

Study of Variation of Bandgaps of Pure and Doped Nickel Oxide Nanoparticles (NiO) prepared in different environments

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ABSTRACT

We report synthesis and characterisation of Nickel Oxide (NiO) nanoparticles and Al doped Nickel Oxide (ANO) nanoparticles prepared by Chemical Bath Deposition (CBD) method. The nanoparticles of NiO and ANO are characterised by XRD (Philips, XPERT PRO) and UV-vis-absorption (Hitachi U-1800) techniques. The NiO nanoparticles are prepared from nickel nitrate and sodium hydroxide solutions. Similarly, the ANO nanoparticles are prepared from nickel nitrate and aluminium nitrate solutions with different Al percentages viz. 2.5, 4.5 and 6.5 as dopant. Both the nanoparticles of NiO and ANO are prepared at room temperature (RT) and subsequently calcined at 473 K and 673 K. At RT the nanoparticles are found to be amorphous in nature and after calcination the nanoparticles get crystallised which is confirmed by the XRD analysis. The direct band gaps calculated from the UV-vis absorption spectra of NiO nanoparticles prepared at RT and 473 K and 673 K temperatures are found to be of the order of 5.79 eV, 5.61 eV and 5.55 eV. But for ANO nanoparticles prepared at RT the direct band gaps are found to be of the order of 4.36 eV, 3.84 eV and 3.82 eV at doping percentage 2.5, 4.5 and 6.5 respectively. It is seen that when the calcination temperatures and doping percentage are increased, the band gaps decreases. Due to the increase in particle size at higher temperatures, the band gaps are reduced. Increase in doping percentages lead to increase in conductivity due to the higher concentration of carriers.

Keywords: NiO nanoparticles, Al doped NiO, Microstrain Band Gap

INTRODUCTION

Nanostructured materials have been showing increasing research interest due to their unique chemical and physical properties [4-7]. The size, shape and band gaps of nanomaterials are greatly affected by these properties. The nanoscale oxide particles of transition metals are gaining continuous importance for various applications such as catalysts, passive electronic components and ceramic devices. Nickel Oxide (NiO) is a wide band gap metal oxide ranging from 3.6 eV to 4.0eV [8-17] with wide range of applications like catalytic, magnetic and conductivity. When particle size decreases, nanoparticles show blue shift but in some reported work the values of optical band gap of nanostructure are found to be less than the optical band gap of bulk NiO nanoparticles [8].

In this work, NiO nanoparticles and ANO nanoparticles are prepared by CBD method. The ANO nanoparticles are prepared using different aluminium doping concentrations.

METHODOLOGY

Preparation of NiO nanoparticles by CBD method:

NiO nanoparticles are prepared by CBD method. 0.019M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (solution1) and 0.5M NaOH (solution2) are dissolved in ethanol under continuous stirring condition at 80°C. Solution1 is added drop wise to solution 2 under continuous stirring condition. The mixture is filtered and the precipitate obtained is allowed to dry for further characterizations.

Preparation of ANO nanoparticles by CBD method:

All chemicals are of analytical reagent grade and are used without further purification. ANO nanoparticles are prepared by chemical precipitation method. The reactants are $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Ethanol is used as the reaction medium in all the synthesis steps. In a typical synthesis, desired molar proportions of $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ (0.2M) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.5, 4.5 and 6.5 at.%) each in 100 ml ethanol are dissolved and stirred for 30 minutes. NaOH (0.25M) solution is added drop wise to the solution under continuous stirring for four hours to get fine precipitation. The obtained precipitate is

filtered and dried at room temperature to obtain Al doped NiO nanoparticles.

CHARACTERIZATION METHODS:

X-Ray Diffraction analysis:

The phase and the structure of NiO nanoparticles and ANO nanoparticles are identified by X-Ray Diffractometer (XRD) which is operated with generator setting of 35mA and 40kV with $\text{CuK}\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation. The XRD is calibrated with a standard silicon sample and broadening of peaks because of instrumental effect is also corrected by Warren rule. The scanning range is from 25-90° (2θ) at a scan speed 1sec/step and 0.02° 2θ is the step size. The diffraction patterns of the NiO nanoparticles and ANO nanoparticles prepared at RT and at different annealed temperatures of 473K and 673K are given in Fig1 and Fig2 respectively. The diffraction patterns of the nanoparticles corresponds to (111), (200), (220), (311) and (222) planes almost match with standard NiO powder (ICCD No. 78-0643). The prepared NiO nanoparticles are cubic with $a=4.176$ and space group $\text{Fm}\bar{3}\text{m}$ (225).

