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Photo physical investigation on Mg / Sn doped ZnO nanoparticles for Gas sensing application

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Abstract - *Mg & Sn doped zinc oxide (ZnO) nanoparticles were successfully synthesized by microwave irradiation method. All the samples were systematically characterized by XRD, FTIR, UV, PL, EDAX and SEM measurements to study the structural, chemical bonding, elemental composition, and optical analysis. From XRD analysis, as prepared samples possess good crystallite nature. FTIR spectra of as prepared samples exhibit the strong absorption peaks aimed at metal oxygen region 500-900 cm^{-1}. The morphology analysis shows highly agglomerated spherical like particles for as prepared samples and good conductivity between them. From optical analysis the Mg and Sn doped nanomaterials absorption maximum was red shifted with respected to ZnO nanoparticle. The emission properties of the doped material should studied from the photoluminescence analysis.*

Key Words: Nanoparticles, Zinc Oxide, Doping, Microwave irradiation, Gas sensing…

1. INTRODUCTION

Zinc oxide nanoparticles have lot of applications in the fields of catalyst, sensing and pharmacological etc., Addition of doping constituents involves increasing the active sites, surface area, wide absorption of photon and reducing the band gap energies of the semiconductor. Because of doping the crystalline size and electron density variation in nanoparticles are the main factors to decide the efficiency of any photonic applications. More metal oxides having active catalysts than noble metals in the majority of applications, metal oxides are more suitable [1].

Enormous growth of environmental effluence due to the fast population growth, industrialization, burning of fuels from automobiles, use of pesticides and insecticides in cultivated sector, leakages of poisonous chemical and gases is an alarming when risk to the surroundings [2]. The suspension of dangerous chemical from industrial effluent and excess water from agricultural lands into running as well as ground water could effect a number of health hazards. Initial discovery and monitoring of these toxic and hazardous gas thus essential for environmental safety purposes. Gas sensors play a significant role for the detection and monitoring of poisonous hazardous gases [3, 4]. In addition, combining two or more metal oxide catalysts could improve or enhance sensing activity. Gas sensor consist of two basic functions, such as receptor functions and transducer functions. Receptor function involving there step primarily the chemical substance, however transducer function changes the chemical signal into electrical signals. This segment deals through the structural properties supporting receptor functions of ZnO responsible for gas sensing performance. Wurtzite structure ZnO is the most favored for gas sensing (5). ZnO has been effectively prepared to detect various gases, such as H_2, NO_2, O_2, H_2S, CH_3CH_2OH and NH_3 [6]. Mg and Sn doped ZnO nanoparticles were prepared here through microwave irradiation method [7].

1.1 Materials and Methods

Chemicals

Reagents used for experiments are Zinc nitrate [Zn $(NO_3)_2$], Tin chloride penta hydrate [Sn (Cl_2). $5H_2O$], Magnesium nitrate [Mg $(NO_3)_2$], Sodium Hydroxide (NaOH) and Ethanol [C_2H_6O]. All reagents were used without further purification. Double distilled water was employed as the solvent.

1.2 Preparation of zinc oxide Nanoparticles

Recently, microwave-assisted synthesis methods have been widely used to produce oxide, hydroxide, sulfide nanoparticles and etc., in a typical procedure, 50ml aqueous solution of 0.95M Zn nitrate was mixed with 30ml aqueous solution of 0.05M tin chloride penta hydrate (or) magnesium nitrate. After stirring for several minutes, 2.5M of NaOH was slowly added to the reaction mixture. It was stirred for ten more minutes. Finally, the mixture was placed microwave irradiation (300 W) for 10 minutes. The product was filtered, washed with distilled water and dried in 80◦C for 12h in air at room temperature. The final product was annealing at 500°C for 1h and grinded the powder can be stored extended period of time.

1.3 Characterization

The phase purity and crystal structure of as synthesized Mg & Sn doped ZnO nanoparticles were identified using powder X-ray diffraction method (XRD). The elemental analysis of nanoparticles was carried out by using an Energy dispersive X-ray (EDAX) analyser associated with a scanning electron microscope (SEM). The optical analysis was obtained by UV-vis spectrophotometer (UV). The photoluminescence (PL) of the samples were recorded over the range, 350–650 nm.

