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# Nanostructured Cerium oxide (Ceria): Electrolyte for IT-SOFC

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## Abstract

Mg and Sm co-doped ceria samples $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ (x = 0.00; 0.05; 0.1; 0.15, 0.175) successfully synthesized by Sol-gel route using citric acid as fuel. Sample pellets were sintered at 1300°C for 4h in air. Bulk density was determined by Archimedes method. X-ray diffraction confirms the single phase cubic fluorite structure. Relative found increasing with increasing Mg content in samarium doped ceria material. The Mg substitution has led to increase crystallite size as determined by XRD data using Scherer's formula. The alkali earth Mg can be used as sintering aid in ceria-based materials. Dense solid solution of ceria are good candidate electrolyte materials for IT-SOFC.

**Keywords:** Nanoparticles, Electrolyte, Cerium oxide (Ceria), X-ray diffraction.

## Introduction

Among the oxides of Lanthanides, the Cerium oxides (ceria, $CeO_2$) has got attention of researchers due to its exotic properties at nanoscale, that it can exist in two oxidization states, $Ce^{3+}$ and $Ce^{4+}$. It crystallizes in Face centered cubic fluorite structure with space group Fm3m. The Frenkel defects in ceria creates oxygen vacancies by introducing a foreign atom for host Ce atom, which are the sites of catalytic reactions and makes them candidate materials to be used as electrolytes of fuel cell, catalysts. Nanoparticles of Ceria has multienzyme, including oxidase, superoxide oxidase, and catalase, and have emerged as a fascinating material in biological fields, such as in antioxidants, Photocatalysis, bioanalysis, etc. The demand for clean energy can be met by Solid oxide fuel cells (SOFC) which has three important parts cathode, anode and electrolyte. The chemically stable electrolyte of SOFC should be dense, high ionic conductivity and zero electronic conductivity at elevated high temperatures and must have low Ohmic losses [1]. Nanostructured ceria has more surface to volume ratio and shows more open structure and shows more ionic conductivity. Ceria is preferred as SOFC electrolyte over Yittria stabilized Zirconia (YSZ) due to its stability and shows high ionic conductivity even at intermediate temperatures 600-800ºC compared to YSZ [2,3]. Ceria doped with alkali metal and rare earth lanthanide metals shows more open structure which further increase ionic conductivity [4]. The cost of raw electrolyte materials and its synthesis plays an important role, keeping this in mind the alkali earth metals are preferred over rare earth lanthanides as dopants nevertheless they are soluble in ceria.

Some of the alkali earth metal oxides used are CaO, MgO, SrO, rare earth oxides $Gd_2O_3$, $Sm_2O_3$ are soluble in ceria lattice. Various methods of synthesis are available for doped ceria includes solid state reaction

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method or ceramic method, hydrothermal, co-precipitation, solvo thermal, sol-gel method etc. The Magnesium doped ceria, calcium doped ceria, Gadolinium doped ceria (GDC), samarium doped ceria (SDC) synthesized by solid state reaction method was studied extensively for the effect of sintering temperature on density, porosity, structural and electrical properties [5-7]. Samarium is one of the best choice among the rare earth metals because it is easily soluble in ceria solid solution due to its close electro negativity and ionic radius to that of ceria [8]. In the present work sol-gel auto combustion methods, for two different ceria dopants and co-dopants have been discussed. Mg and Sr doped ceria, some samples have been prepared by solid state method and sintered at 1400ºC, while Mg and Sm co-doped with formula, $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ (x = 0.00; 0.05; 0.1; 0.15, 0.175) has been synthesized by Sol-gel process to study the effect of sintering temperature on density, structural, and optical properties.

## Experimental Method

For Solid state synthesis, commercially available powders of $CeO_2$, MgO and $SrCO_3$ (AR grade Sigma Aldrich USA, 99.9% purity) were used as starting materials. For Sol-gel synthesis of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$, analytical grade nitrates $Ce(NO_3)_26H_2O$, $Sm(NO_3)_36H_2O$, $Mg(NO_3)_36H_2O$ (99.99% pure) were used as starting materials. The metal nitrates were dissolved and mixed in 100ml de-ionized water in Pyrex beaker. Citric acid (reagent grade) was used as chelating agent and ethylene glycol as gel formation agent. During continuous heating on a hot plate and mixing at around 200°C combustion process occurred leaving a grey fluffy powder. The powder then grounded and pelletized in to disc shaped samples. The samples of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ (x = 0.00, 0.05, 0.1and 0.15) were sintered at 1300°C for 4 h in air. X-ray diffraction (XRD) of the pellet were performed by Shimadzu XRD 700 x-ray diffractometer using Cu Kα radiation (λ= 1.54Å). XRD data further used to confirm the phase and structural properties such as theoretical density and dislocation density.

## Results and Discussion

The bulk densities ($d_B$) of sintered samples were measured by Archenemies principle method. The X-ray diffraction (XRD) shown in figure 1, confirms the phase purity of the samples, $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ (x = 0.00; 0.05; 0.1; 0.15, 0.175) sintered at 1300°C. The samples reveal single phase fluorite cubic structure without any unclear reflections. The diffraction peaks corresponding to plane (111), (200) (220) (311) (222) (400) and (311) provide a clear evidence for the formation of single phase cubic fluorite structure (space group *Fm3m*) of $CeO_2$ JCPDS card No 34-0394 [9]. The Scherrer's formula, $D=\frac{0.9\lambda}{\beta Cos\theta}$ is used to calculate the crystallite size. where λ is wave length of x-rays (λ = 1.54Å), β is FWHM in radians and θ is the Bragg's diffraction angle [10,11]. The lattice parameter 'a' has been determined using formula $a=\frac{\lambda\sqrt{(h^2+k^2+l^2)}}{2\,Sin\theta}$, where λ is the wavelength of incident x-rays and (hkl) Miller indices of the plane. Theoretical x-ray density (dth) was determined by $d_{th}=\frac{nM}{a^3N_a}$, M is molecular weight, a is lattice constant, and Na is Avogadro's number. The percentage of relative density % $D_R$ was calculated using the relation $\%D_R = (d_b/d_{th}) \times 100$. It is observed that relative density increased with increasing Mg concentration indicating that the dense nature of samples. In our earlier studies [12] we observed that the density of ceria-based materials increase with increasing sintering temperature.

