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ON

DEFECT INDUCED BAND GAP NARROWING OF ZINC OXIDE NANOPARTICLE USING Mg^{2+}, Ca^{2+} AND Sr^{2+} METAL IONS AS DOPANT

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Acknowledgment

First of all, I would like to thank the almighty God who by his absolute love and protection I could exist and be able to perform this work. Next, I would like to express my sincere gratitude

Abstract

The main objective of this study was to investigate the lowering of the band gap energy and optical properties of ZnO doped with alkaline earth metals (Ca^{2+}, Sr^{2+}, Mg^{2+}). ZnO nanoparticle

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

1. Introduction

1.1 Background of the study

Zinc oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water, which is widely used as an additive in numerous materials and products. Zinc oxide is amphoteric, that is it reacts with both acids and alkalis. Zinc oxides is a II-VI compound semiconductor with a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [1].

Nanocrystalline materials have attracted a wide attention due to their unique properties and immense potential application in nano device fabrication. Zinc oxide (ZnO) has a direct wide band gap (3.4 eV at Room temperature), which is n -type semiconductor. In the present work undoped and Ni doped ZnO nanoparticles were synthesized by using chemical co precipitation method, which is robust and reliable to control the shape and size of particles without requiring the expensive and complex equipments [2].

ZnO has been effectively used as a gas sensor material based on the near-surface modification of charge distribution with certain surface-absorbed species. ZnO nanorods would provide significant enhancement in sensitivity due to high surface-to-volume ratio. ZnO is also piezoelectric, and is used in surface acoustic wave devices. As with any semiconductor, 1-D ZnO nanostructures provide an attractive candidate system for fundamental quantization and low-dimensional transport studies. The large surface area of the nanorods and bio-safe characteristics of ZnO makes them attractive for gas and chemical sensing and biomedical applications, and the ability to control their nucleation sites makes them candidates for micro-lasers or memory arrays [3].

Transparent conducting oxides (TCO) like ITO, SnO_2, CdO, ZnO, $ZnSnO_4$, NiO, etc., have been widely studied due to their interesting optical and electrical properties. Among these transparent conducting materials, zinc oxide is the most attractive because of its non-toxicity, low cost, chemical stability and facility to doping with a wide variety of ions. ZnO is an n-type, direct band gap3.30 eV semiconductor with high optical transmittance in the visible and near infrared spectral regions and low electrical resistivity (10^{-2} to 10^{-4} Ω cm) [4].

ZnO is a technologically important and environmental friendly semiconductor with many remarkable properties, such as a direct wide band gap of 3.37 eV, large excitonic binging energy,

high electron mobility, large piezoelectric constants, high nonlinear optical coefficients, and radiation hardness. ZnO is promising for many potential applications including thin film transistors, sensors, light emitting diodes, UV photo detectors ,UV lasers, and piezoelectric power generators. Many potential applications rely on the delicate control over the doping of ZnO materials[5].

Zinc oxide is a IIb–VI compound semiconductor. The IIb–VI semiconductors and semimetals comprise the binary compounds of Zn, Cd, and Hg with O, S, Se, and Te and their ternary or quaternary alloys. ZnO is a wide-gap semiconductor with a direct gap around 3.4 eV, i.e. in the near-UV and crystallizes preferentially in the hexagonal wurtzite-type structure. It occurs in nature with the mineral name "zincite". The mineral contains usually a certain amount of Mn and other elements and is of yellow to red color. The ZnO used for the investigations and applications below is exclusively synthetic material. Due to its large band gap pure ZnO is colorless and clear[6].

Due to the ability of absorbing ultra-voilet light because of large and wide band gap, ZnO has found huge applications in sunscreens and also in varistors and pigments. ZnO possess hexagonal wurtzite structure where there is a tetrahedral coordination of Zn atoms with four oxygen atoms. Introducing impurities by an appropriate method in ZnO not only provides an insight into the study of its electronic properties, but also provides a great interest in studying its optical properties[7].

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[8] .

The UV-Vis spectra are usually measured in very dilute solutions and the most important criterion in the choice of solvent is that the solvent must be transparent within the wavelength range being examined. In general, when measuring UV-Visible spectra, we want only absorbance to occur. UV-Visible spectra generally show only a few broad absorbance bands. Although UV-Visible spectra do not enable absolute identification of an unknown, they frequently are used to confirm the identity of a substance through comparison of the measured

spectrum with a reference spectrum. UV-Visible spectroscopy can be used to determine many physicochemical characteristics of compounds and thus can provide information as to the identity of a particular compound[9].

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. This work is aimed for 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. And finally we obtained a metal ion which lowers more to the band gap energy.

2. Review of Related Literature

2.1. Doping

Doping is the process of adding some impurity atoms in the semiconductors. These impurity atoms are known as dopants. In semiconductor production, doping intentionally introduces impurities into an extremely pure also referred to as intrinsic semiconductor for the purpose of adjusting its electrical properties. The impurities are dependent upon the type of semiconductor. Lightly and moderately doped semiconductors are referred to as extrinsic[11].

2.1.1. N-type Doping

ZnO with a Wurtzite structure naturally deviates from its stoichiometry, thus automatically forms an N-type semiconductor due to presence of intrinsic defects such as O vacancies and Zn interstitials. However, undoped ZnO produced by most methods is intrinsically n-type and n-type doping in ZnO is easier to achieve and produces samples with better conductivity than p-type doping. To n-type dope ZnO, aluminum, gallium, and indium are commonly used dopants[12].

2.1.2. P-type Doping

It is very difficult to obtain *p*-type doping in wide-band-gap semiconductors such as GaN, ZnO and ZnSe. The difficulties to form shallow acceptor level arise mainly from low solubility of the dopant in the host material, compensation of dopants by low energy native defects, like Zn interstitials or O vacancies or background impurities and deep impurity level. P-type samples are made using nitrogen, phosphorus, lithium, or sodium as dopants. To overcome those difficulties, one would expect that the *P*-type doping in ZnO may be possible by substituting either group IA elements for Zn sites or group-V elements as N, P, and As for O sites[13,14].

