A Synthesis and Characterization of GD and SR Co-Doped Ceria Electrolytes for LT- SOFC Application

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Abstract - *The energy demand of the world is growing continuously. Current energy production is through the non-renewable source of energy that is going to deplete in a few years, along with that, there is an adverse effect of the exhaust gases liberated from the use of non-renewable energy sources. So, scientists and engineers are finding out different alternatives and finding different ways to use renewable energy sources. In the last few decades, tremendous efforts have been made to use hydrogen as fuel to produce electrical energy by using Solid Oxide Fuel Cells (SOFC). As SOFC has very high energy conversion efficiency (nearly 80%) without exhaust pollutants. But, the major barrier for commercialization in SOFC is its high operating temperature (around 1200^{0}C) of electrolyte. Yttria stabilized zirconia (YSZ) shows very good performance above 1000^{0}C. So, alternatives such as doped ceria show very high conductivity at many low temperatures with rare earth dopants. So, in the current study Strontium and Gadolinium rare earth elements are doped in fluorite structured ceria and their properties are evaluated in 500^{0}C to 1000^{0}C.*

Key Words: LT-SOFC, Ion Conductivity, fluorites, co-precipitation, co-doped ceria, electrolyte.

1. INTRODUCTION

In the past few decades, hydrogen renewable energy source has been found to be the most promising source of energy in a fuel cell without harmful emission from it. Out of all available fuel cells SOFC have high energy conversion efficiency (nearly 80%) [1]. Commercialization of the SOFC is hindered by its high operating temperature [2]. Many scientists and engineers had brainstorming research to reduce the working temperature. Yttria Stabilized Zirconia (YSZ) which is having promising ionic conductivity at high temperatures (1000^{0}Cto1200^{0}C) is replaced with fluorite structured doped ceria [3], [4]. Doped ceria of a few micron thicknesses has high ionic conductivity in intermediate temperature (500^{0}C to 800^{0}C) in practical [5], [6]. However, doped ceria is mixed ionic and electronic (MIEC) conductor due to the reduction of Ce+4 to Ce+3 partially [7]. Various dopants such as Sr+2, Ca+2, Y+3, La+3, Gd+3, and Sm+3 are used with a different percentage in the host ceria. Sm+2 doped ceria is a promising electrolyte in IT applications [8]. Now, research has been moved towards the use of more than one dopant in host ceria and analyzing its conductivity in IT. Although, there is a different alternative to do so by making composite or single-phase pure double doped ceria [9]. In order to synthesize the doped ceria, assorted routes are developed, such as combustion technique, sol-gel method, hydrothermal process, and co-precipitation. Even so, all these ways suffered from complex processes, high cost with very low yield [10]. Out of all, the Co-precipitation method is a simple and cost-effective one.

In present study agglomerate precipitate powders of $Ce_{0.8}(Sr_{1-x}Gd_x)_{0.2}O_{2-\delta}$ (SGDC) for (x= 0.0, 0.25, 0.5, 0.75, 1) produced through oxalate co-precipitation route. The crystal structure of SGDC is analyzed through high-resolution X-ray spectroscopy. Surface morphology of SGDC is applied to analyze dopant percentage and atomic weight variation of dopant in host ceria.

