Chapter II

Objectives of the Work

Co-doping of ceria with two or more aliovalent cations was found to be a good approach to enhance its conductivity in the intermediate temperature range (500-700 ºC). Study of some rare earth co-doped ceria systems has been found in the literature. But rare earth ions are very costly. In the present work, in order to reduce the cost, rare earth ions are partly replaced by the alkaline earth ions. To increase the grains, grain boundaries as well as the total conductivity in the intermediate temperature range, some singly and doubly doped ceria solid electrolytes have been synthesized and characterized. For co-doping, cations have been chosen of different valencies to enhance the number of defects in the ceria lattice. The systems investigated are given below:

1. **$Ce_{1-x-y}La_xSr_yO_{1.925}$ (Total number of oxygen vacancies are fixed).**

Compositions	x and y	Abbreviations
$Ce_{0.85}La_{0.15}O_{1.925}$	x = 0.15, y = 0.00	CLO15
$Ce_{0.87}La_{0.11}Sr_{0.02}O_{1.925}$	x = 0.11, y = 0.02	CL11S2
$Ce_{0.89}La_{0.07}Sr_{0.04}O_{1.925}$	x = 0.07, y = 0.04	CL7S4
$Ce_{0.91}La_{0.03}Sr_{0.06}O_{1.925}$	x = 0.03, y = 0.06	CL3S6

2. **$Ce_{0.85}La_{0.15-x}Sr_xO_{\{2-(0.075+x/2)\}}$ (Total number of oxygen vacancies changed).**

Compositions	x and y	Abbreviations
$Ce_{0.85}La_{0.15}O_{1.925}$	x = 0.15, y = 0.00	CLO15
$Ce_{0.85}La_{0.125}Sr_{0.025}O_{1.9125}$	x = 0.125, y = 0.025	CL125S025
$Ce_{0.85}La_{0.10}Sr_{0.05}O_{1.9000}$	x = 0.10, y = 0.05	CL10S5
$Ce_{0.85}La_{0.075}Sr_{0.075}O_{1.8875}$	x = 0.075, y = 0.075	CL075S075

3. **$Ce_{1-x-y}Sm_xSr_yO_{1.90}$ (Total number of oxygen vacancies are fixed).**

Compositions	x and y	Abbreviations
$Ce_{0.80}Sm_{0.20}O_{1.90}$	x = 0.20, y = 0.00	SDC
$Ce_{0.82}Sm_{0.16}Sr_{0.02}O_{1.90}$	x = 0.16, y = 0.02	2SrSDC
$Ce_{0.84}Sm_{0.12}Sr_{0.04}O_{1.90}$	x = 0.12, y = 0.04	4SrSDC
$Ce_{0.86}Sm_{0.08}Sr_{0.06}O_{1.90}$	x = 0.08, y = 0.06	6SrSDC

4. **$Ce_{1-x-y}Ca_xSr_yO_{2-\delta}$ (Total number of oxygen vacancies changed).**

Compositions	x and y	Abbreviations
$Ce_{0.95}Ca_{0.05}O_{1.95}$	x = 0.05, y = 0.00	CCO5
$Ce_{0.94}Ca_{0.05}Sr_{0.01}O_{1.94}$	x = 0.05, y = 0.01	CC5S1
$Ce_{0.93}Ca_{0.05}Sr_{0.02}O_{1.93}$	x = 0.05, y = 0.02	CC5S2
$Ce_{0.92}Ca_{0.05}Sr_{0.03}O_{1.92}$	x = 0.05, y = 0.03	CC5S3

5. **$Ce_{0.90}Mg_{0.10-x}Sr_xO_{1.90}$ (Total number of oxygen vacancies are fixed).**

Compositions	x and y	Abbreviations
$Ce_{0.90}Mg_{0.10}O_{1.90}$	x = 0.10, y = 0.00	CMO10
$Ce_{0.90}Mg_{0.08}Sr_{0.02}O_{1.90}$	x = 0.08, y = 0.02	CM8S2
$Ce_{0.90}Mg_{0.06}Sr_{0.04}O_{1.90}$	x = 0.06, y = 0.04	CM6S4
$Ce_{0.90}Mg_{0.04}Sr_{0.06}O_{1.90}$	x = 0.04, y = 0.06	CM4S6

The objectives are as follows:

- To synthesize these compositions using citrate-nitrate gel auto-combustion route.
- To study the thermal behavior of the synthesized powders.
- To study the phase and crystal structure of the samples using XRD.

