Investigation of structural, electronic, magnetic and dynamical properties of transition metal doped delafossite-type oxides

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Name of the Student	**:**	Deepak Kumar Upadhyay
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Supervisor:
Prof. Arun Pratap
Department of Applied Physics, Faculty of Technology and Engineering,
The M. S. University of Baroda,
Vadodara-390001

Co-Supervisor:
Prof. P. K. Jha
Department of Physics, Faculty of Science,
The M. S. University of Baroda,
Vadodara-390002

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ABSTRACT

The ABO_2 (A= monovalent cations, B = trivalent cation) delafossite type oxide materials exhibit considerable potential to be used in p-n junction devices, transparent conductor materials, due to their a renewable and sustainable energy sector due to their to their layered structure and suitable band gap. However, the major drawback of delafossite type oxides is their low p-type conductivity as compare to the conventional n-type semiconducting materials. The p-type conductivity of these oxides depends on the p-d hybridization between the monovalent and trivalent cations which lead to the interesting results on the p-type conductivity and transparency of delafossite type oxides. Inspired from their flexible nature (in order to get higher p-type conductivity and bandgap) and performance in various fields researchers and scientists are exploring more and more p-type delafossite type compounds.

In this dissertation, we have systematically studied the pressure dependent structural, electronic, vibrational and elastic properties of bulk 2H- and 3R-$HCoO_2$ using first principles calculations within the framework of density functional theory (DFT). We particularly focus on the structural features, along with the dynamical and mechanical stability for the detailed investigation on structural-property relation between 3R and 2H-$HCoO_2$ under pressure. We also present a group theoretical analysis of the mode compatibility of $HCoO_2$ at symmetry points and in all directions of Brillouin Zone (BZ). Both the 2H and 3R-$HCoO_2$ are observed dynamically stable up to 34.3 and 38.3 GPa pressure respectively. The clear link detected between sheer modulus and phonon modes suggesting a sheer modulus driven dynamical instability in these compounds. The electronic, lattice dynamical and optical properties of $CuMO_2$ (M=H, Li, Na, K, Rb) have also been determined in detail. Our results of $CuMO_2$ indicate that the different alkali atoms have a significant influence on the electronic, lattice

dynamical, as well as on optical properties. The detailed study of optical properties such as dielectric constant, absorption coefficient, refractive index, reflectivity spectra, loss function and extinction coefficients have been carried out. Finally, a combined experimental and theoretical study using density functional theory is performed to analyse the effect of transition metal doping on the structural and electronic properties of the $CuCoO_2$ compound.

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Introduction

The energy demand is rapidly increasing at highest rate due to the in technological and industrial revolution. Humans used to depend on fossil fuels as their prime source of energy. Though, fossil fuel reserves are limited [1] and their production is falling over the time. Also, the fossil fuels have adverse effects on the environment because the gases emitted from burning the fuels trap the solar radiation leading to global warming and threatening the lives of humans and other creatures [2]. For these reasons, scientists are in search of the alternative sources of energy. Solar energy is found to be one of the most feasible options as the amount of solar energy reaching the earth is four orders of magnitude greater than the current world's energy consumption [3]. Over the last few decades, materials with delafossite type structures are extensively explored in photovoltaic and optoelectronic industries due to their broad range of electronic and optical properties [4-5]. Their remarkable optical transparency in the visible region is widely used in display screens, solar cells, smart windows etc. [6-8]. Moreover, their utilization as transparent conducting oxides (TCOs) can substitute conventional n-type conducting materials such as ZnO, In_2O_3 etc. in transparent optoelectronic applications. The discovery of p-type conductivity in delafossite structured $CuAlO_2$ is crucial as all technologically relevant transparent conducting oxides (TCOs) such as In_2O_3, ZnO are n-type semiconductors [9-10]. However, the biggest problem with delafossite $CuAlO_2$ or other p-type TCOs is their poor p-type conductivity and insufficient transparency for technological applications [11-12]. The major obstacle in order to predict the best p-type TCOs is the strong localization of holes at the valence band edge of most of the oxides. The *2p* orbitals of oxygen in metal oxide semiconductors is a main channel of hole transportation at the valence band maximum (VBM), however, the holes are quite localized [13]. This implies not only the difficulties in hole doping but also low hole mobilities due to

