Synthesis and Characterization of Nickel Doped Zinc Oxide Nano Particles by Microwave Oven Method for Novel Applications

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Abstract: **Nickel doped Zinc Oxide nanoparticles were synthesized by Micro-wave assisted technique from the chlorides of Zinc (II) and Nickel (II). Initially 0.2 mol of Aqueous ZnCl2 was taken, added with acetic acid and continuously Stirred at 300 RPM. Later NaOH solution is added to the above prepared solution till it reaches P^H 7. Given Molar Percentage of Nickel Chloride (Pure, 0.01, 0.02, 0.03, 0.04 mol) added for Doping at P^H = 7 of the solution and stirred for 10 minutes. The prepared solution is placed on magnetic stirrer and then heated under Microwave for 20 minutes with 5 minute interval, observed the gel like form and finally prepared powder was filtered. The filtered and dried powder was then calcinated at 500^0 C for 1 hour. The synthesized nanoparticles were characterized for determining the atomic and molecular structure of material by X-ray diffraction, size and morphology by Scanning Electron Microscopy, elemental composition by EDAX, Band Gap by UV-VIS spectroscopy, Mode of Vibration by Raman Spectroscopy. SEM analysis results revealed the formation of Hexagonal nuts like structure of ZnO with porous or rough surfaced Nanoparticles. The doping of Nickel was revealed by the formation of new peaks when compared to that of un-doped ZnO, with average crystallite size of 45nm while smallest size is 8nm. Scanning Electron Microscopy images showed random shape, hexagon nut, morphed plates has hole at center (Nut) and small rods with particles morphology for un doped ZnO to doped ZnO. The change in morphology was observed with addition of Nickel dopant acts as a catalyst for morphology change and self-assembling. UV-VIS spectroscopy shows the increase in band gap due to the replacement takes place of Nickel ions in Zinc matrix. This shows an increase in electrical conductivity activity and higher thermal conductivity in transformer cooling oil application.**

Key Words: **UV, XRD, SEM, RAMAN, EDAX**

INTRODUCTION

Nanotechnology is the application of nano science leading to the use of new nano materials and Nano size components in useful products. Nanotechnology will eventually provide us with the ability to design custom-made materials and products with new enhanced properties, new Nano electronics components, new types of "smart" medicines and sensors, and even interfaces between electronics and biological systems. These newborn scientific disciplines are situated at the interface between physics, chemistry, materials science, microelectronics, biochemistry, and biotechnology. Control of these disciplines therefore requires an academic and multidisciplinary scientific education. At this level, matter exhibits different and often amazing properties and the borders between established scientific and technical disciplines fade. Hence the strong interdisciplinary character is associated with Nanotechnology. Nanotechnology is often described as having a "disruptive" or "revolutionary" potential in terms of its possible impact on industrial production routes. Nanomaterial offers possible solutions to many current problems by means of smaller, lighter, faster and better performing materials, components and systems. This opens up new opportunities for wealth creation and employment. Nanotechnology is also expected to make some essential contributions to solving global and environmental challenges by realizing more specific-to-use products and processes save resources and lower waste and emissions. Scientists currently debate the future implications of Nanotechnology.

Nanotechnology is being used in developing countries to help treat disease and prevent health issues. The umbrella term for this kind of nanotechnology is Nano- medicine. Nanotechnology is also being applied to or developed for application to a variety of industrial and purification processes antibacterial activity.

A Nano particle is a microscopic particle with at least one dimension less than 100nm. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the Nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface Plasmon resonance in some metal particles and super para magnetism in magnetic materials. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. The interesting and sometimes unexpected properties of nanoparticles are not partly due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties.[14] Nanoparticles exhibit a number of special properties relative to bulk materials. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid.

