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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF ALUMINIUM DOPED ZnO NANOPARTICLES.

S. R. Brintha and M. Ajitha.
Department of Chemistry, Annai Velankanni College, Tholayavattam , Tamil Nadu, India.

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Abstract

ZnO nanoparticles were synthesized by aqueous solution method.The synthesized particles were characterized by XRD, SEM and EDX .The X-ray diffraction studies reveals that the synthesized ZnO nanoparticles have wurtzite structure and the particle size varies from 11 to 13 nm. A change in morphology from hierarchical nanostructures in ZnO to nanorods after doping with aluminium has been observed. The Energy Dispersive X-Ray Diffraction Spectroscopy (EDX) reveals that the elemental composition of prepared samples and the incorporation of the Al ions into the ZnO lattice. The antibacterial activities of ZnO and Al doped ZnO nanoparticles were examined using the disc diffusion method against four pathogenic bacteria (Eschericia Coli , Klebsiella Pneumoniae , Bacillus Cereus, and Staphylococcus aureus)

Introduction:-

ZnO is a II-VI semiconductor with wide band-gap (3.37 eV) and exciton binding energy (60 meV) at room temperature. ZnO nanostructures can be synthesized into a variety of morphologies, including nanowires, nanorods, tetrapods, nanobelts, nanoflowers and nanoparticles [1]. It is an inexpensive and environmentally safe host material [2]. In addition to catalytic properties, metal oxide nanoparticles also exhibit electronic, optical and magnetic properties. In the few decades, metal oxide nanoparticles were extensively investigated due to their applications in the field of spintronics, photoelectronic, sensor, lasing devices and light emitting diodes, etc [3]. These remarkable properties make them to find many applications in the field of medicine, electronic devices and in many industries [4]. Zinc oxide has high biocompatibility and fast electric transfer kinetics, such phenomena encourage the use of this material as a bio membrane to immobilize and modify the biomolecules [5].

Nowadays, various routes have been used for the synthesis of ZnO nanomaterials, such as sol–gel synthesis, hydrothermal, solvothermal methods, micro emulsion method, precipitation, and physical vapor deposition [6]. Zinc oxide–soluble starch nano composites were synthesized using water as a solvent and soluble starch as a stabilizer and impregnated onto cotton fabrics to impart antibacterial and UV-protection functions. [7]. Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, is a multifunctional material [8].

ZnO nano powders doped with different ions such as Al, In, Ga, etc. have improved electrical, optical, and catalytic properties. Among these, Al-doped ZnO (AZO) nanopowders are both conductive and transparent in the visible region and thus can be utilized in transparent conductive pastes [9]. The enhancement of conductivity makes Al^{3+} and In^{3+} doped ZnO, a promising candidate for optoelectronic applications [10]. Inorganic nanocrystalline metal oxides such as ZnO are particularly interesting because they can be prepared with extremely high surface areas, and

Corresponding Author:- S. R. Brintha.
Address:- Department of Chemistry, Annai Velankanni College, Tholayavattam , Tamil Nadu, India.

are more suitable for biological applications. ZnO is widely used to treat a variety of skin conditions, in products such as baby powder, barrier creams to treat diaper rashes and in calamine cream, antidandruff shampoos and antiseptic ointments [11].The inorganic antibacterial materials have advantages over organic antibacterial material that the former shows superior durability, less toxicity and greater selectivity and heat resistance [12]. Some researchers have shown the performance of ZnO nanoparticles in degradation of some organic compounds, antibacterial effect and killing human cancer cells [13]. Zinc oxide nanoparticles are known to be one of the multifunctional inorganic nanoparticles with effective antibacterial activity. Antibacterial and antifungal activities of ZnO nanoparticles are observed even at very lower concentrations and also the antifungal activity does not affect soil fertility compared to the conventional antifungal agents [14].

Materials and Methods:-

Materials:-

Zinc acetate, Aluminiun nitrate, Trisodium citrate, Ammonia solution, Sodium hydroxide. All the reagents used were analytical grade, obtained from Merck (Indian) Ltd, and used without further purification.