large hole effective mass. For obtaining such ambiguous materials, delafossites have been extensively explored in the past few years. Motivated from the significant structural-property relations in delafossite family, Hosono [14] proposed some guidelines for obtaining large band gap as well as dispersive valence band maximum (VBM) in p-type TCOs. The closed *d* shell of A^+ cations and presence of p-d hybridization in ABO_2 metal oxides make them an excellent optoelectronic material. The discovery of p-type conductivity in $CuAlO_2$ initialized the experimental and theoretical investigations of other delafossites [15]. The $CuCrO_2$ and $CuGaO_2$ delafossite type oxides exhibit remarkable properties together with the better p-type conductivity [16-17]. Among all delafossites, $CuCr_{1-x}Mg_xO_2$ [18] possesses the highest p-type conductivity of 220 Scm^{-1}. However, transparency in the visible range is only about 30%, which is very much lower compared to the traditional n-type TCOs. To obtain high p-type conductivity several other delafossites were explored for their utilization in solar energy devices. Tiago *et al.* [19] predicted several Cu, Ag, and Au based ternary oxides in delafossite structures. Recently, Burlet *et al.* [20] proposed a new delafossite structure for heterogenite cobalt oxy-hydroxides ($HCoO_2$) using Raman and IR spectroscopic measurements. It was observed that the doping of trivalent metal site with divalent dopants significantly enhances the conductivity of delafossite type oxides. Several attempts have been made to explain the trends in increasing conductivity with doping of different divalent cations [21]. The conductivity increases due to a reduction in ionic radius of the trivalent cations. The electronic bands near the Fermi level is accomplished by hole doping into a wide gap Cu^+ oxide, which has the d^{10} closed shell. Hence, the valence band maximum was expected to have the contribution of Cu-3d with some O- 2p orbitals. The conductivity of these oxides depends on the p-d hybridization; the suitable combination of monovalent and trivalent cations can give interesting results on the conductivity and transparency of delafossite oxides. Aside from this, great deals of efforts are being diverted to predict new chemical

compositions with variety of crystal symmetries aiming low effective mass and high p-type conductivity in delafossites type oxides. Previous studies predicted that the chemical modulation and valence band engineering can improve the p-d hybridization states in common delafossite oxides [22-23]. Motivated by this fact we have investigated the structural, electronic, vibrational and optical properties of new class of delafossite type oxides. Our main interest is to find out the suitable materials having large band gap and high p-type conductivity.

Objectives

The aim of this proposed work is to investigate the structural, electronic vibrational and magnetic properties of various delafossite oxides to provide a better understanding of physical and chemical properties of delafossite compounds, including doping induced characteristic of copper based delafossite. The doping effect will be investigated on electrical conductivity, vibrational properties; and in magnetic properties. The specific objectives of the present work are:

1. To investigate and understand the possible modifications in structural and electronic properties of delafossite compounds by determining the ground state optimization, electronic band structure and density of states (DOS) at ambient and extreme conditions.

2. To investigate the influence of transition metals on magnetic properties of delafossite compounds.

3. To investigate the lattice distortions, dynamical instability and vibrational properties by computing phonon dispersion curve and density of states.

4. To investigate the structural and magnetic transitions of delafossite compounds at different temperatures and pressures.

5. To simulate the pressure dependent Raman spectra to understand the phonon driven phase transition.

Summary of Research Work

The present thesis is organized in the following manner:

Chapter 1 contains the sustainable development and progress of transition metal oxides in the field of p-type transparent conducting oxides (TCOs). Transition metal oxides attract a lot of attention due to a great variety of physical phenomena, most of which go along with the ordering of some microscopic degrees of freedom as a function of temperature, pressure, or doping. Delafossite type oxides are the unique material in the family of transition metal oxides. They show the p-type conductivity and simultaneously transparency in the visible light region. Due to the unique ability of delafossites they are useful in electrodes for hydrogen production by photo-electrochemical (PEC) water splitting and transparent conductive oxides (TCO) in optoelectronic devices. It is the p-type conductivity and good hole mobility which established the delafossites so unique and more attractive in these applications compared to other metal oxides. For instance, due to their p-type nature, the delafossites are resistive against oxidative corrosion. Some recent studies demonstrated that the Cu based delafossites are stable in solution and are capable of H_2 evolution from water. For the application of TCOs, the currently available TCOs, such as ZnO, In_2O_3, TiO_2 are mostly n-type; hence, their utilization is limited to transparent p-n semiconductor devices. The realization of p-type conductivity and good hole mobility in delafossites is because their valence band maximum (VBM) is composed of hybridized Cu d and O p antibonding orbitals. This chapter reviews the recent development of delafossite type oxides in field of optoelectronics and photovoltaic applications. Furthermore, this chapter covers the advantages and disadvantages of the delafossite materials together with the mechanism of p-type conductivity and transparency of these oxides.

The description of methodology used throughout the work is presented in **Chapter 2**. In this chapter, we briefly introduce the basic concepts of density functional theory (DFT) along with its formulation. In particular, we have described all the quantities which are

helpful for the calculation of the electronic, lattice dynamical and mechanical properties of the materials on the basis of DFT are discussed. We present all the basic ideas of many body problems, Born-Oppenheimer, Hartree and Hartree-Fock approximations followed by density based method Thomas-Fermi method and Kohn-Sham equation. Moreover, the use of plane wave to represent electron wave functions and density needed to deal with valance and core electrons implemented in Quantum Espresso simulation code are discussed. We also discuss the Random phase approximation (RPA) which is an important basis for the optical properties. Finally, we describe the formulation of Raman spectra calculation using DFT.

