

Structural, Morphological, Electrical Properties of Mg and Sr Doped Ceria

Koteswararao P^{*a}, M. Buchi Suresh^b, Syed Ismail Ahmed^c, B. N. Wani^d, P. V. Bhaskara Rao^e

^aCentre for Nano Science and Technology, Jawaharlal Nehru Technological University, Hyderabad, Andhra Pradesh, India.

^bCenter for Ceramic Processing, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad, Andhra Pradesh, India.

^cDepartment of Basic Sciences – Physics Division, Ibn Sina National College, Jeddah, Saudi Arabia, Chemistry Division, Saudi Arabia

^dBhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra, India.

^ePhysics Department, St. Mary's Engineering College, Deshmukhi, R.R (DT), Hyderabad, Andhra Pradesh, India

ABSTRACT

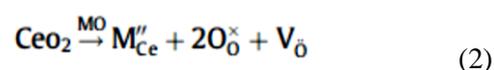
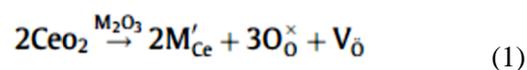
This paper reports the Strontium and Magnesium doped Ceria solid solutions ($Ce_{0.99}Sr_{0.01}O_{1.995}$ and $Ce_{0.99}Mg_{0.01}O_{1.995}$) were synthesized by solid state reaction method. The doped and un-doped CeO_2 samples were sintered at constant Temperature $1400\ ^\circ C$ to investigate their density, structural, morphological, electrical properties. The sintered densities of the samples are above 90%. XRD study reveals the cubic fluorite structure. SEM reveals that the synthesized samples the grains formed are of different size. The grain size depends on sintering temperature and of doping. The EDS spectra show that the samples are free of contaminants. FTIR study reveals well agreement with Pure CeO_2 . A.C. impedance spectroscopy was used to study the ionic conductivity of CeO_2 , $Ce_{0.99}Sr_{0.01}O_{1.995}$ and $Ce_{0.99}Mg_{0.01}O_{1.995}$ samples. The main aim is to study is ($Ce_{0.99}Sr_{0.01}O_{1.995}$ and $Ce_{0.99}Mg_{0.01}O_{1.995}$) compositions showed highest conductivity values than Pure Ceria sample for possible electrolyte for SOFC.

Keywords: Doped ceria, relative density, XRD, SEM, EDS, SOFC.

I. INTRODUCTION

Ceria based materials have been used as catalyst supports, CO reduction catalysts and solid oxide fuel cell (SOFC) Electrolytes because of its special properties than conventional Yttria Stabilized Zirconia (YSZ) such as high thermal stability, oxygen storage capacity and ion conductivity.[1-4].YSZ Commonly used as a electrolyte for Solid oxide fuel cells(SOFC) at high temperatures $1000\ ^\circ C$ which offers high cost, less cell operation life. Mainly Ceria based materials are used for reduction of operating temperatures below $600\ ^\circ C$ for Intermediate temperature SOFC. when Alivalent Cations (Ca^{+2} , Sr^{+2} , Ba^{+2} , Y^{+2} , Ln^{+3} , Sm^{+3} , Gd^{+3} , Nd^{+3} , doped with ceria shows strong candidate for electrolyte for SOFC because its ionic conductivity with low activation energy and its Stability from Room temperature to its melting temperature ($2300\ ^\circ C$) in addition that ionic radius of ceria matches (Sm^{+3} , Gd^{+3} ,

Etc) which creates vacancies leads increase ionic conductivity and less phase instability than un-doped ceria.[5]



Where the symbols are used in accordance with Kroger Vink notation of defects. M^1_{ce} stands for a trivalent ion on Ce^{4+} site, M''_{ce} stands for a divalent ion on Ce^{4+} site V_O is oxygen vacancy with doubly positive effective charge and O_O represents that oxygen ion on O^{2-} site being neutral. Rare earth oxides have high solubility in ceria. Jadhav et al. [6] studied the $Ce_{1-x}Gd_xO_{2-x/2}$ ($x = 0.30$) system which was synthesized by glycine–nitrate process and they found single phase formation in this system and the grain growth of sintered samples was observed to hindered with an increase in Gd content.