Zinc oxide

Zinc oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water. ZnO is present in the Earth's crust as the mineral zincite. That being said, most ZnO used commercially is synthetic.Zinc oxide is commonly found in medical ointments where it used to treat skin irritiations. In more recent times zinc oxide has transcended to use in semiconductors, concrete use, ceramic and glass compositions

Nickel oxide

Nickel(II) oxide is the chemical compound with the formula NiO. It is the principal oxide of nickel. It is classified as a basic metal oxide. Several million kilograms are produced annually of varying quality, mainly as an intermediate in the production of nickel alloys. The mineralogical form of NiO, bunsenite, is very rare. Other nickel oxides have been claimed, for example: Nickel(III) oxide(Ni_2O_3) and NiO_2, but they have yet to be proven by X-ray crystallography in bulk. Nickel(III) oxide nanoparticles have recently (2015) been characterized using powder X-ray diffraction and electron microscopy.

METHODOLOGY

Microwave oven assisted method:

The technique offers simple, clean, fast, efficient, and economic for the synthesis of a large number of organic molecules. In the recent year microwave assisted organic reaction has emerged as new tool in organic synthesis. Important advantage of this technology includes highly accelerated rate of the reaction, Reduction in reaction time with an improvement in the yield and quality of the product. Now day's technique is considered as an important approach toward green chemistry, because this technique is more environmentally friendly. This technology is still under-used in the laboratory and has the potential to have a large impact on the fields of screening, combinatorial chemistry, medicinal chemistry and drug development. This growth of green chemistry holds significant potential for a reduction of the by product, a reduction in waste production and a lowering of the energy costs. Due to its ability to couple directly with the reaction molecule and by-passing thermal conductivity leading to a rapid rise in the temperature, microwave irradiation has been used to improve many organic synthesis.

CHARECTERISATION TECHNIQUES:

1. X-ray Powder Diffraction (XRD)
2. UV-VIS SPECTROSCOPY
3. UV-VIS SPECTROSCOPY
4. Raman Spectroscopy
5. Energy dispersive Analysis X-ray Spectroscopy

MATERIALS

1) Zinc Chloride(anhydrous)
2) Nickel Chloride
3) Distilled water
4) Ethanol
5) Sodium Hydroxide pellets

Synthesis of ZnO nano particles:

Microwave synthesis has been employed as it combines the advantage of speed and homogeneous heating of the precursor materials

Firstly using molarity formula the weight of particular material is calculated. For 0.2M Zinc Chloride it weighs 6.81gm for 50ml of water and 8M of NaOH weighs 16gm for 50ml of water. The chemical is taken accordingly to the calculations and

is added to the 50ml of water. The solution is stirred on magnetic stirrer until it is completely dissolved. NaoH solution is taken in to the burette and this solution is added drop by drop to the Zinc chloride solution while stirring. The pH is occasionally checked when the pH reached 7 the process is stopped and the gel formed is placed in Microwave oven for 1 hour then cooled and filtered using whatman filter paper and the filtered particles are washed for 7 times using distilled water and are dried at room temperature for 2 days. The dried particles are collected and are calcinated in muffle furnace for about 2 hrs at 450^0C and are collected and stored.

The same process is carried out for 4 samples now by doping nickel cholride in zinc chloride samples where the zinc chloride concentrations are 0.19M,0.18M,0.17M,0.16M with 0.01M,0.02M,0.03M,0.04M respectively where NaOH concentration is 8M(CONSTANT)

Synthesis of Ni doped ZnO nano particles:

Four different doping concentrations Zinc and Nickel are done. Firstly 0.19M of Zinc chloride solution and 0.01M of Nickel Chlorode solutions are prepared using 50ml water. These solutions are added and are stirred for 5 min to dissolute completely. 8M of NaOH solution is prepared using 500ml of water. This solution is taken in to the burette and is added drop by drop to the above combined solution .The solutions turned in to a white gel then the NaOH solution inlet is stopped anf then place and in microeave oven for 20 minutes and thengel is filtered. The filtered particles ate washed for 7 times using distilled water . These particles are dried at room temperature and are calcinated at 450^0C for 1hr 30 min. Then particles are stored in a Zip lock. Simillarly this is carried out to Zncl2(0.18,0.17,0.16)M+ NiCl2(0.02,0.03,0.04) M respectively.