In **Chapter 3**, we report the results of systematic study of the newly predicted delafossite $HCoO_2$. This chapter presents the structural, electronics, lattice dynamical and mechanical properties of $HCoO_2$. The study provides the clear picture of the structure-property-relation of $HCoO_2$ with the successfully determination of the existence of two polytypes of $HCoO_2$ in the form of rhombohedral and hexagonal (See Fig. 1). Further, we investigated the high-pressure behaviour of both polytypes of $HCoO_2$ using state of the art density functional theory (DFT) calculations.

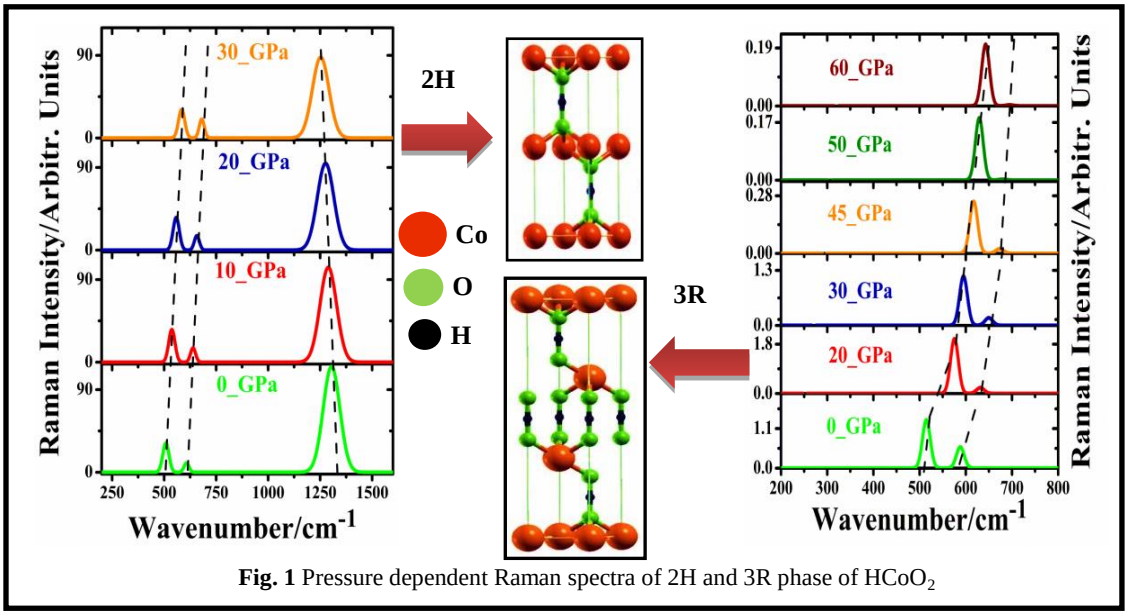

Fig. 1 Pressure dependent Raman spectra of 2H and 3R phase of $HCoO_2$

The local density approximation (LDA) and generalized gradient approximation (GGA) as the exchange correlation functional were taken into consideration. For the calculation of electronic

band structures, we have also used the on-site coulomb interaction U term with LDA calculations and found improvement in our results. The obtained ground state properties for both polytypes agree well with experimental and previously reported theoretical data. The electronic band structure shows that both phases are semiconductor with an indirect band gap in the range of 2.01-2.06 eV. The pressure dependent phonon dispersion curves and elastic constants depict the instability of 2H and 3R phase around 35 and 40 GPa pressure respectively.

Chapter 4 presents the Comparative *ab initio* study of the structural, electronic, dynamical and optical properties of group-I based $CuMO_2$ (M=H, Li, Na, K, Rb) delafossite compounds. The crystal geometry of considered systems are presented in Fig.2. The different alkali atoms have a significant influence on their electronic, dynamical, as well as optical behaviour. By means of first principles based DFT calculations we explore the universality of electronic characteristics, dynamical stability and optical properties of these compounds. The electronic band structures, vibrational frequencies and optical properties have been directly connected with the atomic radius of the alkali atoms. The electronic band gap of $CuMO_2$ (M=H, Li, Na, K, Rb) lies within the range of 0.5—1.0 eV bringing them in the group of low band gap p-type semiconductors. We found a significant increase in the band gap and p-d hybridization as going from H to Rb. Partial density of states (PDOS) revealed strong metal-oxygen (Cu—O) overlap, due to the strong p-d hybridization. The phonon dispersion curves obtained for these compounds confirm the dynamical stability as there is no imaginary frequency observed throughout the Brillouin zone (BZ). The static dielectric constants and refractive index fall within the range of 8.0—12.91 and 1.98—3.55 respectively suggesting usefulness of scrutinized compounds in non-linear optical devices. The optical properties depict that the alkali atoms based delafossites can serve as promising candidates for highly efficient optical devices within a broad range from visible to ultraviolet light of electromagnetic spectra.

