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Effect of Mg^{2+}, Ca^{2+} and Sr^{2+} Ions Doping on the Band Gap Energy of ZnO Nanoparticle

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Abstract

The main objective of this study was to investigate the lowering of the band gap energy and optical property of ZnO doped with Mg^{2+},Ca^{2+} and Sr^{2+} ions. ZnO nanoparticle was synthesize by adding Zinc acetate to aqueous NaOH solution and subjected to ultrasonic irradiation for 2hr after that a white precipitate was obtained which was filtered and washed with ethanol and de-ionized water and dried in an oven at 60 ^{0}C for 3hr. The dried white powder was then calcined at 400 ^{0}C for 2hr and subjected to UV-Vis spectrophotometer to characterize the synthesized ZnO nanoparticle. The band gap energy of ZnO undoped and doped with Mg^{2+},Ca^{2+} and Sr^{2+} ionswas determined. From all dopants 0.006M Mg^{2+} doped ZnO nanoparticles was found to be narrowing band gap more.

Keywords : Alkaline Earth metals; Optical property; ZnO; Dopant

Introduction

Nanocrystalline materials got wide attention due to their unique properties. Transparent conducting oxides like ITO, SnO_2, CdO, ZnO, etc., have been widely studied due to their interesting optical and electrical properties. Among these conducting materials, zinc oxide is the most attractive because of its low cost, non-toxicity, chemical stability, and facility to doping with a wide variety of ions [1]. ZnO is promising for many potential applications including thin film transistors [2,3], sensors [4,5], light emitting diodes UV photo detectors [6,7], UV lasers [8,9], and piezoelectric power generators [10,11]. Many potential applications rely on the delicate control over the doping of ZnO materials [12]. Zinc oxide (ZnO) has a wide direct band gap energy which makes it transparent to visible light and is a promising candidate for blue and ultraviolet light emitting devices (LEDs) and lasers. In general, ZnO with a wurtzite structure is an unintentional n-type semiconductor due to the deviation from stoichiometry [13].

The band gap for pure ZnO is found to be E_g=3.35 eV and for V-doped ZnO samples of 1,5 and 9 % V, it is 3.24, 3.25 and 3.30eV, respectively. The band gap of V_2O_5 is 2.3eV and ZnO is 3.37eV. When V_2O_5 is doped in ZnO, a mixed oxide of ZnV_2O is formed and causes the decrease in the band gap [14]. For Ni-doped ZnO films, the energy gap decreases from 2.95 to 2.72eV as the [Ni]/[Zn] ratio increases from 0 to 0.02 and then increases to reach 3.22eV for [Ni]/[Zn]=0.04 [15]. The value of the band gap energy of undoped nanocrystalline ZnO nanoparticles was 3.26eV and increased by incorporation of Sb doping as it was 3.309eV for doping 1% Sb, 3.318eV for 3% Sb and 3.329eV for 5% Sb [16]. Alkaline earth metals have received great interest due to their attractive electronic, optical and thermal properties as well as catalytic properties and potential applications in the fields of chemistry, physics, biology, medicine, and material science and their different interdisciplinary fields and therefore, the synthesis and characterization of ZnO doped with alkaline earth metals have attracted considerable attention from a fundamental and practical point of view.

The alkaline earth metals are high in the reactivity series of metals, but not as high as the alkali metals of Group I. The metals of Group II are harder and denser than sodium and potassium, and have higher melting points. These properties are due largely to the presence of two valence electrons on each atom, which leads to stronger metallic bonding than occurs in Group I [17]. This work is aimed at a band gap narrowing by doping into ZnO by alkaline earth metals (Mg^{2+},Ca^{2+},Sr^{2+}). UV-Vis experiments were carried out for ZnO undoped and doped with alkaline earth metals. By measuring UV-Vis spectra of the resulting $Zn_{1-x}M_xO$, (x=0.001, 0.003 and 0.006) we tried to investigate how a material's composition affects its electronic band structure and optical properties.

Materials and Methods

All chemicals for this research were used as received without any treatment.