2.2. Optical properties

Optical property of a material is defined as its interaction with electro-magnetic radiation in the visible. Materials are classified on the basis of their interaction with visible light into three categories. Materials that are capable of transmitting light with relatively little absorption and reflection are called transparent materials. Translucent materials are those through which light is transmitted diffusely i.e. objects are not clearly distinguishable when viewed through. Those materials that are impervious to the transmission of visible light are termed as opaque materials. These materials absorb all the energy from the light photons[15].

2.3 Effect of doping on band gap energy

The band gap for pure ZnO is found to be E_g =3.35 and for V doped ZnO samples of 1, 5 and 9 % V, it is 3.24, 3.25 and 3.30 eV, respectively. The band gap of all the V doped samples is lower than the pure ZnO sample. The reason for this decrease in band gap may be explained on the basis of alloying effect between ZnO and V_2O_5. The band gap of V_2O_5 is 2.3 eV and ZnO is 3.37 eV. When V_2O_5 is doped in ZnO, mixed oxide of ZnV_2O is formed and causes the decrease in the band gap[16].

For Ni doped ZnO films, the energy gap decreases from 2.95 to 2.72 eV as the [Ni]/[Zn] ratio increases from 0 to 0.02 and then increases to reach 3.22 eV for [Ni]/[Zn] = 0.04. The decrease of the band gap is attributed to the formation of defect energy level of Ni. It is established that Ni acts as donor impurity, which produces a shallow donor level below the conduction band, reducing the band gap of ZnO. On the other hand, the increase of the band gap energy when the [Ni]/[Zn] ratio varies from 0.02 to 0.04 is resulted to the reduction of the tail in the valence and conduction bands[17].

The value of the band gap energy of undoped nanocrystalline ZnO nanoparticles was 3.26 eV and increased by incorporation of Sb doping as it was 3.309 eV for doping 1% Sb, 3.318 eV for 3% Sb and 3.329 eV for 5% Sb. This enhancement in band gap is due Sb incorporation and the high carrier concentration that moved the optical absorption edge towards lower energy and broadened the energy gap[18]

The measured direct band gap energy of the ZnO films with different Ni concentrations at 3, 5, and 7 % were, 3.06, 2.99 and 2.98 eV, respectively. The band gap value for pure ZnO was found to be 3.23 eV. The absorption edges of the films with increasing Ni concentration shows red shift i.e. decrease in the band gap. The optical absorption at 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. The possible reason for decrease in band gap is put as follows: the impurity states of d-electrons of Ni split under the influence of tetrahedral field of ZnO giving rise to lower energy e_g doublet and higher energy t_{2g} triplet states. The triplet states hybridize with valence p-states forming t{bonding} and t{ant bonding} states[19].

Zinc oxide is a main component of very interesting and technologically important powder and ceramic materials that have been extensively studied and used for decades. Due to its interesting physicochemical properties zinc oxide is a material of wide applications in many fields of industry such as pharmaceutical, ceramics, and rubber production. Among the most studied metal oxides nanoparticles, ZnO stands out due to its exceptional opto-electronical properties, low cost of synthesis, environmentally friendly and highly versatile device fabrication based on the bound magnetic polarons[20].

Zinc oxide (ZnO) has a wide direct band gap energy which makes it transparent in 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. The background free electrons essentially arise from the shallow donor levels associated with the presence of intrinsic defects such as oxygen vacancies and/or zinc interstitials[21].

One interesting feature of ZnO is the ability to band gap tuning by its alloying with magnesium oxide (MgO, $E_g \sim 7.7$ eV) or cadmium oxide (CdO, $E_g = 2.3$ eV). Namely, band gap energy of 3.9 eV ($Mg_xZn_{1-x}O$, $x = 0.33$) can be achieved by doping with Mg^{2+}, while Cd^{2+} decreases the band gap energy to 2.99 eV ($Cd_yZn_{1-y}O$, $y = 0.07$). In addition, the large exciton binding energy of 60 meV of ZnO is of interest to achieve excitonic stimulated emission for the realization of low-threshold lasers at room temperature and even higher temperatures[22].

Based on the results, contrary to the alkaline metal doping, the electronic properties of the ZnO tube are much more sensitive to alkali metal doping so that it is transformed from intrinsic semiconductor with HOMO–LUMO energy gap of 3.77 eV to an extrinsic semiconductor with the energy gap of 1.11−1.95 eV. The doping of alkali and alkaline metals increases and decreases the work function of the ZnO tube, respectively, which may influence the electron emission from the ZnO tube surface[23] .

Nanosized particles of alkaline metals have received great interest due to their attractive electronic, optical, and thermal properties as well as catalytic properties and potential application in the fields of chemistry, biology, medicine and material science and their different inter disciplinary fields and therefore, the synthesis and characterization of ZnO have attracted

considerable attention from a fundamental and practical point of view. The small size is not the only requirement to form nanoparticle[24].

The preparation of ZnO doped with alkaline earths generally involves the chemical reduction of metal salt in aqueous phase. However, the high surface energy of ZnO makes them extremely reactive, and most system under go aggregation without protection of their surfaces.Thus,special precautions have to be taken to avoid their precipitation[25].

ZnO are promising for a wide range of applications due to the combination of unique multifunctional nature and remarkable solution processability. Doping is an effective approach of enhancing the properties of colloidal ZnO nanocrystals in well-controlled manners[26].

In the traditional semiconductor industry, doping generally means the introduction of trace amount of impurities into extremely pure semiconductors to tailor the electrical properties. From a synthetic chemistry point of view, doping for colloidal nanocrystal simply refers to the modification of compositions by the incorporation of dopant atoms into the crystal lattices. The purpose is to enhance the properties, that is, optical, magnetic, or other properties rather than restricted to electrical properties of the nanocrystals. Doping of ZnO films with certain elements (Ga, In and Mg) leads to an increase in the band gap width as well as an increase in the activation energy of donor center and to their stability [27].