The average crystallite size found for $Ce_{0.8}Sm_{0.2}O_{1.9}$ sintered at 1300ºC was 7.14, it is observed that the Mg substitution in SDC has led to increase in the crystallite size. The substitution of smaller ionic radii dopants in ceria shrinks the lattice and hence the lattice parameter decrease according to Vegard's law. It is observed from the XRD pattern that the substitution of Mg in SDC led to shift in the peaks to higher angles, indicating that the lattice parameters are decreased. The lattice parameter, densities and crystallite size are summarized in table 1. The shift in the peaks is due to difference in ionic radii of dopants which produces a strain in the crystal. Since the ionic radius of Mg, $Mg^{2+}$ (0.72 Å) is less than that of Ce and samarium, $Ce^{4+}$ (0.97 Å) < $Sm^{3+}$(1.08 Å), a shift in the XRD peak towards right side has been observed, which indicates the decrease of lattice parameter 'a' as reported in our earlier work [10]. The variation in lattice parameter and $D_R$ are shown in figure 2.

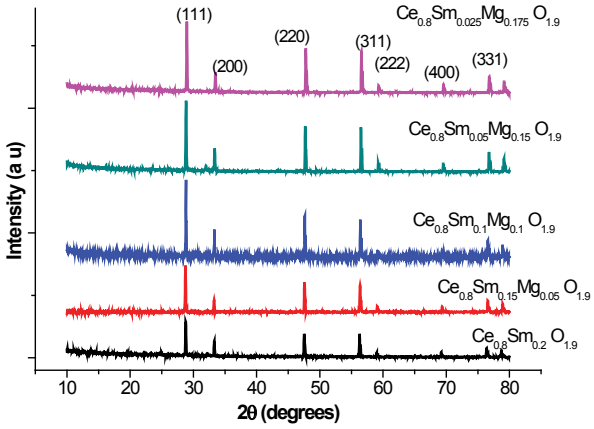


**Figure 1:** X-ray diffraction pattern of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ (x = 0.00; 0.05; 0.1; 0.15, 0.175) sintered at 1300°C.

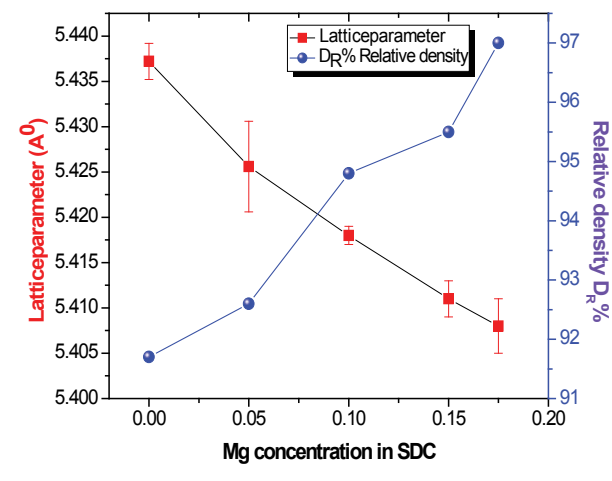


**Figure 2:** Variation of Lattice parameter and relative density DR with Mg concentration.

**Table 1:** Lattice parameter (a); Volume of unit cell; X-ray density ($D_x$); bulk density ($D_b$); % relative density ($D_R$) and Crystallite size (D) of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ (x = 0.00; 0.05; 0.1; 0.15, 0.175) sintered at 1300ºC.

| Sample Composition | a (Å) | Volume of unit cell (Å)$^3$ | $d_{th}$ (g/cm$^3$) | $d_b$ (g/cm$^3$) | % $D_R$ | D (nm) |
|---|---|---|---|---|---|---|
| $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ | 5.4372 | 160.7 | 7.129 | 6.542 | 91.7 | 7.14 |
| $Ce_{0.8}Sm_{0.15}Mg_{0.05}O_{2-\delta}$ | 5.4256 | 159.6 | 6.923 | 6.422 | 92.6 | 17.19 |
| $Ce_{0.8}Sm_{0.1}Mg_{0.1}O_{2-\delta}$ | 5.418 | 159.0 | 6.710 | 6.359 | 94.8 | 17.23 |
| $Ce_{0.8}Sm_{0.05}Mg_{0.15}O_{2-\delta}$ | 5.411 | 158.4 | 6.619 | 6. 3205 | 95.5 | 17.20 |
| $Ce_{0.8}Sm_{0.025}Mg_{0.175}O_{2-\delta}$ | 5.408 | 158.1 | 6.330 | 6.143 | 97 | 17.22 |

## Conclusion

The co-doping of Sm and Mg to ceria leads to change in densities, lattice parameter and crystallite size. The alkali earth metals can be used as sintering aid in ceria. XRD analysis reveals that the lattice parameter decreases, while relative density and crystallite increase with Mg concentration.

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