Preparation of ZnO nanoparticles

The 50ml of aqueous solution of 0.2M Zinc acetate $Zn(CH_3COOH)_2{\cdot}2H_2O$ was added to 10ml of 0.2M aqueous NaOH solution and subjected to ultrasonic irradiation for 2hr. The obtained white precipitate was filtered and washed with ethanol and deionized water and dried in an oven at 60 ^{0}C for 3hr. Then the sample was calcined at 400 ^{0}C for 2hr.

Preparation of Mg^{2+} Ca^{2+},Sr^{2+} doped ZnO nanoparticles

In a typical synthesis, 10ml of Mg^{2+}, Ca^{2+}, Sr^{2+}solution (0.006 M) were added to 0.05g of calcined ZnO. The sample was heated at 110 ^{0}C for 30min. The powder cooled to room temperature, and again calcined at 400 ^{0}C for 2hrs. The product obtained was labeled as Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO. The above procedure was repeated for 0.003M and 0.001M $Mg^{2+}Ca^{2+}$, Sr^{2+}doped ZnO nanoparticles.

Band gap and Optical property determination

The measurement of the absorption spectrum leads to determination of the optical band-gap energy. The optical band gap of the nano powders was determined by applying the Tauc's relationship is given by;

$$(\alpha h\nu) = (h\nu - E_g)n$$

Where; α is the absorption coefficient (α=2.303A/t, A is the absorbance and t is the thickness of the cuvett), E_g is the energy band gap, hν is the energy of the radiation (photon energy), The value of n=½, 3/2, 2, or 3 depending on the nature of the electronic transition responsible for absorption and n=½ for the direct band gap of semiconductor [18].

Results and Discussion

Characterization of ZnO nanoparticles

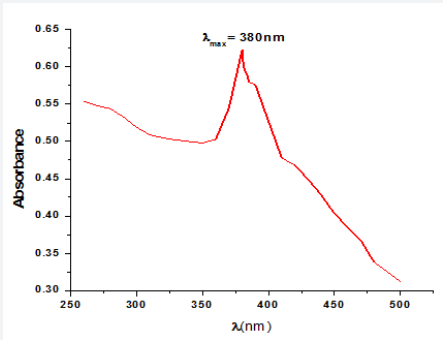

Figure 1: UV-vis absorption spectrum of ZnO nanoparticles.

The absorbance of the ZnO nanoparticles solution was measured using a quartz tube. The UV–visible absorption spectra of ZnO nanoparticles samples were recorded in the wavelength range of 250 to 500 nm; it exhibits a strong absorption band at about 380nm, (Figure 1). The size of the nanoparticles plays an important role in changing the entire properties of materials. UV-Visible absorption spectroscopy was widely being used technique to examine the optical properties of Nanosized particles. The average particle size was calculated from the absorption spectra by using effective mass model where the band gap E can be approximated by [19].

$$E^* = E_g^{bulk} + \frac{\hbar^2\pi^2}{2er^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_o r} - \frac{0.124e^2}{\hbar^2(4\pi\varepsilon\varepsilon_o)^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right)^{-}$$

Where E_g^{bulk} is the bulk band gap expressed in eV, h is Plank's constant, r is the particle radius, m_e is the electron effective mass, m_h is the hole effective mass, m_0 is free electron mass, e is the charge on the electron, ε is the relative permittivity, and ε_0 is the permittivity of free space. Due to the relatively small effective masses for ZnO (m_e= 0.26, m_h= 0.59, m_o= 9.11×10^{-31}Kg, ε_0 = 8.85×10^{-12} F/m, ε = 8.5, Charge of electron = 1.602×10^{-19}C, planks constant = 6.626×10^{-34} m^2kg/s) band gap enlargement is expected for particle radii less than about 4nm. To find the size of the particle using absorbance spectra, the effective mass model, given above, was modified with small mathematical simplification [20],

$$r\,(nm) = \frac{-0.3049 + \sqrt{-26.23012 + \frac{10240.72}{\lambda_p}}}{-6.3829 + \frac{2483.2}{\lambda_p}}$$

Where λ_p is peak absorbance wavelength in nm. The prepared ZnO nanoparticles exhibit an absorbance peak at about 380 nm which corresponds to the particle size of 3.6nm.