RESULTS

X-RAY DIFFRACTION TECHNIQUE

Each and every sample has a particular max full width half maximum and the FWHM of particular peak is taken along for calculation. The strain, MI, dislocation density are tabulated.

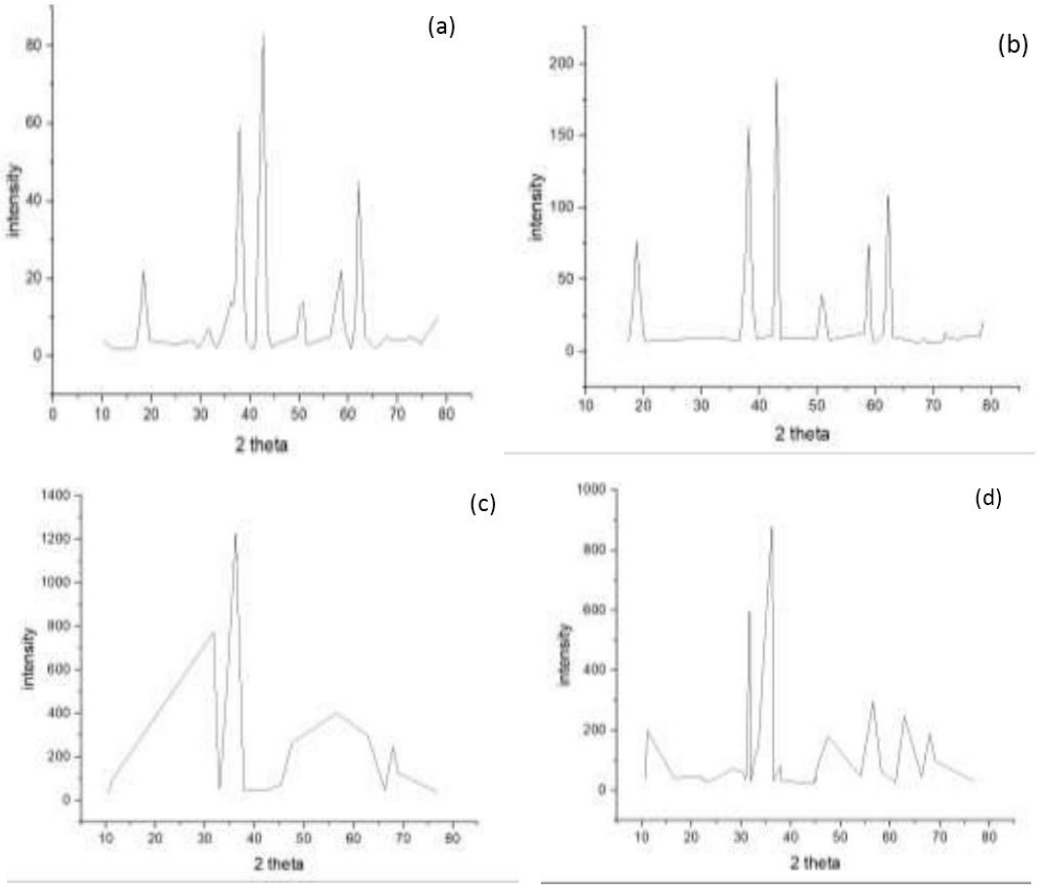


Fig: XRD analysis for (a) 0.2M concentration of Zinc chloride$_2$, (b) 0.01mol Ni doped with 0.19mol ZnCl solution, (c) 0.02mol Ni doped with 0.18mol ZnCl solution (d) 0.03mol Ni doped with 0.17 mol ZnCl solution

The crystalline size of pure ZnO nano praticles of 0.2M concentration of ZnCl, is between 5nm-132nm and for 0.19 molconcentration of Zncl the particle size is between 10nm to 61nm which shows as the concentration of Zncl increases the particle size decreased and from tabular column it is analysed that the strain and crystalline size are inversely proportional.

