A study on the optical properties of transition metal doped ZnO Nanostructures.

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Abstract: -

The optical properties of transition metal doped ZnO nanostructures are studied in reference to different types of growth mechanism and synthesis procedure in this review work. The work emphasized on the optimum growth parameters for the preparation of ZnO nanostructures for enhancement of luminescence properties by doping of transition metal into it. The physics behind the best growth mechanism and doping procedure of transition metals are studied in this work. The changes in optical properties of transition metal doped ZnO nanostructures due to quantum size effect are also explained.

Keywords: - Transition metal doping, Quantum size effect, Luminescence, ZnO nanostructures.

Introduction

Zinc Oxide (ZnO) with its technological importance like wide band gap (Eg=3.37 eV), large exciton binding energy (60 meV) is a n-type doping semiconductor, wurtzite crystal structure and high optical gain at room temperature. ZnO has attractive characteristics for electronics and optoelectronics devices due to its various accessibility of growth method and also due to its unique properties. Applications of ZnO nanowires and nanostructures of this semiconducting oxide have been doped with different metal ions including transition metal elements eg. Mn, Mg, Co, Ni, Li, Fe, Ag etc. Most of the research studies explained Photoluminescence (PL) spectra of ZnO consisting of a sharp exciton. Silver doping is found to be effective for the fabrication of p-type ZnO. Dopants in ZnO, cobalt doped ZnO shows potential in various applications. According to many research, doping cobalt in ZnO creates more zinc vacancies [1-3]. Among many research, sensing response of nickel doped ZnO reported that the response to ethanol has been greatly enhanced by Ni doping ZnO with an

optimal doping concentration is 0.05 at%. Recent literature reported that Mg-doped ZnO nanostructures can exhibit excellent properties for device application. Investigation on doping elements with ZnO showed that the dopants can alter the band gap energy with an increase in the UV-Visible luminescence intensity [4-5].

In this review article, different types of experimental method for the synthesis of ZnO Nanoparticles and transition metal doped ZnO are elaborated. The methods for the synthesis of ZnO nanoparticles and Transition metal doped ZnO nanostructures are the most cost effective, reliable and environmental friendly and it also provides flexibility for controlling the size and shape of synthesized nanoparticles. This review aims to explore the best protocol for synthesis of ZnO nanoparticles and the effect of transition metal doped ZnO nanostructures using cost effective chemicals and standard laboratory equipments along with optical characterization by UV-vis, Photoluminescence.

A review on Experimental Method:-

B Sankara Reddy et al., 2015 proposed an experimental method as all the chemicals used in the experiment are of analytical grade and purchased from Merck, Mumbai, India. Pure ZnO and manganese, silver doped ZnO nanoparticles were synthesized by chemical co-precipitation method at room temperature and for silver and manganese doping silver nitrate ($AgNO_3$), and manganese acetate tetra hydrate have been used. $Zn_{1-x}Mn_xAg_xO$ ($_{x=}$0.00, 0.05) nanostructures were prepared at room temperature as the procedure described below. Initially 0.2 M solution was prepared by using Zinc acetate and KOH. For dopants, $AgNO_3$ and manganese acetate have been added drop wise to the above solution in equal concentration such as 0.00, 0.05 under continuous stirring for 8 hours. Hence, the precipitate was formed and it was filtered out separately, and repeatedly washed with deionized water to remove unnecessary impurities formed during the preparation process. Ag and Mn doped ZnO nanopowders were obtained after drying at 100^0 C for 5 hrs. Then the final products were grinded and annealed at 400^0 C in the furnace for 1 hr. [6].

J El Ghoul et al., 2016 proposed an experimental method as $Zn_{0.89}$ $Al_{0.01}V_{0.1}O$ nanocrystals were prepared by the sol-gel method using 16 g of zinc acetate dehydrate as precursor in a 112 ml of methanol. After 10 min magnetic stirring at room temperature, 0.628 g of ammonium metavanadate corresponding to [V]/[Zn]= 0.10 and an adequate quantity of aluminium nitrate -9-hydrate corresponding to [A]/[Zn] ratios of 0.010 were added. After an

additional 15 min magnetic stirring, the solution was placed in an autoclave and dried under supercritical conditions of ethyl alcohol (EtOH). The obtained powder was then heated in a furnace at 500^0C for 2 hr in air [7].

