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Synthesis and Characterization Studies of Pure ZnO and Bentonite Doped ZnO Nanocrystals

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1. ABSTRACT

The structural and optical properties of bentonite doped ZnO nanoparticles prepared by wet chemical method have been investigated. Since last few years, synthesis of nanoparticles has been attracted considerable attention. The advantages of producing nanoparticles by wet chemical method are is easeful, flexible, fast, cost effective, and pollution free. Nanostructured Zinc Oxide have wide range of applications due to their interesting size-dependent chemical and physical properties compared to particles of size in the range of micrometer such as catalysts, cosmetics, microelectronic device, semiconductors, sporting goods and textiles. Zinc Oxide nanoparticles appear as a white powder. ZnO nanoparticles were synthesized by simple wet chemical method using basic Zinc Chloride as synthesized precursor and NaOH as stabilizing agent. Appropriate molar weight of zinc chloride was dissolved in 50 ml of double distilled water. 5mL of NaOH solution is added in limited intervals while the mixture is stirred by a magnetic stirrer for 3 to 4 hours. The precipitate is washed using ethanol, filtered and finally calcinated at 600^{o} C for 8 hours. In this way Pure ZnO nanoparticles are prepared and the nanoparticles are doped with bentonite using same process by adding desired weight amount (0.5 and 0.005 gms) of the same molar weight. Due to its near-UV emission and visible light transparency, ZnO is useful for the fabrication of light-emitting diodes, UV-radiation detectors, and transparent contacts in solar cells. In order to increase the carrier concentration and modify the optical properties of ZnO nanoparticles, the bentonite doping is proposed in present work. The undoped and bentonite doped ZnO nanoparticles, was successfully prepared by chemical technique. The functional group and structure was confirmed by FTIR and XRD analysis. The optical properties of ZnO and bentonite doped were analyzed by UV-Visible. Scanning electron microscope (SEM) is used to study the surface of prepared nanoparticles.

Key words: Nano crystals, wet chemical, optical properties

2. Introduction

ZnO is a wide-band gap semiconductor of the II-VI semiconductor group. This semiconductor has several favourable properties, including wide bandgap, good transparency, high electron mobility and etc. As a semiconductor, ZnO has a wide direct band gap (Eg = 3.37 eV), with a large excitonic binding energy of 60 meV. Zinc oxide has high refractive index, high thermal conductivity, antibacterial and UV-protection properties. Bentonite is a native, colloidal, hydrated aluminium silicate. Bentonite is a clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. Other smectite group minerals include hectorite, saponite, beidelite and nontronite. Bentonite's adsorption/absorption properties are very useful for wastewater purification. Common environmental directives recommend low permeability soils, which naturally should contain bentonite, as a sealing material in the construction and rehabilitation of landfills to ensure the protection of groundwater from the pollutants. Bentonite is the active protective layer of geosynthetic clay liners. Bentonite is used as an animal feed supplement, Due to its thixotropic properties, bentonite and organoclays function as a thickening and/or suspension agent in varnishes, and in water and solvent paints. Bentonite, as a carrier, has many advantages, such as low cost, big surface area, good adsorption, and high ion exchange. There were many literatures that bentonite as an excellent carrier was applied in the field of catalysis. Nanosized particles of semiconductor materials have gained much more interest in recent years due to their desirable properties and applications in different areas such as catalysts [1], sensors [2], photoelectron devices [3,4], highly functional and effective devices [5]. These nanomaterials have novel electronic, structural, and thermal properties which are of high scientific interests in basic and applied fields. Zinc oxide (ZnO) is a wide band gap semiconductor with an energy gap of 3.37 eV at room temperature. It has been used considerably for its catalytic, electrical, optoelectronic, and photochemical properties [6-9]. ZnO nanostructures have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity [10]. Many methods have been described in the literature for the production of ZnO nanostructures such as laser ablation [11], hydrothermal methods [12], electrochemical depositions [13], sol–gel method [14], chemical vapour deposition [15], thermal decomposition [16], and combustion method [17,18]. Recently, ZnO nanoparticles were prepared by ultrasound [19], microwave-assisted combustion method [20], two-step mechanochemical-thermal synthesis [21], anodization [22], co-precipitation [23], and electrophoretic deposition [24]. In this work ZnO nanoparticles and ZnO-bentonite nanocomposite were prepared by wet chemical method. Microscopic and spectroscopic methods have been used for product characterization.