UV-Visible spectroscopy and Optical properties studies of doped ZnO nanoparticles

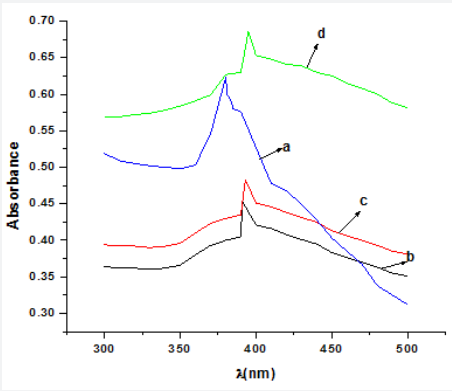

Figure 2: Plots of absorbance vs wavelength of (a) undoped ZnO, (b) $Mg_{0.001}Zn_{0.999}O$ (c) $Mg_{0.003}Zn_{0.997}O$, (d) $Mg_{0.006}$ $Zn_{0.994}O$.

UV-Visible spectra of Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO nanoparticles were obtained by doping different concentration of metal ions in $Zn_{1-x}M_xO$ (M= Mg^{2+},Ca^{2+},and Sr^{2+} ; x = 0.001, 0.003,

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0.006) [21]. Figure 2, shows the UV-Vis spectra of Mg^{2+} doped ZnO nanoparticles along with undoped it can be seen from the figure that the absorption peaks position changes from 380nm to 390nm for 0.001M, 391 for 0.003M and 393nm for 0.006M. With increase in Mg^{2+} concentration, the optical absorption edge slightly shifts towards the longer wave length region which may be attributed to the increase in particle size of ZnO [22]. Figure 3, illustrates that the absorbance plot for various concentrations of Ca^{2+}. It can be observed from the plot that the maxima changes compared from ZnO.

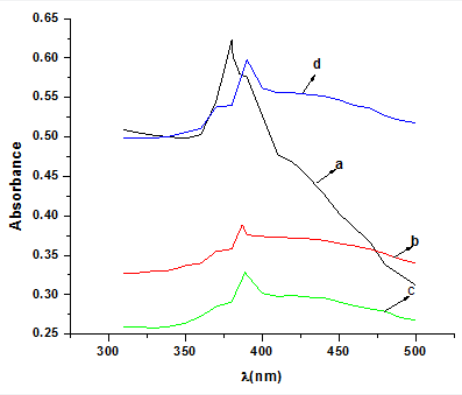

Figure 3: Plot of absorbance vs wavelength of (a) undoped ZnO, (b) $Ca_{0.001}Zn_{0.999}$ O, (c) $Ca_{0.003}Zn_{0.997}$ O, (d) $Ca_{0.006}Zn_{0.994}O$.

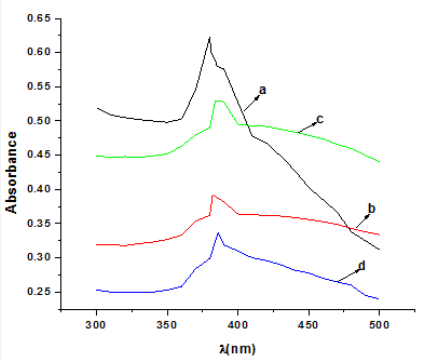

Figure 4: Plot of absorbance vs wavelength of (a) undoped ZnO, (b) $Sr_{0.001}Zn_{0.999}O$ (c) $Sr_{0.003}Zn_{0.997}O$ (d) $Sr_{0.006}$ $Zn_{0.994}O$.

The changes of maxima are 386,387 and 389nm for 0.001, 0.003 and 0.006M respectively. This small shift in absorption band may be due to the doping effect of Ca^{2+}into ZnO [23]. UV-Visible spectra for Sr^{2+} doped ZnO can be seen from Figure 4. ZnO nanoparticles shows the absorption peak at 380nm and the Sr^{2+} doped ZnO nanoparticle with different concentration of Sr^{2+} shows the absorption peaks at 382,383 and 385 nm respectively. The optical absorption edge corresponds to the transition from valence band to conduction band, while the absorption edge shifting to the lower energy relates to some local energy levels caused by some intrinsic defects [24].