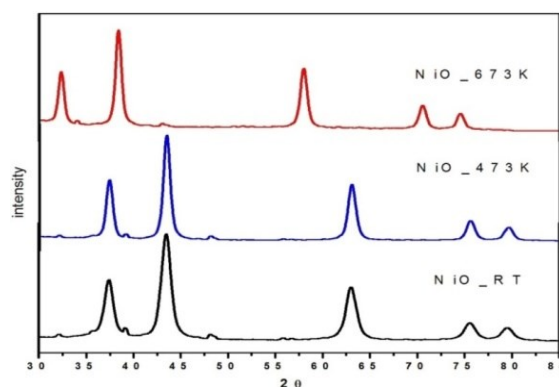


Figure 1: The XRD pattern of NiO nanoparticles prepared at temperatures RT, 473K and 673K

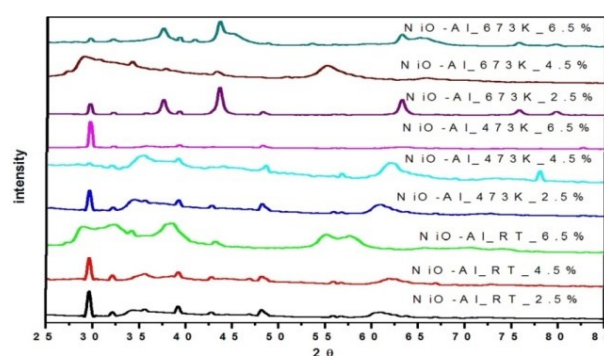


Figure 2: The XRD pattern of ANO nanoparticles

prepared at RT, 473K and 673K.

2.2.1 Microstrain analysis for NiO nanoparticles:

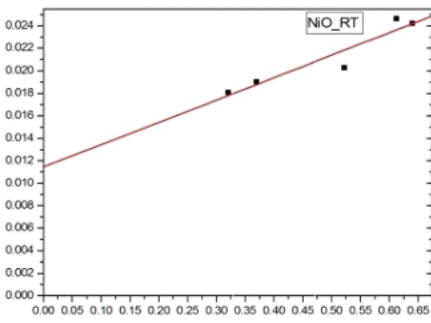


Figure 3

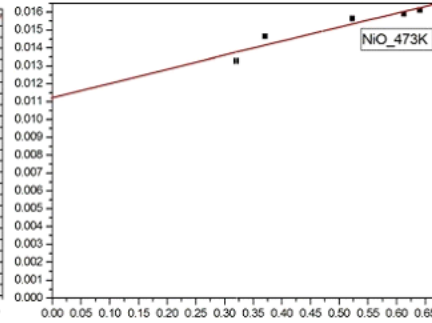


Figure 4

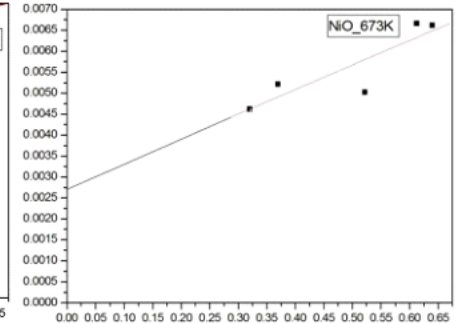


Figure 5

2.2.2 Microstrain analysis for ANO nanoparticles:

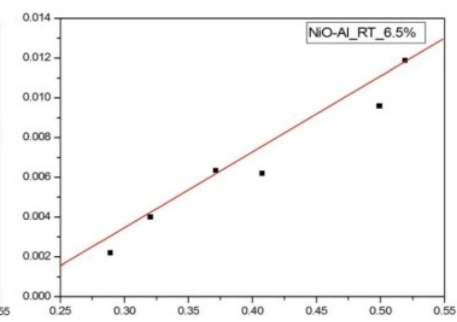
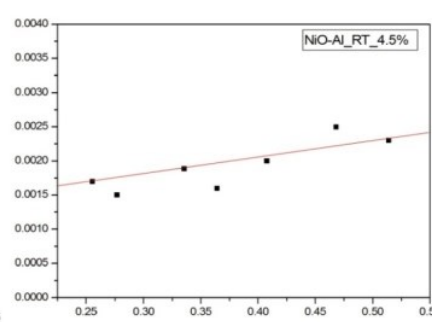
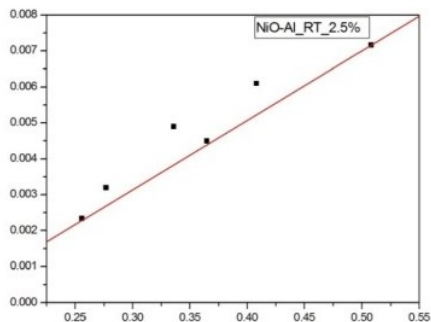


Figure 6: The W_Hall plot to determine grain size and strain of Al doped NiO nanoparticles (2.5%, 4.5% and 6.5%) prepared at RT.