Analyzing an optical and luminescence property of ZnO studied about the oxygen in ZnO, oxygen vacancy is responsible for the intraband luminescent at 510 nm (2.3eV). As studied ZnO crystal energy is transformed from excitons to oxygen vacancies. Under the action of the incident UV radiation, neutral oxygen vacancy which contains two electrons passes to an excited singlet state and then relaxes to an exited triplet state from the center of luminescence[28] .

It was shown that vacancy oxygen centers are analogs of F-center which have been well studied in ionic crystals CaO, BaO, SrO, MgO. As his interpretation the result of the theoretical work which was shown that the formation energy of oxygen vacancy is high and there amount in ZnO can not be large. ZnO is the most attractive because of its non-toxicity, low cost, chemical stability and facility to doping with a wide variety of ions. ZnO is an n-type, direct band gap semiconductor with high optical transmittance in the visible and near infrared spectral regions and low electrical resistivity[29, 30].

These characteristics have made ZnO thin films very adequate for several promising applications. They can be used as gas sensors, transparent electrodes in optoelectronic and solar cells devices, laser diodes and light emitting diodes. However, all these applications are very dependent of intrinsic defects or additional impurities. The conduction of pure ZnO is attributed to native defects or oxygen vacancies and zinc interstitials [31].

The optical band gap of Sr doped ZnO nanorods as prepared, 300°C, 400°C and 500°C annealed temperature was found to be 3.65 eV, 3.45 eV and 3.10 eV respectively. The band gap was found to decrease from 3.65 eV to 3.10 eV, with the increase of annealing temperature from 300°C to 500°C. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with the reduction in porosity and increase in grain size[32].

2.4. Statement of the problem

The electronic and optical property of zinc oxide is not suitable due to it is large band gap but doping with selective elements of alkaline earth metals offers an effective method to enhance and control the electrical and optical properties of zinc oxide by lowering it. This study was to answer the following questions.

- Which alkaline earth metal (Mg^{2+},Ca^{2+},Sr^{2+}) is suitable for band gap narrowing of zinc oxide?

- What lowest concentration can be used to lower band gap by doping alkaline earth metals with(Mg^{2+},Ca^{2+},Sr^{2+}) zinc oxide.

2.5. Objective of study

2.5.1. General objective

The objective of this work is to band gap narrowing of ZnO using Mg^{2+},Ca^{2+},and Sr^{2+} ions by varying concentration and to discuss optical property.

2.5.2 Specific objectives

- To study the band gap narrowing by doping.

- To know the lower band gap by using different concentration of Mg^{2+},Ca^{2+}, and Sr^{2+} ions with ZnO.

- To examine the optical property of ZnO doped with Mg^{2+},Ca^{2+}, and Sr^{2+} ions.

2.6. Significance of the study

In it is normal form zinc oxide is an n-type semiconductor, i.e., conductivity by electrons. Zinc oxide doped with alkaline earth metals improves the conductivity of materials in the area of technology which is used as a charge collector in the solar cells. Doping of ZnO with alkaline earth metals would be a good candidate for the starting materials in solar cell. It can also be a source for future researchers.

3. Materials and Methods

3.1. Experimental Site

The study was conducted in Analytical and Physical chemistry laboratory at Jimma University.

3.2 Chemicals

Magnesium nitrate (Nice,98%),Calcium nitrate (Nice,98%), Strontium nitrate (Finken,99%), Ethanol (Hylux,98%) & Sodium hydroxide (Finken,97%), Zinc acetate di hydrate (Finken,98%). All chemicals for this research were used as received without any treatment.

3.3 Instruments

The following materials were used for this work. Oven (Model GENLAB WIDNES, England), Magnetic stirrer, Centrifuge, Hot plate, Ultrasonic wave irradiation and UV-Vis spectrophotometer (JENWAY 6705 UV-Vis Spectrophotometer) with single beam cell holder.

3.4 Procedure

3.4.1 Preparation of ZnO nanoparticles

The 50ml of aqueous solution of 0.2 M Zinc acetate $Zn(CH_3COOH)_2.2H_2O$ 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 de ionized water and dried in an oven at 60^0C for 3 hr. Then the sample was calcined at 400^0C for 2 hr.

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

In a typical synthesis, 10 ml of **$Mg,^{2+} Ca^{2+}, Sr^{2+}$** Solution (0.006 M) were added to 0.05 g of calcined ZnO. The sample was heated at 110^0C for 30 min. The powder cooled to room temperature, and again calcined at 400^0C for 2 hrs. 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

3.4.4 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;

$$(\alpha h\nu) = (h\nu - Eg)^n$$

Where; α is the absorption coefficient (α_c=2.303A/t, A is the absorbance and t is the thickness of the cuvett), Eg is the energy band gap, hv 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 [33].

3.4.5. Characterization of the ZnO Nanoparticles.

The prepared ZnO nanoparticles were characterized for their optical and nano structural properties. The optical absorption spectra of ZnO, dispersed in water were recorded using UV-VIS Spectrophotometer [34].

4. Result and Discussion

4.1. Characterization of ZnO nanoparticles

The size of the nanoparticles plays an important role in changing the entire properties of materials. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the propertiesof the materials. UV-Visible absorption spectroscopy was widely being used technique to examine the optical properties of Nanosized particles. It exhibits a strong absorption band at about 380nm. The average particle size in a nanoparticle can be calculated from the absorption onset from UV-Vis absorption spectra by using effective mass model where the band gap E can be approximated by [35]

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

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 = 9.11x10^{-31}Kg, ε_o = 8.85x10^{-12} F/m, ε = 8.5, Charge of electron = 1.602x10^{-19}C, planks constant = 6.626x10^{-34} m^{2}kg/s) band gap enlargement is expected for particle radii less than about 4 nm. The following equation was derived from the effective mass model given above with small mathematical simplification which is used to find the size of the particle from the absorbance spectra,

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

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 3.6 nm.

