

# Modification in Morphological and Structural behavior in NiCoO<sub>4-δ</sub> With Cobaltous Oxide Concentration

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## ABSTRACT

In present scenario, the size of user's application decreases with increase of its multi-functionalities. So, therefore, the technology based on nanomaterials will be future prospective material for today's researchers. In this work, Cobalt doped Nickel Oxide nano-crystalline were synthesized via microwave modified chemical co precipitation protocols. Thereafter, various calcined samples were characterized via different tools and comparative studies were made in direction to study its morphological and structural changes with different concentration of doped material. The structural and morphological properties of un-doped and Co doped NiO (Co/NiO) samples with different concentration (5%, 10% & 20%) were studied through XRD, FTIR and FESEM tools etc. The X Ray Diffraction results observed that the most intense peak was noticed at  $2\theta \approx 43.33^\circ$  for NiO pure and 5% Co doped sample, whereas,  $2\theta \approx 31.58^\circ$  were exhibited for Cobaltous concentration 10% and beyond range. Henceforth, the study reflects that a crystalline phase change occurred with Cobaltous concentration 10% and above i.e. FCC to pyramidal. The calculated grain size as calculated by Debye Scherer formulation were 36.35nm, 40.61nm, 34.88nm and 30.61nm for NiO pure, 5% Co/NiO, 10% Co/NiO & 20% Co/NiO nano particulates respectively. The IR absorption peaks at about  $451\text{cm}^{-1}$  &  $575\text{cm}^{-1}$  were assigned to O-Ni-O & O-Co-O lattice vibration. The FESEM spectra reflects that 2D truncated disk-like shape with an average diameter and grain size of around 50 nm and thickness of a few nanometers.

Keywords-Cobalt doped NiO, chemical co-precipitation, XRD, FTIR, FESEM etc.

## INTRODUCTION

The collections of atoms having dimensions in nano-range possess eminently different properties than their bulk counterpart. Metal oxide nanomaterials (MONMs) are widely used in numerous field of technological, material & medical sciences [1]. Iron oxide, Manganese Oxide, Cobalt Oxide etc. metal oxides nanoparticles are extensively used in biomedical application such as drugs delivery, molecular imaging, sensors, electrode formation for energy storage, magneto resistive devices and catalyst [2-4].

Nickel oxide nanoparticles have various applications such as magnetic materials, electro-chromic films. NiO is more significantly focused due to low cost and various applications i.e. as gas sensors, photo-detectors, catalyst, improved life cycle & efficiency of storage battery, dye sensitized solar cell, light emitting diode, antibacterial agent, anticancer activity, water treatment action and so on [5-6]. As Ni and Cobalt transition metal have well known electrical properties and both of these are in category of ferromagnetic substance and have valuable advance application in various field of technology. So, the researcher turning their knee interest to synthesis the samples of different concentration of Cobalt doped NiO nanocrystalline and purpose of this synthesis will have to study the Structural & Morphological change occurred due to Co dopant concentration in NiO lattice.

## EXPERIMENTAL DETAIL

### Synthesis Method

Nickel oxide (NiO) nanoparticles incorporated with appropriate amount of cobalt were synthesized by microwave treated modified chemical co precipitation approach. All the chemicals & salts used in study were highly pure in nature and AR in grade.

The author further declared that no purification were done at laboratory scale. In this method the proper amount of Nickel chloride hexahydrated (NiCl<sub>2</sub>.6H<sub>2</sub>O) & Cobalt Nitrate (5%, 10% & 20%) were mixed & then add the required distilled water for making the