3. EXPERIMENTAL METHOD OF SYNTHESIS OF PURE ZnO DOPED WITH BENTONITE NANOCRYSTALS

Zinc oxide nanoparticles were prepared by wet chemical method using zinc chloride and sodium hydroxide as precursors without further purifications.1M of sodium hydroxide was added drop wise over a period of 2 hours in 1M of Zinc Chloride solution in room temperature. After the completion of reaction, the solution was allowed to settle for 24 hours. The solution was allowed at 4500 rpm, for 10 minutes and washed with ethanol and distilled water to remove the by products for several times. After washing, the material was calcined at 800° C for 24 hours in oven. During calcinations, zinc hydroxide was converted into zinc oxide. The obtained ZnO powder was observed to be white in colour. For the preparation of bentonite doped zinc oxide nanoparticles, the procedure was the same. However, different radio of bentonite (0.005 and 0.5 gms) were dissolved along with 1M of sodium hydroxide solution. The obtained Zno powder was observed to be dirty white in colour which may be due to the addition of bentonite.

4. RESULTS AND DISCUSSIONS

4.1 POWDER XRD ANALYSIS

All diffraction peaks could be perfectly indexed to the wurtzite ZnO reported in JCPDS (2016) (file no. 10.17706). This result suggested that the Nanopowders had a pure hexagonal wurtzite structure with well developed crystallinity. The lattice constants were calculated to be a =3.249 Å, c=5.206 Å. The grown sample shows the peaks of (100) and (101). This is an evidence for creation of internal compressive micro states. Such case was also observed in ZnO annealed in hydrogen atom sphere. It is known that more oxygen content is introduce into the sample. A strong and sharp peak (101) is observed in the Bentonite doped ZnO sample. This is due to the presence of bentonite in the ZnO nano particles. The formation of nanocrystalline ZnO is reflected through the broadening of the XRD characteristic lines for ZnO. The XRD pattern shows the presence of ZnO, due to the reflection peaks. In bentonite doped ZnO the peaks become broder and more intense, which indicates the decrease of particle size and the improvement of crystallinity. By recording the full width at half maxima (FWHM) of these peaks, the average size of the nanocrystallites is determine using the debye-scherrer equation

$$D = k\lambda / \beta \cos\theta$$

Where D is the average crystallite size, k is a constant (0.89 here), λ is the $\times$ of the X-ray radiation (0.154 nm), β is the band broadening (full width at half-maximum) and θ is the diffraction angle. The particle size of pure and bentonite doped ZnO nanoparticles was calculated and given in the Table1.