Umadevi Godavarti et al., 2017 proposed an experimental method as the following high purity chemicals such as zinc acetate dihydrate (Zn $(CH_3COO)_2$ $2H_2O$), Nickel acetate tetrahydrate ($Ni(OCOCH_3)_24H_2O$, sodium hydroxide (NaOH), ethanol and methanol (99.998%) were used as the precursors without further purification. The experimental procedure for the preparation of pure ZnO and Ni doped ZnO samples is as follows: For the preparation of pure ZnO NPs, specific amounts of zinc acetate and NaOH are dissolved in 50 ml methanol separately and NaOH in methanol is added dropwise and then stirred with heating at 325 K for 2 hr. The precipitate is separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 400 K to obtain ZnO nanocrystals. The samples obtained were annealed at 673 K for 8 hr. The same procedure was repeated to obtain Nickel doped ZnO samples by Zinc acetate dihydrate and Nickel acetate tetrahydrate were dissolved in methanol (100 ml) and NaOH in methanol (100 ml) was prepared separately and added by constant magnetic stirring while heating 325 K for 2 hr. The precipitate separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 400 K. the samples obtained were annealed in air for 8 hr at 673 K [8].

Umadevi Godavatri et al., 2017 proposed an experimental method as the following high purity chemicals such as zinc acetate dehydrate (Zn $(CH_3COO)_2$ $2H_2O$), cobalt acetate tetrahydrate (Co $(CH_3COO)_2$ $4H_2O$), sodium hydroxide (NaOH), ethanol and methanol (99.998%)were used as the precursors without further purification. For the preparation of pure ZnO nanoparticles specific amounts of zinc acetate and NaOH are dissolved in 50 ml methanol which is added drop wise and then stirred with heating at 325 K for 2 hr. The precipitate is separated from the solution by filtration, washed several times with distilled water and ethanol then dried in air at 400 K to obtain ZnO nanocrystals. The samples obtained were annealed at 673 K for 8 hr. For the synthesis cobalt doped ZnO, zinc acetate dehydrate and cobalt acetate dehydrate were dissolved in methanol (100 ml) and other containing of NaOH in methanol (100 ml) were prepared and added by constant magnetic stirring while heating at 325 K for 2 hr. Precipitate is then separated from the solution by

filtration, washed several times with distilled water and ethanol then dried in air at 400 K to obtain Co doped ZnO nanoparticles and annealing at 673 K for 8 hr. [9].

I Kazeminezhad et al., 2016 proposed an experimental method as to prepare $Zn_{0.98}TM_{0.02}O$-NPs, zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2$ $6H_2O$), manganese nitrate hexahydrate ($Mn(NO_3)_2$ $6H_2O$), iron nitrate ($Fe(NO_3)_3$ $9H_2O$), chromium nitrate ($Cr(NO_3)_3$ $9H_2O$, gelatin ($(NHCOCH\text{-}R_1)_n$, R_1= amino acid) and deionized (DI) water were used as starting materials. To prepare pare $Zn_{0.98}TM_{0.02}O$-NPs, the specific amounts of zinc nitrate and transition metal nitrate were dissolved in 30 ml of DI water and stirred for 30 min. Meanwhile. 10 g of gelatin was dissolved in 150 ml of DI water and stirred for 30 min at 60^0C to achieve a clear gelatin solution. Then zinc nitrate and transition metal nitrate solution were added to the gelatin solution and the container was moved to a thermostatic oil bath with adjusted temperature at 80^0C. The compound solution was then stirred for 12 hr to obtain a honey -like resin. The resin became hard after the temperature of the container was reduced to room temperature. The final product was calcined at 500^0C in air for 6 hr to achieve $Zn_{0.98}TM_{0.02}O$-NPs [10].

A review on optical Properties:

B Sankara Reddy et al., 2015 reported the optical properties of transition metal doped ZnO nanostructures were estimated from the UV -vis diffuse reflectance spectroscopic studies with a model Varian Cary- 4000 spectrophotometer. The optical absorption spectra of pure ZnO and $Zn_{1-x}Mn_xAg_xO$ ($_x$ = 0.00, 0.05) samples are studied by diffuse reflectance spectrometer (DRS) in the range of 200 to 800 nm. It can be seen that the excitonic absorption peak for undoped ZnO appears around 363 nm and 5 mol% of Ag, Mn doped ZnO nanoparticles shows that the one excitonic peak at 240 nm and other broad peak is observed, which is centered at 336 nm. It is clearly observed that the absorbance of the co-doped ZnO samples decreased for 5 mol% of Ag, Mn concentration and also observed for 5 mol% of Ag, Mn concentration in ZnO nanoparticles, because of the quantum confinement effect.

