SYNTHESIS AND OPTICAL PROPERTIES OF SELF-ASSEMBLED COORDINATION POLYMER OF Zn(II) IONS WITH PHENYLMALONIC ACID AND 4-1H-AMINO- 1,2,4- TRIAZOLE

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ABSTRACT

The coordination chemistry of the phenylmalonic acid and 4-1H- amino- 1,2,4- triazole with Zn(II) ions has been investigated. The coordination polymer was synthesized by slow evaporation method and characterized by FT-infrared spectroscopy, ultraviolet-visible measurements, scanning electron microscopy, Electron Dispersive X-ray analysis and Powder X-ray diffraction studies. The ligands and the resulting metal complex gave intense absorption (λ_{max} = 239 nm) upon irradiation by ultraviolet light, $\{[Zn_2(C_9H_8O_4)_2(C_2H_4N_4)_2(H_2O)_4\}n$ (orthorhombic, and $P2_1/cn$) was obtained. An octahedral structure was proposed for the synthesized Zn(II) complex

Keywords: Synthesis, Optical Properties, Coordination Polymer

INTRODUCTION

Materials with precise electronic structure could be used to assemble electronic devices, and the ability to control electrical property of a material by externally applied voltage is at the heart in modern electronics (Kooti and Noori, 2010; Kani and Aksu, 2010; Onal *et al.,* 2011; Kumar and Rao, 2011; Fultz and Howe, 2013; Hussain and Shabeeb, 2014; Pandian and Anbusrinivasan, 2014). However, conventional electronic material manufactured on industrial scale is expensive with a negative effect on the natural environment, their electronic structure fixed and hard to control for their fixed crystalline structure. Recently, self assembled coordination polymers have been found to provide potential solution for this issue (Kani and Aksu, 2010; Onal *et al.,* 2011). A detailed knowledge and investigation of the linear and non-linear optical properties is required in order to evaluate coordination polymers as promising materials for optoelectronic devices (Kou-Lin *et al.*, 2007; Kumar and Rao, 2011). The optical band gap and extinction coefficient are properties used to determine the atomic structure, electronic band structure and electrical properties (Hussain and Shabeeb, 2014). The study of the optical absorption in the solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations while the higher energy part of the spectrum gives knowledge about the electronic states in the atom (Pandian and Anbusrinivasan, 2014). In this research, a coordination polymer has been synthesized by tailoring the functional groups of phenylmalonic acid and 4-1H- amino-1,2,4- triazole ligands to react with zinc(II) salt. This complex is considered new because it has no search match from the pattern list in the International Centre for Diffraction data (ICDD) library. It is a nano-sized complex, an indication of having many functions in small volumes. This property is very important in nanotechnology in fabricating materials for photoluminescence devices. This complex can help in providing solutions to existing challenges by promoting closer interaction between academia and industry.

MATERIALS AND METHODS

The zinc(II) nanoparticles were synthesized according to the literature method (Eno *et al.*, 2011). Zinc Nitrate (1 mmol, 0.297 g) was dissolved in 10 ml deionized water and added to (5 ml) methanolic solution of 4-1H- amino- 1,2,4-triazole (2.5 mmol, 0.210 g) under stirring. Potassium malonate (generated in situ by reacting 1 mmol (0.180 g) of phenylmalonic acid and 1 mmol (0.138 g) of K_2CO_3 dissolved in 6 ml deionized water) was added drop wise to the

previously resulting solution under continuous stirring with a magnetic stirrer for four hours at a constant temperature of 30 °C and filtered. Colorless crystals of Zn(II) complex were obtained from the filtrate after one week. Yield: 68 %. Anal. Calcd. for $[Zn_2(C_9H_8O_4)_2(C_2H_4N_4)_2(H_2O)_4]$: C 36.10, H 4.38, N 15.32, O 26.26, Zn 17.88 %; Found: C 35.98, H 4.56, N 15.26, O 26.34, Zn 17.86 %.

