Chapter 1

Introduction

A brief description of the origin of the delafossite structure along with its properties is presented here. Also, an impression of various previously published works on these systems has been given. The deficiencies in the reported work led to the motivation and objective of the present thesis work.

1.1 Introduction

A great deal of consideration is shared by the transition metal oxides due to various physical properties exhibited by them mostly because of the ordering of some microscopic degrees of freedom with respect to temperature, pressure, or doping [1]. The noticeable examples are the remarkable metal-insulator changeovers in sesquioxide of vanadium [2–5], cuprates with high T_c superconductivity, or manganates with giant magnetoresistance [6–9]. The manifestation of different spin states in cobaltates also attracted much attention and are potential candidates for thermoelectric uses [10–14]. Since the discovery of mineral $CuFeO_2$ by Friedel [15], this family of ABO_2delafossite compounds has generated significant interest through the pioneering development by Rogers, Shanon and Prewitt. They have reported about the synthesis, structure and properties of the delafossite family of compounds, including $CuFeO_2$, $AgFeO_2$, $PtCoO_2$ and $PdCoO_2$[16–18]. Benko and Koffyberg have reported the optical properties of many delafossite compounds in their studies [19–22]. The demonstration of transparency and p-type conductivity in $CuAlO_2$ thin films was earlier reported [23]. The findings of H. Hosono and his co-workers on copper (I) – based transparent oxides is an important contribution towards this development [23–26]. Pt and Pd-based compounds show metallic behavior, while the Cu and Ag-based compounds show the semiconducting behavior [27]. In addition to the above properties, some of them exhibit good optical transparency which makes them potential candidates for transparent conducting oxides (TCO) [23]. These classes of compounds have generated significant interest in the scientific community due to varied conducting behavior is shown by these from metallic to insulating [23,28,29]. Also p-type or n-type conductivity is shown by them depending on the donor or acceptor impurity [30]. With such a distinctive combination of electrical conductivity and optical transparency, they are potential candidates in the areas of solar energy [31] and photocathodes [32]. The catalytic activity of copper delafossites is applied in hydrogen production [33]. These are also used as anode in lithium-ion batteries [34], antimicrobial compounds [35] and gas sensors [36].

The mineral compound $CuFeO_2$ was first noted by Friedel in 1873 during the analysis of a sample from Siberia [15] and was named Delafossite in honor of the French mineralogist and crystallographer Gabriel Delafosse. The existence of the same was confirmed by Roger in most of the copper mines in America [37,38]. Delafossite structure was first established by Soller and Thompson [39] through the synthetically prepared sample, which was further confirmed by Pabst using a mineral sample [40].

The triangular organization of transition metal atoms in these systems results in the possible frustration effects giving rise to localized magnetic moments. Mekata et al. [41] identified two magnetic phase transitions in $CuFeO_2$ at T_{N1} = 16 K and T_{N2} = 11 K through neutron diffraction data. Ye et al. [42] found structural distortions below 4 k along with magnetic phase transitions leading to the monoclinic lattice with the C2/m space group. A 3D magnetic coupling was hinted at through the analysis of spin-wave spectra [43]. Kimura et al. [44] observed a non-collinear-incommensurate magnetic field which can be a symptomatic multiferroic behavior. Inelastic neutron scattering data also indicated multiferroic behavior [43]. A potential thermoelectric application for Pt doped $CuFeO_2$ was indicated by Ruttapanum et al. [45].

A similar system $CuCrO_2$ is semiconducting with an antiferromagnetic transition observed at T_N = 25 K [46–48]. A large magnetic frustration is suggested in this system through the large difference observed in θ and T_N[46–48]. Mg^{2+} doping on the Cr^{3+}site shows a direct impact on the resistivity curves along with increased magneto-resistance around T_N[49]. The delafossites have a simple chemical formula and may be considered as the classical superlattice. Here the combination of A and B strongly influences the overall behavior of the system. Due to the properties mentioned above and the role of A and B permutation in these systems, they are potential candidates to fulfill the technical application demands and mass production. The processing for this has to be flexible and low cost.

1.2 Delafossite Structure

Monoatomic triangular layers stack to give rise to delafossite ABO_2 structure having space group $R\bar{3}m$ [16–18,29]. The structure is characterized by linear coordination of the monovalent A^+-cations by O^{2-}-anions and octahedral coordination of the trivalent B^{3+}cations by O^{2-} anions. Together with the complementary pseudo-tetrahedral coordination of the O^{2-} ions by three B^{3+} ions and one A^+ ion results in two distinct structural units: Edge-sharing MO_6 octahedral, forming a flat layer, and parallel oriented O-Cu-O dumbbells linking them, resulting in a triangular pattern of A^+ ions [16–18,29].

