Executive Summary

Contents

Summary of Thesis

- The samples of delafossite type oxides comprising of two series $CuFeO_2$ and $CuCrO_2$ have been successfully synthesized by using the conventional solid-state reaction. The in-depth XRD analysis confirmed the good quality of the samples without any impurity phases with the rhombohedral structure having space group R-3m. For the pure and doped $CuCrO_2$ samples the structural parameters correlate more with the expected valance state-based hole or electron doping induced changes in the local electronic structure rather than ionic sizes. SEM micrographs confirm the good crystallinity along with well-defined grain boundaries for both the $CuFeO_2$ and $CuCrO_2$ series samples.
- Minor shifts in the E_g and A_{1g} modes in Raman of $CuFeO_2$ samples were observed due to Ti and Mn doping including a Jahn-Teller distortion-related extra peak around 500 cm^{-1} but with variable strength. Mössbauer's measurement at room temperature confirmed the presence of octahedron distortion and suggested the absence of Fe^{2+} or mixed valence. The optical band gap had no significant changes in these samples.
- Raman studies showed strong local distortions in Mn, Ti and Fe doped $CuCrO_2$ samples which had not been reported earlier. In both E_u and A_{2u} IR, active modes removal of degeneracy is observed, related to T_o and L_o optical modes of vibrations in Mn, Ti, Nb, Ga and V doped $CuCrO_2$ samples. The doping of mixed/or di- or tetra-valent ions reduced the bandgap of $CuCrO_2$ samples, related to changes in p-d hybridizations coupled with Jahn-Teller distortions.
- The dc conductivity studies of the $CuFeO_2$ samples showed a decrease in resistivity with the partial doping of the Fe site which can be correlated to the changes in carrier concentration as well as mobility due to induced charges and MO_6 based distortions. Small-polaron-based conduction was exhibited by the pure and Ti-doped $CuFeO_2$ samples. Moreover, Jonscher's law confirmed non-overlapping small polaron tunneling (NSPT) model-based behavior for conduction.
- The low-temperature electrical conduction behavior of $CuCrO_2$ samples is significantly altered with the electron or hole doping in these predominantly phonon-driven semiconducting systems. Here also a predominantly small polaron hopping process is established through ac conductivity studies. Jonscher's power law analysis showed correlated barrier hopping conduction model for Ti and Mn-doped samples, while the NSPT model for others.

- The magnetic and dielectric studies for pure and Ti-doped $CuFeO_2$ samples demonstrate a significant role of Jahn–Teller effect-based local defects, particularly at low temperatures. The magnetization and dielectric permittivity measurements of the studied pure and doped $CuCrO_2$ samples showed clear evidence of magneto-dielectric coupling. The present correlated study clearly highlights the role of doping level and local distortions in deciding the magnetic and multiferroic nature of this system providing an effective tool to tune its physical and chemical behavior.

Outline of the thesis

The thesis is divided into 7 chapters. A summarized detail of the chapters is as follows:

Chapter 1- The introductory part of the thesis includes briefly, the origin of the delafossite compounds and outcome of 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. Aim and motivation to the current research problem chosen, along with its objectives are explained here.

Chapter 2- This chapter will give the description about the experimental laboratory work carried out for the sample preparation in the bulk sample form as well as about the characterization of the prepared samples. Broadly for both $CuCrO_2$ and $CuFeO_2$ systems modified solid-state reaction technique is used. The details of the same will be described here. Particularly for the $CuFeO_2$ system a novel synthesis route involving a solid-state technique using high vacuum is used, its need is described here. Details of the characterization done under four different categories namely structural characterization (Crystal structure and microstructural studies), optical and near optical measurements, transport measurements and magnetic and dielectric measurements are pesented here.

Chapter 3- This chapter contains the analysis of the crystal structure and microstructure. Details of the crystal structure and the identification of the crystallographic data are presented. This is followed by the details of the refined data of XRD through Rietveld refinement for both $CuCrO_2$ and $CuFeO_2$ systems. Microstructures details of the prepared samples were analysed using scanning electron microscopy.

Chapter 4- Here the optical and near optical studies are presented. The combined results and analysis of the Raman and FTIR measurements are included in this chapter. Further the detailed effects of the local structure variation on the electronic bandgap are presented using the Uv-Visible measurements. Correlations of these results, are presented in this chapter.

Chapter 5- This chapter discusses the observed results of Raman and FTIR studies, which has potential effects on the transport properties. Therefore, in this chapter results of transport measurements are discussed from low temperature to room temperature using the four probe

method. This is followed by the presentation of suitable conduction models to explain the conduction mechanism. The same is correlated with the a.c. conductivities of the samples measured through dielectric measurements.

Chapter 6- Magnetic and dielectric studies of the samples are presented here in detail. Effect of the dopants on the magnetic behaviour of the samples is discussed. This is followed by the dielectric measurements in an identical temperature range probe the multiferroic behavior of the samples.

Chapter 7- This chapter presents the major achievements and the conclusions of the work, which is the outcome of our above experimental characterizations. This is followed by the scope of the above work in future.

