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

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Research Methodology and Key Findings

Present thesis describes the physical properties of newly predicted structures of delafossite as well as the effect of transition metal doped $CuCoO_2$ delafossite. We have investigated the detailed structural and vibrational properties of 3R ($R\bar{3}m$) and 2H ($P6_3/mmc$) phase of $HCoO_2$. The composition of $HCoO_2$ is different from the conventional delafossites however; the structure is similar to the delafossite [1]. Our aim is to investigate the structural, electronic, vibrational and mechanical properties of $HCoO_2$ compound, and to compare these calculated properties with the conventional delafossites. A comparative density functional theory study of the structural, electronic, vibrational and optical properties of group I based delafossite $CuMO_2$ (M = H, Li, Na, K, Rb) is performed. Present work is focused on the idea of the exploration of new structural features of delafossite type oxides with combination of alkali metals [2]. It is well established that the doping of transition metal ions at the place of trivalent cations, results into the high electrical conductivity and the low hole effective mass. In this case $CuCo_{1-x}V_xO_2$ is explored for the structural, electronic and magnetic properties [3].

Chapter 1 describes the importance of delafossite type oxides their propertie**1** | P a g e s and applications. The delafossite type oxides are p-type semiconducting materials used in various applications such as transparent conducting oxides (TCOs), solar cells, catalysis and thermoelectric devices [4]. The origin of p-type conductivity in delafossite type oxides their limitations and improvements are systematically defined in this chapter.

In **Chapter 2**, the overview of the density functional theory (DFT) [5] and the experimental techniques for sample preparation is described. Computational details of the vibrational and optical properties are also described in this chapter. Further, the characterization techniques such as X-ray diffraction, Raman Spectra, X-ray photoemission

(XPS), VSM are discussed. The challenges of the electronic band structure and phonon calculations for the complexes are explained.

Chapter 3, covers the structural, electronic, vibrational and mechanical properties of hexagonal (2H) and rhombohedral (3R) phases of $HCoO_2$ are described. The high-pressure behaviour of both polytypes of $HCoO_2$ is determined using state of the art first principles calculations based on DFT. The details of different exchange correlation functionals such as local density approximation (LDA) and generalized gradient approximation (GGA) and their effects on electronic properties are discussed. The structural properties of both polytypes of $HCoO_2$ are investigated in this chapter. Here, we have explored the structure, electronic and vibrational properties of both the polytypes and compare these properties with the conventional delafossite. Further, the high pressure behaviour of both polytypes of $HCoO_2$ is investigated. For the accurate description of electronic band gap we have used different approximation such as local density approximation (LDA) and generalized gradient approximation (GGA). Additionally, the electronic band structure is calculated using the on-site coulomb interaction U term. These two polytypes exhibits indirect band gap semiconductors with the band gap in the range of 2.01 eV-2.06 eV. Further, the structural evolution with respect to the pressure depicted the change in lattice parameters, volume and the bond length of these polytypes. The linear decrement in O-H bond length with pressure is observed for both phases with pressure. The phonon dispersion curves show the dynamical instability of 2H phase at 35 Gpa while the 3R phase is unstable around 40 Gpa. Raman spectra show that the A_{1g} mode is more sensitive to the pressure. The mechanical stability of these compounds investigated in terms of the stiffness matrix and Born stability criteria. The elastic constants of 2H and 3R-$HCoO_2$ shows the existence of phase transition beginning around 34.3 and 38.3 Gpa pressure derived from the shear modulus.

In **Chapter 4**, a comparative study of the structural, electronic, vibrational and optical properties of the alkali atom based $CuMO_2$ (M= H, Li, Na, K, Rb) is reported. The description of electronic band structure along with the projected density of states (PDOS) is described in terms of hybridization of the orbitals. Finally, the applicability of these compounds is discussed with respect to the optoelectronics applications. Although the similar chemical compositions of group I based delafossites ($CuMO_2$ (M = H, Li, Na, K, and Rb)), display diverse structural, electronic, dynamical, and optical properties. The atomic radii of the different elements of group I, starting from H to Rb has significant influence in their electronic, lattice dynamical and optical properties. We determine the uniqueness of ground state properties of these compounds by means of first principle calculations based on the density functional theory (DFT). The electronic band structures, phonon dispersion curves (PDCs) and the optical properties are profoundly linked with the atomic radii of the group-I atoms. The electronic band gap of $CuMO_2$ (M = H, Li, Na, K, and Rb) found within the range of 0.5-1.0 eV, categorized them in the low band gap p-type semiconductors. The band gap increase with respect to the atomic radii of the alkali atoms like the conventional delafossites. The metal-oxygen (Cu-O) overlap is observed due to the robust p-d hybridization. Dynamical stability is confirmed from the phonon dispersion curves, as there is no imaginary frequency observed in the entire Brillouin zone. The refractive index and static dielectric constants fall within the range of 1.98-3.55 and 8.0-12.91 respectively, suggesting the utility in none-linear optical devices. The optical properties depicted the utility of these delafossites as promising candidates for improved optical devices.

