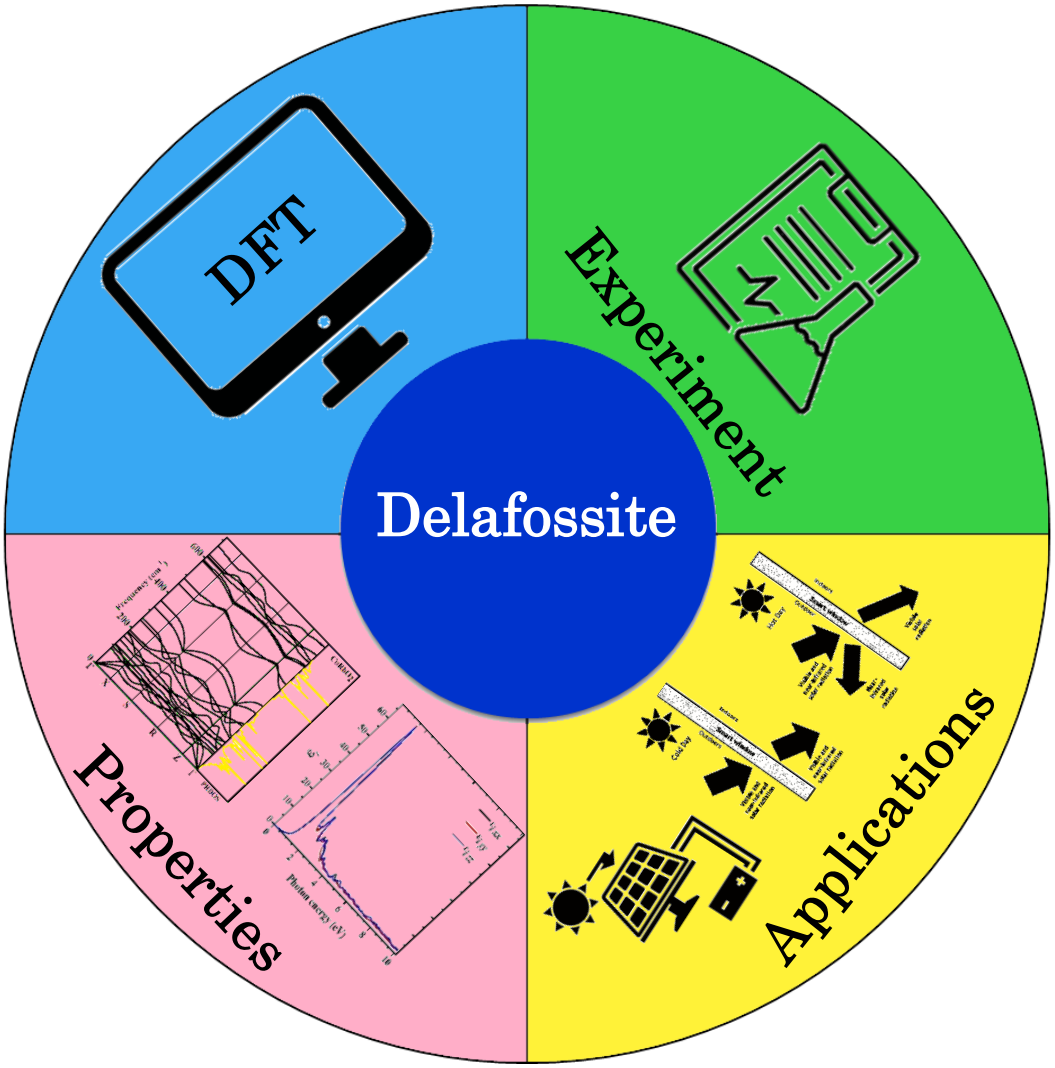
CHAPTER 6

Conclusions and Future Scope



6.1 Conclusions

The entire thesis work aimed to investigate the fundamental properties of novel ABO_2 delafossite type oxides and their applications in transparent conducting oxides (TCOs), solar energy converters and optoelectronics using a combined theoretical and experimental study. 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 the fundamental properties of materials. The findings 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 stand out as a promising candidate for their applications in optoelectronics as well as TCOs. To investigate the effect of substitutional doping on the structural, electronic as well as magnetic properties of these oxides, the idea of transition metal (TM) doping was taken into consideration. We have considered the desirable characteristics of each materials along with their downsides and shown that each of these semiconductors exhibits potential for aimed applications. The results presented in each chapter compared 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 as well as provide a basis for future theoretical and experimental work that can implement these materials in optoelectronic devices.

An introduction to TCOs and other applications of these materials along with their important properties and fabrication methods, are presented in **Chapter 1**. It is followed by a general explanation of the basics of DFT and the experimental synthesis together with the characterization techniques in **Chapter 2**. Further, **Chapters 3, 4 and 5** comprise the main results of the thesis those are concluded below.