Comparative study of effect of doping on band gap energy of undoped ZnO nanoparticles

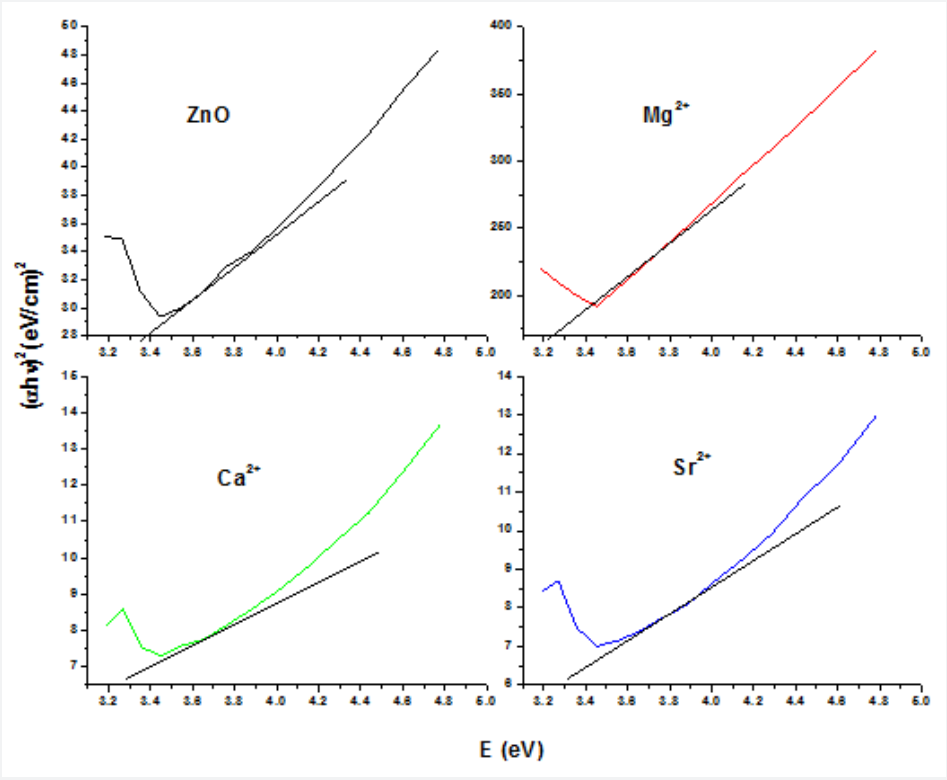

Figure 5: Optical energy plot for undoped ZnO, $Mg_{0.00}$ $Zn_{0.999}O$, $Ca_{0.001}Zn_{0.999}O$, $Sr_{0.001}$ $Zn_{0.999}O$.

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Optical energy plot of pure and Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO at 0.001M shown in (Figure 5). The absorption coefficient α were calculated and plotted for the direct transmission of the ZnO undoped and doped Mg^{2+}, Ca^{2+} and Sr^{2+} at 0.001M concentration. The value of band gap energy of undoped ZnO nanoparticle was 3.263eV. The band gap of a 0.001M Mg^{2+}, Ca^{2+} and Sr^{2+} doping was 3.179, 3.212 and 3.245eV respectively. It can be seen that Mg^{2+} doped narrows the band gap of undoped zinc oxide nanoparticle more than Ca^{2+} and Sr^{2+}[25]. The band gap energies were determined by taking the extrapolated lines from the linear vertical regions near the band edge as shown in Figure 6. The band gap energy for pure ZnO was found to be 3.263eV.

