SYNOPSIS OF

"Structure, Microstructure, Transport, Magnetic and Dielectric studies of some ABO_2 type compounds in Bulk form"

A THESIS

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Introduction:

General formula of delafossite is $A^{+1}B^{+3}O_2^{2-}$ (ABO_2) and are extensively studied due to their potential applications of catalysis [1-3], ozone sensors [4], diluted magnetic semiconductors [5], light emitting diodes [6], and transparent conducting oxides (TCO) [7]. Also they are known to exhibit both multiferroic and Spintronic properties [8]. The findings of H. Hosono and his co-workers on copper (I) – based transparent oxides is an important contribution towards this development [9-12]. These systems are promising candidates to fulfill the technical application demands and mass production. The processing for this has to be flexible and low cost.

The mineral compound $CuFeO_2$was first noted by Friedel in 1873 during the analysis of a sample from Siberia [13] 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 [14, 15]. Delafossite structure was first established by Soller and Thompson through synthetically prepared sample [16].

The delafossite oxides have general formula ABO_2, which 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].

$CuFeO_2$ exhibits both multiferroic and Spintronic properties [8]. Substitutional effects on the Fe site of $CuFeO_2$ have been studied by various research groups. Nozaki et al.[17] showed that the substitution of Ni with less than 2% at Fe sites results in an enhanced electrical conductivity of $CuFeO_2$. On the other hand, doping of 5% Mn at the Fe sites was

found to decrease the thermal conductivity [18]. Hayashi et al. [19] observed no distinct change in the structural parameters, on contrast, a decrease in antiferromagnetic (AF) phase transition temperature is seen with Mn doping. $CuFeO_2$ can be made p-type or n-type semiconductor with Mg and Sn doping, respectively. The mobility is much higher in p-type samples [20]. Ferro-electricity was observed by Singh et al. [21] on doping 50% V at Fe sites that exhibited the features of the glass-like relaxor state. Mössbauer studies found that doping of V at Fe sites affects magnetic behavior, which changes from 2D ferrimagnetic-like one to a 3D antiferromagnetic one with a Néel temperature greater than 4.5 K [22]. Shi et al. [23] observed on doping of Ga^{3+} at Fe sites an expansion of ferroelectric in commensurate state was induced. Elkhouni et al. [24] observed Ca^{+2} doping at the Fe site caused suppression of magnetic properties, while it boosted in the case of Mg^{2+} doping. Seki et al. [25] showed a significant change in the magnetic phase diagram with Al doping at Fe sites, where ferroelectricity became apparent with Al doping up to 2%. These results show that the electronic and magnetic properties of these systems are significantly dependent on the interplay of the microstructure modifications carried out by doping of different ions. In addition to the above mentioned observations, Dordor et al.[26] prepared polycrystalline and single crystals of $CuFeO_2$,which were found to be of n-type with a very low conductivity [$1.9 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ for polycrystalline and for single crystal $6.5 \times 10^{-7}\Omega^{-1}\ cm^{-1}$ (∥) and $3.1 \times 10^{-4}\Omega^{-1}\ cm^{-1}$ (⊥)].

Another interesting and identical delafossite system is $CuCrO_2$, having the same structure but possessing the alternating stacking of layered structure with edge shared CrO_6 octahedra and Cu layers, resulting in antiferromagnetic triangular sublattice [27]. $CuCrO_2$ 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 [28]. Beneath its Neel temperature (T_N= 25 K), $CuCrO_2$ exhibits both antiferromagnetic [29] and

ferroelectric [30] nature. It has been observed that reported 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 percentage of doping. Mg^{2+} substitutions at the Cr site drastically decrease the resistivity without changing the Neel temperature [27]. The doping of Ni at Cr site also increases the conductivity of the $CuCrO_2$ system [31]. A weak ferromagnetism is induced and destabilization of antiferromagnetic ordering of Cr^{3+} occurs due to doping of Al^{3+} ions [32]. Sc doping causes local lattice distortions thereby breaking of the residual magnetic degeneracy occurring in the $CuCrO_2$ system [33]. Correlated variation of (Cr, Rh−O) bonds and shifting of Raman active modes was observed in $CuCr_{1-x}Rh_xO_2$ [34]. 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 [30, 35]. Ferroelectricity is induced in $CuCrO_2$ when it becomes antiferromagnetic (below T_N = 24 K) with non-collinear spin ordering [30, 36].

