SYNTHESIS, RESULTS, PROPERTIES AND APPLICATION OF Mn-DOPED ZnO NANOCRYSTALS

Abstract:

Doped metal oxides play a very important role in many areas of chemistry, physics and materials science. Nanocrystalline pure and Mn doped metal oxide (ZnO) with wide band-gap and large exciton binding energy have potential applications in various fields such as solar cells, light emitting diodes and laser diodes. It is also used as diluted magnetic semiconductors. In the present work, pure ZnO and Mn doped ZnO metal oxide has been synthesized by co-precipitation method. Initial work focuses on optimization of annealing temperature and number of Mn doped of metal oxide (ZnO) substrate. The impact of annealing on structural, optical and photoluminescence properties was systematically studied. It has been found out that ZnO annealed at 450°C shows the best structural and optical properties, which may be used for optical application. Based on the structural and opticals studies by varying the number of layers of ZnO oxide, it was confirmed that the eight layered film shows high crystalline quality, having the prominent (002) peak which is the characteristic peak for the c-axis oriented wurtzite ZnO structure. Again, the morphology of the eight layered sample showed hexagonal shaped grains reflecting the basic unit cell structure. Hence, for the preparation of Mn doped ZnO films, eight layered thickness films annealed at 450°C in open air has been used. The effect of hybrid and open air annealing on the structural and optical properties has been investigated. Due to good crystallinity and enhanced photoluminescence behavior, open air annealing was carried out for the preparation of all doped ZnO nanocrystals.

KEYWORDS: Zinc Oxide Nanoparticle, Mn- doped ZnO, Properties of Mn doped ZnO, Powder X-ray diffraction, Optical and Magnetic Properties, Application

Introduction:

Nanoparticles:

A solid particle in the range of 1-100nm is called nanoparticles. Nanoparticles could be non-crystalline, aggregate of crystallites of a single crystallite. These nanoparticles affect many properties such as- melting point, boiling point, band gap, optical properties, magnetic properties and electrical properties. Therefore, nanoparticles can make materials more chemically reactive and affect their strength or electrical properties and also be arranged into layers on surfaces and hence activity, relevant to a range of potential applications such as catalysts. They have varied applications such as cosmetics, textiles, paints and drug chemistry.

Zinc Oxide Nanoparticle:

Zinc oxide (ZnO) is one type of metal oxide nanomaterials, it is an inorganic compound. On the other hand, ZnO is a white power that is an insoluble in water and its suspension could not be electrostatically stabilized in the preset pH range between 7.2 – 12 and due to formation of unstable Colloidial practices zinc hydroxide. It is widely used as an additive in numerous materials ceramics, lubricants, batteries, cement, glass etc. ZnO is a wide-band gap semiconductor of the II- VI semiconductor group.Most applications exploit the reactivity of the oxide as precursor to other zinc compounds. For materials science applications, zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV protection properties. It is universally known that zinc oxide nanoparticles are antibacterial and inhibit the growth of microorganisms by permeating into the cellmembrane. Since zinc oxide is an amphoteric in nature, it react with both acids and alkali giving Zn (II) ions.

$$ZnO + 2HCL \xrightarrow{\text{acidic medium}} ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \xrightarrow{\text{basic medium}} Za_2ZnO_2 + H_2O$$

$$ZnCl_2 \xrightarrow{\text{aqueous medium}} Zn^{2+} + 2Cl^-$$

Doped Oxide:

Doped oxides have significant physical and chemical properties which are often, sharply improved by combining them in different proportions for making their alloy or compounds or nanocrystals. Doped oxides nanocrystals hold promise for a wide variety of applications if dopant –induced properties can be appropriately harnessed. X-ray photo electron spectroscopy analysis indicated that doped metal is distributed throughout the nanocrystal. On the other hand, Elemental composition analysis, shift and intensity changes in the x-ray diffraction peaks and electronic absorbance spectroscopy suggest that the guest cations are substitution doping in the host matrix.

Mn- doped ZnO:

"The term Mn- doped ZnO" has come from the adding ions against host lattice. The Mn atoms replace few Zn atom and occupy the position in ZnO crystal. The doping with 3d transition metal Mn highly effect in surface area and less amount of the particle size of ZnO nanoparticles. Mn is preferred for the doping of ZnO due to the fact that the d electron of Mn at t2g level can easily overlap with the ZnO's valence bond as compared with other transition elements.

Properties of Mn doped ZnO:

The properties of Mn doped ZnO are significant due to two types of important properties such as optical and magnetic properties. The optical band gap of the ZnO:Mn increases with the decrease of doping concentration. The transmission range of Mn doped ZnO nanoparticles in the visible light range is more than about 88%. The samples with low doping concentration (1-5% of Mn) exhibit paramagnetic and ferromagnetic behaviors.

Synthesis of Mn-doped ZnO Nanoparticles:

Materials

a) Manganese acetate tetra-hydrate
b) Zinc acetate di-hydrate
c) Sodium lauryl sulphate (polymer)
d) Sodium hydroxide (NaOH)
e) Ethanol (EtOH)
f) Distilled water

Calculation	**Compound Molecular weight:**
Zinc (II) acetate di-hydrate	219.498g/mol
Manganese (II) acetate tetra-hydrate	173.026g/mol
Sodium hydroxide	39.997g/mol
Water	18.01528g/mol
Sodium lauryl sulfate	288.372g/mol

Materials Quantity

Zinc (II) 0.5g
Manganese (II) 0.01g
NaOH +EtOH 125mM
EtOH 100ml
H2O 1ml
Polymer 0.4g

Experimental procedure:

0.01g amount of manganese acetate tetra hydrates was dissolved in 1ml of water. This solution was added to 100 ml of ethanol. Then undergoes vigorous stirring.After this maintaining the reaction mixture for a couple of 2 hours at room temperature. Then 0.5g amount of zinc acetate di-hydrates was added and this mixture was heated at 50 degree centigrade. Then it was undergoes to quenched ice and 0.4g polymer was added. The reaction mixture was stirred for 2 hours. Then hydrolyzed by the drop wise mixture (NaOH + EtOH=125mM) under ultrasonic agitation for about 2 hours. This mixture solvent were removed by rotavapourization then the resulting mixture was washed with water. Zn-MnO Nano-crystals was precipitate. This precipitate was centrifuged and dried in a vacuum 10 hour.