4.2 UV-Visible spectroscopy and Optical properties of ZnO nanoparticle

UV−visible absorption spectroscopy is a powerful technique to explore the optical properties of semiconducting nanoparticles. The absorbance is expected to depend on several factors such as band gap, oxygen deficiency, and impurity centers. The sample absorbs the radiations in the UV range up to 380 nm and almost all the visible spectrum radiations are transmitted by the ZnO

nanoparticles. Figure 1, shows the absorbance as a function of wavelength. The exciton absorption is at about 380 nm.
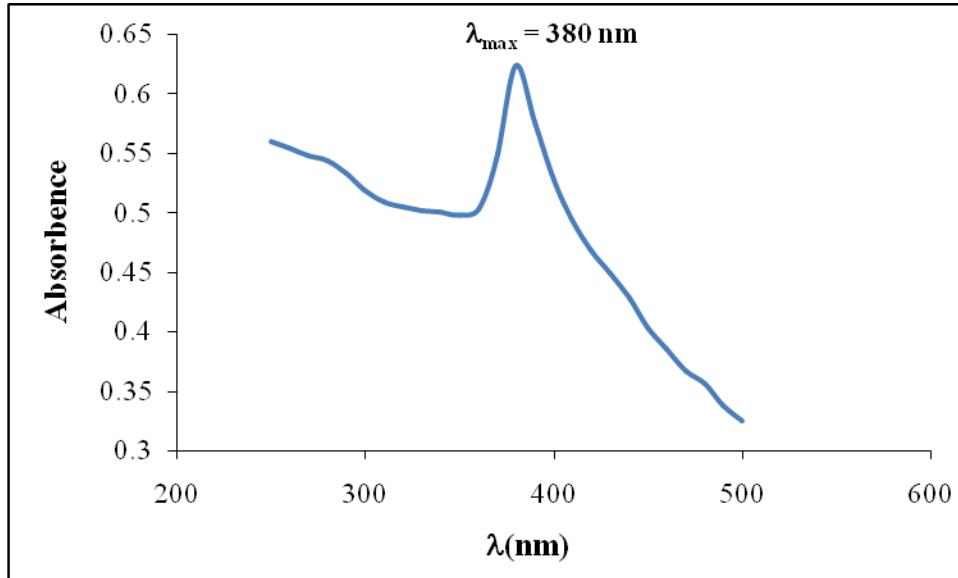
Figure 1: UV-Vis absorption spectrum of ZnO nanoparticles

The band gap energy of the ZnO nanoparticles was obtained by extrapolating the curve drawn between (hv) and $(\alpha h v)^2$.The band gap energy is obtained by extrapolating the straight line portion of the plot to zero absorption coefficient. The band gap energy of ZnO nanoparticles was found to be 3.263 eV.
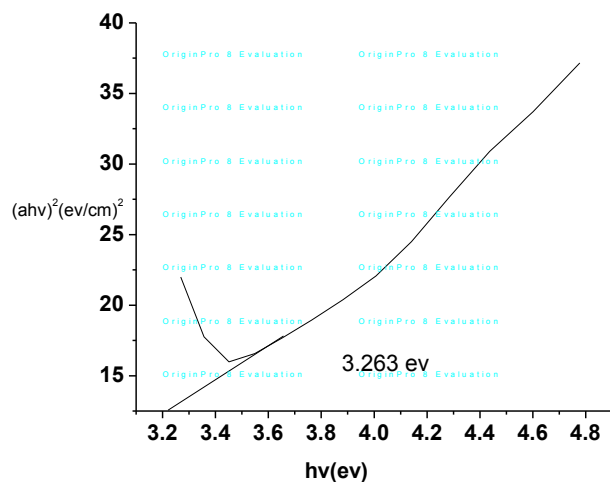
Figure 2. Extrapolation curve for band gap determination of synthesized ZnO nanoparticles.

The band gap energy of the synthesized ZnO nanoparticles was ≈3.263 eV and an absorption band of 380 nm.The band gap of bulk ZnO was 3.37 eV and an absorption band of 368 nm.[36]

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

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, 0.006) [37].

Figure 3. 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 380 nm to 390 nm for 0.001M, 391 nm for 0.003M and 393 nm 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. [38]
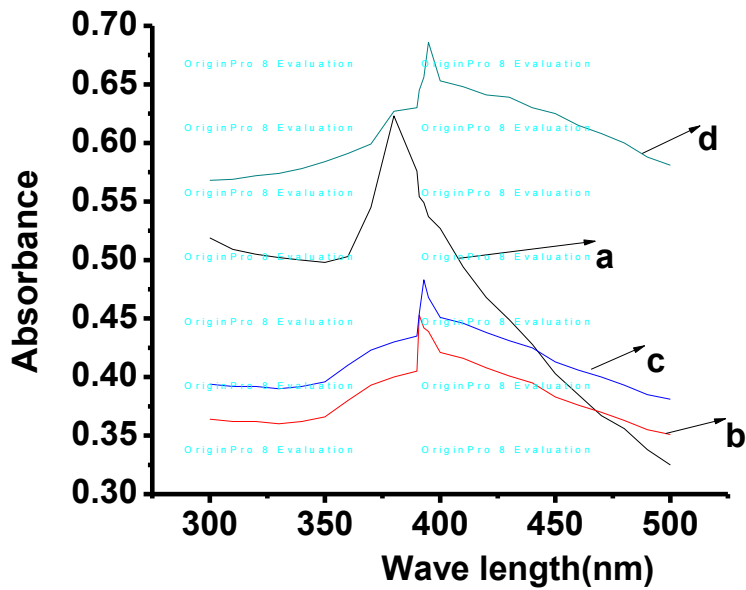
Figure 3. Plots of absorbance vs wavelength of (a) undoped ZnO, (b) $Mg_{0.001} Zn_{0.999} O$ (c) $Mg_{0.003} Zn_{0.997} O$, (d) $Mg_{0.006} Zn_{0.994} O$