The novel oxyhydroxides $HCoO_2$ in delafossite type structure examined in **Chapter 3** named as polymorph exploration of $HCoO_2$ system under high pressure. A systematic investigation of the structural, electronic, vibrational and elastic properties of 2H- and 3R-$HCoO_2$ at high pressure was carried out using first-principles calculations within the DFT. Our results provide an accurate description of the electronic band structure and band gap of the $HCoO_2$ in both hexagonal (2H) and rhombohedral (3R) phases using LDA+U calculations. The calculated phonon dispersion curves (PDCs) and Raman spectra provide a deep understanding of the high-pressure behavior of these polytypes. Pressure-dependent PDCs depict the dynamical instability for both 2H and 3R phases of $HCoO_2$ at 35 GPa and 40 GPa due to the softening of E_{2u} and A_{2u} modes respectively. The mechanical properties as well as stability of these polytypes, have been determined by calculating the elastic constants. The 2H- and 3R-$HCoO_2$ are mechanically stable up to 34.3 and 38.3 GPa respectively. The negative value of elastic constant C_{44} after these pressures display the violation of the Born stability criteria. This study confirms the relation between shear modulus and phonon modes and suggests a shear modulus driven dynamical instability.

As the second step, we have investigated structural, electronic, lattice dynamical and optical properties of the newly predicted novel p-type group-I-based delafossite CuMO2 (M=H ,Li ,Na,K,Rb) in **Chapter 4**. These semiconducting compounds possesses an indirect band gap nature. The band gap of these compounds found lower than the conventional delafossite type oxides. Their unique structural geometry and different bonding nature initiate the significant p-d hybridization and is the main source of p-type conductivity. As we move from H-Rb, increment in the band gap and p-d hybridization provides a clear indication of the alkali atom induced metal-oxygen (Cu—O) overlap. The PDCs and phonon density of states (PhDOS) reveal that the CuMO2 (M=H ,Li ,Na,K,Rb) compounds are dynamically stable. The direction dependent calculations for the dielectric function and optical matrix elements illustrate the

anisotropy in the electronic and optical properties. These results reflected in the band gap value and the near-band-edge optical properties. The fallouts of the dielectric constant and absorption coefficient point out that the $CuMO_2$ with M = Na, K and Rb can be utilized for solar energy converters. While, the value of the static refractive index implies the usefulness of $CuMO_2$ compounds in nonlinear optical devices. In the reflectivity spectra, high-intensity peaks appeared in the visible region and the loss spectra indicate less energy loss by an electron confirm potential applications of these compounds in optoelectronics.

Chapter 5 presents the effects of vanadium (V) doping on the structural, electronic and magnetic properties of $CuCoO_2$ (CCO). This work presents a combined experimental and theoretical investigation on the CCO and its V doped counterpart (CCVO) at different concentrations. The XRD diffraction pattern confirm the pure rhombohedral phase formation of pristine CCO and CCVO. The phase formation and bonding environment are further analysed by Raman and XPS spectroscopies. It was found that the V prefers the tetravalent occupancy (V^{+4}) when doped at Co site. The pristine CCO compound displays an indirect band gap of 1.03 eV which reduces to 0.40 eV when doped with V atom. The modulation observed in valence band maximum (VBM) after doping of V originated from the higher Cu-O overlap. In the electronic band structure and projected density of states (PDOS) of CCVO, notable p-d hybridization was detected which is induced by the V atom. The p-d hybridization observed in CCVO indicates that the substitution of V at the Co site generates more free holes and is supposed to enhance the p-type conductivity. Furthermore, we report the magnetic properties of CCO and CCVO compounds examined by a vibrating sample magnetometer (VSM). The experimental results display paramagnetic behaviour of pristine CCO and doped CCVO compounds. In the case of CCVO, V doping slightly increases the magnetization values and is supported by the theoretical findings as well. It was also examined that the magnetic property of these compounds also depends on the ionic radii of trivalent atoms.

6.2 Future Scope

First and foremost, it is vital 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, the clever engineering of known delafossite compounds, including new processing techniques, nonequilibrium synthesis methods, post-processing, etc., to promote carrier transport and a higher concentration of TM doping in host materials. Additionally, it is beneficial to engineer quasi-molecular structures, where the VBM is more disperse than the conduction band minimum (CBM) and explore band engineering and carrier mobility of low-dimensional materials. Further, the replacement of O atoms (that restrict the p-type conductivity) with the chalcogenide (S, Se, Te) atoms (the mixture of oxygen and chalcogen compounds) known as oxychalcogenides can be explored. Delafossite type transition metal nitrides and their low-dimensional counterpart can provide desirable properties in terms of p-type conductivity and optical transparency. The oxyhydroxides and their monolayers can also be explored within the delafossite type structures and further for their band gap modifications.

Finally, this thesis motivates the continued investigation of interfaces of wide band gap delafossites and their device applications. Developing a theoretical understanding of stability, degradation, and interface modelling of these oxides is essential to decide which material found its applicability to certain devices. In particular, the band alignment of the systems remained undetermined and distinguishability of its nature will be crucial for tailoring materials to particular device applications. The idea of substitutional doping of TM in delafossite type compounds can be a potential approach to achieve desired p-type conductivity. Incorporating both n-type and p-type materials into existing devices as well as carving new device

architectures of these unique materials, could lead to higher performances and enhanced efficiencies. Together, this suite of future advances into p-type delafossite materials and devices containing such materials could be a key part in accelerating society's renewable energy transformation and enabling future technological advances. Also, at the theoretical front, it would be an important future work to apply the electron-phonon coupling method to investigate the carrier dynamics in selected delafossite compounds.