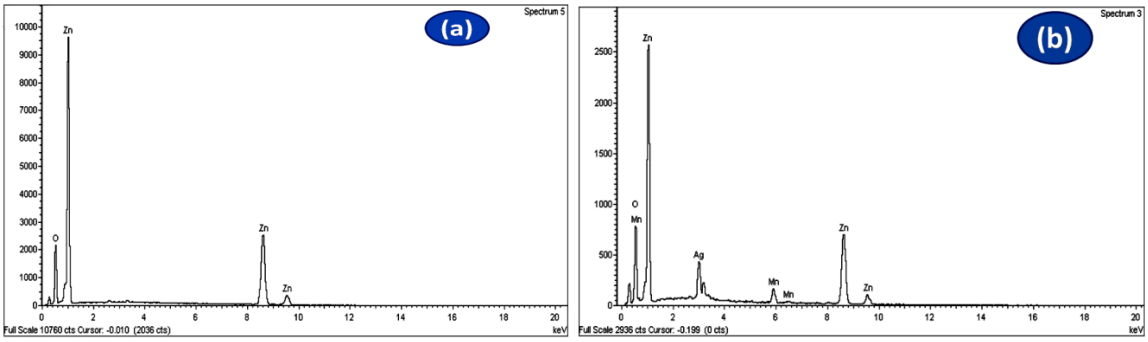

Fig. 1: EDAX spectra of (a) pure ZnO, (b) $Zn_{1-x}Mn_xAg_xO$ nanoparticles (Reproduced from Ref. no. 6)

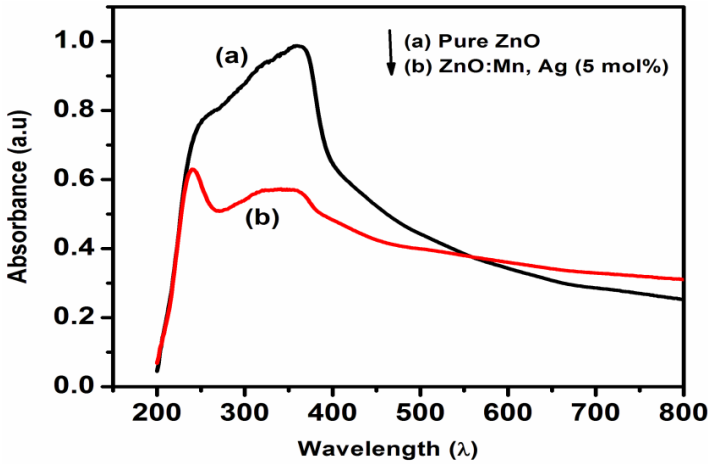

Fig.2. UV-vis absorption spectra of (a) pure ZnO and (b) 5 mol% of Ag, Mn doped ZnO nanoparticles (Reproduced from Ref. no. 6)

J El Ghoul et al., 2016 reported the optical properties of transition metal doped ZnO nanostructures as the spectra are characterized by high transmittance in the visible range and an intense fundamental absorption due to nanoparticles ZnO in the spectral range between 300 and 400 nm. The band gap decreases in the case of the doped ZnO samples. Regarding the doped samples, the highest average visible transmittance of 89% and the lowest resistivity of $6.7*10^{-3}$ Ω cm. PL spectra of the nanopowder showed strong yellow - red luminescence band. From the analysis of the PL (AIVZ) and PLE spectra (AIVZ), it can be concluded that the contents of defect complexes involved by oxygen excess which introduced as interstitial oxygen due to charge equilibrium, associated with the presence of dopants in the powder was responsible of this luminescence band.

