CHAPTER 6
SUMMARY AND SUGGESTIONS FOR THE FUTURE WORK

6.1 SUMMARY

The main objective of this work was related to the solid oxide fuel cell, especially ceria based electrolytes, the materials were synthesized by citrate nitrate auto-combustion method. The aim of the present investigation is to develop materials with increased oxygen vacancies and ionic conductivity with ceria-based composites by doping of rare earth elements such as Er, Nd, Pr, Sc, La, Yb and Y, for fuel cell applications.

Recently, many efforts have been committed for the preparation of rare-earth doped CeO$_2$ nanoparticles. Rare-earths doped ceria solid solutions can be synthesized by a variety of techniques such as the conventional ceramic route or chemical methods. In general, citrate nitrate auto-combustion (CNA) method has the advantage over conventional ceramic techniques. In this combustion technique, a principle of the propellant chemistry is used for a thermally induced redox reaction takes place between an oxidant and a fuel. Citrate nitrate auto-combustion synthesis is a very popular solution combustion method, where the fuel is citric acid and metal nitrates are used as metal and oxidant source. Also, the combustion technique is capable of producing highly pure, homogeneous and ultra-fine nanopowders at intermediate temperature. This method has the advantage of low cost, relative simplicity and no
supporting materials for sintering were included. Moreover, this method has proved to be quite effective in producing high sinterable ceramic powders.

In this work, the rare earth ions doped ceria (RE$_{3+}$:CeO$_2$) nanopowders such as (Ce$_{0.9}$La$_{0.1}$O$_{1.95}$), (Ce$_{0.9}$Sc$_{0.1}$O$_{1.95}$), (Ce$_{0.9}$Yb$_{0.1}$O$_{1.95}$), (Ce$_{0.9}$Er$_{0.1}$O$_{1.95}$), (Ce$_{0.9}$Nd$_{0.1}$O$_{1.95}$), (Ce$_{0.9}$Pr$_{0.1}$O$_{1.95}$), and (Ce$_{0.9}$Y$_{0.1}$O$_{1.95}$) were successfully synthesized by citrate nitrate auto-combustion method at 500 °C using citric acid as fuel for the combustion reaction. The nitrates of the respective precursors were used as the host metal ions. The as prepared RE$_{3+}$:CeO$_2$ powders were calcined at 700 °C for complete crystallization. The calcined powders were kept in uni-axial compression to fabricate cylindrical discs and subsequently sintered at 1200 °C to make dense cylindrical electrolyte.

The as synthesized nanopowders and sintered bodies were studied by various characterization techniques in order to analyze their physical, optical, surface and functional properties. The powder X-ray diffraction (XRD) studies were carried for the RE$_{3+}$:CeO$_2$ powders using Rich-Seifert diffractometer with CuK$_α$ (λ=1.5405 Å) radiation over the range of 10–70° at a scanning rate of 1°/min. The average particle size of the particles was calculated from full width at half-maximum (FWHM) using Debye-Scherrer’s equation for (111) crystal face of the nanoparticles. FT-IR spectra of the nanopowders were recorded for wavenumber regions 4000–500 cm$^{-1}$ using PerkinElmer FT-IR spectrometer. Raman spectra in the range of 100–5000 cm$^{-1}$ were carried out using BRUKER-RFS27 FT-Raman spectrometer. Photoluminescence
measurements were performed on confocal micro-Raman microscope MonoVista 750 CRS. He-Cd ultraviolet laser was used for excitation emitting a wavelength of 325 nm. The measurement system includes Olympus BX51 optical microscopes, monochromator with focal distance of 750 mm and cooled back-illuminated CCD camera ProEM:1600×200. The LMU-15X-UVB objective lens was used for focusing of the beam and collecting signals at ambient room temperature. The structure, surface morphology, shape, size and crystalline planes of the nanoparticles were examined by scanning electron microscope (FEI, Nova NanoSEM 200) and transmission electron microscope (TEM-JEOL JEM 2200 FS). Cyclic voltammetry (CV) was employed to investigate the effectiveness of ceria and doped ceria. The nanopowders were dispersed into colloidal suspensions and further dip-coated on a glassy carbon (GC) plate as working electrode. A Platinum wire and Ag/AgCl containing transparent glass were used as counter electrode and reference-electrode, respectively.