Chapter 5 deals with the effects of vanadium doping on the structural, electronic and magnetic properties of $CuCoO_2$. The method of sample preparation, characterization techniques, and the brief description of the computational parameters are provided in this chapter. The XRD diffraction patterns confirm pure rhombohedral phase formations of

pristine CCO and V doped CCO. The V prefers the tetravalent occupancy (V^{+4}) when doped at Co site. The VBM modulation is observed during V doping due to higher metal oxygen overlap. The pristine CCO compound shows an indirect band gap of 1.03 eV while it reduced to 0.40 eV when doped with V atoms. Furthermore, we report a study of magnetic properties of delafossite CCO and CCVO by a vibrating sample magnetometer (VSM). The pristine CCO and doped CCVO compounds shows paramagnetic behavior. The V doping slightly increases the magnetization values confirmed by the theoretical calculations. The magnetic properties of these compounds are also depends on ionic radii of trivalent atoms. The electronic band structure and the PDOS of these compounds indicated the p-d hybridizations induced by the V doping. The p-d hybridizations observed in V doped CCO indicated that the substitution of V at the Co site generates more free holes and it is good for better p-type conductivity. The results of dielectric constant and absorption coefficient of pristine and V doped CCO indicate that these compounds can be used in optoelectronics. Refractive index spectra increase in the visible region and the reflectivity spectra show maximum peaks in the ultraviolet region, and the loss spectra indicate the least energy loss by an electron in the visible region, confirming potential applications of these compounds in optoelectronic applications.

Conclusion

The thesis has focused on novel ABO_2 delafossite type oxides for their fundamental understanding and applications in transparent conducting oxides (TCOs), solar cells and optoelectronics. A combined theoretical and experimental study is carried out to explore the novel delafossite type oxides. Theoretical techniques such as density functional theory (DFT) and density functional perturbation theory (DFPT) formed the basis for our predictive first-principles calculations. Additional theories and methods were utilized to capture additional physics and to calculate fundamental materials properties. The results of the thesis provide a

substantial foundation for the intrinsic electronic and high pressure stability of novel $HCoO_2$ and their polytypes. The group-I (alkali atoms) based delafossites have been proven to be a good candidate for optoelectronics as well as TCOs applications. Further, the idea of transition metal doping has been utilized to investigate the effects of doping on the structural, electronic as well as magnetic properties of these oxides. We have considered the desirable material characteristics with the downsides to each material and shown that each of these semiconductors shows significant promise for the aimed applications. Each chapter compares the results with existing theoretical and experimental data in addition to significantly expanding the available knowledge. The results contained herein advance the field of p-type semiconductors and TCOs in materials science and provide a basis for future theoretical and experimental work which can implement these materials in optoelectronic devices.

Future Scope

First, it will be important to synthesize and characterize computationally predicted transparent conducting p-type materials (e.g, group-I based oxides, halogen atom based compounds etc.). Second, we suggest continued research into combining known compounds with complementary properties to tune desired functionality. This involves continued investigation into anion and cation alloying in the materials. Third, clever engineering of known delafossite compounds, including new processing techniques, nonequilibrium synthesis methods, post processing, etc., to promote carrier transport and high doping in delafossite host materials. Additionally, it is beneficial to engineer quasi-molecular structures, where the VBM is more disperse than the CBM, and explore band engineering by thinning materials to tune band gaps and mobilities. Further, the replacement of oxygen atoms (that restrict the p-type conductivity) with the chalcogenide (S, Se, Te) atoms together with the mixed oxygen and chalcogen compounds better known for oxychalcogenides can be explored. Delafossite type transition metal nitrides (MCN_2; M = Ni, Co, Fe, etc.) and their

low dimensional counterparts can provide desirable properties in terms of p-type conductivity and optical transparency. The oxyhydroxides and their monolayers can be explored for the delafossite type structures and further their band gap modifications.

Finally, this thesis motivates continued investigation of interfaces of wide band gap delafossites and their device applications. Developing a theoretical understanding of stability, degradation, and interface modeling in these oxides are essential to decide which materials can be used in devices. In particular the band alignment of the systems we have discussed remain undetermined, and understanding them will be critical to tailoring materials to a particular device applications. The idea of co-doping in delafossite type compounds can be a potential approach to achieve desire p-type conductivity. Incorporating both n-type and p-type materials into existing devices, as well as designing new device architectures using these unique materials, could lead to significantly higher performances and efficiencies. Together, this suite of future advances into p-type delafossite materials and devices containing such materials could be a key component in accelerating society's renewable energy transformation and enabling future technological advances. Another future work would be to apply the electron-phonon coupling method to investigate the carrier dynamics in selected delafossite compounds.

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