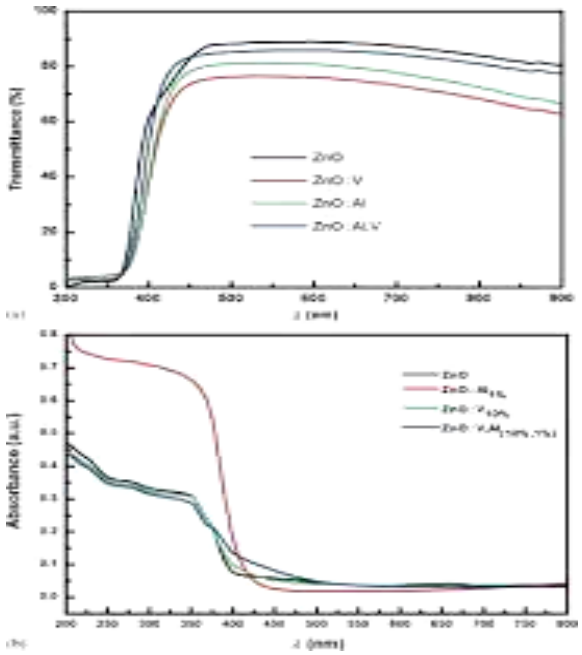

Fig.3. (**a**) Transmittance and (**b**) absorbance of ZnO, AlZ, VZ and AlVZ nanoparticles (Reproduced from Ref. no. 7)

a) b)

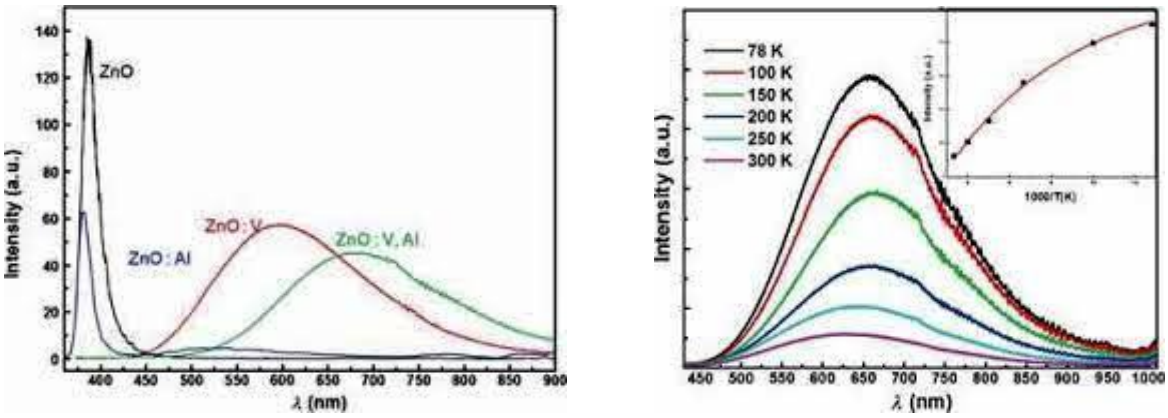

Fig.4. a) PL spectra of ZnO, AlZ, VZ, and AlVZ NPs at 78 K

b) PL spectra of AlVZ at different temperature measurements. The inset showing the integrated intensity as a function of 1000/T (Reproduced from Ref. no. 7)

Umadevi Godavarti et al., 2017 reported the optical absorption/transmission spectra of ZnO and Ni substituted ZnO nanoparticles were recorded using a UV-NIR-3600 spectrophotometer. The photoluminescence (PL) spectrum of the undoped and Ni doped ZnO nanoparticles have been measured using a Perkin Elmer 45 fluorescence spectrometer. The sensing response was recorded over a wide range of temperature by measuring the change in

its electrical resistance with an electrometer (196, Keithley, Germany) .The PL spectrum of all the samples using an excited wavelength of 300 and 400 nm, respectively. The defects could affect the position of the band edge emission as well as the shape of the luminescence spectrum. In general, the reported defects present in ZnO based nanostructures are oxygen vacancies with different charged states, Zn vacancies, Zn interstitials, and adsorbed molecules. Previous studies indicated that the resulting defect -related emissions for these defects typically occur near approximately 480-550 nm, approximately 550-610 nm, and approximately 610-750 nm regions. Therefore, to obtain a detailed understanding of the effect of individual defects on the magnetic properties of the ZnO nanostructures, a three-peak (Gaussian) fitting method of the broad visible emission was adopted. The peak in the range of 380-390 nm in all samples that is attributed to the band edge excitonic luminescence of ZnO and doped ZnO. Therefore, the UV emission at approximately 390 nm was due to exciton recombination through an exciton-exciton collision process. For undoped ZnO there are two emission bands in the range of 420-425 nm and at 488 nm. Emission in the range of 420-425 nm is usually attributed to near band edge (NBE) emission due to free exciton recombination. The emission at about 488 nm is related to deep level emissions (DLE). This emission in ZnO has been frequently ascribed to several intrinsic and extrinsic defects that are due to electron recombination in the oxygen vacancy with a hole in the valence band. There are two emission bands at 530 and 590 nm. These bands are related to oxygen vacancies. Similar results were reported by Darvish-nejad et al. and Motaung et al..