Preparation of ZnO nanoparticles:-

ZnO nanoparticle was synthesized by aqueous solution method using zinc acetate as a precursor. The entire process was carried out with double distilled water. About 2.1 g of zinc acetate was dissolved in 200 ml of double distilled water along with varying amounts of aluminium nitrate (1.5-2.5 %).After 10 minutes of magnetic stirring about 1.5g of trisodium citrate in 10 ml water and 4.2 ml of 25% ammonia solution are added. Then, 20 ml of 2M NaOH solution was added drop wise with vigorous stirring. The temperature of the contents are raised to 80^0C and kept at this temperature for about 6 hours. The contents are centrifuged and the precipitate was washed with distilled water and then dried at 60^0C to get aluminium doped ZnO nanoparticles.

Undoped ZnO was synthesized with a similar procedure except the addition of doping materials.

Characterization of synthesized nanoparticles:-

The structural properties including structure and crystalline size of the samples are determined by x-ray diffractometer. The powder x-ray diffraction (XRD) was performed using automated x-ray diffractometer (X-PERTPRO Philips system) operating CuK_α at wavelength 1.54056 Å. The average crystallite size (D) has been calculated using Schrerer's relation $D = K\lambda/\beta\cos\theta$, where the constant K is taken to be 0.94, λ is the wavelength of X-ray used and β the full width of half maximum (FWHM). The morphology of the zinc oxide samples were characterized by scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX) to analyse the elemental composition of the synthesized materials. The FT-IR spectra was recorded using a SHIMADZU instrument. Antimicrobial activities of the samples are determined by well diffusion method. Four pathogenic bacterial strains namely Escherichia coli, Klebsiella pneumonia, Bacillus cereus and Staphyloccocus aureus are used in this investigation.

Results and discussion:-

X-ray diffraction analysis:-

Structural parameters of zinc oxide nanoparticles are calculated from the XRD pattern.
Fig: 1(a) shows seven diffraction peaks at 2θ values of 31.6811^0, 34.3596^0, 36.1769^0, 47.4835^0, 56.5269^0, 62.8115^0 and 67.9130^0. The peaks are identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Schrerer equation the average crystallite sizes of the nanoparticles are observed as 13 nm. All the peaks are indexed and found to be well matched to wurtzite structure of ZnO having hexagonal phase, which is in good agreement with the standard JCPDS (Card No. 36-1451).

Fig: 1(b) shows seven diffraction peaks at 2θvalues of 31.5972^0, 34.4634^0, 36.1142^0, 46.7427^0, 56.4519^0, 61.4925^0 and 67.8332^0. The peaks are identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Schrerer equation the average crystallite sizes of the nanoparticles are observed as 11 nm.

Fig: 1(c) shows seven diffraction peaks at 2θvalues of 31.8818^0, 34.2000^0, 36.4000^0, 47.8697^0, 56.5628^0, 63.0000^0 and 68.2000^0. The peaks are identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Scherrer equation the average crystalline sizes of the nanoparticles are observed as 12 nm.

Fig: 1(d) shows seven diffraction peaks at 2θvalues of 31.6811^0, 33.4524^0, 35.2516^0, 46.9672^0, 55.5432^0, 61.4356^0 and 67.8976^0. The peaks are identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Scherrer equation the average crystalline sizes of the nanoparticles are observed as 13 nm.