Figure 4. 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. The changes of maxima are 386,387 and 389 nm for 0.001, 0.003 and 0.006 M respectively. This small shift in absorption band may be due to the doping effect of Ca^{2+} in to ZnO [39].
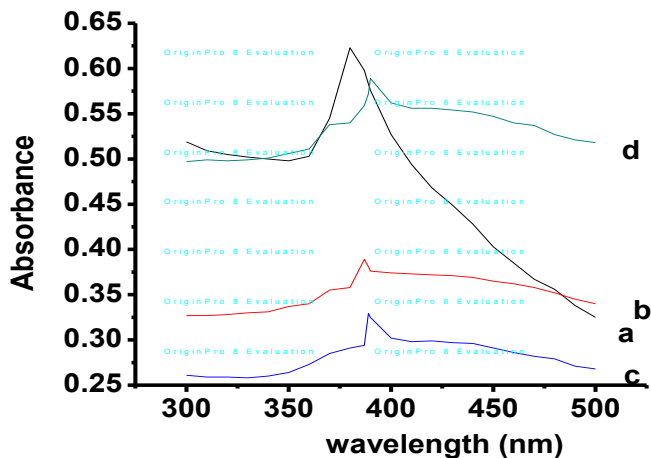
Figure 4: Plot of absorbance vs wavelength of (a) undoped ZnO, (b) $Ca_{0.001}Zn_{0.999} O$, (c) $Ca_{0.003}Zn_{0.997} O$, (d) $Ca_{0.006}Zn_{0.994}O$

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UV-Visible spectra for Sr^{2+} doped ZnO can be seen from Figure 5. ZnO nanoparticles shows the absorption peak at 380 nm 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[40].

Figure 5: 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) $Sr_{0.006}Zn_{0.994}O$.
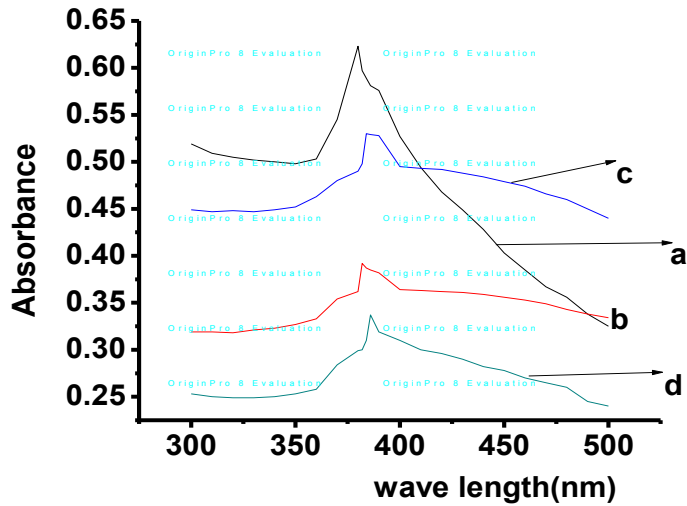
Table 1 demonstrates the absorption maxima for doped ZnO nanoparticles.

Table 1: Absorption maxima for doped ZnO

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

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

Optical energy plot of pure and Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO at 0.001M shown in Fig. 6. 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 3.263 eV. The band gap of a 0.001M Mg^{2+}, Ca^{2+} and Sr^{2+} doping was 3.179, 3.212 and 3.245 eV 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+} [41].
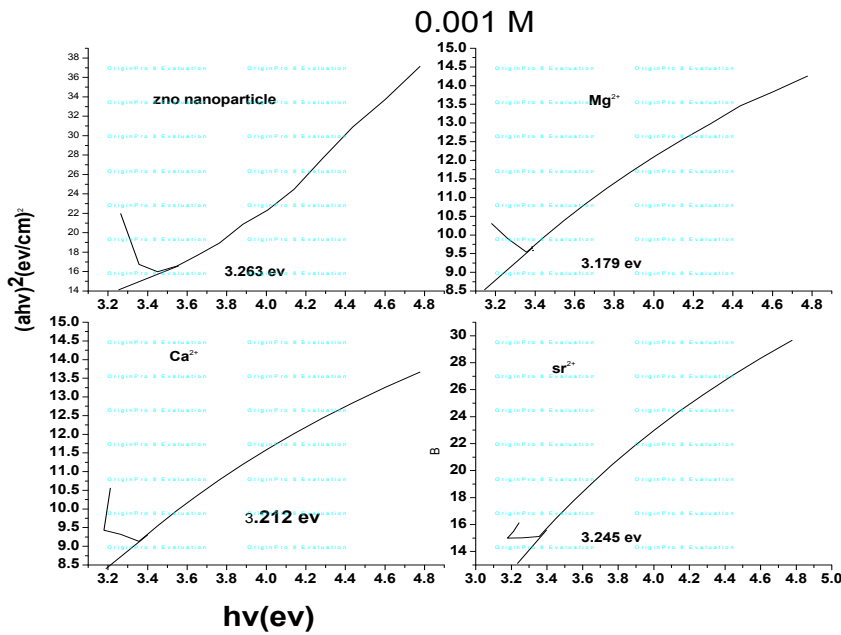
Figure 6. Optical energy plot for undoped ZnO, $Mg_{0.00}Zn_{0.999}O$, $Ca_{0.001}Zn_{0.999}O$, $Sr_{0.001}Zn_{0.999}O$. The band gap energies were determined by taking the extrapolated lines from the linear vertical regions near the band edge as shown in Figure 7. The band gap energy for pure ZnO was found to be 3.263 eV. 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 3.22 eV respectively. In a 0.003M of Mg^{2+}, Ca^{2+} and Sr^{2+} doped ZnO nanoparticle a band gap of Mg^{2+} with 3.17 eV narrows the band gap of undoped ZnO nanoparticle than that of a 3.203 eV of Ca^{2+} doped ZnO nanoparticle and a 3.203 eV of Ca^{2+} doped ZnO nanoparticle narrows the band gap undoped ZnO than that of a 3.22 eV of Sr^{2+} doped ZnO nanoparticles [42].
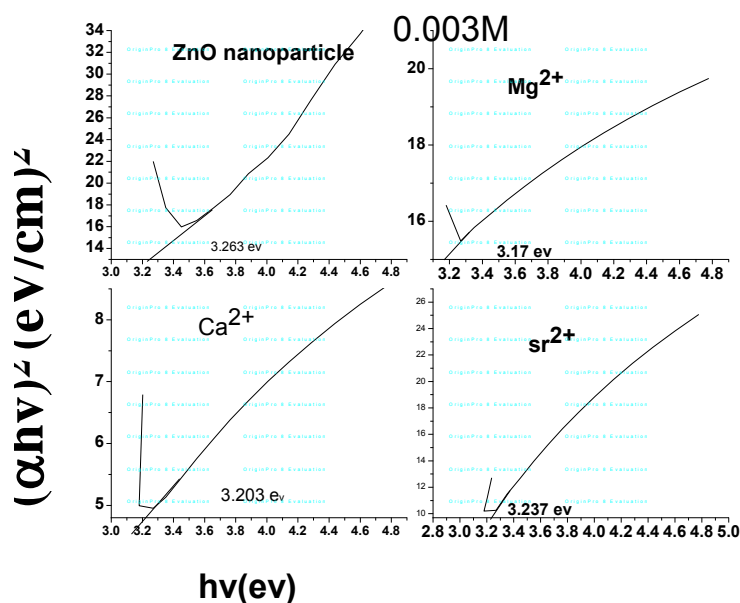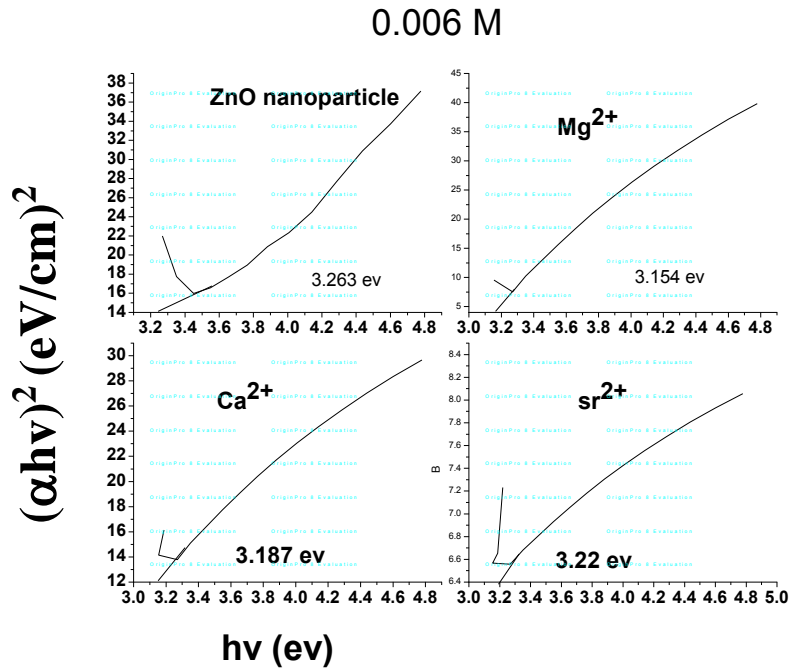
Figure 7. Optical energy plot for undoped ZnO, $Mg_{0.003}Zn_{0.997}O$, $Ca_{0.003}Zn_{0.997}O$, $Sr_{0.003}Zn_{0.997}O$