The crystalline size of Zn doped ZnO nano particles is in the range of 17-55nm for 205 of zinc doping concentration and for doping concentration the crystalline size ranged from 18nm -54nm. The observed diffraction peaks were well matched with the typical single crystalline periclase phase of bulk ZnO and also in good agreement with the JCPDS file for ZnO- (JCPDS, Card No.74-0534).

UV-VISIBLE SPECTROSCOPY

Uv visible spectroscopy technique is used to calculate the energy bang gap of the particular material and Tauc's plot is drawn to analyse the wavelength of the particular nano particle.

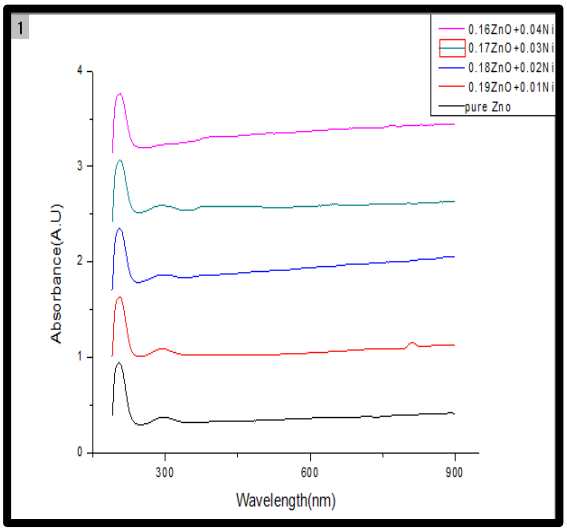


Fig: UV-VIS Absoption Spectra's of Samples

UV-VIS spectrum is a technique to explore the optical properties of nano particles. The absorption spectra of pure and cobalt doped zinc oxide nanoparticles are investigated and optical properties are as shown in Fig.6.2. The absorbance of the nanoparticles is expected to depend on several factors like band gap, oxygen deficiency, surface roughness and impurities center. The absorbance spectra exhibited absorbance at around 200-250 nm. The absorption of different samples slightly changes as concentration of Ni in the ZnO nanoparticles.