2. RESULTS AND DISCUSSION

The present work is mainly focused on the preparation of heterogeneous material to increase the sensitivity and selectivity of the ZnO nanoparticles. Fortunately, the doping semiconductor particles with difference in band-gap energy could increase the charge separation and extend the energy range of photo excitation, hence doping semiconductor exhibited higher sensing activity. Sn or Mg doped ZnO semiconducting materials as one of the most preferable semiconductor gas sensor due to their high sensitivity and chemical stability [8].

The Powder X- ray diffraction patterns of Sn doped ZnO nanoparticles and Mg doped ZnO nanoparticles are shown in Figure 1(a) and 1(b) respectively. All the diffraction peaks are good agreement with the hexagonal wurtzite phase of ZnO nanoparticles with p63mc space group and corresponding JCPDS card no is 36-1451. Interestingly, in both the cases we observed broadening of peak widths and also absence of secondary phases like SnO /Sn and Mg which indicates that dopants are well dispersed in the ZnO lattice or lattice distortion due to the introduction of dopant ions. Additionally, the highly crystalline nature of the as synthesized ZnO nanoparticles was further evidenced from their strong intensity and sharpness of their diffraction peaks. In the present study, in both the cases Mg or Sn doped ZnO nanoparticles we noticed that the negligible peak shifting as compared to pure ZnO (according to literature report). This negligible shift also corresponds to the non-uniform stress/ strain with the replacement of Zn^{2+} with Mg^{2+} and Sn^{2+} in their crystal structure due to the effect of ionic radii of respective metal ions. Hence we believe that the substitutonal presence of Mg^{2+} and Sn^{2+} in the ZnO lattice can be visualized as a broadening of characteristic diffraction peaks such as (100), (002) and (101).

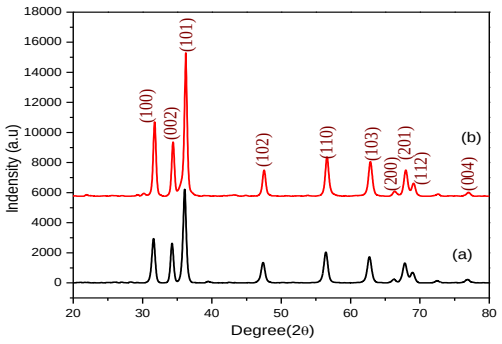

Fig. -1: XRD patterns of (a) Sn doped ZnO & (b) Mg doped ZnO NPs.

From the FTIR spectra both samples broad peak observed in the region of 1375-1357 cm^{-1} is related to the Zn-O bending modes, in particularly Zn-OH bending vibrations. Additionally a small peak at 1654 cm^{-1} and 1664 cm^{-1} in both Mg and Sn doped ZnO is corresponds to the stretching mode of OH group. In general this peak is observed in the at 1380 $cm^{-1}$and notably this peak is more broadening in Mg-doped ZnO nanoparticles because of overlapping of Mg-O stretching vibrations, which is mostly occurred 1348 cm-1. The presence of this OH group indicates the presence of bound H_2O on the surface. Vibrational peaks exist in the region of 2930, 1790 & 835 cm^{-1} are due to the functional groups of organic residuals (CH_2).

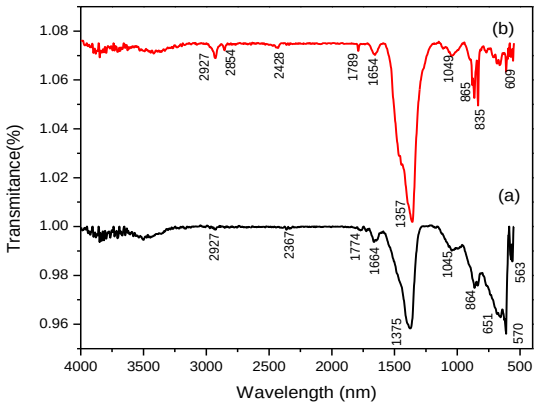

Fig. – 2: FTIR spectrum of (a) Sn doped ZnO & (b) Mg doped ZnO NPs.

Therefore FTIR spectrum clearly confirms the Mg or Sn doped ZnO nanoparticles via the Mg-O, Sn-O stretching and both stretching and bending of Zn-O bonds.

UV-vis absorption spectra were measured and it is shown in Figure 3. The absorption peaks of Sn- doped

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ZnO and Mg-doped ZnO nanoparticles are located at 297 nm and 290 nm, respectively. The increase of optical band gap energy with Mg or Sn doping may be attributed to electrons generated by oxygen vacancies (it is termed as Moss-Burstein effect) [9].