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 Fig 8 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 8 for 0.006M concentration was 3.154, 3.187 and 3.237 eV 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 3.187 eV of Ca^{2+} narrows the band gap of undoped Zinc oxide nanoparticles than that of 3.22 eV Sr^{2+} doped ZnO nanoparticle [43].

0.006 M

ZnO nanoparticle — 3.263 ev

Mg^{2+} — 3.154 ev

Ca^{2+} — 3.187 ev

sr^{2+} — 3.22 ev

$(\alpha h v)^2$ $(eV/cm)^2$

hv (ev)

Figure 8: 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

Fig 9. Illustrated that the difference in band gap energy for each (Mg^{2+}, Ca^{2+}, and Sr^{2+}) ion with the concentration starting from 0.001M,0.003M and 0.006 M shows variation decreasing of band gap linearly as the concentration increases to 0.006 M however, when the concentration of the dopant raised to 0.007 M the band gap becomes increased slightly .

0.007 M

zno nanoparticle — 3.263 ev

Mg^{2+} — 3.161 ev
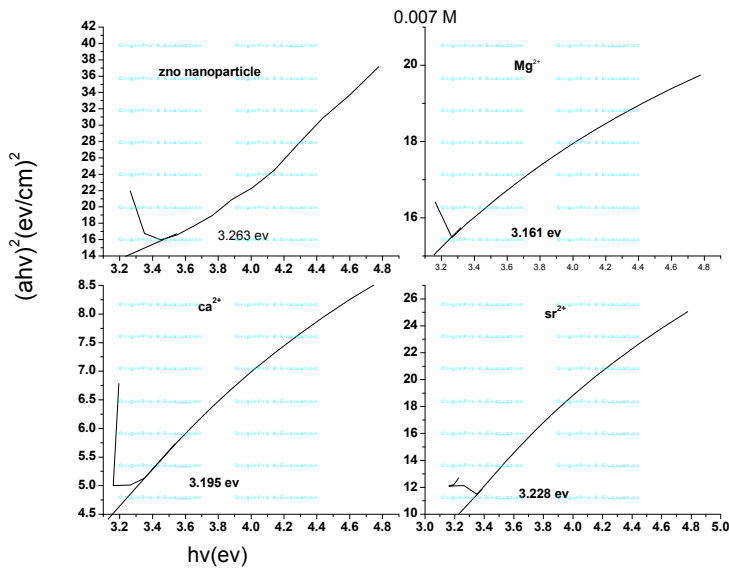
ca^{2+} — 3.195 ev

sr^{2+} — 3.228 ev

$(ahv)^2$ $(ev/cm)^2$

hv(ev)

Figure 9 Optical energy plot for undoped ZnO, $Mg_{0.007}Zn_{0.993}O$, $Ca_{0.007}Zn_{0.993}O$, $Sr_{0.007}Zn_{0.993}O$

The band gap of Mg^{2+} doped ZnO for different concentration was around 3.179, 3.17 and 3.154 eV 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 table 2. Moreover, since ZnO and Mg^{2+} atoms have strong mismatch in electro negativity was a reason for decrease of the band gap. 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[43].