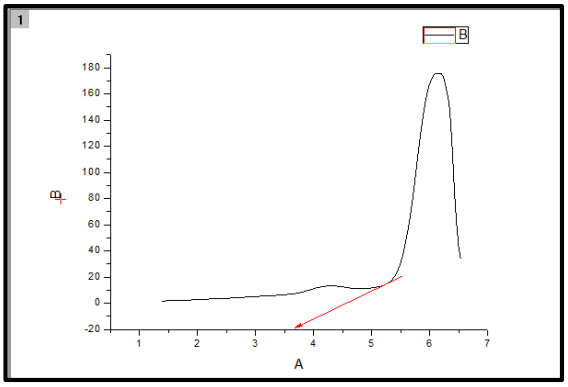


Fig 5.7 Tauc plot of pure ZnO sample

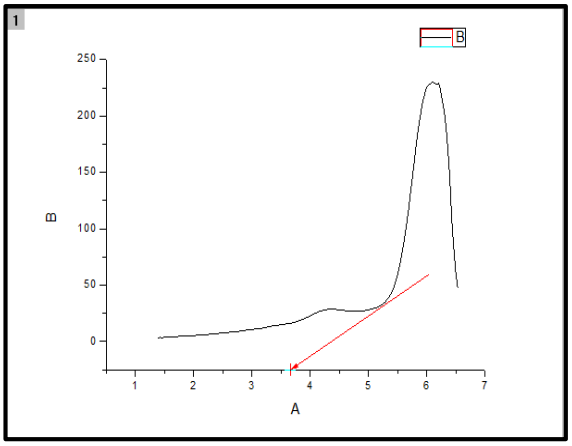


Fig 5.8 Tauc plot of 0.19M ZnO+0.01M Ni sample

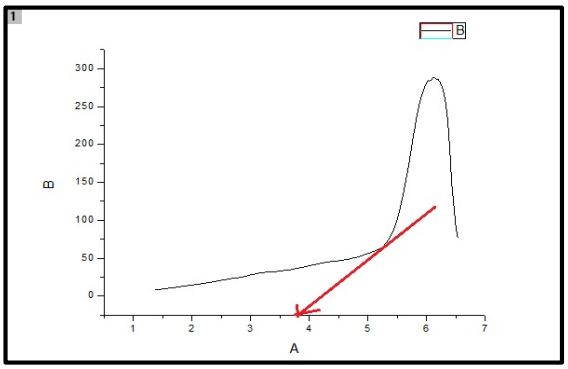


Fig: Tauc plot of 0.18M ZnO+0.02M Ni sample

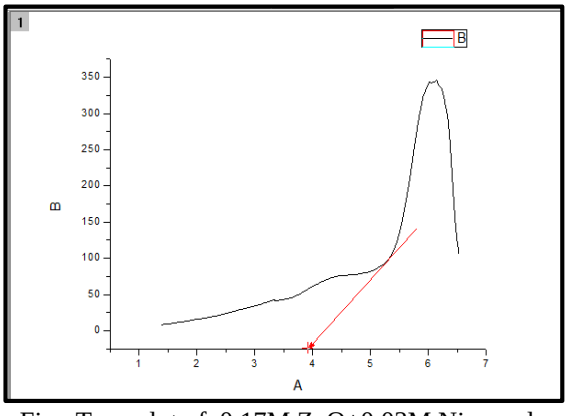


Fig : Tauc plot of 0.17M ZnO+0.03M Ni sample

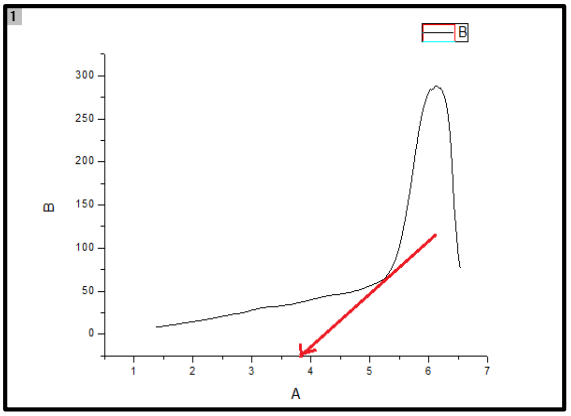


Fig: Tauc plot of 0.16M ZnO+0.04M Ni sample

The obtained energy band gap of pure zinc oxide and Nickel doped zinc oxide as shown fig.6.3 and the value of pure zinc oxide 3.6eV. Due to doping of Ni^{2+} ions to ZnO the energy band gap is increased. The calculated band gap energies Nickle doped zinc oxide was observed in 3.62eV,3.73eV,3.80eV and 3.85eV respectively as shown in the Fig.6.3.

RAMAN SPECTROSCOPY

Raman spectroscopy is used to find chemical structure and identify the materials. Firstly prepare the sample and take it in a transparent zip lock cover so that while taking the readings the equipment will not touch the material directly. After opening the software initially subtract the dark then select the specifics like laser intensity, time of reading in ms etc., after selecting place the laser gun on the material containing cover and hold it until the time specified is completed, then the Raman shift can be seen.