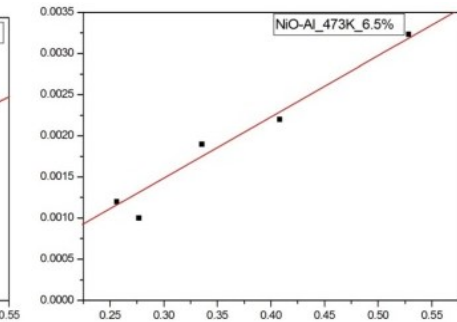
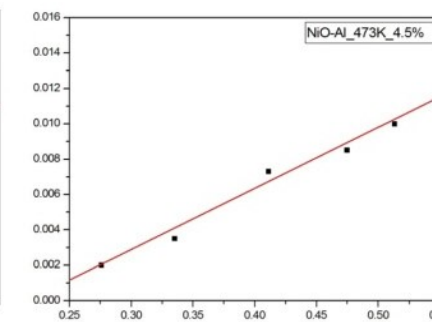
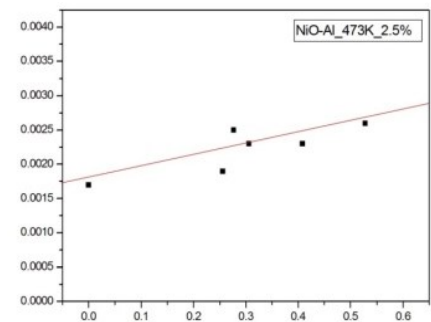


Figure 7: The W_Hall plot to determine grain size and strain of Al doped NiO nanoparticles (2.5%, 4.5% and 6.5%) prepared at 473K.

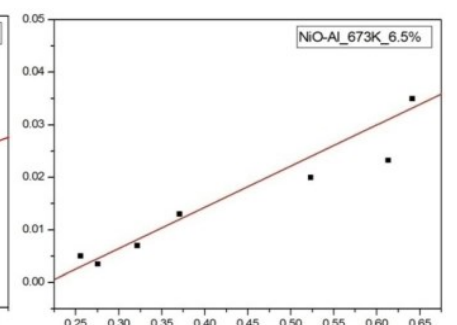
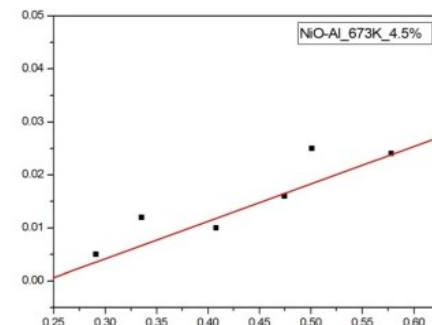
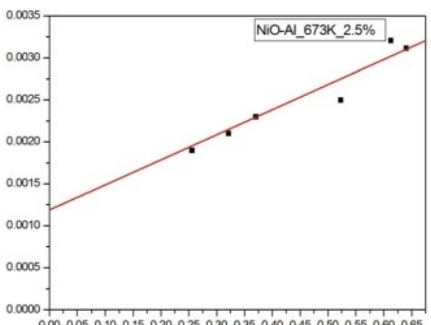


Figure 8: The W_Hall plot to determine grain size and strain of Al doped NiO nanoparticles (2.5%, 4.5% and 6.5%) prepared at 673K.