Picture 1 – Synthesis process (step1-step10)

Results and discussion: (Physical Properties)

Powder X-ray diffraction patterns of undoped ZnO and Mn doped ZnO are shown in below.The characteristic peaks with high intensities corresponding to the planes(100), (002), (101) and lower intensities at (102), (110), (103), (200), (112) and (201)indicated the annealed product is of high- purity hexagonal ZnO wurtzite structure. It is evident from the XRD data that there are no extra peaks due to manganese metal, other oxides or zinc manganese phase, as indicating the samples are single phase. The Mn(II) was doped to the ZnO, No changing the wurtzited like structure at 500° to 550$^{o.}$of 1hours 30minitues. The graph of the X- ray diffraction method was doped samples are slightly changes to left as compares to the undoped ZnO. This shows that small variation in the lattice parameters occurs as Mn concentration. In the sample increases, The result shows that the lattice constant of Mn doped ZnO were slightly larger than those of undoped ZnO, because ionic radius of Mn(II)(0.66) is larger than that of Zn(II)(0.60)**.** The sample grain size was estimated below. The crystal size of undoped ZnO decreases on doping 1mol% of Mn and subsequent doping shows an increasing tendency below.

The sample grain size was estimated:

Samples	**Grain Size (nm)**
UndopedZnO	19.21
1mol% Mn doped ZnO	15.80
2mol% Mn dopedZnO	17.66
3mol% Mn dopedZnO	18.32

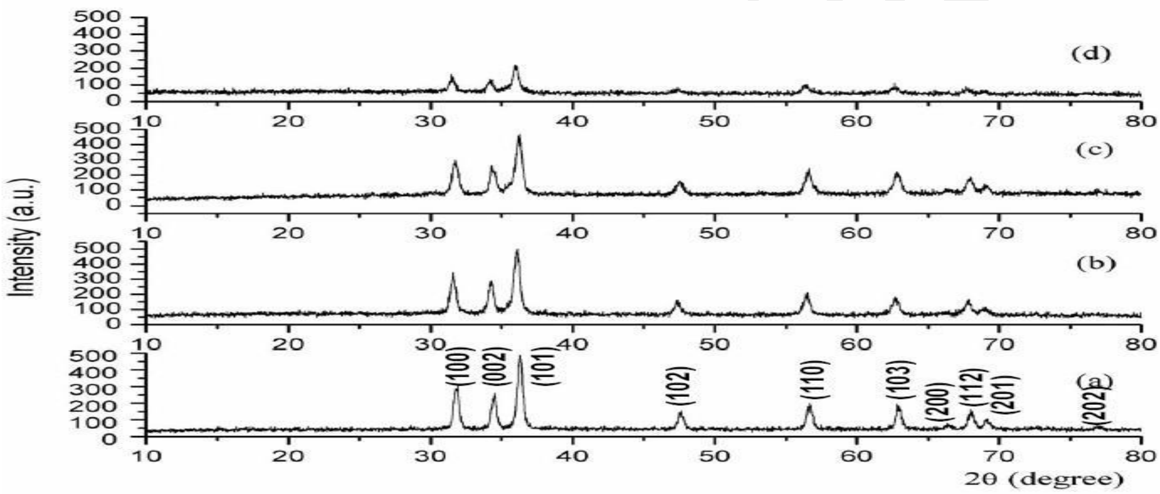

Fig-1 XRD method in samples are annealed inambient air at 500^o to 550^o 1hours30 mints.. (a) undoped ZnO; (b) 1mol% Mn doped ZnO; (c) 2 mol% Mn doped ZnOand (d) 3 mol% Mn doped ZnO.

Optical properties:

- UV- absorption spectra of free-standing ZnO and Mn-doped ZnO nanocrystals, both with an average diameter of 10.7nm.
- The band gap thus obtained for the ZnO nanocrystals corresponds to 3.38ev (367nm), indicating a blue shift of about 0.1ev compared to the bulk band gap of 3.3ev (373nm), due to confinement effect.

Magnetic properties:

- Shows EPR spectra of the doped Nano crystal samples with different Mn concentrations. The EPR spectrum from the uncapped, free-standing Mn doped sample.

Application:

[1] This nanoparticles use on the polyester fabric dyes.
[2] It is used in semiconductor in Nanotechnology.
[3] It is used in the Cosmetics, Nutraceutical and Pharmaceutical industries.

Conclusion:

Mn-doped ZnO nanocrystals have been synthesized by colloidal co-precipitation method with varying manganese compositions. The properties of as -synthesized ZnO and Mn-doped ZnO nanocrystals are expected in above. . The XRD measurement suggests that Mn doped ZnO in the crystals without changing the wurtzite like structure, but with the lattice parameters varying slightly with the extent of doping. We also observed on doping the grain size reduces drastically reducing to nano-scale i.e., doping hinders the grain growth and not to be phases were observed for the simple co- precipitation method work for the doped ZnO samples upto 18.35 wt% of Mn doping.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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