Table 1. Particle size of synthesized sample

Sample	Particle size (nm)
ZnO	40
ZnO/0.5 bentonite	35
ZnO/0.005 bentonite	27

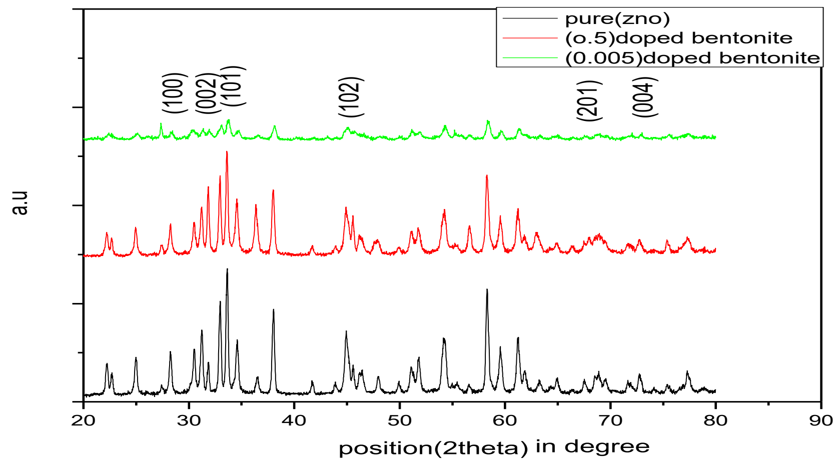


Fig: 1 XRD spectrum of pure ZnO and Doped bentonite

4.2 FT-IR ANALYSIS OF ZnO AND BENTONITE DOPED ZnO NANOPARTICLES

The FTIR spectrum of the pure and bentonite doped ZnO, synthesized by wet chemical method, which was acquired in the range of 400-4000 cm^{-1}. The band between 450 cm^{-1} - 500 cm^{-1}. Correlated to metal oxide bond (ZnO). The broad band starting at 3455 cm^{-1} corresponds to the O-H bond. The peak at 1619cm^{-1} corresponds to O-H bonding of absorbed water. The main absorption band between bentonite doped samples. The absorption band at 3491, 3455, 1040,908, 531, 468 cm^{-1} are due to the coexistence of bentonite in ZnO. The absorption at 3455 cm^{-1} is attributed to stretching vibration of OH groups. It was reported that the Al-Al-OH stretching frequency is observed at 3455 cm^{-1}, while the bending frequency is at 908 cm^{-1}. This can be considered as characteristic of dioctahedral clay. While absorption at the frequencies at 1040 cm^{-1}, 566 cm^{-1} and 468 cm^{-1} are attributed to Si-O-Mg bending respectively. While that at 3491 cm^{-1} has been assigned to OH groups bonded to absorption water. However we have not estimated precisely the quantity of the dopant present in the material.