2. EXPERIMENTATION

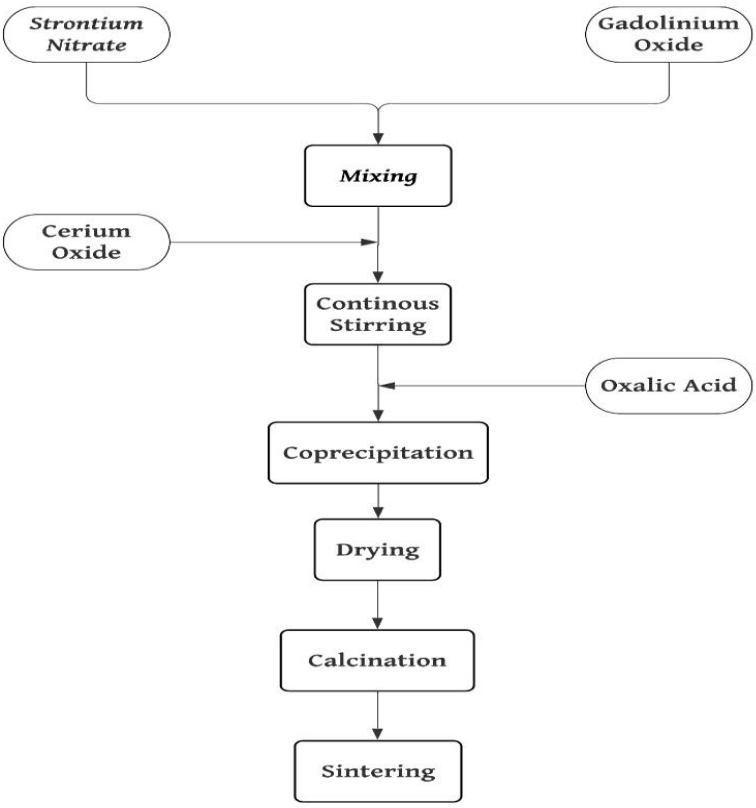
Strontium and Gadolinium doped ceria is prepared through the co-precipitation method and five compositions are named as in table 1. The chemicals used are, Gadolinium Oxide (Gd_2O_3), Strontium Nitrate ($Sr(NO_3)_2$), Cerium Nitrate ($Ce(NO_3)_3.6H_2O$), and Oxalic Acid powder ($C_2H_2O_4.2H_2O$) for the synthesis of SGDC powders. The processes and the experimental setup involved in the Co-precipitation method are shown in figure 1.

Table 1: DGDC Samples Names and their Compositions

Sample Name	Composition
SGDC-0	$Sr_{0.2}Ce_{0.8}O_{2-\delta}$
SGDC-5	$Sr_{0.15}Gd_{0.05}Ce0_{.8}O_{2-\delta}$
SGDC-10	$Sr_{0.1}Gd_{0.1}Ce0_{.8}O_{2-\delta}$
SGDC-15	$Sr_{0.05}Gd_{0.15}Ce0_{.8}O_{2-\delta}$
SGDC-20	$Gd_{0.2}Ce0_{.8}O_{2-\delta}$

Gadolinium oxide (Gd_2O_3)was nitrated with concentrated Nitric acid (HNO_3) and these nitrated cations dissolved in distilled water to prepare 0.05M solution. Strontium Nitrate ($Sr(NO_3)_2$) was diluted with distilled water directly to prepare 0.05M solution. The 0.05M solution of cerous nitrate ($Ce(NO_3)_3.6H_2O$) mixed directly with 0.05M nitrated cation solutions and then drop wise addition of 0.05M oxalic acid($C_2H_2O_4.2H_2O$) solution was done (precipitating agent) on a magnetic stirrer. The speed of magnetic stirrer was maintained at 1000 RPM.

Fig-1: Block Diagram of Co-precipitation Method



Various samples of powder were prepared by mixing the strontium nitrate and gadolinium Oxide in different proportions. The five different proportions are tabulated in table 2.

Table- 2: Five different proportions of Gadolinium and Strontium to manufacture Gd and Sr Co-doped electrolyte material

Sample	Gadolinium Oxide (Gd_2O_3) in gm	Strontium Nitrate ($Sr(NO_3)_2$) in gm	Cerium Nitrate ($Ce(NO_3)_3$) in gm	Composition
SGDC-0	0	0.8465	6.9476	$Sr_{0.2}Ce_{0.8}O_{2-\delta}$
SGDC-5	0.3625	0.6349	6.9476	$Sr_{0.15}Gd_{0.05}Ce0_{.8}O_{2-\delta}$

SGDC-10	0.7250	0.4233	6.9476	$Sr_{0.1}Gd_{0.1}Ce0_{.8}O_{2-\delta}$
SGDC-15	1.0875	0.2116	6.9476	$Sr_{0.05}Gd_{0.15}Ce0_{.8}O_{2-\delta}$
SGDC-20	1.4500	0	6.9476	$Gd_{0.2}Ce0_{.8}O_{2-\delta}$

In agglomeration reaction precipitate of $Ce_{0.8}(Sr_{1-x}Gd_x)_{0.2}O_{2-\delta}$ for (x= 0.0, 0.25, 0.5, 0.75, 1.0) were formed. Precipitates were then heated on hot plate for 1 hour at 100°C to remove water from solution. The dried precipitates are then calcined at 700°C for 2 hours in a muffle furnace to obtain dense composite powders.