The band gap of Ca^{2+} doped ZnO for different concentration was around 3.212, 3.203 and 3.187 eV respectively. With 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+} .[44]

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

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
Zn^{2+}	1.65	74	-	-	-	

4.4. Comparison of the obtained results with reported values

The obtained result for Ca^{2+} and Sr^{2+} were compared with other reported values for ZnO thin films and nanorods doped with Ca^{2+} and Sr^{2+} was shown in Table, 3. The band gap energy of Ca^{2+} doped with ZnO thin films were higher than undoped thin films. But, in this study it was observed that the band gap energy of ZnO nanoparticles has narrowed when it doped with different concentration of either Ca^{2+} or Sr^{2+}. In general the findings of the present study revealed that use of alkaline earth metals as dopant for ZnO nanoparticles exhibited reduction of the band gap energy.

Table 3. The obtained result for Ca^{2+} and Sr^{2+} as compared with other reported values for ZnO thin films and nanorods doped with Ca^{2+} and Sr^{2+}

Conc. (M)	band gap (eV)	dopant	type	Ref
undoped ZnO	3.30			
1%	3.31			
2%	3.32	Ca	(ZnO:Ca) thin film	
3%	3.33			44
Temp.(ºC)				
undoped ZnO	3.88			
300	3.65		(ZnO: Sr) nanorods	
400	3.45	Sr		
500	3.10			32
Conc.(M)				
undoped ZnO	3.263			
0.001	3.212		(ZnO:Ca) nanoparticle	
0.003	3.203	Ca		
0.006	3.187			This work
0.001	3.245			
0.003	3.237	Sr	(ZnO: Sr)nanoparticle	
0.006	3.220			

Conclusion

ZnO nanoparticles were successfully synthesized by addition of aqueous solution of zinc acetate dihydrate with aqueous sodium hydroxide. The UV-Visible spectra for ZnO nanoparticle synthesized in aqueous media exhibited excitonic absorption peak at 380 nm. The band gap obtained for the synthesized of ZnO nanoparticles was determined by extrapolation to the X-axis was ≈3.263 eV. 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 ionicity between ZnO and Mg^{2+}. It may also due to a strong mismatch of electronegativity 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.

References

1. Lu, J. G., Ye, Z. Z., Zeng, Y. J., Zhu, L. P., Wang, L., Yuan, J., Zhao, B. H., Liang. Q. L. Structural, optical and electrical properties of (Zn,Al)O films over a wide range of compositions. *App. Phys.* **2006,** *100*, 073714.

2. Ruby Chauhan, A. K., and Ram Pal Chaudhary., Synthesis And Optical Properties Of Nickel doped Zinc Oxide Nanoparticles. *Tech. Educ. and Res. Integ.Inst.* **2011,** *319*, 1-3.

3. Heo, Y. W., Norton, D.P., Tien, L.C., Kwon, Y., Kang, B.S., Ren, F., Pearton, S.J. Laroche. ZnO nanowire growth and devices. *Mat. Sci. and Eng.***2004,** *47*, 1-4.

4. A. Bouaoud, A. R., F. Ouachtari, A. Louardi, T. Chtouki, B. Elidrissi H. Erguig. Transparent Conducting properties of Ni doped zinc oxide thin films prepared by a facile spray pyrolysis technique using perfume atomizer. *Mat. Chem. Phy.* **2013,** *137*, 843-847.

5. Yizheng Jin, 2 Yuping Ren,1 MoTao Cao, and Zhizhen Ye. Doped Colloidal ZnO Nanocrystals. *J. Nanomat.* **2012**, 1-9.

6. C. Klingshirn. ZnO, From basics towards applications. *phys. stat. sol.* **2007,** *244*, 3027-3073.

7. Tanveer A. Dar, A. A., Pratimasen. Pulsed Laser Deposited Nickel Doped Zinc Oxide Thin Films: Structural and Optical Investigations. *J. Nanoelec.phy.* **2013,** *5*, 02024(3).

8. Shakhashiri, B. Z. I. .A handbook of chemistry for teachers. *The university of wisconnsin Press* **2009**.

9. Li Hui-Lui, H. Y.-x., LI Zhi-min, YAO Yin-Hua, ZHANG Shu-yuan. Preparation and infrared emissivities of alkali metal doped ZnO powders. *J. Cent. South Univ.* **2014,** *21*, 3449-3455.

10. Mote, V. D., Dole, B. N. Crystallographic and Magnetic Properties of Mn Doped ZnO Nanocrystals Via Solid State Reaction Technique. *Uni. J. Phy.App.* **2014,** *8*, 10-13.

11. Takashi, K., Yoshikawa, A., Sandhu, A., *Wide band gap semiconductors: Wide band gap semiconductors: Fundamental properties and modern photonic and electronic devices. Springer Link.* **2007**.

12. Moezzi, A. M., Andrew M.; Cortie, Michael B. Zinc oxide particles: Synthesis, properties and applications. Zinc oxide particles: Synthesis, properties and applications. J.*Chem. Eng.* **2012,** *185-186*, 1-22.

13. Su-Huai Wei and S. B. Zhang, Chemical trends of defect formation and doping limit in II- VI semiconductors: The case of CdTe. *Phys. Rev.* **2002,** *66*, 155211.

14. Ali Ahmadi Peyghan a, M. N., The alkali and alkaline earth metal doped ZnO nanotubes: DFT studies. *J.Phy.* **2014,** *432*, 105-110.

15. Razeghi, M. Optical properties of semi-conductors. *Fundamentals of Solid State Eng*. **2009**, 1-53.

16. Joshi, R., Kumar, P., Gaur, A., Asokan K., Asokan. Structural, optical and ferroelectric properties of V doped ZnO. *Appl. Nanosci.* **2014,** *4*, 531-536.

17. Mondal, S., Mitra, P. Preparation of Ni doped ZnO thin films by SILAR and their characterization. *J. Phys.* **2013,** *87*, 125-131.

18. Shashi B, R., Amarpal Singh, Satbir Singh. Characterization and optical studies of pure and Sb doped ZnO Nanoparticle. *Int. J. Nanoelec.and Mat.* **2013,** *6*, 45-57.