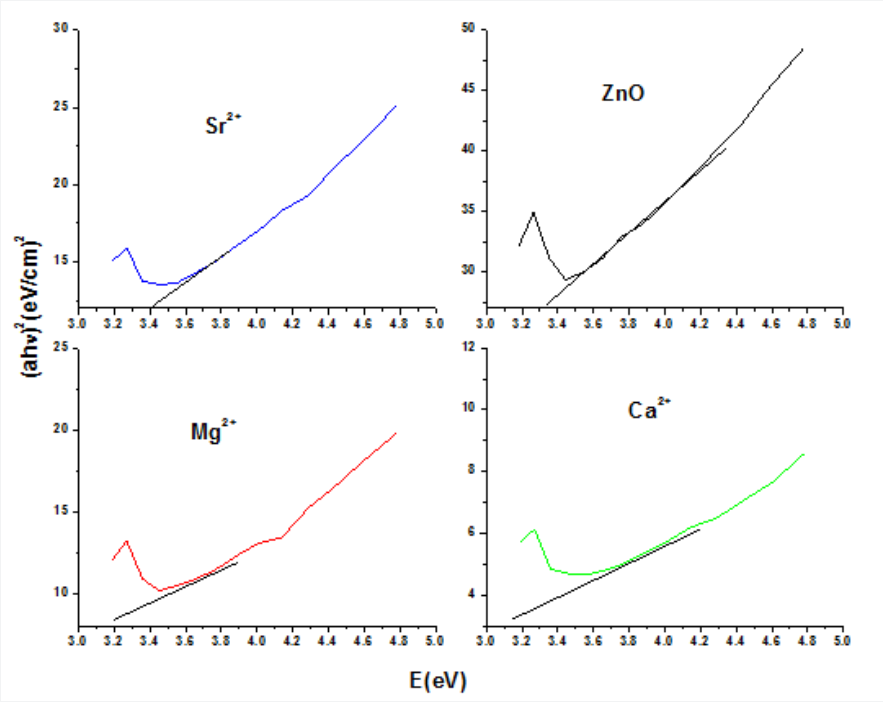

Figure 6: Optical energy plot for undoped ZnO, $Mg_{0.003}$ $Zn_{0.997}O$, $Ca_{0.003}Zn_{0.997}O$, $Sr_{0.003}Zn_{0.997}O$.

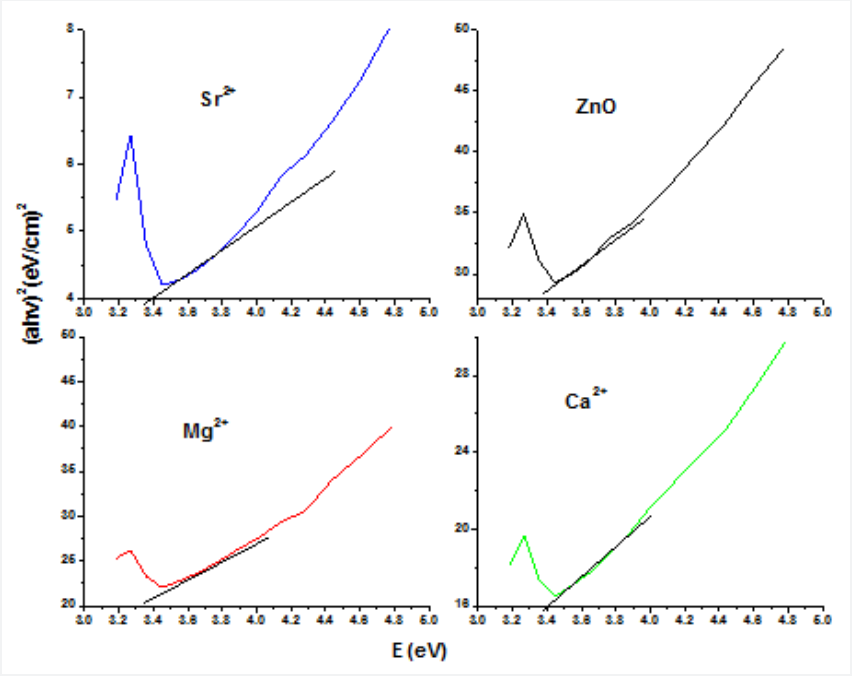

Figure 7: Optical energy plot for undoped ZnO, $Mg_{0.006}$ $Zn_{0.994}O$, $Ca_{0.006}Zn_{0.994}O$, $Sr_{0.006}$ $Zn_{0.994}O$.