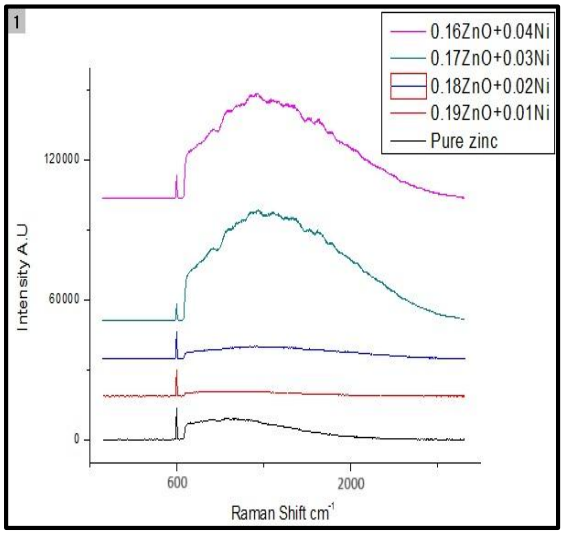
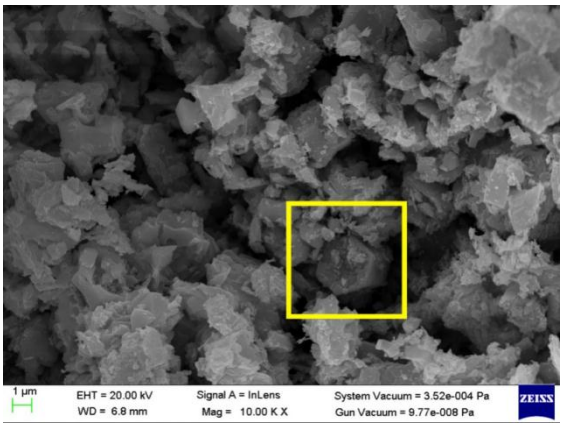


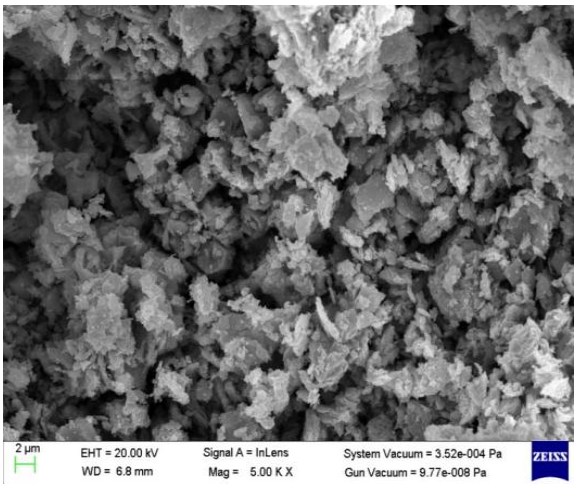
Fig. Raman Spectra of Sample

According to the figure 7.4 When we doped the Nickel into pure zine oxide nano particulars that Raman peak are gradually changed with respectively concentration such as Pure, 0.01%, 0.02%, 0.03%, 0.04% of molar Nickel doped ZnO, with their characteristics bands corresponding to 595cm^{-1}. The above Raman peak is gradually decreases and the peak 620cm^{-1} is gradually increases due to the Nickel doping into host lattice. So related to intrinsic host lattice defects which is become a spectroscopically vibrational active.