19. Tanveer A. Dar, A. A., Pratima Sen. Pulsed Laser Deposited Nickel Doped Zinc Oxide Thin Films: Structural and Optical Investigations. *J. Nano-and elect.phy* .**2013,** *5*, 1-3.

20. S. L. Mammah, F. E. O., F. B. Sigalo, S. C. Ezugwu, F. I. Ezema. Effect of Concentration on the Optical and Solid State Properties of ZnO Thin Films Deposited by Aqueous Chemical Growth (ACG) Method. *J. Modern Phy.* **2012,** *3*, 1516-1522.

21. Siva Vijayakumar, S. K., S. Vasanth, Arul Ganesh, G. Bupesh, R. Ramesh M.Manimegalai, and P. Subramanian. Synthesis of Silver Doped Zinc Oxide Nanocomposite by Pulse mode Ultrasonication and its characterization studies. *J. Nanosci.* **2013,** (*Article ID 785064*), 1-7.

22. Fu-Chien, C. Conduction Mechanism in Resistance Switching Memory devices Using transport boron doped zinc oxide thin films. *Mat. Chem. and Phy.* **2014,** *7,* 7339-7348.

23. Heberto Gómez-Pozos 1, J. L. G.-V. Gonzalo Alberto Torres. Chromium and Ruthenium-Dope Zinc Oxide Thin Films for Propane Sensing Applications, *Sensor*. *mat. chem.* **2013,** *13*, 3432- 3444.

24. Agnieszka Koodziejczak-Radzimska and Teofil Jesionowski. Zinc oxide from synthesis to application. *Mat. Chem. and Phy.* **2014,** *7* (4), 2833-2881.

25. Fan, Z., Lu, Jia G. Zinc oxide nanostructure, synthesis and properties. *J. Nanosc. Nanotechnol* **2005,** *5(10*), 1561-73.

26. Yizheng Jin, Y. R., Mo Tao Cao, and Zhizhen Ye. Doped Colloidal ZnO Nanocrystals. *J. Nanomat.* **2012,** *Article ID 985326*, 1-8.

27. Y. Jin, J. W., B. Sun, J. C. Blakesley, and N. C. Greenham. Solution-processed ultraviolet photo detectors based one colloidal ZnO nanoparticles. *Nano Let* **2008,** *8*, 1649-1653.

28. Govender, K., Boyle, D.S., O'Brien, P., Binks, D., West, D., Coleman, D., Room-temperature lasing observed from ZnO nanocolumns grown by aqueous solution deposition.*Adv. Mate.* **2002,** *14*, 1221-1224.

29. Z. A. Peng and X. Peng. Nearly mono disperse and shape controlled CdSe nanocrystal. *J. Amer.Chem. Soc.* **2002,** *24,* 3343-3353.

30. Ueda, K., Tabata, H., Kawai, T. Magnetic and electric properties of transition-metal -doped ZnO films. *App. Phy. Let.* **2001,** *79*, 988-990.

31. P.Gowthaman a , M. S. a., M.Venkatachalam , J.Deenathayalan ,S.Shankar. Doping effects of Strontium on ZnONanorods and their Photocatalytic properties. *J.Nano sci.andNanoTechn.***2014,** *2*, 1-7.

32. Hiten Sarma, D. C., K.C. Sarma. Structural and Optical Properties of Zno Nano Particles. *J. App. phy.* **2014,** *6*, 2278-4861.

33. Achuthanunni., N. M. a. A. Structural and optical properties of undoped and co doped ZnO nanostructured thin film. *J.sci.Technol.* **2010,** *18*, 81-88.

34. Satyanarayana Talam, S. R. K., and Nagarjuna Gunnam. Synthesis, Characterization, and Spectroscopic Properties of ZnO Nanoparticles. *ISRN Nanotech.* **2012**, 1-6.

35. M. Haase, H. W., and A. Henglein. Photochemistry and radiation chemistry of colloidal semiconductors. Electron storage on zinc oxide particles and size quantization. *J. Phys. Chem.* **1988**, *92,*482-487.

36. J. Mohapatra, D. K. M., S. K. Kamilla, V. R. R. Medicherla. Ni-doped ZnO: Studies on structural and magnetic properties. *J.phy. Stat.sol .***2011**, 248,1352-1359.

37. Chewki Zegadi, K. A., Denis Chaumont, Mohamed Adnane,Saad Hamzaoui. Influence of Sn Low Doping on the Morphological, Structural and Optical Properties of ZnO Films Deposited by Sol Gel Dip-Coating. *Adv.in mat.phy.and chem.* .**2014**, 4, 93-104.

38. Saber Farjami shayesteh and Armin Ahmadi. Effect of doping and annealing on the physical propertiesof ZnO:Mg nanorods. *J.phy.stat.sol* **2013,** *81*, 319-330.

39. Eskandaria, V. A. M., The Effect of magnesium doping concentration on morphology and optical property of ZnONanorods. *J.ICNS4.* **2012**, 1-3.

40. Elilarassi, R., Chandrasekaran, G.Synthesis and optical properties of Ni-doped zinc oxide nanoparticles for optoelectronic applications. *Optoelec. Let* **2010,,** *6*, 1-10.

41. Ruby Chauhana, Ashavani Kumarc and Ram Pal Chaudhary. Synthesis and Characterization of Copper doped ZnO nanoparticles. *J.chem.pharm.Res.* **2010,** *4*, 178-183.

42. S. Udayakumar, V. R., K.Kavitha. Structural, optical and thermal studies of cobalt doped hexagonal ZnO by simple chemical precipitation method. *J.chem.and pharm.Res.* **2012,** *4*, 1271-1280.

43. Talaat M. Hammad, J. K. S., Roger G. Harrison, Rolf Hempelmann, Nasser K. Hejazy. Optical and magnetic properties of Cu doped ZnO nanoparticles. *J .Mater Sci: Mater Elec.* **2013**, *24*, 2846-2852.44.

44. Ayadi,Z.B.L.EIMir,JEI Ghoul,K.Djessas,S.Alaya.Structural and optical properties of calcium doped ZnO sputtered from nanopowders target material.J.Nanoelec.and mat.2010,3,87-97.