A.10: Structural, optical and electronic properties of $Ni_{1-x}Co_xO$ in the complete composition range

The bivalent transition metal oxides, NiO and CoO, are wide band gap (NiO: ~4 eV; CoO: ~2.2 eV) p-type semiconductors having cubic rock-salt crystal structure above Neel temperature (NiO: 523K; CoO: 291 K). These oxides and their ternaries have applications in photo-detection, resistive switching, batteries, transparent electrodes, antiferromagnetic spintronics and solar cells. Since, a systematic study of the variation of the physical properties, specifically band gap of $Ni_{1-x}Co_xO$ ternary over complete composition range is not available; we have studied the crystallographic, optical and electronic properties of the mixed system of NiO–CoO for their possible applications in band gap engineering and transparent anti-ferromagnetic spintronics with tunable Neel temperature.

A series of $Ni_{1-x}Co_xO$ (x= 0, 0.10, 0.20, 0.30, 0.39, 0.50, 0.59, 0.68, 0.78, 0.87 and 1.0) ternary solid solutions with varying Co composition has been synthesized using solid state reaction method. The crystalline structure, lattice parameters and the phase purity of the samples were determined by x-ray diffraction (XRD) measurement at extreme conditions x-ray diffraction (ECXRD) beamline (BL-11), Indus-2, using a beam of wavelength of ~0.5 Å. The lattice parameters of phase pure $Ni_{1-x}Co_xO$ is found to increase linearly with "x", following the Vegard's law. EXAFS measurements were performed, at Ni and Co K-edges, at the scanning EXAFS beamline (BL-09), Indus-2, under ambient condition. The near neighbor (Ni/Co–O) and next near neighbor (Ni–Ni/Co–Co/Ni–Co) bond lengths are found increasing linearly with "x". The variation of these bond lengths nearly follow the variation of bond lengths evaluated from virtual crystal approximation (VCA), which is unlike most conventional ternary semiconductors, where the distortion in the local structure around the constituent atom is observed. The variation of Neel temperature and the optical gap with composition have been determined by differential scanning calorimetry (DSC) and diffuse reflectivity spectroscopy (DRS) measurements, respectively. Even though a linear variation of structural parameters and Neel temperature are observed with composition variation, throughout the complete composition range, the variation of the optical gap deviates significantly from a linear behavior, which is quite different from the ones that are reported in nearly all the ternary semiconductors (FigureA.10.1(b)). With increase in "x", upto x=0.5, the gap decreases slowly from 4.1 eV to 3.7 eV. Beyond x=0.5, the gap falls sharply to 2.1eV, and beyond x=0.68, it again remains almost constant at ~2.1 eV. This variation of the optical gap has been explained by investigating the conduction band using x-ray absorption near edge spectroscopy (XANES) measurement at O K-edge, at soft x-ray absorption beamline (BL-01), Indus-2, for different values of "x". Figure A.10.1(a) shows the XANES spectra at O K-edge. The conduction band edge is determined by finding the onset values of the features A and A' of Figure A.10.1(a), which is shown in Figure A.10.1(b) along with the optical gap.

The edge remains almost at the same position for x upto 0.59 indicating the dominance of Ni 3d *(eg)* state, beyondx=0.59, the edge moves to lower energies, due to the dominance of Co 3d *(t2g)* state. The trend in the variation of conduction band edge is similar to the variation of optical gap, which implies that the variation in the optical gap with "x" is strongly governed by the variation in the conduction band minima with "x". For more detail, please see RSC Adv., 2020,10, 43497-43507.

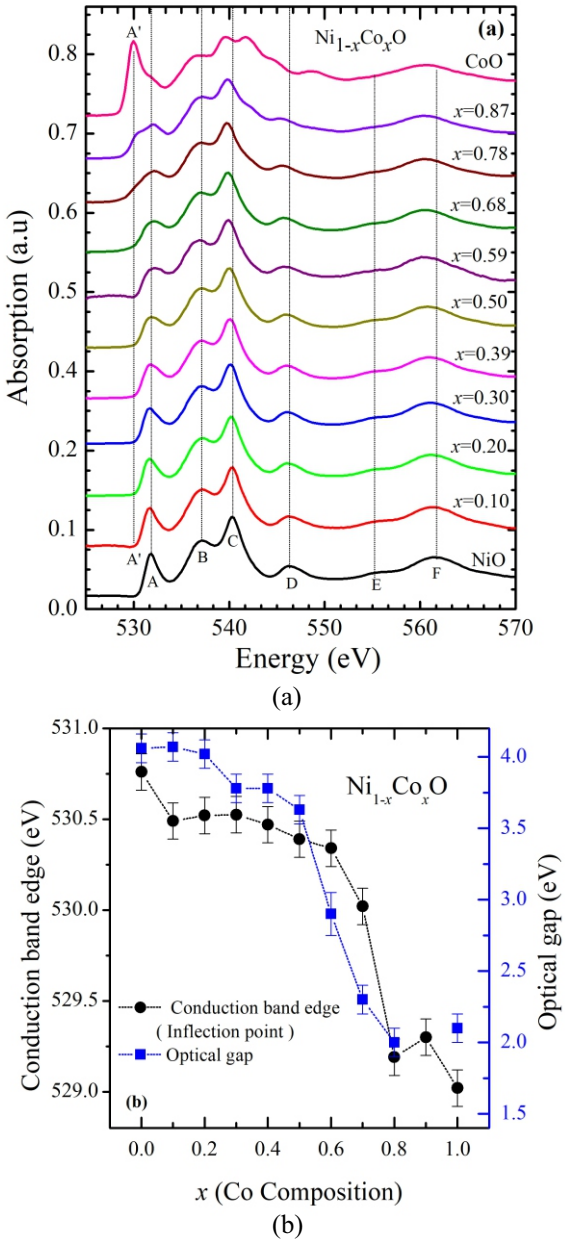

Fig. A.10.1: (a) XANES spectra at O K-edge for $Ni_{1-x}Co_xO$ solid solutions as a function of Co content. (b) Conduction band edge and optical gap as a function of Co content in $Ni_{1-x}Co_xO$.

Reported by:
Kiran Baraik (kiranb@rrcat.gov.in)