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The measured direct band gap energy of ZnO with 0.003M concentration of Mg^{2+}, Ca^{2+} and Sr^{2+} was 3.17, 3.203 and 3.22eV respectively. In a 0.003M of Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO nanoparticle a band gap of Mg^{2+} with 3.17eV narrows the band gap of undoped ZnO nanoparticle than that of a 3.203eV of Ca^{2+} doped ZnO nanoparticle and 3.203eV of Ca^{2+} doped ZnO nanoparticle narrows the band gap undoped ZnO than that of 3.22eV of Sr^{2+} doped ZnO nanoparticles [26]. The UV-Vis absorption spectra of the pure and 0.006M Mg^{2+}, Ca^{2+}, Sr^{2+} doped ZnO nanoparticle were investigated at room temperature. As shown in Figure 7, we can find that the optical absorption spectra changes after doping of Mg^{2+}, Ca^{2+}, Sr^{2+}. In order to evaluating the band gap presents the dependence of α as a function of hv for the pure and Mg^{2+} Ca^{2+}, Sr^{2+} doped ZnO nanoparticle.

The band gap obtained by extrapolation from the Figure 6 for 0.006M concentration was 3.154, 3.187 and 3.237eV respectively. Since the band gap of Mg^{2+} was small compared to the band gap of Ca^{2+} and Sr^{2+}, it narrows the band gap of undoped ZnO nanoparticle, So Mg^{2+} is a suitable dopant for ZnO nanoparticle and it conducts electricity more than that of Ca^{2+} and Sr^{2+}. A band gap of 3.187eV of Ca^{2+} narrows the band gap of undoped Zinc oxide nanoparticles than that of 3.22eV Sr^{2+} doped ZnO nanoparticle [27]. The band gap of Mg^{2+} doped ZnO for different concentration was around 3.179, 3.17 and 3.154eV respectively. As the Mg^{2+} concentration increases the absorption edge slightly shifts towards the longer wave length region which may be attributed to the decrease in band gap. This decrease of the band gap after doping of Mg^{2+} was probably related to the difference in ionicity between Zn^{2+} and Mg^{2+} bonds Tables 1 & 2. Moreover, since ZnO and Mg^{2+} atoms have strong mismatch in electro negativity was a reason for decrease of the band gap.

Table 1: Absorption maxima for doped ZnO nano particles.

Dopants	Concentrations		
	0.001M	0.003M	0.006M
Mg^{2+}	390nm	391nm	393nm
Ca^{2+}	386nm	387nm	389nm
Sr^{2+}	382nm	383nm	385nm

Table 2: Summary of band gap energy for different concentrations of Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO nano particles.

Metal ion	Electro-negativity	Ionic Size (pm)	Band gap (eV)			
			0.001M	0.003M	0.006M	0.007M
Mg^{2+}	1.31	65	3.179	3.17	3.154	3.162
Ca^{2+}	1	99	3.212	3.203	3.187	3.195
Sr^{2+}	0.95	113	3.245	3.237	3.22	3.228

It was seen that the energy band gap decreases with the increase dopant conc. of Mg^{2+} which can be explained as the narrowing of band gap energy is possibly due to the existence of more Mg^{2+} impurities in the ZnO crystallites, which induces the formation of new recombination centers with lower emission energy [27]. The band gap of Ca^{2+} doped ZnO for different concentration was around 3.212, 3.203 and 3.187eV respectively. With the increase in the Ca^{2+} concentration, the optical absorption edge shifts slightly towards the longer wavelength region which may be attributed to the slightly decreases band gap. The reason for the decrease in the band gap may be explained on the basis of alloying effect between ZnO and Ca^{2+} [28].

Conclusion

ZnO nanoparticles were successfully synthesized by addition of aqueous solution of zinc acetate dehydrate with aqueous sodium hydroxide. The UV-Visible spectra for ZnO nanoparticle synthesized in aqueous media exhibited excitonic absorption peak at 380nm. The band gap obtained for the synthesized of ZnO nanoparticles was determined by extrapolation to the X-axis was ≈3.263eV. From all dopants Mg^{2+} doped ZnO nanoparticles were showing narrowing more band gap energy compared to Ca^{2+} and Sr^{2+} doped ZnO nanoparticle. As the concentration increases, the band gap slightly decreases. This decrease in band gap energy after doping of Mg^{2+} was related to difference in iconicity between ZnO and Mg^{2+}. It may also due to a strong mismatch of electro negativity in ZnO and Mg^{2+}. The existence of more Mg^{2+} impurities in ZnO crystallites which induces the formation of new recombination centers with lower emission energy.

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