SCANNING ELECTRON MICROSCOPE

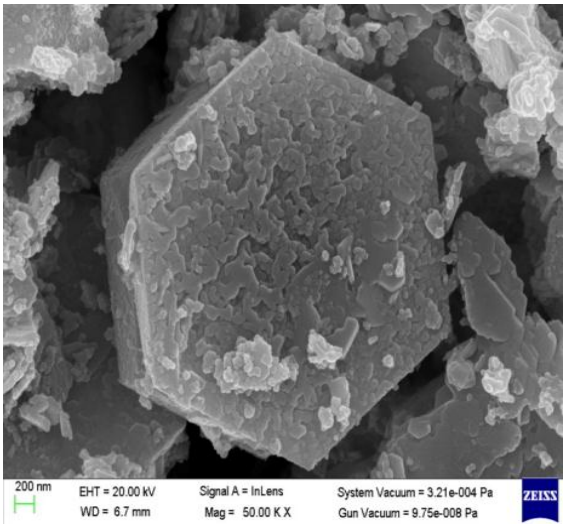


a)1 µm

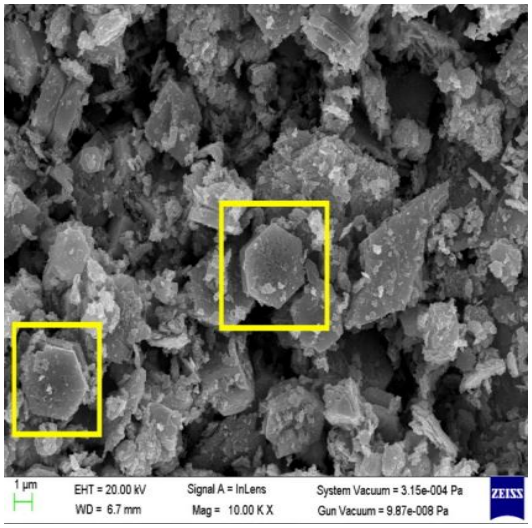


b)2 µm

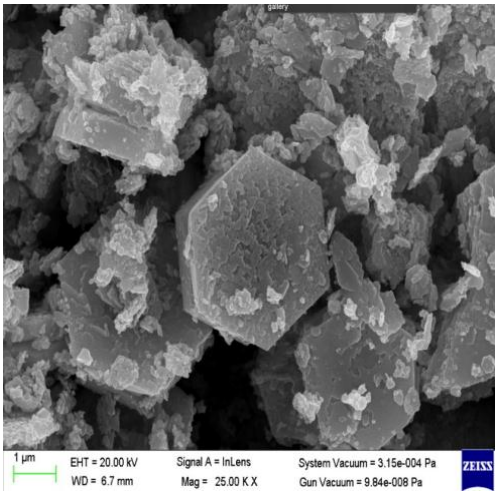
Fig : SEM images (a,b,) of pure ZnO nano particles.

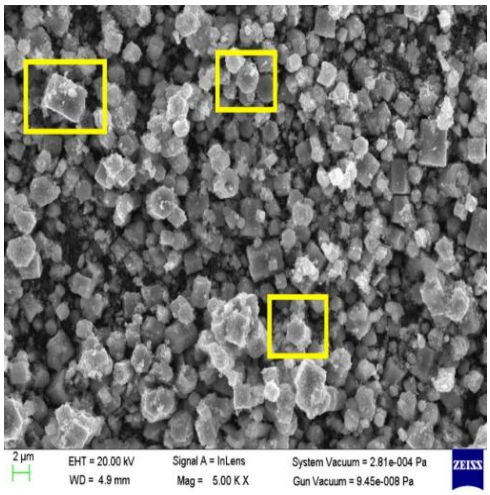


(a)

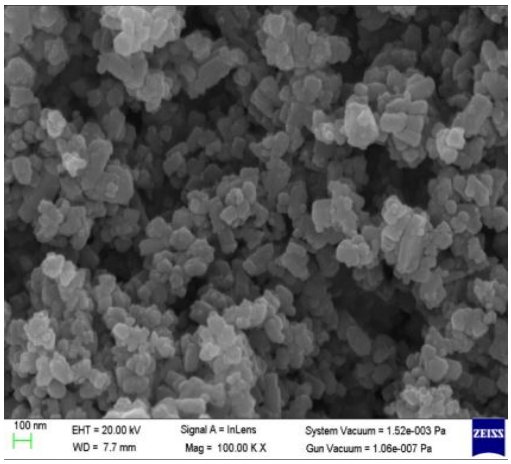


(b)

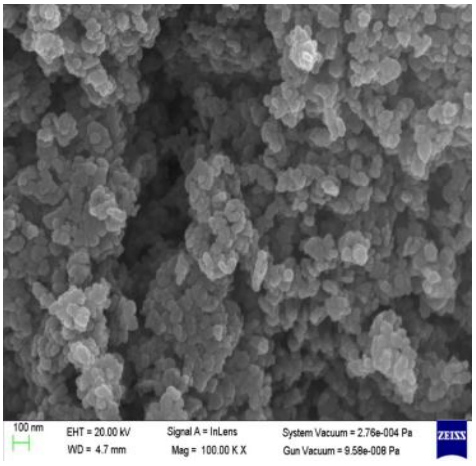




(c)



(d)



(e)