Motivation:

In the 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 and how observed changes in order may affect transport and magnetic properties in these technologically important systems. It is therefore desirable to establish 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 changes in ionic radii, valence and bond length of these systems having p-type and n-type dopings.

Therefore it motivated us 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 delafossites where M = Fe or Cr. We also desire to observe the effects of such a 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.

Moreover, the methods to prepare $CuFeO_2$ through solid-state reaction also require inert atmosphere provided by gases like nitrogen, argon, etc.,[18-25], which are expensive and hazardous. As an economical alternative we proposed to prepare pure and doped $CuFeO_2$ compounds through a novel synthesis route involving a solid-state technique using high vacuum.

Objectives and scope:

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 novel synthesis route 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.

- Majority of the samples are maintained with maximum doping level of 4%, as majority of the ions in these compounds has the same maximum substitutional limits [17, 23, 24].
- 1% V has been added to the compositions to limit the phase formation temperature. Such a reduction in the phase formation temperature has been reported earlier [37, 38].
- The considered ionic charge and ionic radii are based on the assumption that the dopant is expected to prefer the valence state whose radii is closest to the parent elements radii (Cr^{3+} and Fe^{3+}).
- In 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 provide a better insight into these compounds with respect to the role of defects/distortion in the physical properties.

  Here attempts are made to explain the role of dopants on the long and short-range crystalline order in the above systems, through 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.

Proposed content of the thesis:

The proposed thesis will comprise of the following chapters.

Chapter 1

The introductory part of the thesis is includes, in brief, 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 are presented. Further, the deficiencies in the work done and work needed to be done is highlighted in this chapter. Motivations to the research problem chosen, along with its objectives are clearly explained here.

Chapter 2

In this chapter experimental laboratory work will be discussed. It starts with the sample preparation technique used for the preparation of the bulk samples. Broadly for the 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 the 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 heating element. Particularly for $CuFeO_2$ system a novel synthesis route 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

Structural characterization is done using the X-ray diffraction (XRD) and scanning electron microscopy.

Optical studies include Uv-visible technique; Raman and Fourier transform Infrared spectroscopy (FTIR) study.

Transport measurements include d.c. conductivity measurements using the four probe technique and a.c. conductivity.

Magnetic characterization of the samples was carried out using the squid magnetometer (quantum design). Dielectric measurements were carried out by measuring the capacitance as a function of temperature.

Chapter 3

In this chapter the analysis of the crystal structure and microstructure is presented. Details of the crystal structure and the identification of the crystallographic data are presented. The rietveld refinement technique through the Fullprof software [39] is used for the 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.

Chapter 4

In this chapter 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 band gap were also studied using the Uv-Visible measurements. Correlations of these results, obtained from above measurements, are presented in this chapter.

Chapter 5

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

Chapter 6

In this chapter the magnetic and dielectric studies of the samples are presented in detail. Magnetic studies are 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 were also been performed and analyzed in identical temperature range.

Chapter 7

In this chapter all the major achievements and the conclusions of the work are compiled. At the end future scope of the above work is discussed.

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List of Publications:

1. " Structure, microstructure and dielectric studies of PVA/$Sr(Co_{1/3}Nb_{2/3})O_3$ polymer composites" by **Nishant Barot**, Bhagwati Bishnoi, Sagufta Jahan, Prashant K. Mehta and N. L. Singh, Invertis Journal of Science and Technology, Vol. 10, No. 2, pp. 64-72 (2017).
2. "Structure, I-V Characteristics and Optical studies of Delafossite $CuFeO_2$ and $CuFe_{0.96}Ti_{0.03}V_{0.01}O_2$ Prepared Under High Vacuum" by **Nishant Barot**, Prashant K. Mehta, Devang D. Shah and C. J. Panchal, AIP Conf. Proc. 1837, 040031-1–040031-4 (2017).

3. "Effects of iso- and polyvalent substitutions on the short/long-range crystalline order in $CuCrO_2$ compounds" **Nishant Barot**, Prashant K. Mehta, Ashok Rao, Riya Thomas, and Yung-Kang Kuo, Journal of Alloys and Compounds, 701, 134-143 (2019).

4. "Role of charge doping and distortions onthe structural, electrical, and magneticproperties of modified $CuFeO_2$ compounds" **Nishant Barot**, Prashant K. Mehta, Ashok Rao, Riya Thomas, Yung-Kang Kuo, and S. K. Mishra, Journal of Applied physics, J. Appl. Phys. 127, 175704 (2020).

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