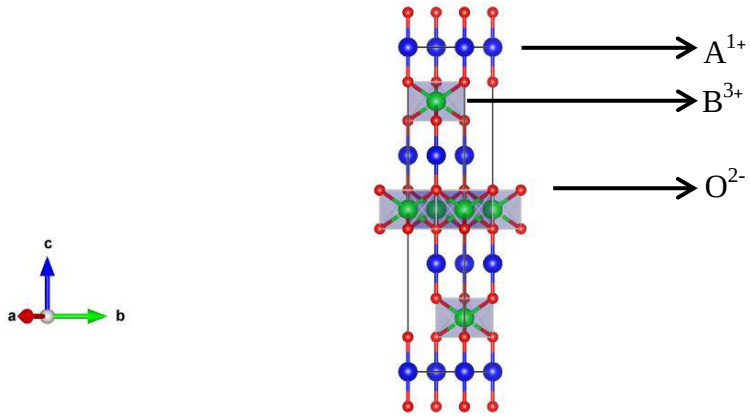

Figure 1.1: A delafossite type structure

1.3 Literature Survey

A large number of delafossite materials having general formula ABO_2 is possible where A = Cu^{1+}, Ag^{1+}, Pd^{1+} or $Pt^{1+}$and B = Ga, Sc, Al, Fe, In, Cr, Rh, etc. But as already discussed earlier, the arrangement of transition metal ions on a 2D triangular lattice gives rise to one of the most attractive properties, which facilitates the study of frustration effects, commensurate and incommensurate non-collinear magnetic ordering, multiferroic behavior and unusual spin coupling. And for this scientific interest, $CuFeO_2$ and $CuCrO_2$ are the appropriate candidates and are therefore considered in this thesis work.

$CuFeO_2$ exhibits both multiferroic and spintronic properties [50]. Several research groups have studied the substitutional effects on the Fe site of $CuFeO_2$ have been studied by . Superior electrical conductivity was observed on doping 2% Ni at Fe site of $CuFeO_2$ by Nozaki et al. [51]. In contrast, doping 5% Mn at the Fe sites decreased the thermal conductivity [52]. Hayashi et al. [53] detected a reduction in antiferromagnetic (AF) phase transition temperature without any change distinctive change in the structural parameters, on Mn doping. $CuFeO_2$ on Mg and Sn doping becomes p-type or n-type semiconductors, with much higher mobility of p-type samples [22]. Glass-like ferro-electricity was witnessed by Singh et al. [54] on doping Fe sites by 50% V. On doping Fe sites with V the magnetic behavior changes from 2D ferromagnetic to a 3D antiferromagnetic one with a Néel temperature more than 4.5 K, identified through Mössbauer study [55]. Shi et al. [56] observed on doping of Ga^{3+} at Fe sites an expansion of ferroelectric in the commensurate state was induced. Elkhouni et al. [57] observed Ca^{+2} doping at the Fe site caused suppression of magnetic properties, while it boosted on Mg^{2+} doping. A analogous result was observed in the case of Sc doping at Fe sites of polycrystalline $CuFeO_2$[58]. Seki et al. [59] presented a noteworthy change in the magnetic phase diagram with Al doping at Fe sites, where

ferroelectricity became apparent with Al doping up to 2%. Naka-in et al. [60] showed a moderate decrease in resistivity along with weak ferromagnetism at 300 K on doping Fe^{3+} sites with Ge^{3+}. Dai et al. [41] observed a significant effect of cationic vacancies on magnetic properties and optimized this for 2% doping of Eu at Fe sites in $CuFeO_2$. PreetiPokhriyal et al. [61] showed large dielectric permittivity around room temperature for the $CuFeO_2$ sample. These results show the importance of the electronic and magnetic properties of these systems. These properties are considerably reliant on the interplay of the microstructure modifications carried out by doping of different ions. In addition to the above cited observations, Dordor et al. [28] prepared single crystals and polycrystalline samples of $CuFeO_2$, which were of n-type with a very low conductivity [single crystal $6.5 \times 10^{-7} \Omega^{-1}$ cm^{-1} (∥) and $3.1 \times 10^{-4} \Omega^{-1}$ cm^{-1} (⊥) and for polycrystalline 1.9×10^{-5} Ω^{-1} cm^{-1}].