Fig : SEM images (a,b,c,d,e) of Ni Doped Zinc Oxide Nano particles of different concentrations

DISCUSSION

SEM technique provides the morphology of nanocarriers by scanning the surface with a focused beam of electrons, along with revealing data concerning the chemical composition, crystalline structure, and orientation of materials of which the specimen is made; and significantly less information regarding size distribution, true population, and its average. Characterization of particles using SEM requires conversion of the nanocarrier solution into dry powder first, then the

sample is mounted on a specimen holder or stud utilizing a conductive adhesive, and sputter coated with a conductive metal, such as platinum, gold, graphite osmium, tungsten, iridium, chromium, or gold/platinum alloy. Thereafter, the sample is scanned with a focused fine beam of electrons. The emitted secondary electrons from the sample surface deliver the surface characteristics.

The size and shape morphology of Ni doped ZnO Nanoparticles were investigated using SEM
In SEM images most of the nano particles showed agglomeration crystallinity of any particle is not specifically found .Well dispersed corrosive rock like structures and patterns are observed with normal reflectivity. Grouped patterns are clearly formed with small particles such less than 1 µm. The SEM image clearly reavels the transformation of Nanoparticles into Nano hexagonal rod like structures and also hexagonal plates turn towards nut like structures are also observed. The particles are quasi spherical and agglomerated and have flower like structures.It is clearly evident that particles appear in uniform and consistent shape with slightly constricted size distribution.

5.5 Compositional Analysis by Energy Dispersive X-ray Spectroscopy:

S.NO	Element (% wt.) and doping Molarity (x=0.01,0.02,0.03,0.04)	Zn	O	Ni	Other elements	Total
1	pure	76.6	23.4	-	-	100
2	$ZnO_{0.19}+Ni_{0.01}$	85.3	14.3	0.4	-	100
3	$ZnO_{0.18}+Ni_{0.02}$	80.9	17.8	1.3	-	100
4	$ZnO_{0.17}+Ni_{0.03}$	84.5	11.8	3.6	-	100
5	$ZnO_{0.16}+Ni_{0.04}$	71.6	25.5	2.9	-	100

Table: Calculated Parameters of pure ZnO and Co-dopped ZnO from XRD analysis

The results shown that the nano powders were almost stoichiometric based on the ZnO nanoparticles. Weight% Zn, and O for Pure is 76.6% and 23.4% respectively .Whereas for diluted ZnO,O,Ni are 85.3%,14.3%,0.4% are respectively for Ni doped ZnO. The produced pure and Ni-doped ZnO nanoparticles can be referred from above data.

CONCLUSION

1)Nickel doped zinc oxide Nano particles (Zn0.2-xNix (x=Pure, 0.01, 0.02, 0.03, 0.04) were successfully synthesized by Microwave oven method.
2)The XRD spectrum showed a good match with the standard JCPDS file for ZnO. (JCPDS74 –0534). It confirms the hexagonal wurtzite crystalline structure.
3)Specific amount of Ni concentrations and the properties of micro-strain are decreases by increasing the Ni concentration.
4)SEM analysis reviled that ZnO and Co doped ZnO have the hexagonal shape, some of the flakes with rod like structure, at the percentage of 0.03 and 0.04 molar doping concentrations it shows rod like structure collectively with flower surface.
5)From UV visible spectroscopy characterization gives us energy band gap ZnO has 3.1eV, when cobalt doped zinc oxide nano particles were also had 3.71eV and is changed little bit and it accepts the blue shift conditions.
6)In Raman spectroscopy, for Pure Zn Oxide nanoparticleshighest peak occurred in 595cm^{-1} then Nickel dopped zinc oxide nanoparticles have highest peak in 789 cm^{-1} so that cobalt doping is tailoring the vibration modes of the materials
Future scope:
The pure ZnO nano particle crystalline size can be controlled using specific synthesis methods and these nano particles have high scope in using as anti bacterial agent and also Zn doped nano particles have wavelength in visible range which can be processed for photocatalysis.

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