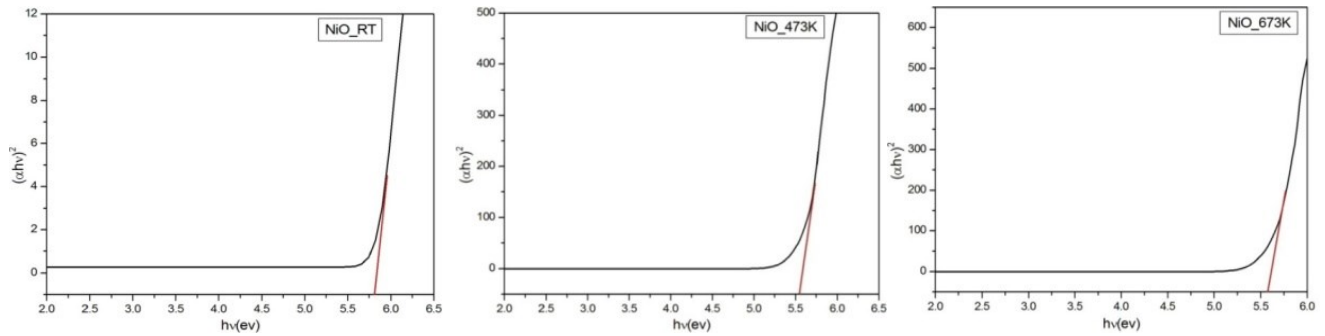


Figure 9: The direct band gaps of the NiO nanoparticles calculated from the UV-vis-absorption at temperatures RT, 473K and 673K.

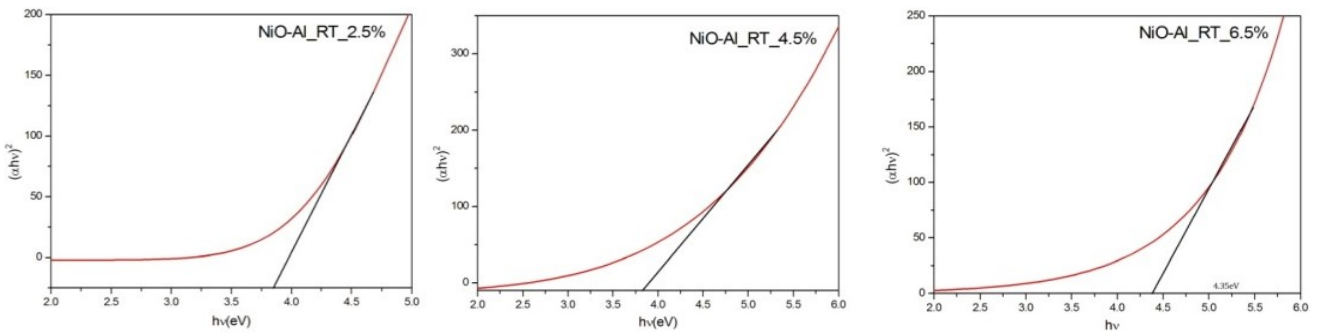


Figure 10: The direct band gaps calculated from the UV-vis-absorption of Al doped NiO nanoparticles prepared at RT.

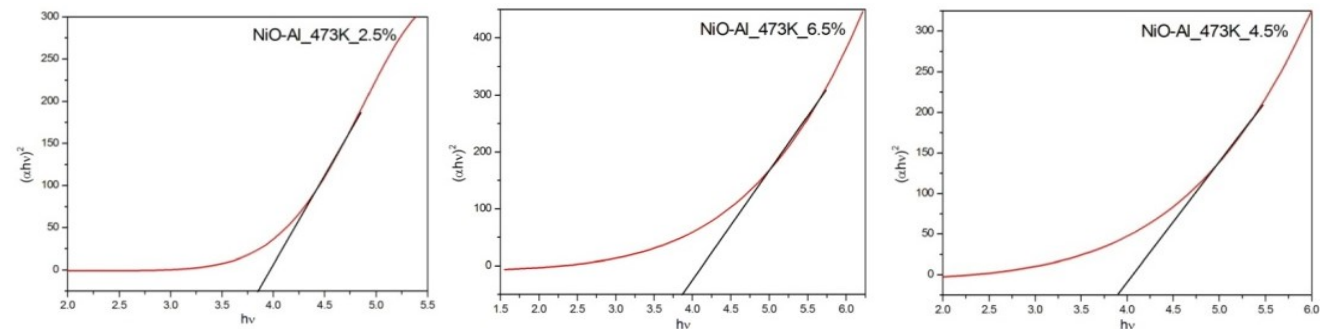


Figure 11: The direct band gaps calculated from the UV-vis-absorption of Al doped NiO nanoparticles prepared at 473K.