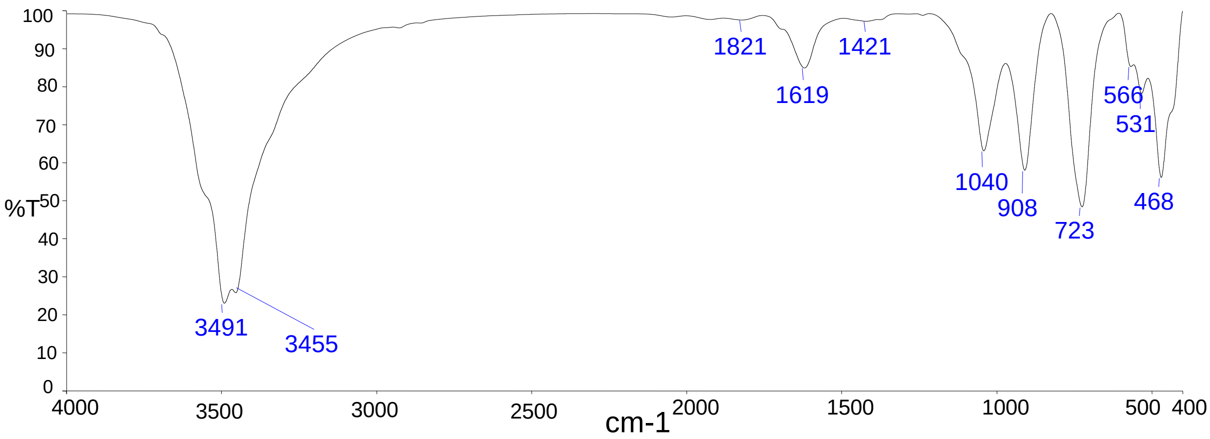


Fig: 2 FTIR spectrum of pure ZnO nanoparticles

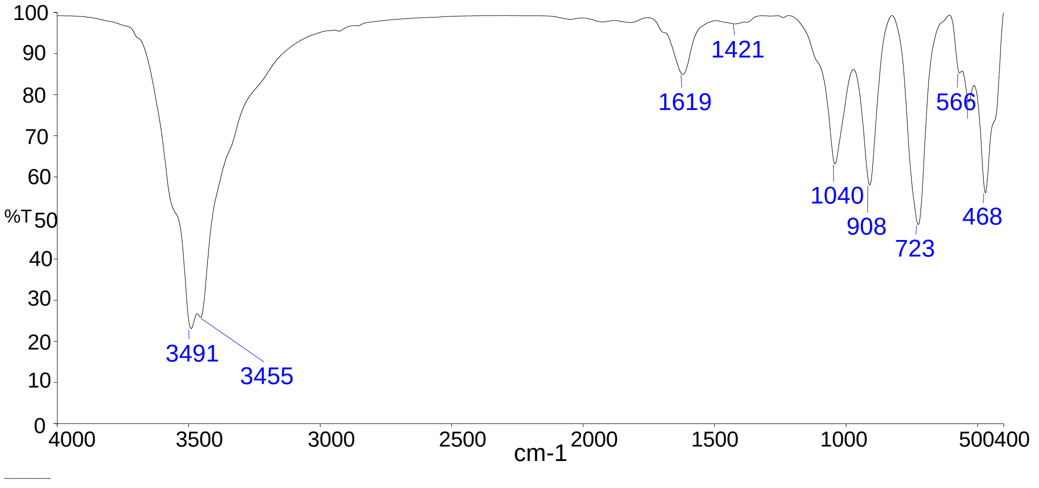


Fig: 3 FTIR spectrum of zno/0.5 bentonite nanocrystals

4.3 UV-VISIBLE SPECTRA ANALYSIS OF ZnO AND BENTONITE DOPED ZnO NANOPARTICLES

The UV absorption peaks of the prepared pure ZnO sample are shown in Fig. 4 UV-Vis spectrum was recorded the in the range of 200-1200 nm. Confirmation of the synthesized ZnO nanoparticles was exhibited by the blue shifted absorption maximum at 340 nm. Bulk ZnO exhibits absorption maximum around 380 nm approximately. The absorption peaks of pure ZnO are 220 nm to 370 nm. The absorption and transmission peaks of bentonite doped ZnO and their absorption peaks are 320 to 372 nm. The transmission peaks of bentonite doped ZnO are transparency. The plots of variation of $(\alpha h\nu)^{1/2}$ verses hv for the pure and Bentonite doped ZnO nano particles are presented. These plots are known as the Tauc's plots and they are used to find the accurate optical band gap value by the extrapolation of the linear part. The band gap values found for the pure and Bentonite doped ZnO nano particles. As a consequence of wide band gap , the pure and Bentonite doped ZnO nano particles have the large transmittance in the visible region. This suggest that the optical transition in the sample is a direct transition. From these graph we are calculating the band gap energy for pure ZnO nano particle is 3.3 eV and for Bentonite (0.5) doped ZnO nano particles is 2.7 eV, respectively. The peak absorption spectrum of and the corresponding absorption energy is 2.9 eV. In theoretical method the band gap was calculated using the formula,