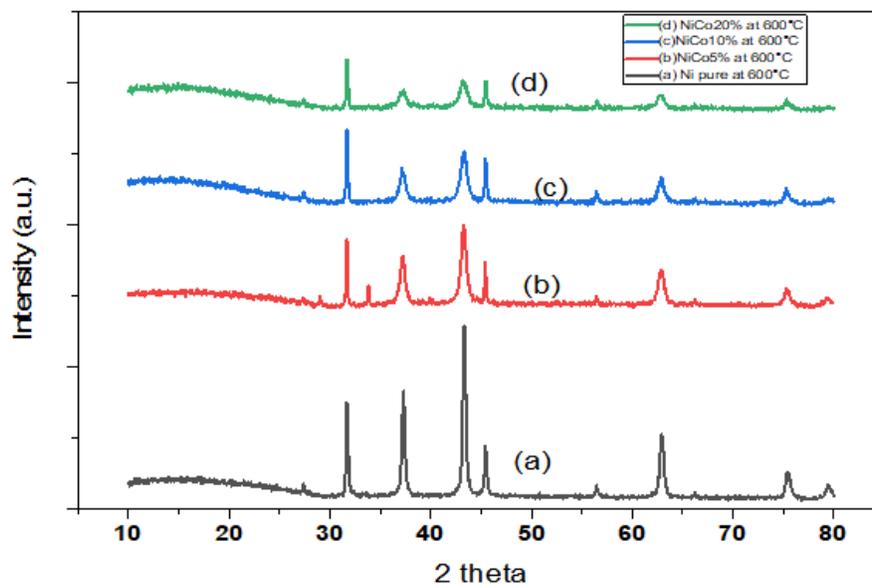
clear solution separately in three beakers. In another beaker prepared NaOH (2.0 M) solution and then was added into resulted aqueous solution of Nickel chloride & Cobalt Nitrate solution drop-wise with stirring until pH of resulting samples become 9.0 which was measured by electrode pH-meter. Thereafter, keep the resulted solution for 24 hours for aging process. The consequential precipitated solution was filtered through standard Watt-man filter paper and the resultant cake was washed with ethanol and distilled water to remove chloride based impurities & contaminants. Thereafter filtrate and then dried the sample in microwave oven at 100°C for 15 minutes of two sittings so that all moistures were removed. The resultant dried specimens were transferred in high temperature oriented crucible disk and put it in electric muffle furnace for calcination at 600°C for 2 hours. The calcined samples were crushed in mortar until or unless it turn out to be powdered form. At last, the powdered sample was kept in sample holder tube for further characterization and analysis.

### Characterization Techniques:-

The various calcined samples were analyzed with X-Ray Diffractometer (XRD) with CuK $\alpha$  radiation having wavelength  $\lambda=0.1542\text{nm}$  & the diffraction pattern was recorded by taking diffraction angle in  $2\theta$  range  $10^\circ$  to  $80^\circ$  for studying the structural properties. Fourier Transform Infrared Spectrum (FTIR) was determined by Diamond ATR & Pallet accessory (Perkin Elmer) spectrometer by plotting the wave-number in the range of  $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$  on horizontal axis Vs transmittance rate on vertical axis for the confirmation of compositional elements formed with NiO nanoparticles. The morphological and structural changes were examined by electron microscopy such as FESEM tools.

## RESULT AND DISCUSSION

The various Co concentrated NiO powdered samples were characterized by X-Ray diffraction for finding the information about structural properties and crystallite size of the nanoparticles. This technique provide information about whether the material is crystalline or amorphous in nature. Presently, the samples were scanned by CuK $\alpha$   $\lambda=1.5406\text{\AA}$  having  $2\theta$  in range  $10^\circ$ - $80^\circ$ . The Co(5%, 10% & 20%) doped NiO samples calcined at 600°C/2hours were examined via diffraction of X-Rays. The comparative results of study were shown in figure-1.



**Figure -1** XRD spectrum of CoO doped NiO with variation in dopant concentration (a) NiO pure (b) CoO5% dope NiO (c) CoO 10% in NiO (d) CoO 20% in NiO.

