A.16: Structural analysis of $Ni_{1-x}Zn_xO$ and its correlation with XANES data from Indus-2

NiO has a wide optical gap (3.7-4.0 eV) with p-type conductivity, which is suitable for p-type transparent conducting oxide. There are some reports on ternary $Ni_{1-x}Zn_xO$ in the form of thin films prepared by sol-gel technique. The optical gap of $Ni_{1-x}Zn_xO$ cubic rock salt solid solutions was found to decrease from 3.65 eV (x = 0.0) to 3.35 eV (x = 0.31), thus suggesting that $Ni_{1-x}Zn_xO$ solid solutions can have applications in UV photo-detectors in the 320-400 nm wavelength range. Besides the above, nickel oxide (NiO) is also an important anti-ferromagnetic insulator with a Neel temperature of 523 K. It finds various applications in catalysis, rechargeable batteries, electro-chromic films, giant magneto-resistive (GMR) spin valve structures, fuel cells, gas sensors, resistive switching random access memory devices etc.

In this work, several $Ni_{1-x}Zn_xO$ solid solutions have been synthesized through standard solid state reaction technique. The starting precursors are 99.999% pure NiO and ZnO powders. The composition of Zn (x) was varied from 0 to 35% by mixing ZnO powder in different molar ratios with NiO powder. The mixture was ground in a mortar and pestle (made of Agate) for about 4-5 hours to yield better homogeniety and then the mixture was pressed into pellets of 10 mm diameter by applying ~8 tons pressure. Thereafter, the pellets were annealed in air at ~900°C for about 18 hours. The crystalline quality and the lattice parameter were determined by x-ray diffraction (XRD) measurements using Cu Kα laboratory source (Bruker D8 diffractometer). The symmetry of substituted Zn atoms in ternary solid solution was determined from the x-ray absorption near edge spectroscopy (XANES) measurements performed on the scanning EXAFS beamline (BL-09) on Indus-2 synchrotron source.

Figure A.16.1 shows 2θ scan from $Ni_{1-x}Zn_xO$ ternary solid solutions, where eight Bragg reflections related to $Ni_{1-x}Zn_xO$ ternary solid solutions are observed. One does not observe any signature of wurtzite (WZ) ZnO in any of the ternary solid solution for Zn composition up to 30%. However, a secondary phase of WZ ZnO is noted for the Zn composition of 35% in the XRD data (graph not shown here). This observation indicates that the ternary solid solutions are single phase for the Zn compositions up to 30%. Inset to Fig. A.16.1(a) shows 2θ scan from (420) Bragg reflection of $Ni_{1-x}Zn_xO$ ternary solid solution. It is noted that the Bragg peak shifts to lower angle with increase in the Zn composition indicating that the lattice parameter increases with the Zn composition. The lattice parameter is determined by LeBail fitting of the XRD data and is presented in Fig. A.16.1(b), where it increases linearly with the Zn composition. The solid line represents the lattice parameter variation following Vegard's law. This shows that the lattice parameter of ternary solid solution of $Ni_{1-x}Zn_xO$ clearly follows Vegard's law. The symmetry of Zn atoms in the cubic lattice of $Ni_{1-x}Zn_xO$ has been determined by the Zn K-edge XANES measurements which are shown in Fig.A.16.1 (c), where the XANES data from the WZ ZnO powder is also displayed for the comparison. It is noted that the near edge features from $Ni_{1-x}Zn_xO$ ternary solid solutions are quite different from those of WZ ZnO, thus confirming that Zn atom has replaced Ni atom to fit in the cubic lattice of $Ni_{1-x}Zn_xO$ ternary solid solution.

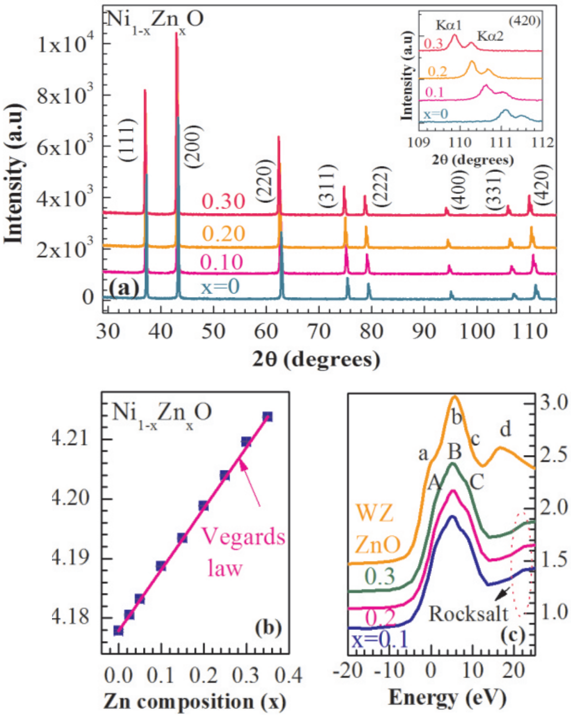

Fig. A.16.1: (a) 2θ scans from $Ni_{1-x}Zn_xO$ cubic rock salt ternary solid solutions for different Zn compositions. Inset figure shows 2θ scan of (420) Bragg reflection. (b) Variation of lattice parameter with Zn composition; solid line is lattice parameter given by Vegard's law. (c) XANES spectra from wurtzite ZnO and $Ni_{1-x}Zn_xO$ ternary at Zn K-edge.

In conclusion, $Ni_{1-x}Zn_xO$ ternary solid solutions are single phase for Zn compositions up to 30% and the lattice parameter variation is perfectly governed by the Vegard's law. The Zn K-edge XANES data confirms the rock salt symmetry of $Ni_{1-x}Zn_xO$ ternary solid solutions (For more details, please refer to S. D. Singh et al., Dalton Transactions 44, 14793, 2015).

Reported by:
S.D. Singh (devsh@rrcat.gov.in), and T. Ganguli