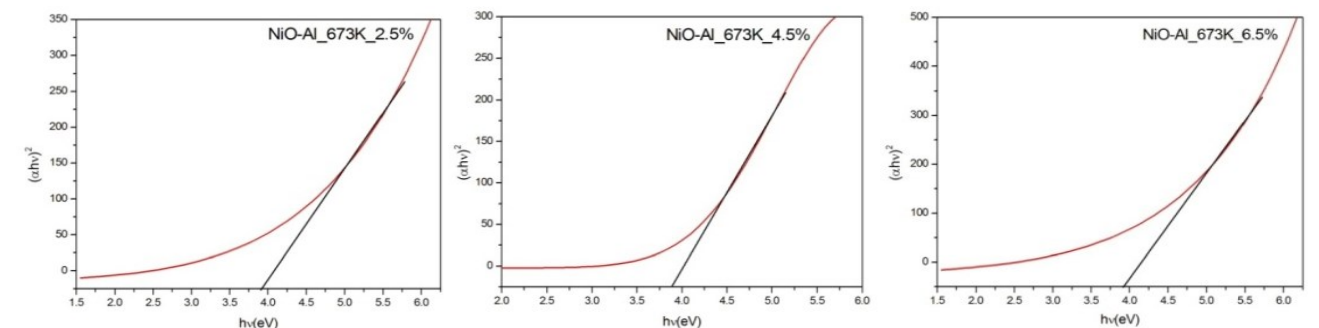


Figure 12: The direct band gaps calculated from the UV-vis-absorption of Al doped NiO nanoparticles prepared at 673K.

Table 1: Comparison of bandgaps, particle sizes and microstrains of NiO and ANO nanoparticles.

Sample code	Doping conc.	Band Gap (eV)			Particle size(nm)			Microstrain		
		RT	473K	673K	RT	473K	673K	RT	473K	673K
NiO		5.79	5.61	5.55	12.05	13.50	54.55	0.013	0.0052	0.0027
	2.5%	4.36	3.83	3.80	6.30	8.16	11.66	0.0075	0.0017	0.0031
	4.5%	3.84	3.81	3.79	8.67	12.61	13.87	0.0023	0.0135	0.0160
ANO	6.5%	3.82	3.80	3.75	9.25	15.41	17.82	0.0148	0.0029	0.0173

Microstrain analysis:

The observed peak shifts in the peaks of the nanoparticles are because of the development of defects in the nanoparticles at higher calcination temperatures. The broadening in the diffraction peaks occur due to inhomogeneous microstrain induced by strain broadening or because of shrinkage of coherent scattering volume (size broadening). The strain and size broadening can be separated by W_H plotting. The specimen broadening in XRD lines broaden due to small grain size and strain. The Williamson-Hall technique is adopted where microstrain ' ϵ ' and grain size is related as:

$$\beta \cos\theta = \epsilon \sin\theta + \lambda/D$$

β where is the full width at half maxima of the peak (in radians), θ is the diffraction angle, λ the wavelength of X-ray. The slope of the graph between $\beta \cos\theta$ and $\sin\theta$ gives the microstrain and the intercept on Y-axis gives λ/D . The particle sizes and microstrains of the NiO/ANO at RT and different calcination temperatures calculated from the W-H plots are given in the Table. 1. Figure 3: The W_Hall plot to determine grain size and strain of NiO nanoparticles prepared at RT. Figure 4: The W_H plot to determine grain size and strain of NiO nanoparticles prepared at 473K. Figure 5: The W_Hall plot to determine grain size and strain of NiO nanoparticles prepared at 673K.

2.3 UV-vis characterization:

UV-vis absorption spectroscopy is one of the most important techniques to investigate the energy structures and optical properties of nanocrystalline semiconductors and has widely been studied [22]. The strong absorption in the UV region can be assigned to the band gap absorption of nanostructured NiO. The plots of $(ah\nu)^2$ vs $h\nu$ for NiO and ANO nanoparticles corresponding to different annealing temperatures calculated from absorption data are shown in Fig 9,10

and 11. The linear nature of the plots indicate the involvement of direct transition and thus the prepared NiO nanoparticles fall on the group of direct band gap metal oxide [23]. UV-vis spectra are taken from the NiO nanoparticles and ANO nanoparticles (2.5%, 4.5% and 6.5%) at RT, 473K and 673K. The direct band gaps of NiO and ANO nanoparticles calculated from the UV-vis-absorption at RT, 473K and 673K are given in Table 1. UV-vis spectra are taken from the ANO nanoparticles (2.5%, 4.5% and 6.5%) at RT, 473K and 673K. The direct band gaps calculated from the UV-vis-absorption are given in Table 1.

CONCLUSIONS

1. ANO and CNO nanoparticles are prepared successfully and matched with the standard data.
2. With change in doping concentrations and temperatures, size of the nanoparticles increases.
3. With decrease in size, band gap and microstrain increases.

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