Preface

The global need for energy production from renewable resources and the effect of green house gas, especially carbon-dioxide is increasing day-by-day. Statistical survey shows that about 60% of the energy lost in vain worldwide, in the form of waste heat. The conversion of this waste heat into useful energy form will certainly play a major role in alternative energy technologies, to reduce our fossil fuel dependence and greenhouse gas emissions. Thermoelectric (TE) materials have drawn vast attentions, due to their ability to interconvert the gradients in electrical potential and temperature. So this technology can be used for both refrigeration and power generation. Thermoelectric materials can harvest waste heat from automobiles, factories, combustion of fossil fuels, nuclear decay etc. and can convert this into electrical energy. The development of high efficiency TE materials for waste-heat-recovery systems is necessary to bring vast economic and environmental benefits. The efficiency of the thermoelectric materials is determined in terms of figure of merit, $ZT = \frac{S^2\sigma T}{\kappa}$ (S – Seebeck coefficient, $\sigma$ – electronic conductivity, T-temperature and $\kappa$- thermal conductivity). So the main challenge of researchers is to create materials with high $ZT$ value. This can be achieved by increasing both the Seebeck coefficient and electrical conductivity and reducing the thermal conductivity. The methods of synthesis i.e. control over particle size, plays an important role in controlling the properties of thermoelectric materials. The nanostructuring of thermoelectric materials can enhance the efficiency by quantum confinement effect and phonon scattering. By nanostructuring, the electrical conductivity of thermoelectric materials can be enhanced by quantum confinement effect and the thermal conductivity can be reduced by phonon scattering at the interfaces, thereby increasing the figure of merit. Rare earth based perovskites especially, rare earth cobaltates are potential candidate for thermoelectric applications, due to their fascinating electrical, mechanical and thermal properties. The thesis entitled “Synthesis and studies of nanostructured thermoelectric perovskite materials” is a report on the synthesis of nanopowders of multinary perovskites for thermoelectric applications.

The first chapter presents a brief description about the perovskites, its electronic structure, exchange interactions, nanostructured materials, thermoelectric materials, the motivation and objective of the present work. From the literature review, it is confirmed that
an alternative energy technology is very much essential for our future generation. So thermoelectric materials with high efficiency should be fabricated. Rare earth cobaltates show good thermoelectric property due to the spin dependent electrical, mechanical and thermal properties. It is observed that, by nanostructuring better performance is obtained when compared to the bulk materials. TE materials in nanostructured form can enhance the ZT by quantum confinement effect and phonon scattering.

Chapter II describes the method of synthesis and the experimental tools used in the present study for the characterization of nanosized perovskite materials. The Bi and Sr doped \( \text{RCO}_{0.6}\text{Fe}_{0.4}\text{O}_3 \) (R – La, Pr, Nd) perovskites are synthesized by citrate-sol-gel-auto combustion method. The characterization of nanopowders are done using X-ray diffractometer (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS), particle size analyser, Impedance spectrometer, LCR-meter, Vibrating sample magnetometer (VSM), Physical property measurement set up (PPMS) and finally the dc electrical conductivity and Seebeck coefficient is measured by SEM-3 thermoelectric measurement set up.