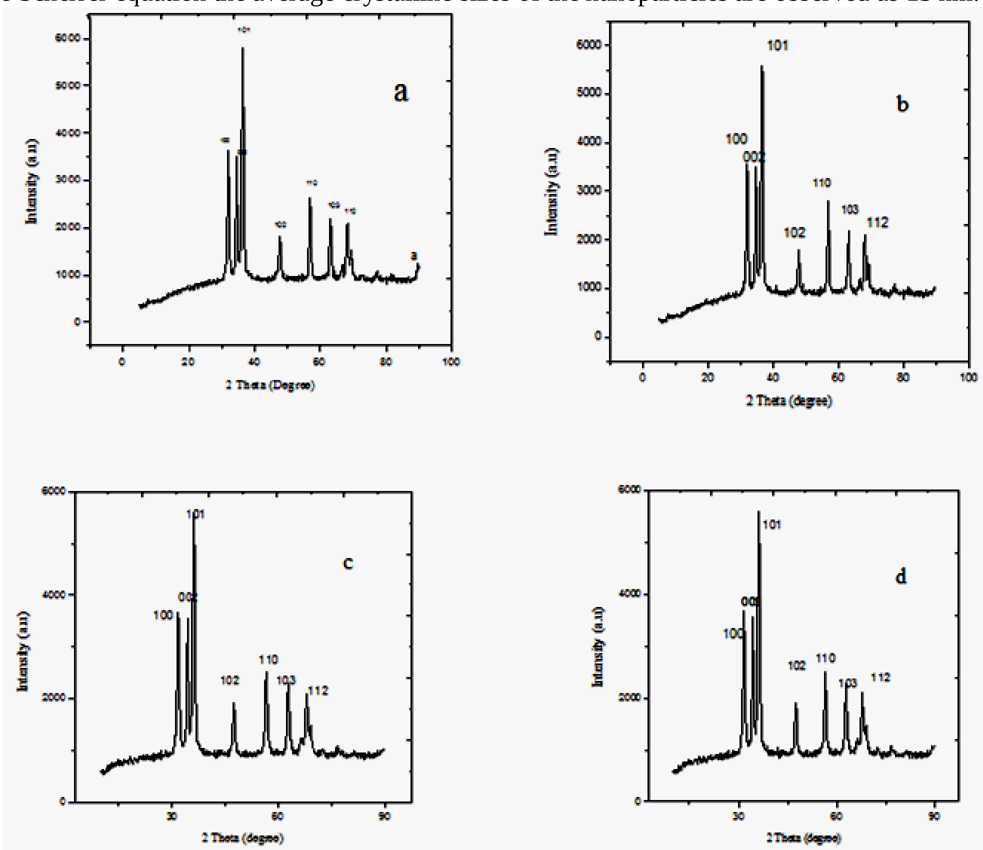
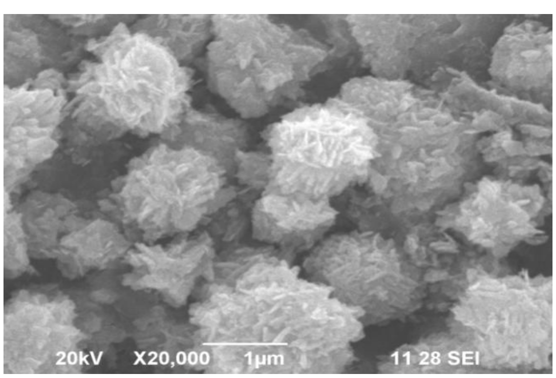


Fig: 1(a):- XRD patterns of undoped ZnO, (b) Al (1.5%) doped, (c) Al (2%) doped and (d) Al (2.5%) doped ZnO nanoparticles by aqueous solution method.

SEM analysis:-
Scanning electron microscopy (SEM) was employed to analyse the morphology and the growth features of prepared nanoparticles.

Fig: 2:- shows the SEM images of pure zinc oxide and Aluminium doped zinc oxide nanoparticles. The images show change in morphology of particles from hierarchical nanostructures in pure zinc oxide to distorted hierarchical nanostructures ($[Al^{3+}]$ =1.5%) and then to rods ($[Al^{3+}]$ =2.5%).



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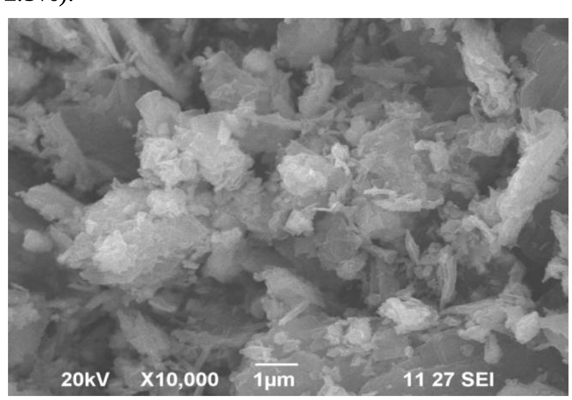

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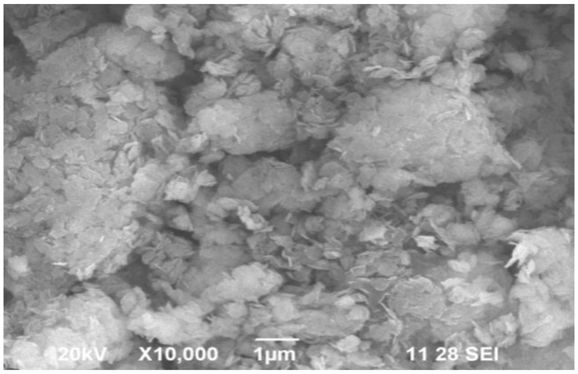