The results of XRD spectrum revealed that the peaks were observed at position  $2\theta \approx 31.7^\circ, 37.4^\circ, 43.3^\circ, 45.3^\circ, 62.8^\circ$  &  $79.4^\circ$  which were attributed by the formation of Face Centered Cubic structured NiO nano crystalline & were confirmed by JCPDS file no-47-1049[7-8]. However some additional peaks were observed at about  $2\theta \approx 32.3^\circ$  &  $56.4^\circ$  corresponds to the existence of Co concentration doped in NiO nanomaterials. Whereas, it was found that crystallite size of newly samples was highly dependent on the cobaltous concentration in NiO lattices. Moreover, the crystallite size initially increased up to 5% concentration of Co which might be due to crystal deformation occurred at this stage with no phase change occurrence (i.e.

most intense peak position not be changed), whereas the significant changes in shifting of most intense peak position were noticed beyond 5% concentration of Co i.e. NiO lattice transformed from FCC to Cobalt pyramidal shape with smaller size. Some XRD parameters for the quantitative analysis of the effect of dopant concentration in NiO nano-particulates were recorded in table no-1.

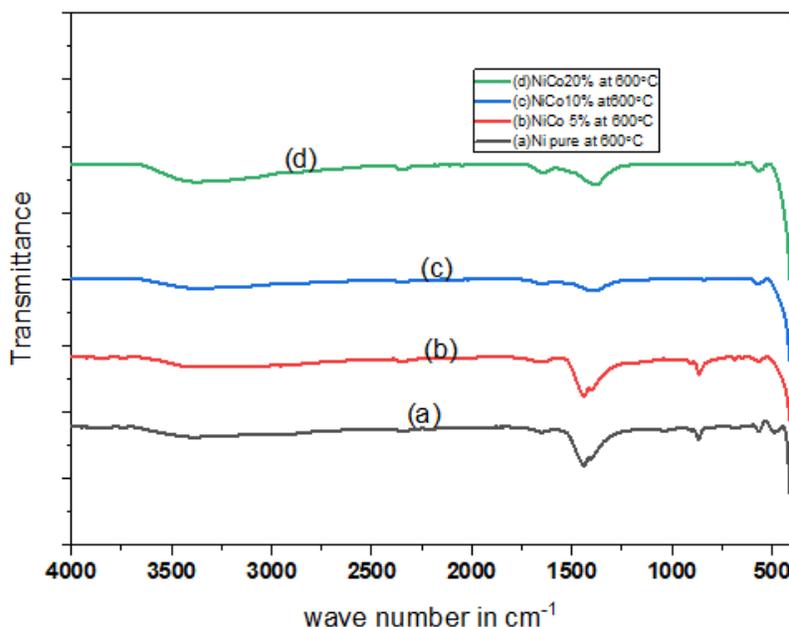
**Table-1 Recorded data of most intense peak of various cobaltous doped NiO crystalline calcined at 600°C for 2 hours.**

Name of Sample	Angle 2θ (in degree)	Interplanar distance(d)	FWHM (in radian)	Size(D) (in nm)
NiO pure	43.33	2.086	0.334	36.35
NiO+CoO 5%	43.27	2.089	0.435	40.61
NiO +CoO 10%	31.58	2.089	0.435	34.88
NiO+CoO20%	31.70	2.82	0.234	30.61

The above tabular data reflects that the calculated crystallite size from Debye Schere formula were found as 36.35nm for pure NiO ,40.61nm for 5% Co /NiO ,34.88nm for 10% Co/NiO & 30.61nm for 20% Co/NiO calcined at 600°C for 2 hours.The alteration in size or initially increment (for 5% Co doping in NiO) in the crystallite size may be caused due to  $Co^{3+}$  ion replace the  $Ni^{2+}$  ion in NiO lattice. However, beyond 5% Co concentration the size decreases rather it increases and it might be due to phase reversal take places from FCC to pyramidal shape of novel substance[8-10].

**FTIR Result Analysis**

The IR spectroscopy was used to determine the vibrational energy of various groups present in the samples. In present work the Co(5%,10%&20%) doped NiO samples calcined at 600°C/2 hours were scanned through IR spectrum ranging from  $400cm^{-1}$ - $4000cm^{-1}$  and comparative analysis were shown in graphical form in figure no-2.