Kim et al. [7] studied the scavenging effect of SrO. It reacts with SiO₂ and the resultant material gathers at triple point junction of the grain boundaries. This reduces the grain boundaries resistance. However, only a few reports on MgO doped ceria exist in the literature. Limited solubility of MgO in ceria has been reported to be due to difference in ionic radius of Ce⁺⁴ (0.97 Å) and Mg⁺² (0.89 Å). Solubility of SrO in ceria is between 5 and 10 Mol% for similar reason (ionic radius of Sr⁺² is 1.26 Å) [8]. Ceria doped with alkali earth metals such as CaO and SrO has been studied extensively [9, 10] Ceria solid solutions with formula Ce_{1-x}M_xO_{2-δ}, where M is rare earth metal or lanthanides shows more open structure and more oxygen ion conductivity and are potential candidates as electrolyte for IT-SOFC. [11, 12] In order to explore simple and cheaper synthesis method of SOFC electrolyte and to study the structural, Morphological, Electrical Properties of un-doped and Mg and Sr doped ceria, some samples have been prepared and investigated.

II. METHODS AND MATERIAL

2. Experimental

2.1 Sample preparation:

Commercially available powders of CeO₂, MgO and SrCO₃ (AR grade Sigma Aldrich USA, 99.9% purity) were used as starting materials. The powders of CeO₂ and SrCO₃ were mixed in appropriate stoichiometric proportion to make (1 mole %) Ce_{0.99}Sr_{0.01}O_{1.995} composition. The mixture was grinded in agate and mortar to get a homogenized powder. The powder was calcinated at 800°C for 2 hours for decomposition of SrCO₃ and re grounded. 2 mole% of polyvinylperidine was added to the powder as binder and was mixed thoroughly. The powder sample was uniaxially pressed by a pressure of 10 tons/ sq inch to get a disc shaped pellets. Similarly Ce_{0.99}Mg_{0.01}O_{1.995} and un-doped CeO₂ pellets were prepared. The prepared pellets were sintered at 1400°C for 2 hours in air at ramp of 2°C/minute and cooled to room temperature by the same ramp. The prepared un-doped CeO₂, Sr doped and Mg Doped pellets were identified as CE14, SC14 and MC14 which have been sintered at temperature 1400°C used for characterization, results and discussion.

2.2 Characterization:

2.2.1 Density

The bulk densities (d_B) of sintered samples were measured by Archimedes principle method. The theoretical densities were measured by formula

$$d_{th} = \frac{4}{A^3 N_a} [0.99M_c + 0.01M + 1.995M_o] \text{-----(1)}$$

Where, M_c and M_o and 'M' are atomic wt. of ceria, oxygen and the dopants Sr and Mg, and A is lattice parameter.

2.2.2 Structure and morphology

The phase and structural properties of the sintered pellets were studied by powder X-ray diffraction (XRD) using Cu Kα radiation (λ=1.54 Å) radiation source at 40 kV and 30 mA. The crystalline size 'D' was measured

$$\text{by Scherrer's formula } D = \frac{0.94\lambda}{\beta \cos\theta} \text{-----(2)}$$

where β is FWHM of the peak and θ is Bragg angle. The Lattice parameter was calculated by using relation

$$a = d\sqrt{h^2 + k^2 + l^2} \text{-----(3)}$$

The sintered pellets were polished and gold coated for microstructure analysis using a scanning electron microscope (ZEISS Evo series SEM) at operating voltage 15 kV) equipped with an energy dispersive X-ray spectrometer (EDX) analyzer. The surface morphology was characterized by Scanning electron microscopy (. The grain size was measured from higher magnification SEM micrographs.

2.2.3 Impedance : The AC impedance spectra of the samples (CE-14, MC-14, SC-14) were recorded using Agilent precision impedance analyzer (4294 A) as a function of temperature (300–700 °C) in air in a measuring frequency range from 40 Hz to 1 MHz. Silver paste was brushed to each side of the samples, which was subsequently dried at 600 °C for 20 min, producing solid silver electrode on both sides of the pellet.