$$E = hc / \lambda$$

Where,

h-planck's constant (6.626×10^{-34} J),

c – Velocity of light (3×10^{8} m/s),

λ - Cut off wavelength

Calculated band gap value is =2.99 eV

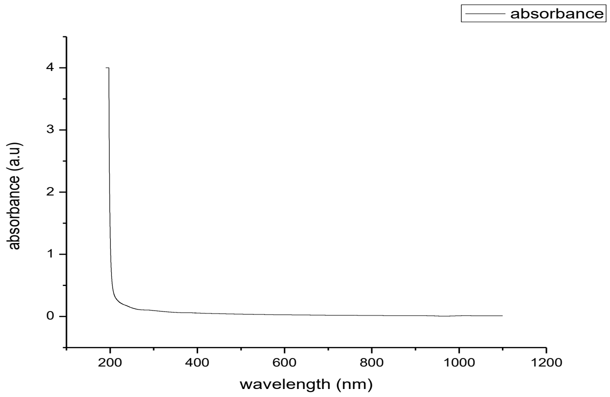


Fig: 4 absorption spectrum of pure ZnO

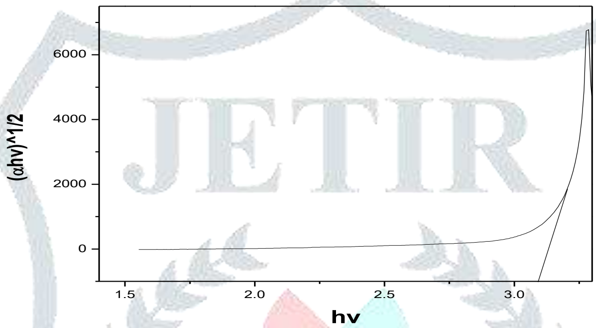


Fig : 5 (a) Tauc's plot for pure ZnO nano particles