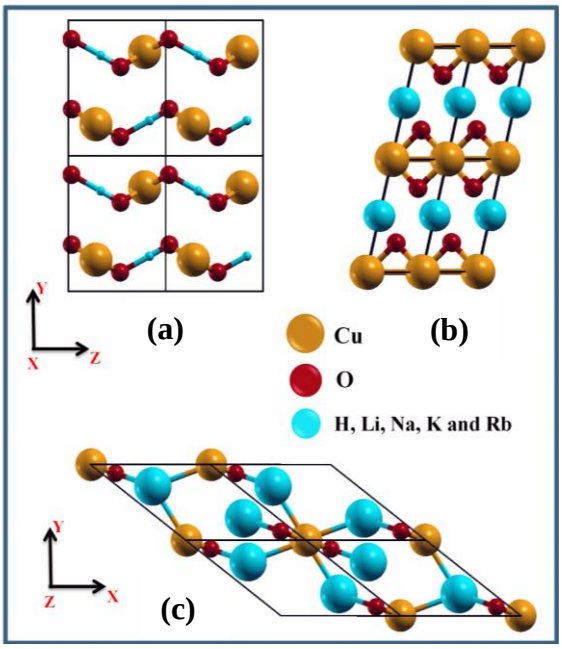

Fig 2. Crystal geometry of (a) $CuHO_2$ (b) $CuLiO_2$ and (c) $CuMO_2$ (M=Na, K and Rb)

In **Chapter 5**, we have analysed the effect of vanadium (V) doping in $CuCoO_2$ delafossite. We have successfully analysed the structural and electronic modulation of $CuCoO_2$ when doped with V atom. This chapter contains the combined experimental and DFT study of the $CuCoO_2$. We have used the solid-state reaction method for the synthesis of $CuCoO_2$. X-Ray diffraction confirms the pure phase formation of this oxide, and also provides the evidence of V doping at cobalt site. The X-ray photoelectron spectroscopy (XPS) confirms the p-d hybridization of V doped $CuCoO_2$ which is confirmed by the theoretically calculated electronic density of states (DOS) and also reveals the metal-oxygen (Cu-O) overlap near the Fermi level.

The results of DFT calculations on structural, electronic, lattice dynamical and mechanical properties of various delafossite type oxides have been summarized in **Chapter 6**. The obtained unique properties of these oxides presented in previous chapters systematically summarized and linked with their potential applications such as TCOs solar cell and optoelectronics. Finally, the thesis concluded with a brief discussion on possible future work.

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List of Publications Related to Thesis

1. **Deepak Upadhyay**, A. Pratap and P. K. Jha, A first principles study on structural, dynamical, and mechanical stability of newly predicted delafossite $HCoO_2$ at high pressure, *J. Raman. Spectrosc.* **50,** (2019) 603. DOI: 10.1002/jrs.5538.
2. **Deepak Upadhyay**, A. Patel, A. Pratap and P. K. Jha, Electronic properties and stability criteria of rhombohedral $HCoO_2$, *AIP Conf. Proc.* **1942,** (2018) 090027. DOI: 10.1063/1.5028942.
3. **Deepak Upadhyay**, A Pratap, P. K. Jha, Electronic and optical properties of ferromagnetic $CuCrO_2$, $AgCrO_2$ and $AuCrO_2$, *AIP Conf. Proc.* **2115,** (2019) 030516. DOI: 10.1063/1.5113355.
4. **Deepak Upadhyay**, N. Joshi, A Pratap and P. K. Jha, Comparative *ab initio* study of the structural, electronic, dynamical and optical properties of group-I based $CuMO_2$ (M=H, Li, Na, K, Rb) *J. Appl. Phys*. **128,** (2020); DOI: 10.1063/5.0019961.
5. **Deepak Upadhyay**, A. Pratap and P. K. Jha, Computational Insights into the electronic and optical properties of newly predicted delafossite $CuFO_2$ (In Press, *AIP Conf. Proc.*).

List of Publications Non-Related to Thesis

1. B. Roondhe, **Deepak Upadhyay**, N. Som, S. B Pillai, S. Shinde and P. K. Jha, Structural, Electronic and Dynamical Properties of Curium Monopnictides: Density Functional Calculations, *J. Elect. Mater.* **46** (2017) 1842. DOI: 10.1007/s11664-016-5247-1
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