III. RESULTS AND DISCUSSION

Table 1 gives the relative densities of samples sintered at 1400°C temperatures. It is observed that the substitution of Sr in ceria leads to increase in

the density of ceria solid solution. The relative density is about 93% of theoretical density at temperature 1400°C for Ceria and 94% for strontium doped Ceria. The substitution and increase in the content of Sr in ceria [13] However in the case of Mg doped ceria (MC-14) no great change in density has been observed, probably because of its size mismatch and lesser atomic wt. Mg(0.79A) and Ce(0.97A). It is evident from Fig 1.a)

Table-1 Sample identification and densities

Sr no.	Sample Code	Temperature (°C)	Composition	d _m (g/cc)	d _{th} (g/cc)	% relative density
1	CE 14	1400	CeO ₂	6.680±0.022	7.186	93
2	SC 14	1400	Ce _{0.99} Sr _{0.01} O _{1.995}	6.591±0.027	7.013	94
3	MC 14	1400	Ce _{0.99} Mg _{0.01} O _{1.995}	6.550±0.021	7.122	92

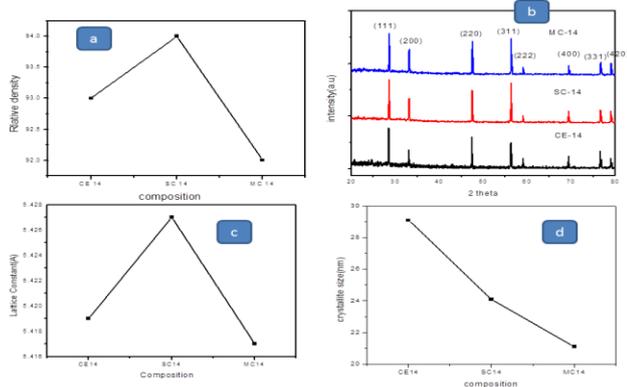


Figure 1. a) Relative density Vs. composition
b) XRD patterns of Ce-14, SC-14, and MC-14
c) Lattice constant Vs. composition
d) crystallite size Vs composition

b) shows X-ray diffraction patterns obtained for CE14, SC14 and MC14 are shown in Fig3. All the samples were in single phase fluorite structure. The results were compared with JCPDS card no. 81-0792. The samples shows the presence of (111) (200) (220) (311) (222) (400) and (331) diffraction peaks in the scanning range of $2\theta = 20 - 90^\circ$. The crystalline size and lattice parameters were calculated using eq (2) & eq (3) Table-2 Lattice parameters, grain size and crystallite size of samples sintered at 1400°C. It is evident from Fig 1.b), the (111) diffraction peak shifts angle due to Mg and Sr comparing to Pure ceria due to mismatch of Ionic Radius Ce (0.97A) and Sr (1.21A) than Mg(0.79A). The

lattice parameters increased for Sr doped ceria due to Sr Ionic radius is greater than Ceria as result Lattice expansion take place comparing MC-14(It is evident from Fig3.c). The deviation of lattice parameter Δa ($\Delta a = |a_{CE} - a_{doped}|$) from undoped ceria CE14 was found maximum (0.008) for SC14 and minimum for MC14 as shown in Fig.3.d). The crystal size ranges from 29 to 21 nm was observed.

The micro structures of the sintered pellets are shown in the Fig 5. No pores are observed in high temperature sintered sample which is consistent with their measured densities. The linear intercept method was applied and higher magnification micrographs were used to measure the grain sizes. The average grain size for CE14 was 5.5 μm and that of SC14 was 3 μm. It is evident that the, substitution of Sr in Ceria lattice decreases the grain size which may be due to mismatch of size of atomic radii of Ce⁺⁴ and Sr⁺². But in case of Mg doped ceria the grain size (6.3 μm) increases, it could be due to r_{Mg} (0.72A) < r_{Ce} (0.96A).