- To determine the % of theoretical density of the sintered specimens using Archimedes principle.
- To determine the theoretical values of lattice parameter of the system having one rare earth and one alkaline earth dopants in ceria to verify the experimental values and also to determine the radii of oxygen vacancies formed due to doping of divalent and trivalent cations.
- To study the microstructure and energy dispersive spectra of the sintered pellets employing SEM/EDX.
- To determine the electrical conductivity of the samples employing complex plane impedance analysis.
- To correlate the electrical behavior of the samples with the microstructure.

To further enhance the conductivity of co-doped ceria based electrolytes, nanocomposites of a few samples have been prepared. In the present work, the compositions which have highest total ionic conductivity in the series investigated have been chosen for the nanocomposites. Compositions for the nanocomposites are given below:

6. **$Ce_{0.89}La_{0.07}Sr_{0.04}O_{1.925}/(Li\text{-}Na)_2CO_3$ (CL7S4/LNCO)**

Compositions	**Abbreviations**
CL7S4/20 wt.% $(Li\text{-}Na)_2CO_3$	CL7S4/20LNCO
CL7S4/30 wt.% $(Li\text{-}Na)_2CO_3$	CL7S4/30LNCO
CL7S4/35 wt.% $(Li\text{-}Na)_2CO_3$	CL7S4/35LNCO

7. **$Ce_{0.85}La_{0.125}Sr_{0.025}O_{1.9125}$ /$(Li\text{-}Na)_2CO_3$ (CL125S025/LNCO)**

Compositions	Abbreviations
CL125S025/20 wt.% $(Li\text{-}Na)_2CO_3$	CL125S025/20LNCO
CL125S025/30 wt.% $(Li\text{-}Na)_2CO_3$	CL125S025/30LNCO
CL125S025/35 wt.% $(Li\text{-}Na)_2CO_3$	CL125S025/35LNCO

8. **$Ce_{0.82}Sm_{0.16}Sr_{0.02}O_{1.90}$/$(Li\text{-}Na)_2CO_3$ (SSDC/LNCO)**

Compositions	Abbreviations
SSDC/20 wt.% $(Li\text{-}Na)_2CO_3$	SSDC /20LNCO
SSDC/30 wt.% $(Li\text{-}Na)_2CO_3$	SSDC /30LNCO
SSDC/35 wt.% $(Li\text{-}Na)_2CO_3$	SSDC /35LNCO

9. **$Ce_{0.93}Ca_{0.05}Sr_{0.02}O_{1.93}$/$(Li\text{-}Na)_2CO_3$ (CC5S2/LNCO)**

Compositions	Abbreviations
CC5S2/20 wt.% $(Li\text{-}Na)_2CO_3$	CC5S2 /20LNCO
CC5S2/30 wt.% $(Li\text{-}Na)_2CO_3$	CC5S2 /30LNCO
CC5S2/35 wt.% $(Li\text{-}Na)_2CO_3$	CC5S2 /35LNCO

10. $Ce_{0.90}Mg_{0.06}Sr_{0.04}O_{1.90}/(Li\text{-}Na)_2CO_3$ (CM6S4/LNCO)

Compositions	Abbreviations
CM6S4/20 wt.% $(Li\text{-}Na)_2CO_3$	CM6S4 /20LNCO
CM6S4/30 wt.% $(Li\text{-}Na)_2CO_3$	CM6S4 /30LNCO
CM6S4/35 wt.% $(Li\text{-}Na)_2CO_3$	CM6S4 /35LNCO

The objectives are as follows:

- To prepare the nonocomposites by mixing nanocystalline co-doped ceria powders with binary mixture of carbonates.
- To study the thermal behavior of the synthesized composite powders.
- To study the phase and crystal structure of the composite powders using XRD.
- To determine the % of theoretical density of the sintered specimens.
- To study the microstructure and energy dispersive spectra of the sintered pellets employing SEM/EDX.
- To determine the electrical conductivity of the samples employing Complex plane impedance analysis.
- To correlate the electrical behavior of the samples with the microstructure.