a) b) c)

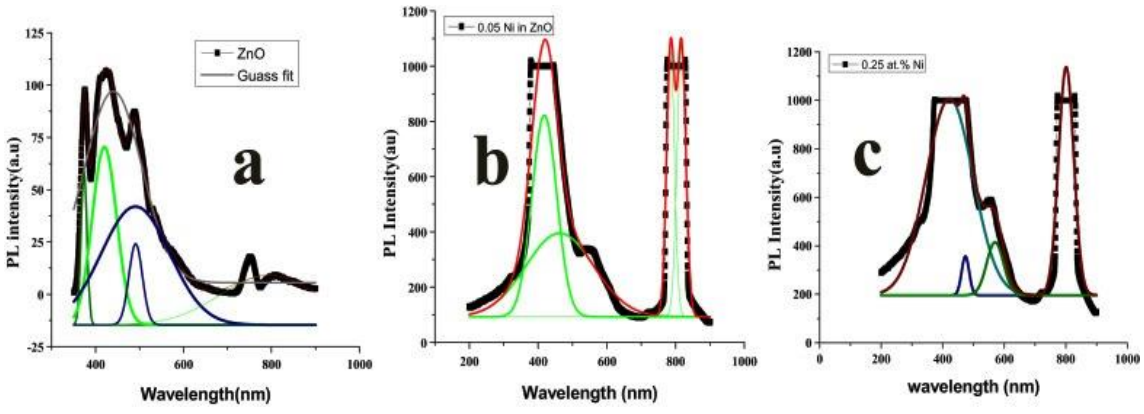

Fig.5. PL spectroscopy (a) ZnO, (b) 0.05 at% Ni and (c) 0.25 at% Ni doped ZnO (Reproduced from Ref. no. 8)

I Kazeminezhad et al., 2016 reported that UV-vis spectroscopy (Perikin-Elmer spectrometer) was applied for considering the optical properties. Raman measurements (Jobin Yvon Horiba HR 800 UV) were carried out to study the crystallinity of the obtained products. The Raman spectra of nanoparticles with different TM dopants are shown the peak around 330 cm-1 for different dopant indicates the E_{2H} - E_{21}. (Multi-phonon process) mode, which determinds that the nanoparticles are single crystals. This peak for Mn-doped ZnO NPs is sharper in comparison with the other samples indicating that most of the Mn- doped ZnO NPs are single crystals. All spectra show a sharp and strong peak around 434 cm^{-1} that is assigned to E_2 (high) mode and it is a characteristic peak of wurtzite hexagonal ZnO, confirming that the TM doped ZnO NPs have wurtzite hexagonal structure. The peak at 572, 524,574,115,583,149 and 583,149 for Fe, Co, Cr and Mn respectively, referred to be E_1 (LO) mode, confirming associated with the impurities and formation of defects such as oxygen vacancies that are increased by incorporating dopant. Thus, doped ZnO NPs with Cr, Co, Fe and Mn enhanced the oxygen vacancies. Infact, the Raman results show more oxygen vacancies for the samples with bigger strain. The UV-vis absorption spectra of the ZnO NPs at room temperature are revealing a characteristics absorption peak for ZnO at wavelengths from 376 nm for the undoped ZnO to 373 nm for the doped. This can be attributed to the intrinsic band gap absorption of ZnO, owing to the electronic transitions from the valence band to the conduction band ($O_{2p}\rightarrow Zn_{3d}$). In addition, the direct band gap can be estimated from the maximum of the first derivative of the absorbance plot vs. Energy also from intersection of the second derivative with energy axle. It can be seen that absorption peak is due to TM element. In fact these elements as metal can increase electron concentration that cause to widen the band gap ZnO NPs.