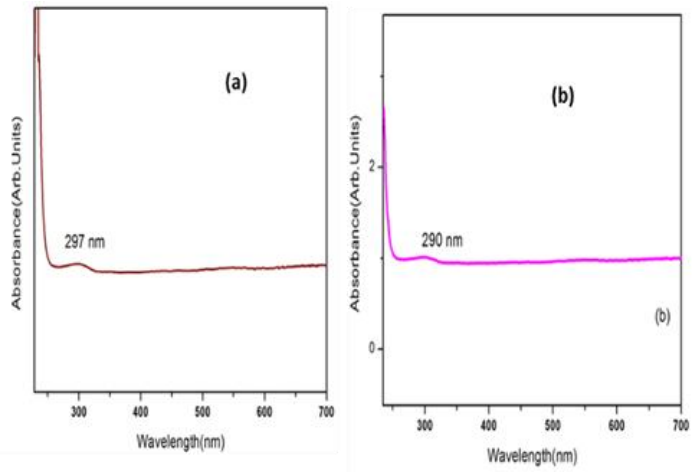

Fig. – 3: UV spectra of (a) Sn doped ZnO ¬ & (b) Mg doped ZnO NPs.

Because substitution of Zn by Mg or Sn increase more oxygen vacancies and electron concentration due to the electronegativity and ionic radius difference between the Zn and Mg or Sn [10].

Photoluminescence spectroscopy was employed for further understanding of the optical properties of Mg or Sn doped ZnO nanoparticles. From the PL spectrum we can infer the recombination of photo induced charge carriers, information regarding the presence of surface states, efficiency of charge carrier trapping and their recombination kinetics [11].

The peak shifting may be due to the oxygen vacancies, dopant may be introduced defect sites and causes the s interfacial energy transfer [12].

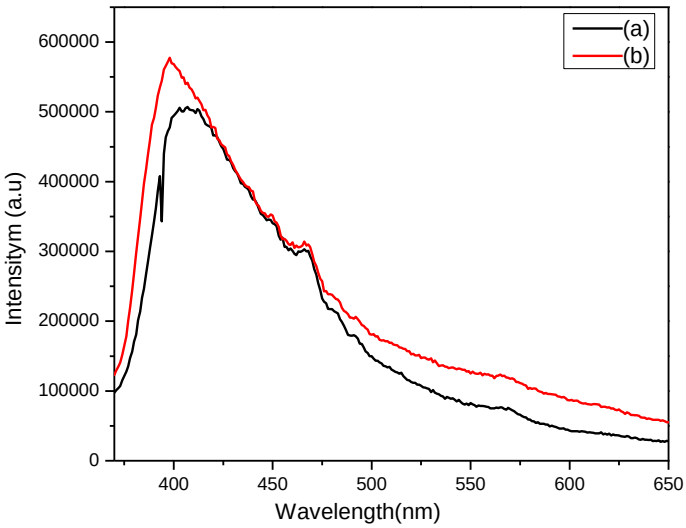

Fig. – 3: PL spectrum of pure (a) Sn doped ZnO & (b) Mg doped ZnO NPs.

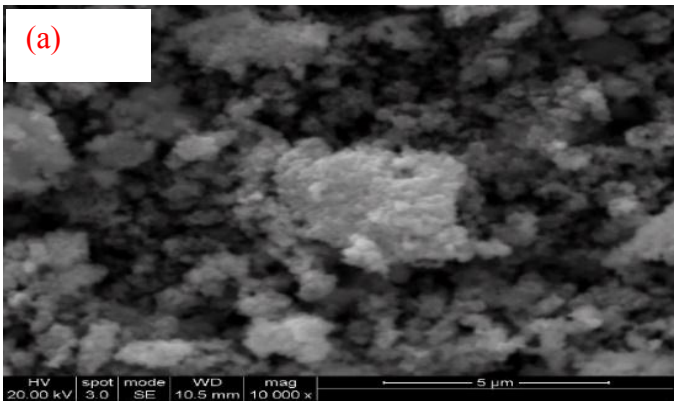

Fig. – 4: (a) Morphology of Sn doped ZnO NPs.