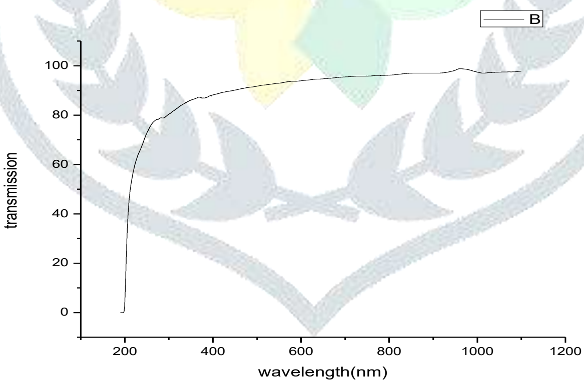


Fig: 6 Transmission spectrum of ZnO Nano Particles

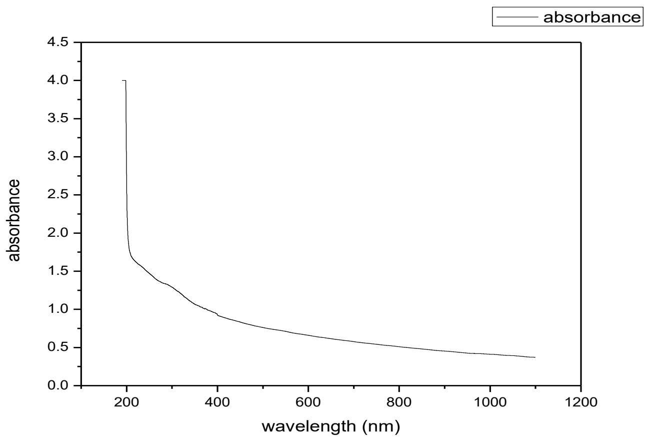


Fig : 7 Absorbance spectrum of bentonite doped ZnO Nano Particles

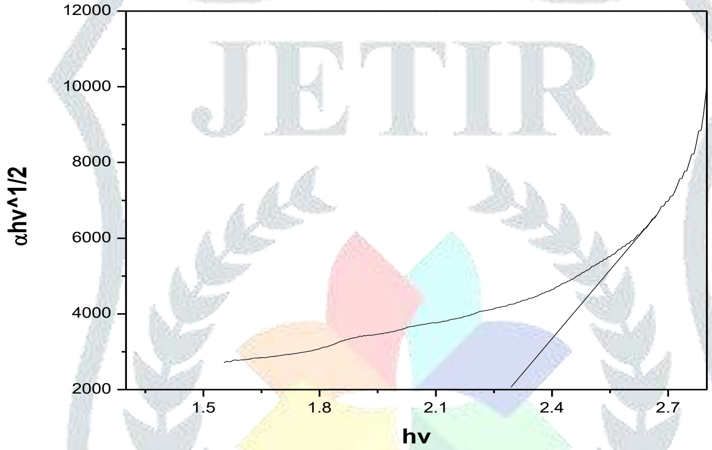


Fig: 8 (a) Tauc's plot for Bentonite doped ZnO Nano Particles

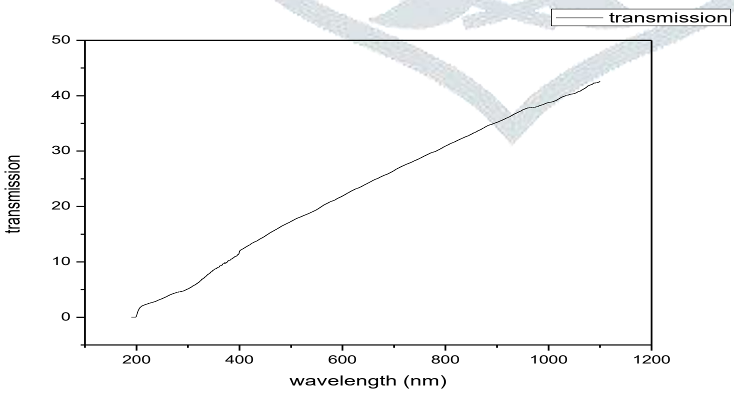
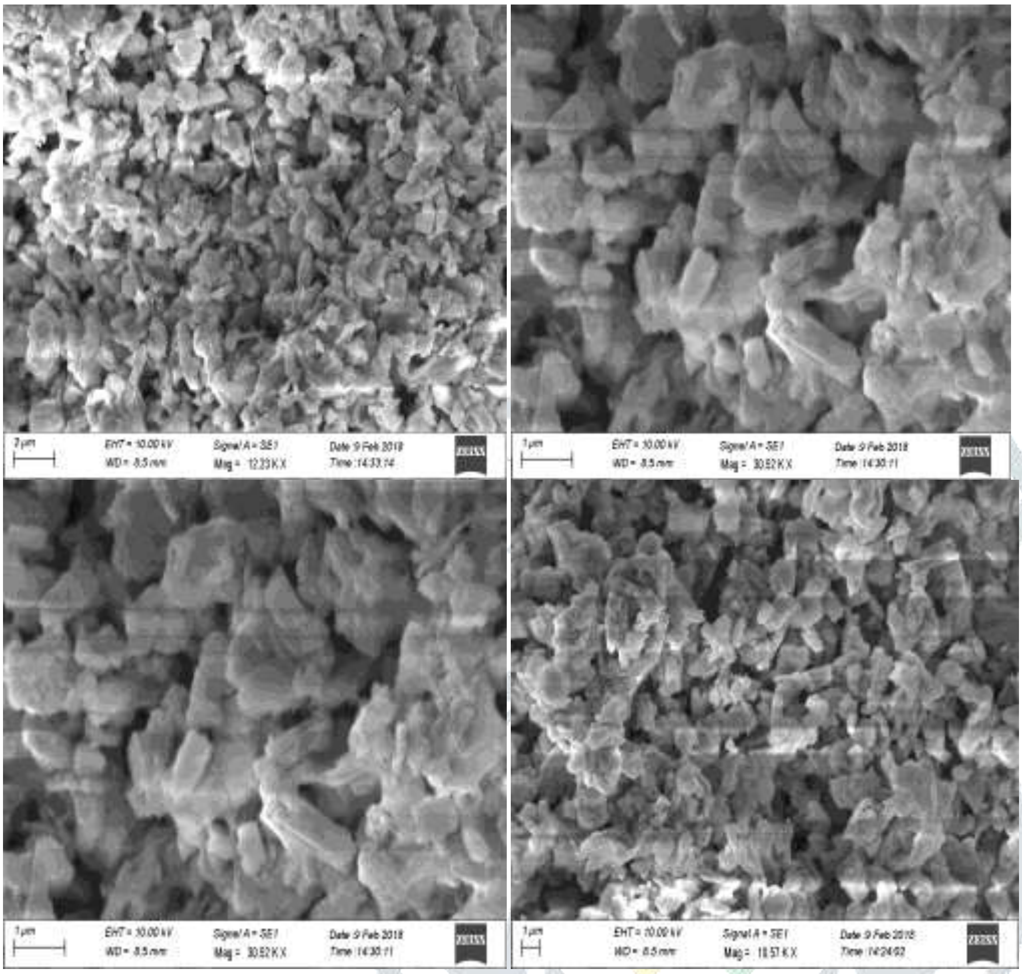