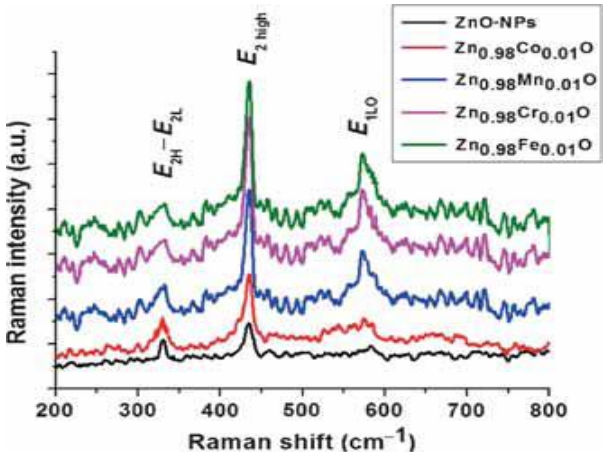

Fig.6. Raman spectra of the undoped and TM-doped ZnO nanoparticles

(Reproduced from Ref. No. 10)

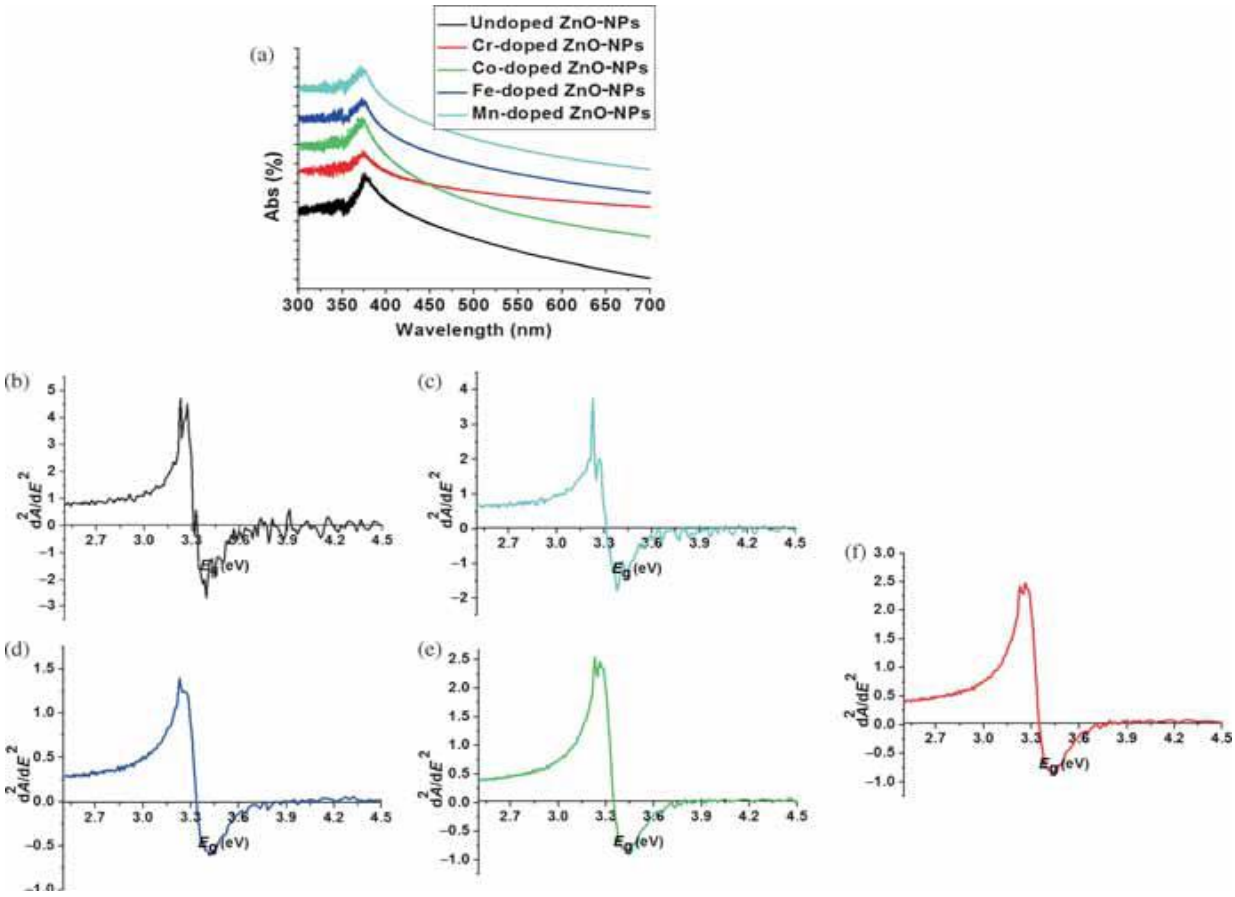

Fig.7. (a) Second derivative of the UV–Vis absorption spectra of the undoped and TM-doped ZnO-NPs. (b–f) the band gap of the undoped and TM-doped ZnO-NPs estimated from second derivate and energy excel intersect (Reproduced from Ref. No. 10)

Umadevi Godavarti et al.2017 was not reported the optical properties of Transition metal doped ZnO nanostructures (Cobalt doping) in their article.

Discussion: The different synthesis method were discussed in the review study of the effect of transition metal doped ZnO nanostructures along with the optical properties on various metal doped ZnO nanostructures were explained. B. Sankara Reddy et al. 2015 were synthesized Pure ZnO and manganese, silver doped ZnO nanoparticles by chemical co-precipitation method at room temperature and for silver and manganese doping silver nitrate ($AgNO_3$), and manganese acetate tetra hydrate have been used. Ag and Mn doped ZnO nanopowders were obtained after drying at 100^0 C for 5 hrs. Then the final products were grinded and annealed at 400^0 C in the furnace for 1 hr. The absorbance of co-doped ZnO nanosamples decreased for 5 mol% of Ag, Mn concentration because of quantum

confinement effect. J El Ghoul et al., 2016 $Zn_{0.89}$ $Al_{0.01}V_{0.1}O$ nanocrystals were prepared by the sol-gel method using zinc acetate dehydrate as precursor in methanol. The obtained powder was heated in a furnace at 500^0C for 2 hr in air. The band gap decreases of Al, V doped ZnO samples in which the highest average visible transmittance of 89%, the lowest resistivity and provide some useful references for the potential application of the samples in optoelectronic devices. Umadevi Godavarti et al., 2017 were synthesized pure ZnO, Ni doped ZnO and Co doped ZnO using following high purity chemicals such as zinc acetate dehydrate, Nickel acetate tetrahydrate, Cobalt acetate tetrahydrate, sodium hydroxide (NaOH), ethanol and methanol as the