Summary and Conclusions

The samples of delafossite type oxides comprising of two series $CuFeO_2$ and $CuCrO_2$ have been successfully synthesized by using the conventional solid-state reaction. The $CuFeO_2$ series is prepared by doping Ti, Mn, Ga and V at the Fe site was prepared with the help of a cost-effective solid-state technique under a high vacuum. $CuCrO_2$ series doped with Mg, Ti, Mn, Ni, Ga, Nb and V at Cr sites were also prepared. The in-depth XRD analysis confirmed the good quality of the samples without any impurity phases with the rhombohedral structure having space group R-3m. For the pure and doped $CuCrO_2$ samples the structural parameters correlate more with the expected valance state-based hole or electron doping induced changes in the local electronic structure rather than ionic sizes. Crystallite size along with induced lattice strain was also determined from XRD patterns for both series. SEM micrographs confirm the good crystallinity along with well-defined grain boundaries for both the $CuFeO_2$ and $CuCrO_2$ series samples.

Minor shifts in the E_g and A_{1g} modes in Raman of $CuFeO_2$ samples were observed due to Ti and Mn doping. A Jahn-Teller distortion-related extra peak was observed around 500 cm^{-1} but with variable strength. Mössbauer's measurement at room temperature confirmed the presence of octahedron distortion and suggested the absence of Fe^{2+} or mixed valence. The optical band gap had no significant changes in these samples. The phase purity of these samples prepared through the cost-effective solid-state reaction under high vacuum was further confirmed by the FTIR, Raman, and Mössbauer studies. Raman studies showed strong local distortions in Mn, Ti and Fe doped $CuCrO_2$ samples which had not been reported earlier. In both E_u and A_{2u} IR, active modes removal of degeneracy is observed, related to T_o and L_o optical modes of vibrations in Mn, Ti, Nb, Ga and V doped $CuCrO_2$ samples. The doping of mixed/or di- or tetra-valent ions reduced the bandgap of $CuCrO_2$ samples. These observed reductions in the band gap are related to changes in p-d hybridizations coupled with Jahn-Teller distortions rather than changes in bond distances, crystallite size, or unit cell volumes.

The dc conductivity studies of the $CuFeO_2$ samples showed a decrease in resistivity with the partial doping of the Fe site which can be correlated to the changes in carrier concentration as well as mobility due to induced charges and MO_6 based distortions. Small-polaron-based conduction was exhibited by the pure and Ti-doped $CuFeO_2$ samples. Moreover, Jonscher's law-based calculations through the exponent 'n' values showed an increasing trend for both the samples confirming non-overlapping small polaron tunneling (NSPT) model-based

behavior for conduction. The low-temperature electrical conduction behavior of $CuCrO_2$ samples is significantly altered with the electron or hole doping in these predominantly phonon-driven semiconducting systems. Here also a predominantly small polaron hopping process is established through ac conductivity studies. Jonscher's power law analysis here instead showed that for Ti and Mn-doped samples, the conductivity is attributed to the correlated barrier hopping model, while for samples with other substitutions it is related to the NSPT model.

The magnetic and dielectric studies for pure and Ti-doped $CuFeO_2$ samples demonstrate a significant role of Jahn–Teller effect-based local defects, particularly at low temperatures. The magnetization and dielectric permittivity measurements of the studied pure and doped $CuCrO_2$ samples showed clear evidence of magneto-dielectric coupling. Moreover, the 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 superexchange between $M^{3+/4+}$- Cr^{3+} mediated by oxygen at low temperatures. The present correlated study clearly highlights the role of doping level and local distortions in deciding the magnetic and multiferroic nature of this system providing an effective tool to tune its physical and chemical behavior.

Future Plans

Technological advances in the fields of optoelectronics, photonic and magnetic devices are incomplete without thin-film materials. In the form of thin films, the materials can be easily integrated into devices. The thermal stability and reasonably hard nature of thin films add to their usefulness. Semiconductors in the form of thin films are easy to study in terms of optical studies and charge concentration studies.

In the present samples due to large resistivity and inbuilt inhomogeneity when taken as pallets inconsistent results of Hall measurements were obtained. Such a problem can be solved with a well-characterized thin film. Also, X-ray absorption spectroscopy measurements can be performed for studying the fraction of transition metal cations in different spatial locations, their oxidation states, structural disorder, etc. Therefore, in order to obtain a better understanding of the present samples, some of the thin films have already been prepared using the pulsed laser deposition technique.

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List of Publications

A. Publications in Peer-Reviewed Journals

1. **Effects if 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, 791 (2019)134-143***.
2. **Role of Charge doping and distortions on the structural, electrical and magnetic properties 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 127 (2020) 175704***.

B. Publications in Proceedings of the International and National Conferences

1. **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**

   Nishant Barot, Prashant K. Mehta, Devang D. Shah and C. J. Panchal ***AIP Conference Proceedings 1837 (2017) 040031*.**
2. **Structure, microstructure and dielectric studies of PVA/$Sr(Co_{1/3}Nb_{2/3})O_3$ polymer composites**

   Nishant Barot, Bhagwati Bishnoi, Sagufta Jahaan, Prashant K. Mehta and N. L. Singh ***Invertis Journal of Science and Technology 10 (2017) 64-72.***
3. **Dielectric Behavior of Nanostructured $Y_{0.95}Ca_{0.05}MnO_3$: Role of Sintering Temperature**

   Zalak Joshi, Davit Dhruv, Sanjay Kansara, Megha Vagadia, **Nishant Barot**, P.K. Mehta, P.S. Solanki, D.G. Kuberkar, and N.A. Shah ***AIP Conference Proceedings, 1591 (2014) 1306-1308.***