Another interesting and identical delafossite system is $CuCrO_2$, having the same structure but possessing the alternate stacking of layered structure with edge shared CrO_6 octahedra and Cu layers, resulting in antiferromagnetic triangular sublattice [49]. $CuCrO_2$ exhibits a bandgap of 3.1 eV with *p*-type nature as revealed by the Seeback measurements, while the mobility of charge carriers is too low for the Hall Effect measurement [62]. Beneath its Neel temperature (T_N= 25 K), $CuCrO_2$ exhibits both antiferromagnetic [63] and ferroelectric [64] nature. It has been observed that earlier studies mainly focused on the effects of doping on the structural, electrical and magnetic properties in the $CuCrO_2$ system, but with no consistency on the percentage of doping. Mg^{2+} substitutions at the Cr site drastically decrease the resistivity without changing the Neel temperature [49]. The doping of Ni at the Cr site also increases the conductivity of the $CuCrO_2$ system [65]. Weak ferromagnetism is induced and destabilization of the antiferromagnetic ordering of Cr^{3+} occurs due to doping of Al^{3+} ions [66]. Sc doping causes local lattice distortions, thereby breaking the residual magnetic degeneracy occurring in the $CuCrO_2$ system [67]. Correlated variation of (Cr, Rh−O) bonds and shifting of Raman active modes were observed in $CuCr_{1-x}Rh_xO_2$[68]. The $CuCrO_2$ compound exhibits spin-induced ferroelectricity and polarization below the magnetic phase transition temperature T_N in the absence of a magnetic field [56,69]. Ferroelectricity is induced in $CuCrO_2$ when it becomes antiferromagnetic (below T_N = 24 K) with non-collinear spin ordering [64,70]. On doping, the Cr site with Fe in $CuCrO_2$ showed the presence of superconducting transition up to 118 K [71]. Hydrothermally synthesized nanocrystals of Fe and Mg-doped $CuCrO_2$ showed the doping limit of 3% for both the samples beyond which spinel phases were observed [72]. A dimensional crossover of low energy magnetic excitation from anisotropic

3D antiferromagnetic magnon to that of 2D antiferromagnetic excitation was observed by Elkhouni et al. [73]. The substitution of Rh, Sc, or Ga in the Cr site showed steric effects and magnetic dilution interaction,resulting in the modification of macroscopic magnetic behavior and ferroelectric properties [74,75]. Also, recently, through Green's Function technique, it has been shown that there is a strong magneto-electric (ME) coupling in $CuCrO_2$, and the related materials can be the potential ME sensors [76].

1.4 Motivation

In view of the above findings, it was realized that isolated dopings were carried out but no concrete efforts have been made to understand the effect of iso- and polyvalent substitutions on short and long-range crystalline order. The idea is to observe changes in the order that may affect transport and magnetic properties in these technologically important systems. It is therefore desirable to establish a better correlation between long-range structural changes and local distortions with various isovalent and non-isovalent dopants. This requires the careful selection of dopants based on the ionic radius, coordination number, valence state to achieve p-type or n-type carrier and optimization of dopant concentration. The resultant effort is likely to provide a better understanding of the role of ionic radii, valence and bond length in these systems having p-type and n-type semiconducting behaviour.

Therefore the main motivation of this work is to perform a detailed investigation with doping of iso- or poly-valent elements at the M site to shed light on the long and short-range crystalline order in $CuMO_2$ type delafossite where M = Fe or Cr. We also desire to observe the effects of such doping on the local polarizations/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, preparation of $CuFeO_2$ through solid-state reaction also require an passive atmosphere provided by gases like argon, nitrogen, etc., [22,52–58], which are expensive and hazardous. As an economical alternative, it is proposed to prepare pure and doped $CuFeO_2$ compounds through a novel synthesis route comprising a solid-state technique incorporating a high vacuum.

1.5 Objective and Scope of the work

In the present study, the effects of local structure variations due to doping of iso- and poly-valent elements at the M site of $CuMO_2$ (M = Fe/Cr) are correlated to the micro-and macro-structural properties of compounds. This has been analyzed through the crystal structure, microstructure, optical studies, transport, magnetic and dielectric measurements.

Two delafossite systems were selected:

- $CuFeO_2$ system:

  Samples of $CuFeO_2$, $CuFe_{0.96}M_{0.03}V_{0.01}O_2$ (where M= Ti, Ga, and Mn), and $CuFe_{0.96}V_{0.04}O_2$ were prepared through a novel synthesis method involving a solid-state technique using high vacuum.