The obtained powder is pressed into a pellet (9.5mm-diameter and 1mm-thickness) on power press by applying10 tons cm^{-2} pressure for 25 minutes. The phase purity and crystal structure were examined by x-ray diffraction (XRD) with a Bruker D8 advance x-ray diffractometer using CuKα radiation (k = 1.5418 A °) in the 2Θ range from 20° to 80°. The stoichiometric cation distribution in the sample was confirmed by energy-dispersive x-ray spectroscopy (EDXS).

3. RESULT AND DISCUSSION

3.1 Phase Analysis

Phase formation of the calcined oxide powder was determined by X-ray diffraction (XRD) analysis using CuKα radiation at room temperature. Oxide powders were confirmed by XRD analysis to be single-phase fluorite structure. Chart 1 to 5 shows the X-ray diffraction (XRD) pattern of SGDC pellet $Ce_{0.8}(Sr_{1-x}Gd_x)_{0.2}O_{2-\delta}$ for (x= 0.0, 0.25, 0.5, 0.75, 1.0).

3.2 Particle Size Analysis

Chart 6 is the combined graph of SGDC powder at different compositions of Sr and Gd. The average particle size distribution for SGDC composite electrolyte can be calculated by analyzing charts 1,2,3,4 and 5. Particle size distribution suggests that obtained powder was in the range of angstroms. The average size distribution for SGDC electrolytes was 5.57 A^0 which is as per literature [5].

XRD pattern confirm the formation of cubic fluorite structure. No phase other than cubic fluorite structure was found in the XRD diffraction pattern. All peak positions are corresponding to cubic fluorite structure. Peaks of XRD pattern shift to lower angle with an increasing amount of Gd (corresponding decrease in Sr concentration) which is noticed in the chart 6. A small shift in peaks depending on dopant ion indicates the formation of single-phase solid solution with a marginal increase in lattice parameter [11].

Apart from average particle size confirmation, The XRD analysis also helps in the calculations of crystallite size and lattice parameters of five different samples of SGDC as shown in Table 3.