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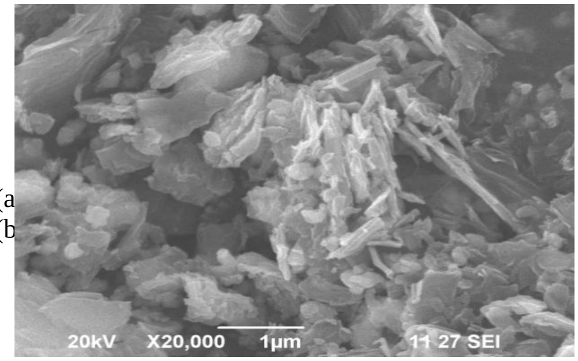


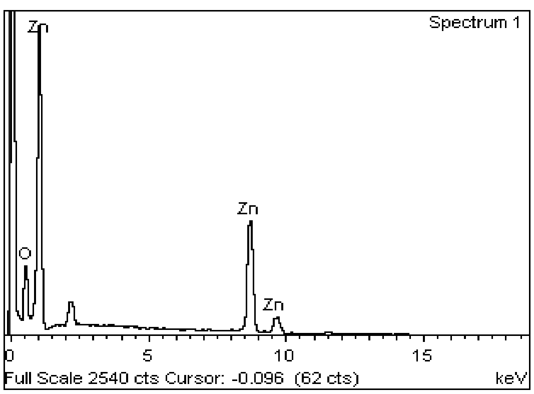
c) d)

Fig: 2 (a) SEM image of undoped ZnO, (b) SEM image of Al (1.5%), (c) SEM image of Al (2%) and (d) SEM image of Al (2.5%) doped ZnO nanoparticles.

Energy Dispersive X-Ray Diffraction Spectroscopy (EDX) :-

The elemental composition of the undoped ZnO and Al ion doped ZnO nanoparticles, at different concentrations were carried out by EDX spectroscopy.

Fig: 3(a) shows the EDX spectrum of undoped ZnO nanoparticles. The strong peaks observed in the spectrum related to Zn and oxygen. The prepared ZnO nanoparticles have atomic percentage of 40.90 of Zn and 59.10 of oxygen. This confirmed the formation of ZnO nanoparticles. In fig: 3(b) The prepared Al-doped **(1.5%) zi**nc oxide nanoparticles have atomic percentage at 17.73 of Zn, 75.27 of oxygen and 7 of Al. In fig: 3(c) Al (2%) doped The prepared Al (2%) doped zinc oxide nanoparticles have atomic percentage at 77.65 of oxygen, 14.58 of Zn, and 7.77 of Al. In fig: 3(d) Al (2.5%) doped zinc oxide nanoparticles have atomic percentage at 11.10 of Zn, 78.91 of oxygen and 9.99 of Al. This confirmed the doping of Al ion into the zinc oxide lattice.



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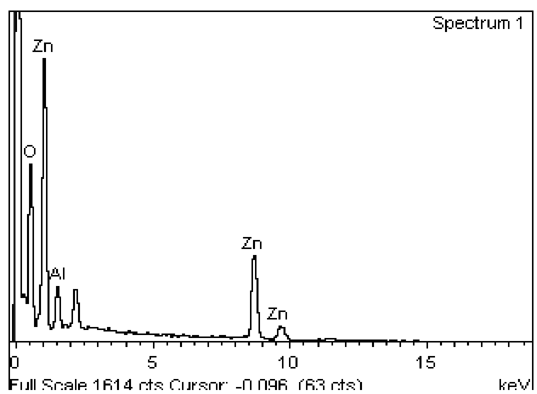

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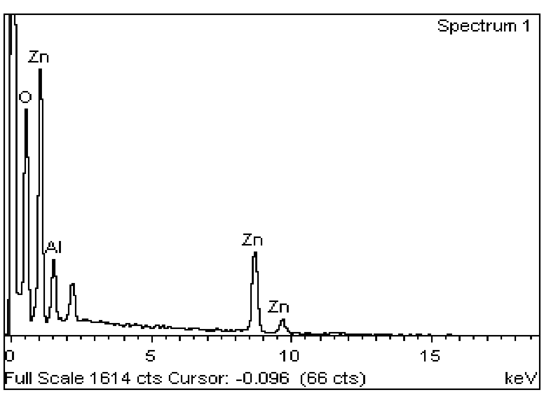