- $CuCrO_2$ system:

  Samples of $CuCrO_2$, $CuCr_{0.96}M_{0.03}V_{0.01}O_2$ (M = Ti, Mn, Ga, and Nb), $CuCr_{0.96}V_{0.04}O_2$, $CuCr_{0.97}Mg_{0.03}O_2$, $CuCr_{0.97}Ni_{0.03}O_2$ and $CuCr_{1-x}Fe_xO_2$ (x = 0.03, 0.06 and 0.09) were prepared by conventional solid-state technique.

- The majority of the samples were maintained with a maximum doping level of 4%, as the ions in these compounds have the same maximum substitutional limits [56,57,77].
- 1% V has been added to the compositions to bound the phase formation temperature. Such a drop in temperature for the phase formation has been reported previously [78,79].
- The considered ionic charge and ionic radii are based on the notion that the dopant is anticipated to favor the valence state whose radii are closest to the parent elements radii (Cr^{3+} and Fe^{3+}).
- In the case of $CuFeO_2$ systems, room temperature Mossbauer spectroscopy is performed to confirm the spin state of Fe and can be correlated to Raman observations to offer a superior understanding with respect to the role of defects/distortion in the physical properties of these compounds.

Here attempts are made to explain the role of dopants on the long and short-range crystalline order in the above systems. This has been done by the combined study of Raman and Fourier transformed Infrared spectroscopy (FTIR) along with long-range order dependent X-ray diffraction (XRD). Observed changes in the local polarizations/dipole moments and crystal structure can lead to changes in the electronic structure-related physical parameters at room temperature as well as at low temperatures which were investigated using the optical

measurements, electrical resistivity measurements, magnetization measurements, and dielectric measurements for these samples.

Content of the thesis

In chapter 1, the introductory part of the thesis includes briefly, the origin of the delafossite compounds and modification to parent compounds to be investigated will be introduced here. The mineral group delafossite is introduced in detail with its structure, properties and other features. The detailed literature survey on the previous work done on the mineral group delafossite and the observed results along with their explanation is presented. Aim and motivation to the research problem chosen, along with its objectives are clearly explained here.

In chapter 2 chapter experimental laboratory work is discussed. It starts with the sample preparation technique used for the preparation of the bulk samples. Broadly for both $CuCrO_2$ and $CuFeO_2$ systems solid-state reaction technique is used. This technique along with its details is described here. Sample preparation starts with stoichiometric weighing, uniform mixing (wet mixing), calcination, sintering and finally annealing of the samples. This method requires high temperature muffle furnace with super kanthal (melting temp ~ 1200 ^{o}C) as the heating element. A novel synthesis route for the $CuFeO_2$ system involving a solid-state technique using high vacuum is used which is described here.

Characterization of the prepared samples was done under four different categories:

1. Structural characterization (Crystal structure and microstructural studies)
2. Optical and near optical measurements
3. Transport measurements
4. Magnetic and dielectric measurements

Chapter 3 describes the analysis of the crystal structure and microstructure is presented. Details of the crystal structure and the identification of the crystallographic data are reported. The Rietveld refinement technique through the Fullprof software [80] is used for crystallographic studies. Crystallographic parameters like, space group, lattice parameters, Wyckoff position of each element, etc are determined for both $CuCrO_2$ and $CuFeO_2$ systems using the refined data. Scanning electron microscopy (SEM) is used to study the microstructures of the prepared samples.

In chapter 4, the optical and near optical studies are presented. The effect of doping on the local structure of the samples is studied in detail using the Raman and FTIR techniques. The combined results and analysis of the Raman and FTIR measurements are presented in this chapter. Further the effects of the local structure variation on the electronic bandgap were also studied using the Uv-Visible measurements. Correlations of these results, obtained from the above measurements, are presented in this chapter.

Chapter 5 discusses the observed local distortions and changes in dipole moments due to doping were observed through Raman and FTIR studies. This can have potential effects on the transport properties. Therefore, in this chapter results of transport measurements are also been presented from low temperature to room temperature using the Four probe method. Suitable conduction models were fitted to explain the conduction mechanism. The same is correlated with the a.c. conductivities of the samples measured through dielectric measurements.

In chapter 6, the magnetic and dielectric studies of the samples are presented in detail. Magnetic studies were performed within the temperature range of 25 K to 300 K. Effect of the dopants on the magnetic behaviour of the samples has been discussed here. In order to probe the multiferroic behavior of the samples, dielectric measurements have also been performed and analyzed in an identical temperature range.

Chapter 7 presents the major achievements and the conclusions of the work. In the end future, the scope of the above work has been discussed.

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