Table-2. Lattice parameters, grain size and crystallite size of samples sintered at 1400°C

Sr. no	Sample	Crystallite size (nm)	Lattice parameter (Å)	Grain Size (μm)
1	CE-14	29.08	5.419	5.5
2	SC-14	24.08	5.427	3.0
3	MC-14	21.11	5.417	6.3

Microstructure:

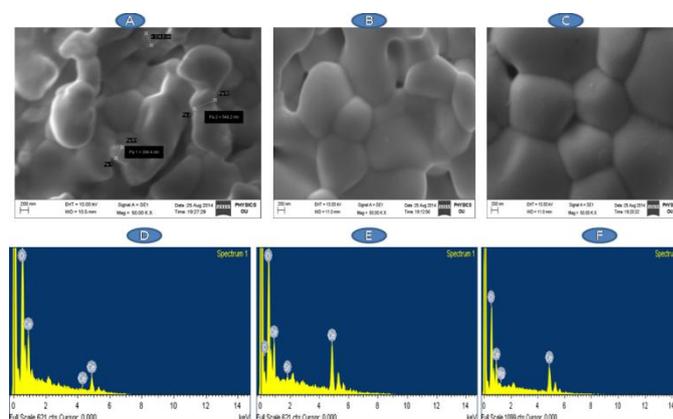


Figure 2. a) (A,D) SEM,EDAX of CE-14,b)(B,E) SEM,EDAX OF SC-14,c)(C,E) SEM ,EDAX OF MC-14

FIG -2 Shows micro structures of the sintered pellets are shown in the Fig 4. All samples shows homogenous and less porosity observed which is consistent with their measured densities. The linear intercept method was applied and higher magnification micrographs were used to measure the grain sizes. The grains observed were of varying size. The average grain size for CE14 was 5.5 μm and that of SC14 was 3 μm . It is evident that the, substitution of Sr in Ceria lattice decreases the grain size which may be due to mismatch of size of atomic radii of Ce^{+4} and Sr^{+2} and Sr acts as a grain growth inhibitor. Grain boundaries are regions of high energy because of disordered present in them. Therefore, the dopant ions can be accommodated in the grain boundaries with minimum expenditure of extra energy i.e. dopants tends to segregate to the grain boundaries. This needs, however, to be confirmed using EDAX. The reason for increasing the grain size for the sample CM14 is not clear. But in case of Mg doped ceria the grain size (6.3 μm) increases, it could be due to r_{Mg} (0.72A) $<$ r_{Ce} (0.96A). However as sintering temperature increases an increment in the grain size was observed.

FTIR:

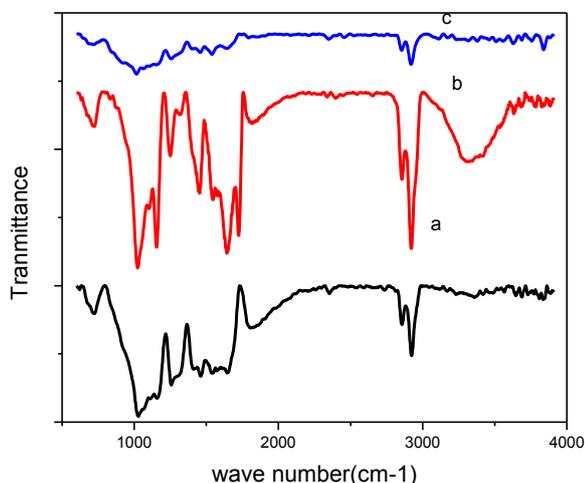


Figure 3. FTIR spectrum of pure CE-14, MG-14, SC-14

The observed band positions are in good agreement with the earlier reported values on similar systems [14]. The FTIR spectrum of the ceria exhibits strong broad band at 720 cm^{-1} due to the δ (Ce–O–C) mode. The peaks at 2348 and 2920 cm^{-1} are due to the CH_2 vibrations. In the FT-IR spectrum the peaks at about 1542, 1256, 1160 and 1028, cm^{-1} are similar to those of commercial CeO_2

powders and CeO_2 nano particles 720, 1028, 1160, 1256, 1461, 1542, 1645, 1806, 2348, 2855, 2920, 3360 The characteristic absorption band of CeO_2 is observed at 1461 cm^{-1} , which was attributed to the stretching vibration of Ce-O. The broad absorption band around 3430 cm^{-1} is designated to O–H stretching mode of hydroxyl group and another broad peak at 1645 cm^{-1} is also due to δ (OH) vibration. [15].