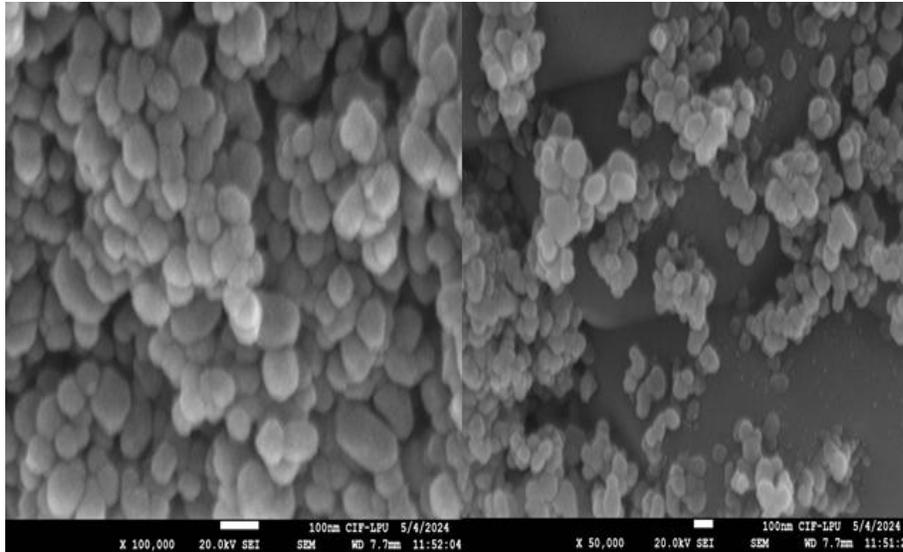
**Figure- 2. IR Spectrum of calcined samples of CoO - NiO nano-crystalline with Cobalt concentration [A] (a)0%(pure NiO ), (b) 5%, (c) 10% & (d)20% at calcination temperature 600°C for 2 hrs.**

The perusal of above IR spectrum express that a sharp peaks at about  $451cm^{-1}$  was observed which corresponds to O-Ni-O vibrational peak. However some additional peaks on doping of CoO in NiO were occurred nearby  $575cm^{-1}$  which was

attributed by O-Co-O vibration. A broad band at nearly  $1400\text{cm}^{-1}$  was observed which was due to the presence of O=C=O[11]. On further increasing (10%, 20%) the concentration of the CoO in the material the peak position corresponding to the CoO shift towards lower wavenumber means red shift was occurred and the size of crystallites decreases.

### **FESEM Image Analysis**

The Field effect Scanning Electron Microscopy is used to study the morphological behavior of Co-doped NiO nanoparticles which include examination of their surface structure, size, shape, and general physical appearance of the sample[12]. This study is peculiar to understand how the incorporation of Co ions influences the properties of NiO nanoparticles.



**Figure 3-The FESEM spectra of 10% Co doped NiO nanoparticles and of pure NiO nanoparticles respectively.**

The FESEM spectra of the prepared samples demonstrate that 2 D truncated Disk like structure with thickness in few nanometer and average diameter /grain size about 50 nm. The FESEM results supports the XRD results of researcher i.e. formation of Co doped NiO samples at nanoscale.

### **CONCLUSION**

The microwave-irradiated chemical co-precipitation approach successfully produced Cobalt incorporated Nickel oxide nanoparticles of different concentration i.e.5%, 10% & 20%. According to the XRD data, the size of pure Ni was 36.35 nm. However, when the concentration of Co increases, the size of the crystallites firstly increases and then decreases, which might be due to replacement of  $\text{Ni}^{2+}$  ion by  $\text{Co}^{3+}$  ion from their lattice position.

The IR spectrum shows the sharp peaks at about  $451\text{cm}^{-1}$  &  $575\text{cm}^{-1}$  which corresponds to the vibration of O-Ni-O & O-Co-O in the prepared samples spectroscopy. The morphological study was done by FESEM tool and found that the shape of 10% Co incorporated in NiO sample was 2 D truncated disk-like structures with an average diameter and grain size of around 50 nm with a thickness of a few nanometers. The XRD results were confirmed by FESEM spectrum results.

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