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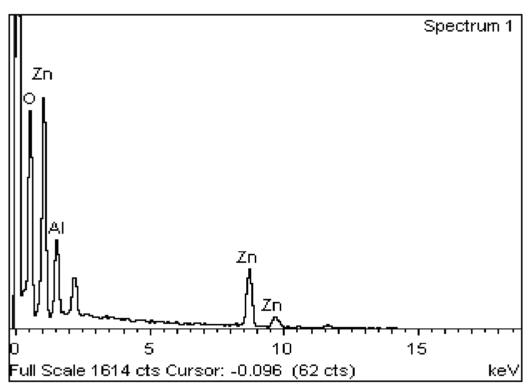


d)

Fig: 3 (a):- Energy dispersive x-ray diffraction spectrum of undoped ZnO (b) Al-doped (1.5%) ZnO (c) Al-doped (2%) ZnO and (d) Al-doped (2.5%) ZnO nanoparticles.

Table 1:- The atomic content of the different type of nanoparticles obtained from the EDX measurements

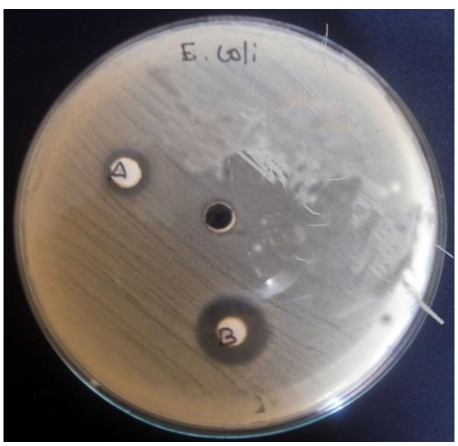
Type of nanoparticles	**EDX results**		
	Oxygen (at%)	**Aluminium (at%)**	**Zinc (at%)**
Undoped ZnO	59.10	-	40.90
1.5% Al doped ZnO	75.27	7.0	17.73
2% Al doped ZnO	77.65	7.77	14.58
2.5% Al doped ZnO	78.91	9.99	11.10

Antibacterial activity:-

Antibacterial activities of ZnO nanoparticles, were examined using the disc diffusion method. Antibacterial activities were studied against four pathogenic bacteria (Eschericia Coli, Klebsiella Pneumoniae, Bacillus Cereus, and Staphylococcus aureus).The ranges of bacterial strains for undoped and doped ZnO nanoparticles were shown in table 2. Al doped zinc oxide nanoparticles shows more activity in all four pathogenic bacteria than undoped zinc oxide nanoparticles.

Table 2:- Various ranges of bacterial strains for undoped and aluminium doped ZnO nanoparticles from aqueous solution method.

S. No	**Name of bacteria**	**Inhibition zone for samples**	
		Undoped ZnO	**Al doped ZnO**
1	Escherichia Coli	9	13
2	Klebsiella Pneumoniae	8	12
3	Bacillus Cereus	8	12
4	Staphylococcus Aureus	8	12



a)

b)

c)

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Fig. 4 (a):- Antibacterial activity against E-Coli, (b) Bacillus Cereus, (c) Klebsiella Pneumoniae and (d) Staphylococcus Aureus [A- undoped ZnO, B-Al doped ZnO]

Conclusion:-

Zinc oxide nanoparticles and Aluminium doped ZnO doped nanoparticles are prepared by aqueous solution method and the prepared nanoparticles are characterized by XRD, SEM, EDX. The crystalline size of the prepared nanoparticles determined by Debye-shrerer's equation was found to be in the nanometer range and show preferred growth orientation along (101) plane. All the nanoparticles showed wurtzite structure. The surface morphology of the ZnO nanoparticles characterized by SEM analysis suggested different morphological structures. Chemical purity and stoichiometry of the samples were investigated by EDAX Spectroscopy, inorder to confirm the presence of Zn, O, and Al ions in the material.

The synthesized ZnO nanoparticles are moderately sensitive to antibacterial organisms. Al doped zinc oxide nanoparticle is found to be more active against four pathogenic bacteria (Eschericia Coli, Klebsiella Pneumoniae, Bacillus Cereus, and Staphylococcus aureus). Thus it can be used for further medicinal applications.

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