Electrical Properties

A.C. impedance spectroscopy is an important tool to study the electrical properties of solid electrolytes and to study the grain, grain boundary and electrode contribution to the overall ionic conductivity. High frequency semi-circle corresponds to grain resistance (R_g), intermediate frequency semi-circle corresponds to grain boundary resistance (R_{gb}) and low frequency incomplete arc corresponds to electrode resistance (R_e). In general, the total conductivity (σ_t) of rare-earth element doped ceria is the sum of ionic conductivity (σ_i) and electronic conductivity (σ_e). The main contribution of the conductivity of ceria-based compounds in air is the ionic conductivity and contribution of the electronic conductivity is negligible ($\sigma_i \approx 10^{-2}$ S/cm; $\sigma_e \approx 10^{-5}$ S/cm $<$ 800°C)

In general, the total conductivity (σ_t) of rare-earth element doped ceria is the sum of ionic conductivity (σ_i) and electronic conductivity (σ_e). The main contribution to the conductivity in ceria-based compounds in air is the ionic conductivity and contribution of the electronic conductivity is negligible ($\sigma_i \approx 10^{-2}$ S/cm; $\sigma_e \approx 10^{-5}$ S/cm $<$ 800 °C). The contributions by grain, grain boundary and electrode to the overall ionic conductivity can be estimated by recording ac impedance spectrum. The sample total resistance, R_t can be obtained from impedance spectroscopy at different temperatures as,

$$R_t = R_g + R_{gb}$$

The total electrical conductivity σ was then calculated using equation,

$$\sigma_t = \frac{1}{R_t} * \frac{l}{A}$$

Where l is the thickness, A is the cross sectional area of the sample.

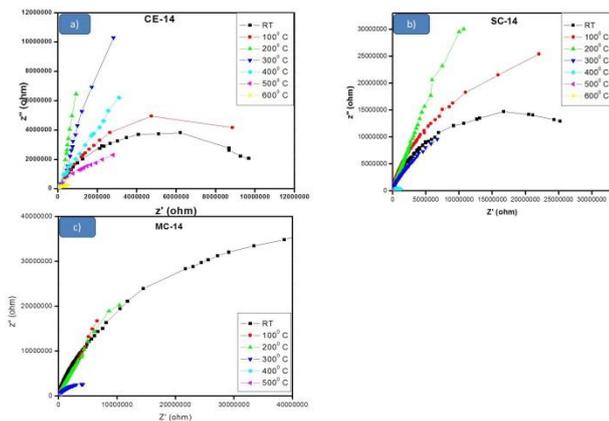


Figure 4. a) Nyquist Plots of CE-14, SC-14, MC-14

Table-3 Conductivity values of CE-14, SC-14, MC-14

Temperature range	Sample Code		
	CE-14	SC-14	MC-14
RT	1.45481E-08 S/Cm	7.2047E-09 S/Cm	3.69278E-06 S/Cm
100	1.46E-08 S/Cm	6.47E-09 S/Cm	2.36E-08 S/Cm
200	3.22E-06 S/Cm	9.86E-08 S/Cm	9.09E-09 S/Cm
300	4.51E-08 S/Cm	8.41E-08 S/Cm	1.9E-08 S/Cm
400	1.43E-10 S/Cm	1.05E-07 S/Cm	1.13E-06 S/Cm
500	6.96E-07 S/Cm	5.06E-06 S/Cm	8.44E-06 S/Cm
600	1.84E-06 S/Cm	2.08E-05 S/Cm	---

The conductivity was then calculated from resistance, thickness l , and cross

Sectional area A , samples by using this formula $\sigma = l/RA$. The respective values of the conductivities at different temperatures are given in the Table 3. From above table it is observed that after doping Mg and Sr shows higher than Pure ceria due to increasing of oxygen vacancies in Pure ceria crystal Lattice.

Increasing of conductivity or decreasing of conductivity depends on the following reasons:

Due to doping of Sr or Mg configurationally entropy originates. Due to partial substitution of Mg or Sr in CeO_2 , ordering of oxygen vacancies is suppressed. This leads to a decrease in the activation energy for migration of O^{-2} ions, leading to an increase in the conductivity.