precursors without further purification. In this method, they obtained ZnO nanocrystals at 400K and Co doped ZnO nanoparticles and Ni doped ZnO nanoparticles were obtained at 673K. The defects present in ZnO-based nanostructures are oxygen vacancies with different charged states, Zn vacancies, Zn interstitials, and adsorbed molecules as noticed from PL studies are responsible for the enhanced gas sensing studies. Operating the sensor at 100°C is regarded as an optimal temperature for gas sensing mechanism in our studies and a rapid response and recovery time are noted for ethanol gas sensing is due to the diffusion and its oxidation with O^- or O^{2-} occur very speedily. I Kazeminezhad et al., 2016 were used Sol gel method to prepare $Zn_{0.98}TM_{0.02}O$-NPs. Zinc nitrate hexahydrate, Cobalt nitrate hexahydrate, manganese nitrate hexahydrate, iron nitrate, chromium nitrate, gelatin and deionized (DI) water were used as starting materials. The final product was calcined at 500^0C in air for 6 hr to achieve $Zn_{0.98}TM_{0.02}O$-NPs. The UV-vis absorption spectra of the ZnO NPs (Cr, Co, Fe, Mn) at room temperature are reveal a characteristics absorption peak for ZnO at wavelengths from 376 nm for the undoped ZnO to 373 nm for the doped. This can be attributed to the intrinsic band gap absorption of ZnO and these elements as metal can increase electron concentration that cause to widen the band gap ZnO NPs.

Conclusion: The luminescence properties of ZnO nanostructures are found to be the function of transition metal doping. The quantum size effect also played a vital role in the absorption and the luminescence properties of ZnO nanoparticles. The absorption peaks are gradually decreasing with the higher concentration of doping element while the intensity of the luminescence spectra are increasing in higher concentration of metal doping. The lowest absorption peak is observed at 240 nm for 5 mol% of Ag and Mn doped ZnO nanoparticles and the highest peak of luminescence spectra is found at 670 nanometer for AlVZ nanoparticles.

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