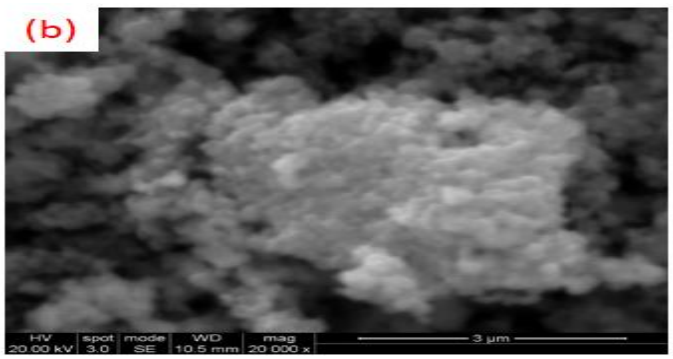

Fig -4: (b) Morphology of Mg doped ZnO NPs.

Fig 4(a) displays the PL spectrum of Sn doped ZnO and Fig 4(b) represent the Mg doped ZnO nanoparticles. In the present case the doped samples emission peaks are observed at 407 and 397 nm for Sn doped and Mg doped ZnO nanoparticles respectively. According to literature report the near band-edge transition of the ZnO is observed at 370.

Table -1: Elemental composition of as-synthesized Samples.

Elements	Sample a		Sample b	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
O	21.51	53.58	27.01	55.87
Sn	5.25	1.76	8.39	11.42
Zn	73.24	44.66	64.61	32.71
Total	100	100	100	100

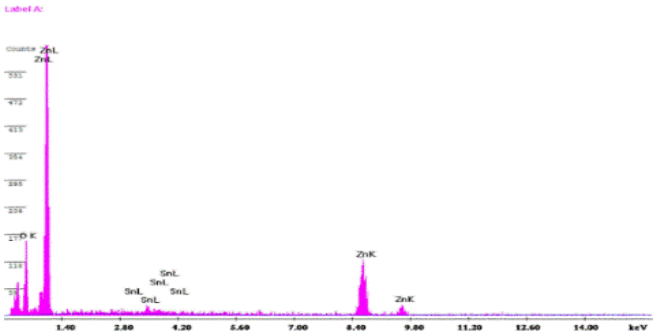

Fig. -5: (a) EDX spectrum of Sn doped ZnO NPs.

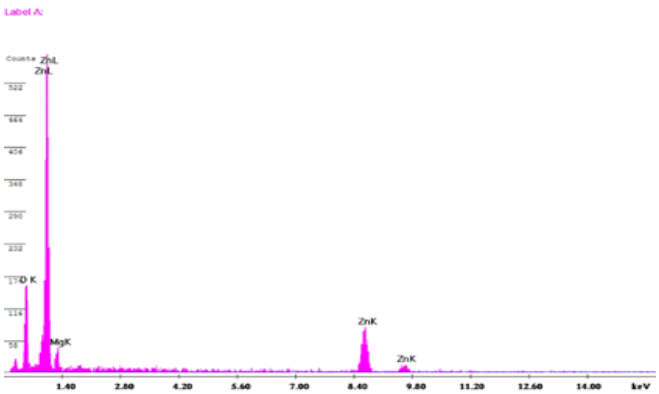

Fig -5: (b) Mg doped ZnO NPs.

However the observed red shift is contradictory for our UV-Visible results [13]. From the morphology analysis as synthesized Sn, Mg doped ZnO nanoparticles consist of fine tiny spherical nanoparticles. The Zn-doped SnO_2 nanoparticles appear to be slightly agglomerated spherical particles. The molar ratio and atomic ratio of Sn, Mg doped in Zinc oxide was tabulated with the use of EDAX spectrum. From this result Sn and Mg dopants are presents in the ZnO nanoparticles.

3. CONCLUSION

Sn/Mg doped ZnO nanoparticles were successfully synthesized through microwave assisted synthesis with help of NaOH precursors. Powder XRD patterns confirms that pure wurtzite phase of hexagonal ZnO materials. The absence of secondary peaks MgO or SnO/Sn further evidence the lattice distortion produced by the dopant ions and it is observed in terms of ionic radius of Mg or Sn ions. FTIR spectrum supports the presence of various characteristic frequencies of Sn-O, Mg-O and Zn-O stretching and bending vibrations. UV-Visible studies demonstrated the existence of blue shifting due to the excess oxygen vacancies created by the doping elements. In addition PL studies also carried out to understand the emission behavior of the as synthesized samples. SEM analysis gives the morphology of as synthesized nanoparticles. EDAX spectrum confirm the presence of precursor with doped molecules in as prepared nanoparticles. From this we hope that, the above mentioned materials will show better gas sensing activity.

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BIOGRAPHIES

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