Secondly, on substitution of Sr^{+2} , the binding energy of oxygen decreases as compared to that in CeO_2 . This decreases the activation energy for diffusion of oxygen ions, leading to an increase in conductivity.

The number of associated defect pairs increases with an increase in Sr^{+2} substitutions. This leads to a decrease in the ionic conductivity. The lattice parameter increases with increasing concentration of Sr^{+2} .

This increases the elastic strain in the lattice, leading to an increase in the activation energy for diffusion of O^{-2} ions. This causes a decrease in the conductivity.

IV. CONCLUSION

Doping of Sr and Mg to ceria leads to a change in densities, lattice parameter, and grain size. Alkali earth metals can be used as sintering aids in ceria. XRD analysis reveals a cubic fluorite structure. The grain size of cerium oxide decreases with the doping of Sr than Mg-doped ceria. All samples show above 90% density at 1400°C. Sr-doped ceria and Mg-doped ceria show maximum conductivity than pure ceria observed. However, increasing temperature shows conductivity increasing linearly.

V. ACKNOWLEDGEMENTS

The author is gratefully thanking to the "UGC-DAE CSR Mumbai Centre for providing sintering facility for my samples" and also thank you to Dr. Manojkothwale for his valuable suggestions.

VI. REFERENCES

- [1] A. Trovarelli, C. de Litterburg, M. Boaro, G. Dolcetti, Catal. Today 50 (1999) 353–367.
- [2] D. Waller, J.A. Lane, B.C.H. Steele, Solid State Ionics 86 (1996) 767–772.

- [3] T. Suratwala, R. Steele, M.D. Feit, L. Wong, P. Miller, J. Menapace, P. Davis, J. Non-Crystalline Solids 354 (2008) 2023–2037.
- [4] A. Tsoga, A. Gupta, A. Naoumidis, P. Nikolopoulos, *Acta Mater.* 48 (2000) 4709–4714
- [5] s.zha,c.xia,G.Meng,J.Power sources115(2003)44.
- [6] L.D. Jadhav, M.G. Chourashiya, A.P. Jamale, A.U. Chavan, S. P. Patil, Synthesis and characterization of nanocrystalline $Ce_{1-x}Gd_xO_{2-x/2}$ ($x = 0.30$) solid solutions, *J. Alloys Comp.* 506 (2010) 739–744.
- [7] Y.H. Cho, P.S. Cho, G. Auchterlonie, D.K. Kim, J.H. Lee, D.Y. Kim, et al., Enhancement of grain-boundary conduction in gadolinia-doped ceria by the scavenging of highly resistive siliceous phase, *Acta Mater.* 55 (2007) 4807.
- [8] H. Yahiro et al., Electrical properties and microstructure in the system ceria–alkaline earth oxide, *J. Mater. Sci.* 23 (1988) 1036–1041.
- [9] Ong PohShing, Mechanical synthesis and Characterization of Calcium doped Ceria oxide ion Conductor. *Material Science and Engineering* 17(2011).
- [10] Yamashita K, Hydrothermal Synthesis and Low temperature Conduction properties of substituted Ceria ceramic. *Solid State Ionics* 81(1995) 53-60
- [11] NandiniJaiswal, Devender Kumar, SahilUpadhyay ,Cerita doped with Calcium and Strontium (Sr) : A potential candidate for intermediate temperature fuel cell. *Ionics.* 20(2014) 45-54.
- [12] Chatchai Veranitisagul, Attaphon Kaewvilai, Worawata Wattanathana, Nattamon Koonsaeng, and ApiratLaobuthee, Electrolyte materials for solid oxide fuel cells derived from metal complexes: Gadolinia doped Ceria. *Ceramic International.*38 (2012)2403-2409.
- [13] NandiniJaiswal,Devender Kumar, SahilUpadhyay ,Cerita doped with Calcium and Strontium (Sr) : A potential candidate for intermediate temperature fuel cell. *Ionics.* 20(2014) 45-54.
- [14] Benson K Money, Ph.D. Thesis, Dept. of Physics, I.I.T. Madras, India, (2010).
- [15] S. Narender Reddy, Ph.D Thesis, Dept. of Physics, O.U, India (1990).