

List of Figures

Figure 1.1: The schematic shows the band gap for transparent conducting oxides (TCOs). Incident visible photons induced excited holes and electrons.	2
Figure 1.2: Schematic representations of Chemical Modulation of the Valence Band methods.	4
Figure 1.3 : (a) Primitive and (b) conventional cell of delafossite structures.....	5
Figure 1.4 : (a) Effective mass versus band gap for the p-type and n-type semiconductors, (b) bar graph shows the effective mass distribution for electrons and holes in oxides, (c) graphical representation of the electrical conductivity (σ) and optical transparency (T_{vis} %) [37]	6
Figure 1.5 : Schematic representations of the applications of delafossite oxides in environmental applications such as catalysis, sensors, and CO ₂ reduction, dye sensitized solar cells etc.....	12
Figure 2.1: Schematic representation of the sample preparation methodology.....	37
Figure 2.2: Schematic diagram depicting the working of vibrating sample magnetometer. ..	39
Figure 3.1: Crystal structure of (a) Hexagonal (2H) and (b) Rhombohedral (3R) HCoO ₂	45
Figure 3.2: Pressure dependent O-H bond length for 2H and 3R-HCoO ₂ . Blue line shows the linear fitted curve: $y = (1.19 \pm 0.00008) - (0.00123 \pm 0.000003)x$	45
Figure 3.3: Reduced lattice parameters (a , c) and reduced volume (v) as a function of pressure of (a) 2H-HCoO ₂ and (b) 3R-HCoO ₂ . a_0 , c_0 and v_0 are the lattice parameters and volume at 0 GPa.....	46
Figure 3.4: The electronic band structure and density of states (DOS) calculated by LDA+U for (a) 2H-HCoO ₂ (b) 3R-HCoO ₂ . The Fermi energy is set to zero.	47
Figure 3.5: Pressure dependent electronic band gap of 2H- and 3R-HCoO ₂ . Red dots and black squares indicate our calculated value and the corresponding lines show the polynomial fitted curve with equation: $y = 2.012 + 0.00632x - (1.21 \times 10^{-5})x^2$	47
Figure 3.6: Phonon dispersion curves and phonon density of states of 2H-HCoO ₂ at (a) 0 GPa and (b) 35 GPa. Inset shows the imaginary wavenumber of 2H-HCoO ₂ at 35 GPa between Γ - K	50
Figure 3.7: Phonon dispersion curves and phonon density of states of 3R-HCoO ₂ at (a) 0 and (b) 40 GPa.	51
Figure 3.8: Pressure-dependent Raman active modes of (a) 2H-HCoO ₂ and (b) 3R-HCoO ₂	51
Figure 3.9: Calculated Raman spectrum of (a) 2H-HCoO ₂ and (b) 3R-HCoO ₂ at different pressures.....	53

Figure 3.10: Calculated elastic constants of (a) 2H-HCoO ₂ and (b) 3R-HCoO ₂ at different pressures. (c) Pressure-dependent C ₄₄ elastic mode of 2H- and 3R-HCoO ₂ .	55
Figure 3.11: Elastic moduli, bulk (B), shear (G), and Young's (E) modulus as a function of pressure for (a) 2H- for peer review HCoO ₂ and (b) 3R-HCoO ₂ .	55
Figure 4.1: Crystal geometry of (a) CuHO ₂ (b) CuLiO ₂ and (c) CuAO ₂ (A= Na, K and Rb).	63
Figure 4.2: Electronic band structure of CuMO ₂ compounds (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	65
Figure 4.3: Projected density of states (PDOS) of CuMO ₂ compounds (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	66
Figure 4.4: The phonon dispersion curves of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	68
Figure 4.5: Real part of a dielectric function of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	72
Figure 4.6: Imaginary part of a dielectric function of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	74
Figure 4.7: Absorption coefficient of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	75
Figure 4.8: Refractive index of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	75
Figure 4.9: Extinction coefficient of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	77
Figure 4.10: Reflectivity spectrum of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	78
Figure 4.11: Loss Spectrum of (a) CuHO ₂ (b) CuLiO ₂ (c) CuNaO ₂ (d) CuKO ₂ and (e) CuRbO ₂ .	78
Figure 5.1: (a) Crystal geometry of delafossite type structures where brown, blue yellow and red balls represent the Cu, Co, O and V atoms respectively. The conventional unit cell, primitive unit cell and 2×2×1 supercell. (b) Comparative simulated and observed XRD patterns of pristine CCO. (c) XRD Pattern of Pristine and vanadium doped CuCoO ₂ .	87
Figure 5.2: (a) Overall core level XPS spectra of the CCO and CCVO samples. (b) XPS spectra of the Cu 2p (c) Co 2p (d) O 1s and (e) V 2p.	89
Figure 5.3: (a) Spin polarised electronic band structures of pristine CCO (b) V doped CCVO (0.08) (c) Projected density of states (PDOS) of CCO (d) V doped CCO compounds.	90
Figure 5.4: (a) Experimental and theoretical Raman spectra of pristine CCO compound (b) The phonon dispersion curves (PDCs) of CCO unit cell. Right panel of the graph shows the	

vibrational modes in perpendicular and parallel direction. (c) Phonon eigen vectors with the frequency of CuCoO_2 at zone center.	92
Figure 5.5: M–H curves of CuCoO_2 (CCO) and $\text{CuCo}_{1-x}\text{V}_x\text{O}_2$ (CCVO) (0.06) powders measured at 300 K.	95
Figure 5.6: Real part of dielectric functions of (a) pristine CCO and (b) vanadium doped CCO.	97
Figure 5.7: Imaginary part dielectric functions of (a) pristine CCO and (b) vanadium doped CCO.	97
Figure 5.8: Absorption coefficient α ω of (a) pristine CCO and (b) vanadium doped CCO. .	98
Figure 5.9: Refractive index n (ω) of (a) pristine CCO and (b) vanadium doped CCO.	99
Figure 5.10: Extinction coefficient k (ω) of (a) pristine CCO and (b) vanadium doped CCO.	100
Figure 5.11: Optical reflectivity spectra of (a) CCO and (b)) vanadium doped CCO.	100
Figure 5.12: Energy loss spectra of (a) CCO and (b)) vanadium doped CCO.	101

List of Tables

Table 3.1: Calculated lattice parameters of 2H- and 3R- HCoO_2 along with reported experimental (Exp.) and theoretical data	44
Table 3.2: Calculated Raman Modes of 2H- and 3R- HCoO_2 along with experimental (Exp.) data.	54
Table 3.3: Pressure dependent elastic constants, bulk (B), shear (G) and Young’s (E) modulus as well as B/G ratio and Poisson’s ratio of 2H- HCoO_2	56
Table 3.4: Pressure dependent elastic constants, bulk (B), shear (G) and Young’s (E) modulus as well as B/G ratio and Poisson’s ratio of 3R- HCoO_2	56
Table 4.1: Lattice parameters (a, b, c in Angstrom) of CuMO_2 (M=H, Li, Na, K, Rb).	64
Table 4.2: Character Table of CuHO_2 and CuLiO_2	68
Table 4.3: Character table of CuNaO_2 , CuKO_2 and CuRbO_2	69
Table 4.4: Born effective charges Z^* in atomic units of CuMO_2 (M=H, Li, Na, K, Rb).....	70
Table 4.5: Static (ϵ_0) and high frequency (ϵ_∞) dielectric constant in parallel and perpendicular directions, dielectric tensor ($\Delta\epsilon_0$) along with refractive index $n(0)$ and degree of birefringence $\Delta n(0)$ of CuMO_2 (M=H, Li, Na, K, Rb).	73