ABSTRACT

Transition Metal oxides (TMOs) perovskite compounds are the maximum multifunctional metal oxides. As they exhibits multifarious properties such as Mott transition, high temperature superconductivity, ferromagnetism, antiferromagnetism, ferroelectricity, colossal magneto-resistance / giant magneto-resistance, charge ordering, spin orbital coupling, multiferroic compounds, catalysis, solid oxide fuel cell, electrodes in battery, supercapacitors and etc., which has provided potential technological applications in the recent past years. Recently, the great deal of interest on these compounds was simulated by novel property called magneto-electric. Thus, TMOs is seen as posterity device applications in memory storage, detectors and etc.

The high tunability of TMOs perovskite compounds through site substitution and preparation methods continued to be a field of interest in academic research till now, which anticipates a break-through in fine tuning of physico-chemical properties of perovskite compounds.

Thus, this thesis involves about some selected site-substitution of TMOs perovskite compounds of LaFeO$_3$, LaCrO$_3$ and BiFeO$_3$ synthesized by citrate combustion and modified solid state reaction. The substitution effects of the prepared compounds are investigated on structure, magnetic and electrical properties, respectively.

The chapter 1 and chapter 2 describes the introduction and experimental part, comprising of TMOs oxides, its classification, applications, and the motivation of the present work and further it involves various preparation and characterization methods, its basic principles and working aspects were described in detail.

A detailed study on structural, magnetic and electrical behavior of LaFe$_{1-x}$Cr$_x$O$_3$ of x=0.0, 0.1, 0.3 and 0.5 synthesized by citrate combustion method is carried out in chapter 3. The structure and chemical phase analysis of the prepared compound is studied using XRD, Raman and FTIR spectra. The
powder XRD shows a $Pbnm$ structure and calculated crystallite size of the prepared compound follow a decreasing trend on Cr substitution. SEM and EDAX are used to depict the morphology and composition of the prepared samples. Further, the unusual Raman mode at \( \sim 676 \text{ cm}^{-1} \) is observed in Raman analysis, indicating the Raman signature of Cr-O-Fe in LaFeO$_3$ compound. The presence of LaCrO$_4$ as an impurity phase is identified using Raman and FTIR analysis. The temperature dependent magnetization, such as FCC-ZFC and M(H) were carried out to understand the magnetic behavior of the prepared samples using SQUID-VSM. The M(H) curve measured at 300 K and 5 K was found to show a weak ferromagnetism on Cr substitution in LaFeO$_3$. The temperature dependent magnetic investigation shows irreversibility in the FCC-ZFC curve due to competition between antiferromagnetism and ferromagnetism (AFM/FM). On Cr substitution the interaction of Cr-O-Cr enhances, which is observed as a transition in FCC-ZFC curve for LaFe$_{0.7}$Cr$_{0.3}$O$_3$ and LaFe$_{0.5}$Cr$_{0.5}$O$_3$ at \( \sim 117 \text{ K} \). The electrical conductivity spectra $\sigma'(f)$ measured between 100 Hz – 1 MHz exhibit a double power law, on Cr substitution. Also, the Cr substitution and temperature transforms the double power law into a single power law.