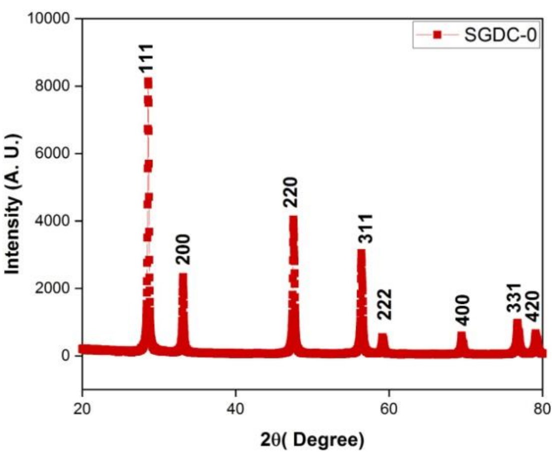


Chart-1: SGDC-0

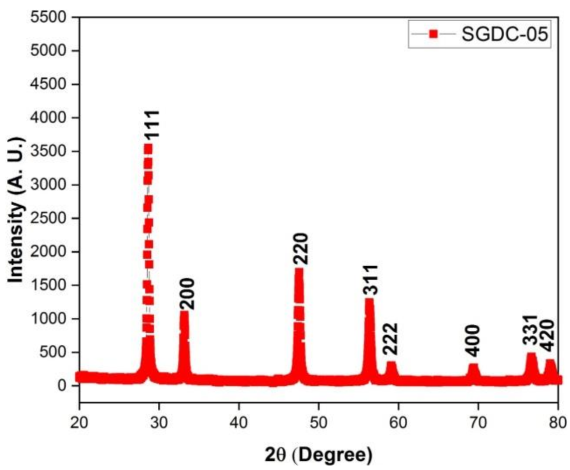


Chart-2: SGDC-05

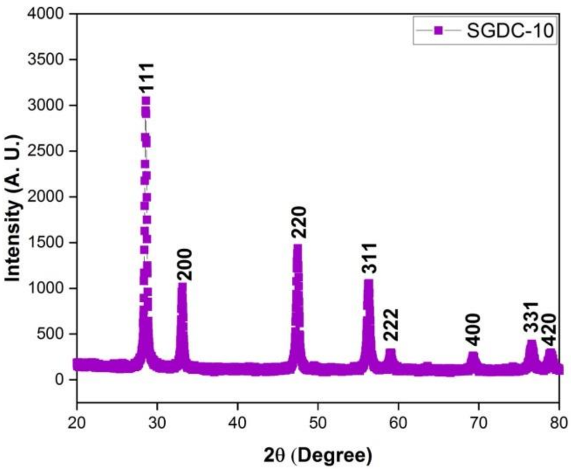


Chart-3: SGDC-10

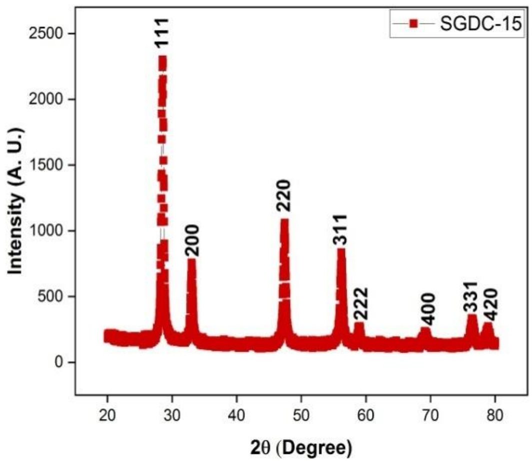


Chart-4: SGDC-15

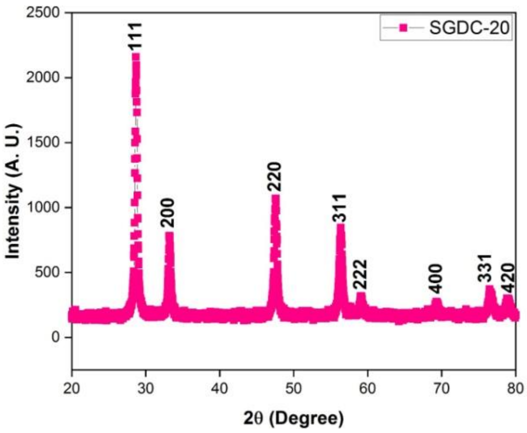


Chart-5: SGDC-20

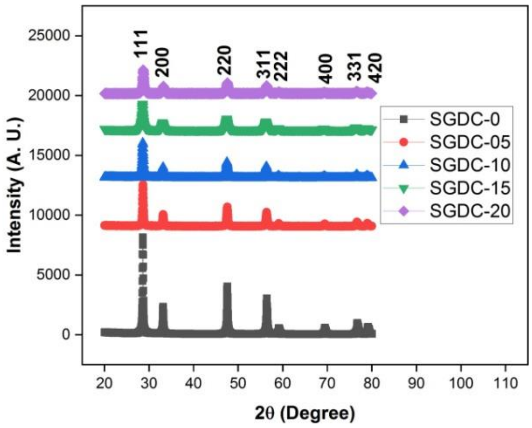


Chart-6: Combined Graph

Table-3: FWHM, Crystallite Size and Lattice parameters of $Ce_{0.8}(Sr_{1-x}Gd_x)_{0.2}O_{2-\delta}$ (SGDC) for (x = 0.0, 0.25, 0.5, 0.75, 1.0)

Sr. No.	Sample	2θ(deg)	FWHM (β) in deg	d(A°)	t(mm)	a(A°)
1	SGDC-0	28.5967	0.1498	3.2186	1207.9907	5.5748
2	SGDC-5	28.6395	0.1712	3.2142	1054.4228	5.5671
3	SGDC-10	28.5967	0.2140	3.2186	845.5935	5.5748
4	SGDC-15	28.5539	0.2782	3.2230	650.1919	5.5824
5	SGDC-20	28.6823	0.2568	3.2098	705.2364	5.5595

4. CONCLUSION

Author's successfully synthesized Powder of $Ce_{0.8}(Sr_{1-x}Gd_x)_{0.2}O_{2-\delta}$ (SGDC) in different compositions (x = 0.0, 0.25, 0.5, 0.75, 1.0) by co-precipitation method. From XRD information it is confirmed that no other phases than cubic fluorite are present and there are no impurities in the material. More compact structure is witnessed from the particle size so there will be more oxygen ion migration. For the composition with zero percentage of Gadolinium the particle size is 5.5748 A° and for the composition with zero percentage of strontium the particle size is 5.5595 A°. This implies that the composition with single dopant have smaller particle size than others. But, for the SGDC-10 composition not only the particle size is smaller 5.5748 A° but also both the dopants are available and that will create more dislocation defects and increases the conductivity. Hence, SGDC-10 is one of the best substitutes in the host ceria for more ion migration

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