Chapter IX

Conclusion and Scope for the Future Work

9.1 Conclusion

The aim of the present work was to replace the rare earth ions by alkaline earth ions to reduce the cost of the solid electrolyte as compared to using rare earth ions only as dopants and also to enhance the conductivity in the intermediate temperature range (500-700 °C). The compositions which have the maximum conductivity in the investigated series have been chosen to prepare the nanocomposites for use in LT-SOFCs. Following conclusion has been drawn from this study.

- All the samples of singly doped, co-doped ceria and ceria/carbonate nanocomposites prepared by citrate nitrate auto-combustion processing route show single phase formation having fluorite structure similar to ceria.

- In the ceria/carbonate nanocomposites, carbonates are present as an amorphous phase.

- Single phase doped and co-doped ceria samples have density more than 93 % and the composite samples have density in the range 82-85 % of the theoretical value.

- SEM micrographs of single phase ceria samples show a dense morphology with distinct grains and grain boundaries with average grain size in the range 1.0-5.0 µm.

- EDS spectrum of the doped ceria samples show the presence of SiO_2 at the grain boundary whereas in Sr co-doped samples SiO_2 is scavenged off and segregates at the triple point junction.

- In nanocomposites ceria grains are fully covered by the molten carbonate phase and the average grain size is in the range 100-150 nm.

- Impedance analysis has been employed to determine electrical conductivity of the ceria based solid electrolytes.
- Composition, $Ce_{0.82}Sm_{0.16}Sr_{0.02}O_{1.90}$ (2SrSDC) shows the highest ionic conductivity among all the series investigated. Its value is higher than the values reported for SDC and GDC.
- This may make 2SrSDC as a potential solid electrolyte for IT-SOFCs which will also reduce the cost as compared to SDC and GDC.
- Comparison of the conductivity in the compositions ($Ce_{0.85}La_{0.10}Sr_{0.05}O_{1.90}$, $Ce_{0.82}Sm_{0.16}Sr_{0.02}O_{1.90}$ and $Ce_{0.90}Mg_{0.04}Sr_{0.06}O_{1.90}$) having the same concentration of oxygen vacancies with respect to their effective radius ratio, effective ionic index, configurational entropy and activation energy is given as below in the Table 9.1.

Table. 9.1 Radius ratio (r_d/r_h), effective ionic index (E_i), configurational entropy (S), total conductivity (σ_t) at 600 °C and activation energy (E_a)

Compositions	r_d/r_h	E_i	S J/mol-K	σ_t (S/cm)	E_a (eV)
CL10S5	1.23	0.93	4.30	8.19×10^{-3}	0.98
2SrSDC	1.13	0.84	4.50	2.67×10^{-2}	0.66
CM4S6	1.15	0.85	3.26	5.26×10^{-3}	0.87

- It is noted from the Table. 9.1 that the compositions having the same number of oxygen vacancies follow the criteria of configurational entropy. Composition 2SrSDC has the highest value of S and hence shows the highest ionic conductivity with minimum activation energy of conduction.
- It is also concluded from the above mentioned data that any single criteria (radius ratio or effective ionic index or configurational entropy) is not sufficient to optimize the conductivity for any particular system.

- A jump in the conductivity plots has been observed in all the composites. This is called as superionic transition at the interfaces.
- The superionic phase transition is ascribed to the interfacial interaction between the two phases. This provides a high conducting path for diffusion of the ions.
- CTE values of the composite samples have been found to be the order of 10^{-6} /K in the temperature range 303-923 K.
- Conductivity of composites is more above the transition temperature and less below the transition temperature than that of the single phase ceria based electrolytes.
- Conductivity of the composite electrolytes has been found in the range 10^{-2}-10^{-1} S/cm with very low activation energy of conduction in the temperature range 450-500 ºC.
- Composition CM6S4/35LNCO shows the highest conductivity 0.4 S/cm at 500 ºC with an activation energy 0.23 eV among all the composites.
- This may make these electrolytes as a potential candidate for LT-SOFCs as these will be reduce the cost.

9.2 Scope for the future work

- HR-TEM equipped with EELS and STEM analysis of these samples will be useful to know the exact composition and morphology of the silicate phases at the triple points.
- Study of conductivity as a function of partial pressure of O_2 will be useful to find the partial pressure range of O_2 in which the conductivity will be only ionic in nature.
- Conductivity measurement in H_2 atmosphere is important to confirm the multi-ion conduction in the composites.
- Study of performance of single cell of these samples will be useful to confirm their suitability for use as potential electrolytes.