[14] S. Lubke, H.-D.Wiemhofer,1999 *Solid State Ionics* **117** 229.
[15] H. Yoshida, H. Deguchi, K. Miura, M. Horiuchi, 2001 *Solid State Ionics* **140** 191.
[16] H. Inaba, H. Tagawa, 1996 *Solid State Ionics* **83** 1
[17] J.V. Herle, D. Seneviratne, A.J. McEvoy,1999 *J. Eur. Ceram. Soc.* **19** 837
[18] R.D. Shannon, 1976 *Acta Crystallogr.* A **32** 751–767.
[19] Tsung-Her Yeh and Chia-Chen Chou,2007 *Phys. Scr.* **129** 303–307.
[20] Renjie Zhou, Yunfei Bu, Dandan Xu and Qin Zhong, 2014 *Int. J. Ionics* **20** 721–727.
[21] José Márcio Siqueira Júnior and Marta Eloisa Medeiros, 2012 *Mater. Chem. Phy.* **135** 957-964.
[22] M.J. Godinho, R.F. Gonçalves, E.R. Leite, 2007 *Materials Letters* **61** 1904–1907
[23] Jose Marcio Siqueira Junior, Luiz Fernando Brum Malta, 2012 *Materials Chem. Phy.* **135** (2-3)