The effect of rare earth magnetic ions in La$_{1-x}$R$_x$FeO$_3$ ($x=0.0$ & $0.5$, R= Nd, Sm & Gd) is synthesized by citrate combustion method. The structural magnetic and electrical conductivity studies of the prepared compounds were given in chapter 4. The XRD, Raman and FTIR spectra were utilized in assessing the structure and purity of the prepared compounds. The substitution of Nd, Sm and Gd in LaFeO$_3$ increases the structural distortion and creates a complexity in the Raman modes as observed in the region 100 - 450 cm$^{-1}$. The Raman and FTIR analysis show their corresponding local vibrations of FeO$_6$ influenced by rare earth magnetic ions substitution. SEM was used to depict the morphology of the prepared samples, to confirm their stoichiometry, EDAX analysis was carried out on the prepared compounds. The temperature dependent magnetization, such as FC - ZFC and M(H) of La$_{1-x}$R$_x$FeO$_3$ ($x=0.5$, R=Nd, Sm & Gd) at 20, 150 and 300 K were carried out to understand the
magnetic behavior of the prepared samples using VSM. The Nd and Gd doped compounds behave like paramagnetic at low temperature between 20 K and 100 K due to weak Nd/Gd-Fe interactions. However, Sm doped compound show an strong ferromagnetism as result of anisotropy of random Sm-O-Fe interactions. The EPR study at room temperature show the changes in the magnetic behavior of Fe$^{3+}$ ions. EPR line shows ferromagnetic signal for La$_{0.5}$Sm$_{0.5}$FeO$_3$, which indicates the different spin structure, whereas for LaFeO$_3$, La$_{0.5}$Nd$_{0.5}$FeO$_3$ and La$_{0.5}$Gd$_{0.5}$FeO$_3$ show an antiferromagnetism. The temperature dependent electrical conductivity spectra $\sigma'(f)$ measurement was done between 100 Hz and 1 MHz using impedance analyzer on the prepared samples. The temperature dependent electrical conductivity spectra $\sigma'(f)$ exhibit a typical double power law behavior in between 100 Hz and 1 MHz.

The isovalent Nd substitution effect of La$_{1-x}$Nd$_x$CrO$_3$ ($x=0.00, 0.05, 0.10$ and $0.15$) is synthesized by citrate assisted combustion method, dealt in chapter 5. The structure and purity of the prepared compounds were assessed using XRD, Raman and FTIR. The X-ray diffraction (XRD) and Raman spectral studies clearly show the structural distortion upon Nd substitution. SEM was used to show the morphology of the prepared samples. The temperature dependent magnetization, such as FCC-ZFC and M(H) were carried out to understand the magnetic behavior of the prepared samples using SQUID-VSM. The magnetic study reveals the canted antiferromagnetic ordering at 5 K. Also, the Neel temperature ($T_N$) decreasing upon Neodymium substitution i.e., 282, 277, 274 and 271 K for La$_{1-x}$Nd$_x$CrO$_3$ ($x=0.00, 0.05, 0.10$ and $0.15$), respectively. The field cooled measurements shows the temperature dependent magnetization reversal (MR) due to the antiparallel ordering of Nd-O-Cr magnetic ions, which enhance the negative magnetization below spin reorientation temperature ($T_{SR}$) as observed for the applied field of 100 Oe in FCC mode. The temperature dependent electrical conductivity spectra $\sigma'(f)$ measurement was done between 100 Hz and 1 MHz using impedance analyzer on the prepared samples. The samples exhibit single power law behavior in the measured temperature range of 303-453 K. The activation energy throws a light
on the type of charge carrier involved in the conduction mechanism. The impedance analysis shows the dominant role of grain boundary and semiconducting nature of the samples in the measured temperature range.

The results of Ti$^{4+}$ substituted Bi$_{0.8}$Ba$_{0.2}$Fe$_{1-x}$Ti$_x$O$_3$ (x=0.0, 0.1 & 0.2) prepared by modified solid state reaction technique is presented in chapter 6. On Ti$^{4+}$ substitution the structural change was observed and confirmed through X-ray diffraction, FTIR and Raman spectra analysis. The high temperature differential scanning calorimeter (DSC) measurement was done to investigate the phase transition and decomposition nature in the prepared samples. DSC shows an anomalous phase transition present at 1173 K for Bi$_{0.8}$Ba$_{0.2}$FeO$_3$ sample. Further, the absence of ferroelectric transition and an enhancement in the decomposition temperature is observed from the DSC data. Magnetization behavior such as M(H) at room temperature and FC-ZFC were recorded using VSM. The VSM study shows that both antiferromagnetic and ferromagnetic phases coexist in the M(H) curve. Upon Ti$^{4+}$ substitution in Bi$_{0.8}$Ba$_{0.2}$FeO$_3$, the antiferromagnetism dominates over the ferromagnetic phase. Further, the room temperature dielectric measurement reveals the decrease of dielectric constant and loss tangent (δ) on Ti$^{4+}$ substitutions.

Finally, the chapter 7 deals with the consolidated parts obtained from this thesis, which is presented as summary and conclusions, and also it discuss the future scope of the prepared compounds.