Preface

In the recent times, intensive investigations have been carried out on delafossite compounds being represented by $A^{1+}B^{3+}O_2^{2-}$. These compounds exhibit a wide range of physical properties, that have several applications in the field several applications in the field of solid state devices. These compounds are interesting as they show metallic to insulator type of conducting behavior. These metal oxides have potential device applications of catalysts, ozone sensors, dilute magnetic semiconductors and light emitting diodes. Also, metal oxides which are stable and have wide band gap with environment friendly nature are being studied as silicon electronics substitutes. These compounds also show spintronics and multiferroic properties. A spectrum of compounds are possible, where A site is having monovalent elements Cu, Ag, Pt and Pd, and B site is trivalent with elements Ga, Sc, Al, Fe, In, Cr, Rh, etc. Out of these the Pt and Pd based delafossites show metallic conductivity and Cu and Ag based compounds show semi conducting behavior. Combination of A and B strongly influences the overall behavior of the system. But particularly in case of $CuFeO_2$ and $CuCrO_2$, the triangular 2D arrangement of transition metal ions gives rise to spin frustration effects leading to localized magnetic moments. Also these compounds exhibit multiferroic behavior.

The previously reported work on these systems show isolated dopings, but no concrete efforts have been made to understand the effect of iso- and polyvalent substitutions on short and long range crystalline order. The observed changes in order may affect transport and magnetic properties in these technologically important systems. In the present study the effort is to establish better correlation between long-range structural changes and local distortions with various isovalent and non-isovalent dopants. A critical study has been done to understand the effects of such a doping on the local polarizations or dipole moments and crystal structure leading to changes in the electronic structure related physical parameters, at room temperature as well as at low temperatures. Additionally, the $CuFeO_2$ system until now was prepared through solid-state reaction under inert atmosphere provided by gases like nitrogen, argon, etc., which are expensive and hazardous. In present, pure and doped $CuFeO_2$ compounds were synthesized through a novel synthesis route involving a solid-state technique using high vacuum.

The entire work of this thesis can be summarized as follows:

The first chapter contains the general introduction of the thesis containing in brief about the origin of delafossite compounds. The structure, properties and features of the delafossite group are also been discussed. A detailed review of literature on the previous work done on the $CuFeO_2$ and $CuCrO_2$ systems with the observed results has been presented. The objectives and motivation for the material selection and research problem chosen have been evidently explained.

The second chapter is about the experimental work, starting with the synthesis technique used for preparing the material and later various characterization tools. Broadly for both the $CuFeO_2$ and $CuCrO_2$ systems high temperature solid state reaction method is used. But for $CuFeO_2$ system a novel synthesis route involving high vacuum is described here. Brief working principles for various characterizations like X-ray diffraction (XRD), scanning electron microscopy (SEM), Uv-vis spectroscopy, Raman, Fourier transform Infrared spectroscopy (FTIR), four probe technique for dc conductivity, electrical, and magnetic measurements are discussed here.

The third chapter describes the detailed results and analysis of the crystal structure and micro structure. The details of the crystal structure along with the identification of crystallographic data are presented. Crystallographic parameters like space group, lattice parameters, Wyckoff positions of elements were determined using the refined data by performing reitveld refinement. In depth XRD analysis established the good quality of samples, without any impurity phases, with rhombohedral structure having space group $R\bar{3}m$. SEM micrographs also confirmed the good crystallinity along with well-defined grain boundaries for both the series of samples.

The fourth chapter describes the effect of doping on the local vibrational structure of the samples through Raman and FTIR techniques. The Uv-Visible studies showing the effect of local structure on electronic band gap. The FTIR, Raman, and Mössbauer studies confirmed phase purity of the $CuFeO_2$ samples prepared through the cost-effective solid-state reaction under high vacuum. Mn, Ti and Fe doped $CuCrO_2$ samples showed strong local distortions through Raman studies, which have not been reported earlier. Removal of degeneracy was observed for Mn, Ti, Nb, Ga, and V doped samples in both E_u and A_{2u} IR active modes, related to the transverse (T_o) and longitudinal (L_o) optical modes of vibrations. Changes in p-d hybridizations coupled with Jahn-Teller distortions, rather than changes in bond distances,

crystallite size or unit cell volumes, resulted in reductions in the band gap in doped $CuCrO_2$ samples.

Chapter five presents the result of transport measurements, which are affected by the observed local distortions represented in Raman and FTIR studies. $CuFeO_2$ samples showed decrease in resistivity with the partial doping of Fe site found to correlate with expected changes in carrier concentration as well as mobility due to induced charges and MO_6 based distortions. Small-polaron based conduction can be seen in pure and Ti doped $CuFeO_2$ samples along with NSPT model-based conduction behavior, confirmed by Jonscher'slaw based calculations of ac conductivity data. $CuCrO_2$ samples show significantly altered low-temperature conduction behavior with electron or hole doping in these principally phonon-driven semiconducting systems. In these samples also small-polaron behavior was observed. The Jonscher's law analysis showed correlated barrier hopping model based conductivity in Ti and Mn-doped samples, while NSPT model based conductivity for others.

In chapter six mangetic and dielectric studies have been described in detail. For pure and Ti doped $CuFeO_2$ a significant role of Jahn-Teller based local defects is seen particularly at low temperatures. Pure and doped $CuCrO_2$ samples showed the clear evidence of magneto-dielectric coupling. It is proposed that optimization of the phonon-induced localized carrier hole density along with the reduction in helical disorder around MO_6 octahedra through suitable electron/hole doping is an effective way to enhance the double exchange along with the Cr-O-M-O linkages or super exchange between $M^{3+/4+}$-Cr^{3+} mediated by oxygen at low temperatures.

Thus, the present correlated study clearly highlights the role of doping level and local distortions in deciding the crystal structure, micro structure, vibrational modes, transport and multiferroic nature of this system providing an effective tool to nurture its physical and chemical behavior.