The third chapter discusses the synthesis of \( \text{LaCo}_{0.6}\text{Fe}_{0.4}\text{O}_3 \) (L0), \( \text{La}_{0.9}\text{Bi}_{0.1}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3 \) (L1), \( \text{La}_{0.8}\text{Bi}_{0.2}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3 \) (L2) and \( \text{La}_{0.8}\text{Bi}_{0.1}\text{Sr}_{0.1}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3 \) (L3) nanosized perovskites by citrate-sol-gel auto combustion method. Powder X-ray diffraction patterns revealed that, the synthesized samples have rhombohedral crystal structure with \( \bar{R}3c \) space group and L2 has the presence of secondary peak due to the crossing limit of solubility of Bi. The microstrain is extracted from the slope of Williamson’s-Hall plot. The dislocation density, specific surface area and the crystallite size are calculated from the XRD data. Tolerance factor which determines the stability of perovskites are obtained using Goldschmidt formula. The SEM and EDAX analysis revealed the surface morphology and the chemical composition of the compounds. The grain size is determined from the particle size analyser. The narrow scan core level XPS spectra is calibrated by C1s reference spectra provided a vital information regarding the variation of binding energies and the oxidation states of elements in the compounds. The impedance measurement at room temperature shows that, L2 has the high impedance due to the secondary peak of Bi and L3 has no impedance. The presence of relaxation is evident in the Nyquist plot. From the combined impedance and dielectric measurements at room temperature, the process of relaxation in
these systems due to the grain and grain boundary effect, is well explained by Maxwell-Wagner Model. From the magnetic studies, an existence of phase transition and small spontaneous magnetic moment seen in L0 is suppressed by the substitution of Bi and Sr. The power factor of L0 is found to be considerably improved by the substitution of Bi (x=0.1), L1 sample and is good for thermoelectric applications. From the Jonker analysis, the theoretical value of maximum power factor is calculated and it is found to be in good agreement with the experimental results.

Chapter IV deals with the experiments and studies of PrCo_{0.6}Fe_{0.4}O_{3} (P0), Pr_{0.9}Bi_{0.1}Co_{0.6}Fe_{0.4}O_{3} (P1), Pr_{0.8}Bi_{0.2}Co_{0.6}Fe_{0.4}O_{3} (P2) and Pr_{0.8}Bi_{0.1}Sr_{0.1}Co_{0.6}Fe_{0.4}O_{3} (P3) nanosized perovskites. The synthesis of the material was accomplished in the same experimental conditions described previously. The XRD results shows that all samples have orthorhombic crystal structure with pbnn space group and Bi(x=0.2) has the presence of secondary peak. From SEM images, dense nanostructures with well shaped grain boundaries are obtained. The EDAX confirms the elemental composition. The oxidation state of each elements and the number of oxygen vacancies are calculated from the XPS spectra. The variation of impedance, dielectric constant and ac conductivity shows similar behaviour as we discussed in previous chapter. The impedance is high for P2 and P3 has no impedance. The existence of relaxation phenomena is well explained by Maxwell-Wagner model. The magnetization of the P0 is reduced by the substitution of Bi and Sr. From thermoelectric measurements, replacing La by Pr enhances the power factor. P1 is found to have high power factor and is good for thermoelectric application.

Chapter V describes the details of NdCo_{0.6}Fe_{0.4}O_{3} (N0), Nd_{0.9}Bi_{0.1}Co_{0.6}Fe_{0.4}O_{3} (N1), Nd_{0.8}Bi_{0.2}Co_{0.6}Fe_{0.4}O_{3} (N2) and Nd_{0.8}Bi_{0.1}Sr_{0.1}Co_{0.6}Fe_{0.4}O_{3} (N3) nanosized perovskites. The synthesis and characterisation of samples are similar to that we have discussed in previous chapters. The XRD patterns show that all samples have orthorhombic crystal structure with pbnn space group and N2 has the presence of secondary peak. The impedance is high for N2 and N3 has no impedance. The variation of dielectric constant and ac conductivity shows similar behaviour as we discussed in previous chapters. The presence of phase transition due to the domain pinning effect is evident in the magnetic studies. The phase transition is suppressed in both Bi and Sr doped sample, N3. The compound N1 has found to have high power factor than the P1 and L1.
Sixth chapter comprises the summary of all the properties studied. It is concluded that the bismuth (Bi, x=0.1) doping enhances the power factor of the material. From the whole studies Nd_{0.9}Bi_{0.1}Co_{0.6}Fe_{0.4}O_3 (N1) is found to have high power factor than other compounds and is suitable for thermoelectric applications. The thermal conductivity has to be measured to find the efficiency of these materials for thermoelectric applications. The dimensions of these materials can be further reduced by choosing different chemical routes such as hydrothermal method, precipitation from homogenous solutions etc. which are expected to show better thermoelectric properties. The size dependent thermoelectric properties of these materials have to be studied. The thin films of the samples can be made using sputter deposition or pulsed laser deposition and the properties have to be studied. Thermoelectric measurements in various ranges of temperatures have to be studied.