The structural and spectral analysis of the rare earths doped ceria nanopowders were studied in detail. Crystalline phase and structure of the RE$^{3+}$:CeO$_2$ was confirmed by powder X-ray diffraction. The XRD patterns confirm the typical cubic fluorite structure which coincides well with the standard powder diffraction data of CeO$_2$ (JCPDS references). The diffraction peaks correspond to (111), (200), (220), (311), (222) and (400) were observed, and the diffraction peak (111) at 2θ=28.36° was used to estimate the average isotropic crystallite size of the nanoparticles using Scherrer's formula.
The crystallite size range from 10 to 30 nm was calculated from X-ray line broadening method the (111) crystal plane. The existences of molecular vibrations due to elemental compositions, adsorbed water and other impurity contaminations were studied by FT-IR and Raman spectra. The characteristic band of CeO₂ from FT-IR was found to be \(~545\) cm\(^{-1}\) is assigned for Ce–O stretching vibration. The Raman active mode at \(~460\) cm\(^{-1}\) is attributed to the CeO₂ cubic fluorite lattice. The small peaks due to the absorption of oxygen vacancies were observed in the region 500–650 cm\(^{-1}\). The photoluminescence spectra of the nanoparticles exhibit a broad band in the blue - green region of wavelength range from 480 to 560 nm. The conversion efficiency of the Er\(^{3+}\):CeO₂ is more predominant than other dopants. The red to green up-conversion emissions were observed at \(~540\) nm and \(~690\) nm, respectively.

In addition to the optical and spectral properties, the surface morphology and micro-structural analyses of the rare earth elements doped ceria were analyzed in detail. The nanopowders of cluster morphology and grain distribution of calcined and sintered bodies, respectively, were studied by scanning electron microscopy (SEM). The grain sizes of the sintered material were found to be in the range from 100 nm to 500 nm. The transmission electron microscope (TEM) images revealed the presence of truncated octahedral, sphere-like shape of the nanoparticles with average size about 10–30 nm, showing good correlation with the particle size values calculated from X-ray peak broadening method. The presence and distribution of elements in rare earths doped ceria nanopowders were analyzed by SEM and TEM.
attached EDX elemental analyses and mapping. The lattice planes and interplanar spacing and crystalline nature of the nanoparticles were analyzed by high resolution transmission electron microscope (HR-TEM).

Cyclic Voltammetry (CV) is one of the electrochemical studies, which was performed on electrolyte material to investigate the effectiveness of ceria and doped ceria. The increasing current density with sweep scan potential in the cyclic voltammograms confirmed that the RE$^{3+}$:CeO$_2$ can be used as an electrolyte in solid oxide fuel cells. From the calculation of specific heat capacitance, it was found that the Y$^{3+}$:CeO$_2$ has higher value of capacitance 375 F/g comparing with the other REs doped CeO$_2$ nanocomposites. The specific capacitance range of the rare earths doped ceria electrolytes, Er$^{3+}$:CeO$_2$, Pr$^{3+}$:CeO$_2$, Y$^{3+}$:CeO$_2$ and Nd$^{3+}$:CeO$_2$ were calculated as (12.9–86.5), (20–72.4), (80–375) and (0.92–4.22), respectively.

6.2 SUGGESTION FOR FUTURE WORK

In the present work, rare earths doped ceria (RE$^{3+}$:CeO$_2$) nanoparticles were prepared by citrate nitrate auto-combustion (CNA) technique at 500 °C using citric acid as fuel. Attempts can be made to prepare the materials using other fuels and dopants in order to increase the oxygen vacancies. Ceria based materials having high ionic conductivity at high temperature are not stable with electrolyte like Li$^{3+}$ based salts and acid based electrolyte. Further attempts can be made to stabilize the materials. The present investigation focussed on the preparation of sintered cylindrical dense bodies. The attempts will also be made
for the preparation of tubular or stacked type of ceria electrodes. Doping can be done with other rare earth materials, and some transition metals. Efforts will also be made to make the perovskite type bilayer, trilayer and multilayer in order to increase the efficiency of electrode suitable for acid base electrolytes.

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