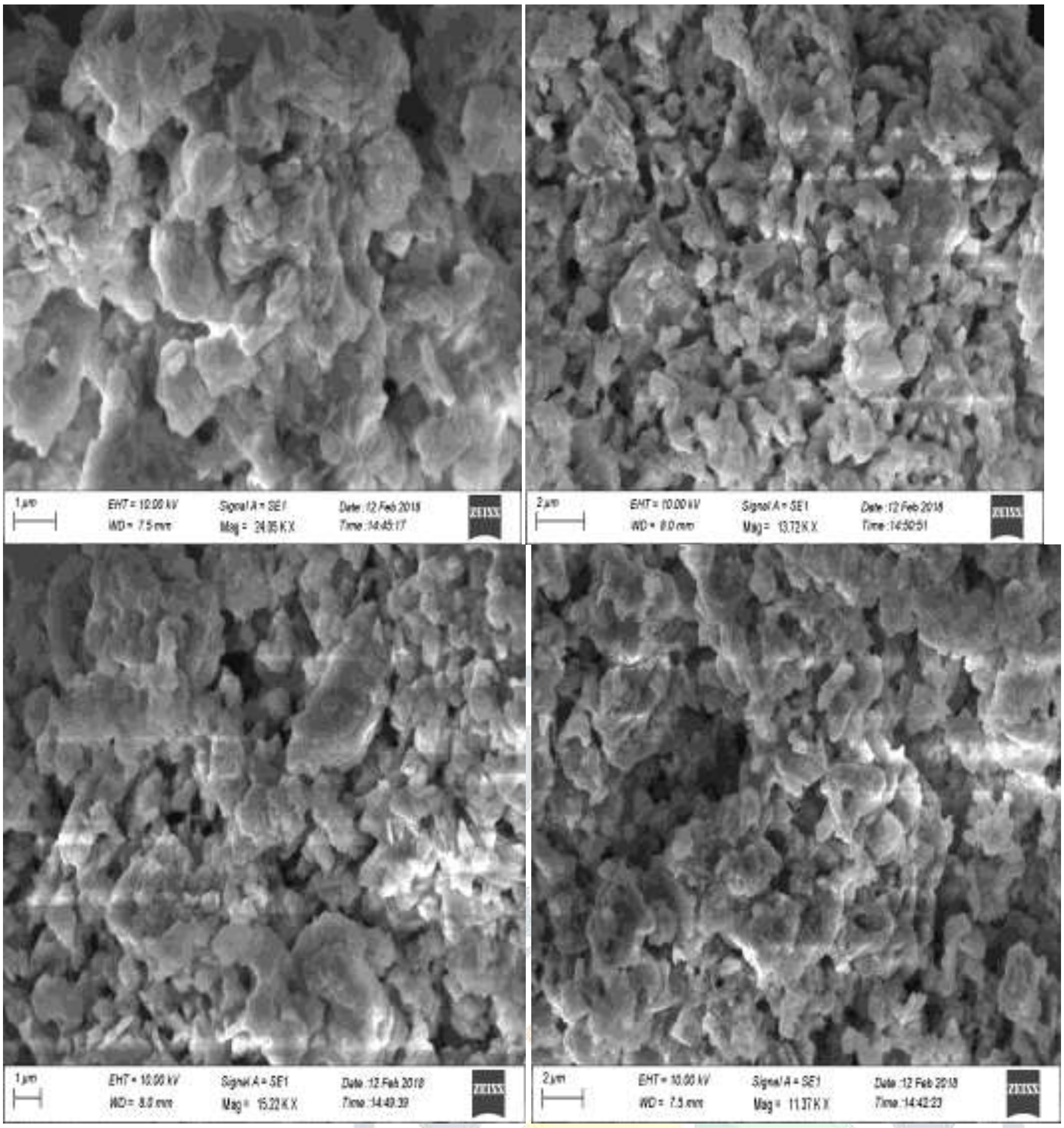
Fig: 9 Transmission spectrum of bentonite doped ZnO Nano Particles

4.4 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

The SEM analysis was used to determine the structure of the reaction products that were formed. SEM image has showed individual zinc particles a well as a number of aggregates. The SEM image showed relatively spherical shape nanoparticles formed with diameter range



SEM image of pure ZnO



SEM image of ZnO/BENTONITE

5. Conclusion

Bentonite doped ZnO nano particles was prepared by wet chemical method powder XRD, FTIR, UV and SEM studies confirmed that the bentonite was doped in ZnO. XRD result showed that the obtained ZnO nanoparticles were hexagonal system. The particle size decreases while increasing the concentration of bentonite. Because of the large surface-to-volume ratio of bentonite doped ZnO particles, efficient and fast trapping of photo-generated holesat surface sites. This concluded that bentonite doped ZnO will have improvement in photoluminescence property. This preliminary idea which confirms that bentonite doped ZnO acts as a good photocatalytic agent due to the presence of large oxygen deficiency. Powder X-ray diffraction pattern shows that nanoparticle nature of sample. This result suggested that the Nanopowders had a pure hexagonal wurtzite structure with well developed crystallinity. The lattice constants were calculated to be a = 3.249 Å, c = 5.206 Å. FTIR spectrum shows the characteristic peaks of prepared nanoparticle. The FTIR spectrum of the pure and bentonite doped ZnO, synthesized by wet chemical method, which was acquired in the range of 400-4000 cm^{-1}. The band between 450-500 cm^{-1}. UV spectrum shows the good transparent nature of nanoparticle and the value of cut off wave length and optical band gap are determined. The transmission peaks of bentonite doped ZnO are transparency. The plots of variation of $(\alpha h\nu)^{1/2}$ verses hv for the pure and Bentonite doped ZnO nano particles are presented. These plots are known as the Tauc's plots and they are used to find the accurate optical band gap value by the extrapolation of the linear part. The band gap values found for the pure and Bentonite doped ZnO nano particles. As a consequence of wide band gap, the pure and Bentonite doped ZnO nano particles have the large transmittance in the visible region. SEM images show the surface morphology of prepared nanoparticle in the magnification of different micrometer. SEM images are spherically flower like shape.

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