The morphology of the synthesized compound was analyzed by scanning electron microscopy using JSM 840-A SEM. The presence of Zn^{2+} in the complex compound was confirmed by energy dispersive X- ray analysis (EDAX coupled to JSM 840-A SEM). Powder X-ray diffraction pattern was recorded using Pan Analytical X-PERT instrument by means of a slowly moving radiation detector with a scan speed of 2°/min in the range of 10-80° where monochromatic wavelength of 1.54060 Á (Cu Kα) was used. The crystalline nature and particle size of the Zn(II) complex was characterized by Powder X-ray diffraction analysis. The Infrared spectrum of complex was recorded over the range 4000- 450 cm^{-1} using a FT-IR 1725X Perkin Elmer spectrometer. The sample was prepared as KBr disc. UV–Vis electronic absorption measurements were made in solution (dimethylsulfoxide) with a spectro–UV-Vis Dual Beam 8 auto cell UVS–2700 LABOMED, INC, US spectrophotometer in the range 200-700 nm at room temperature.

RESULTS AND DISCUSSION

The diffractogramm for the Zn(II) complex in Figure 1 shows a crystalline single phase system. The particle size *D* of the Zn(II) complex was determined using the Debye - Scherrer equation (Hussain and Shabeeb, 2014):

$$D = \frac{R\lambda}{\beta \cos\theta} \quad (1)$$

Where, R is a constant equal to 0.89, β is the full width half maximum height of the diffraction peak at angle θ and λ is wavelength. A dimensional particle size of 42.15 nm was determined from the Debye-Scherrer equation for the synthesized Zn(II) complex. The other crystallographic data and structure refinement for the Zn(II) complex is given in Table 1.

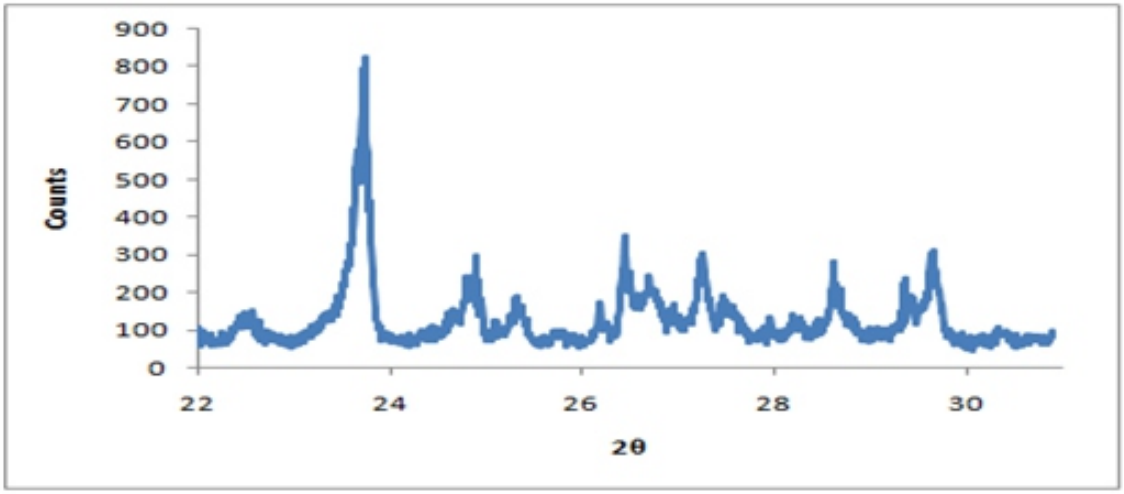

Fig.1: Powder X-ray Diffractogramm of Zn(II) Complex

Table 1: Crystallographic Data and Structure Refinement for the Zn(II) Complex

Empirical formula	$C_{11}O_2N_4H_{1.3}Zn$
Formula weight	598
Temperature (K)	293
Wavelength (A °)	1.54060
Crystal system	$P2_1/cn$
Space group	orthorhombic
Z	8
Theta range for data collection	10-80
Completeness to theta(27.48)	99.40%
Absorption correction	None
Strain value	-0.1689378
Particle size (nm)	42.15

The SEM micrograph shown in Figure 2 depicts that the Zn(II) nanoparticles are in cluster like structure and possess porosity.

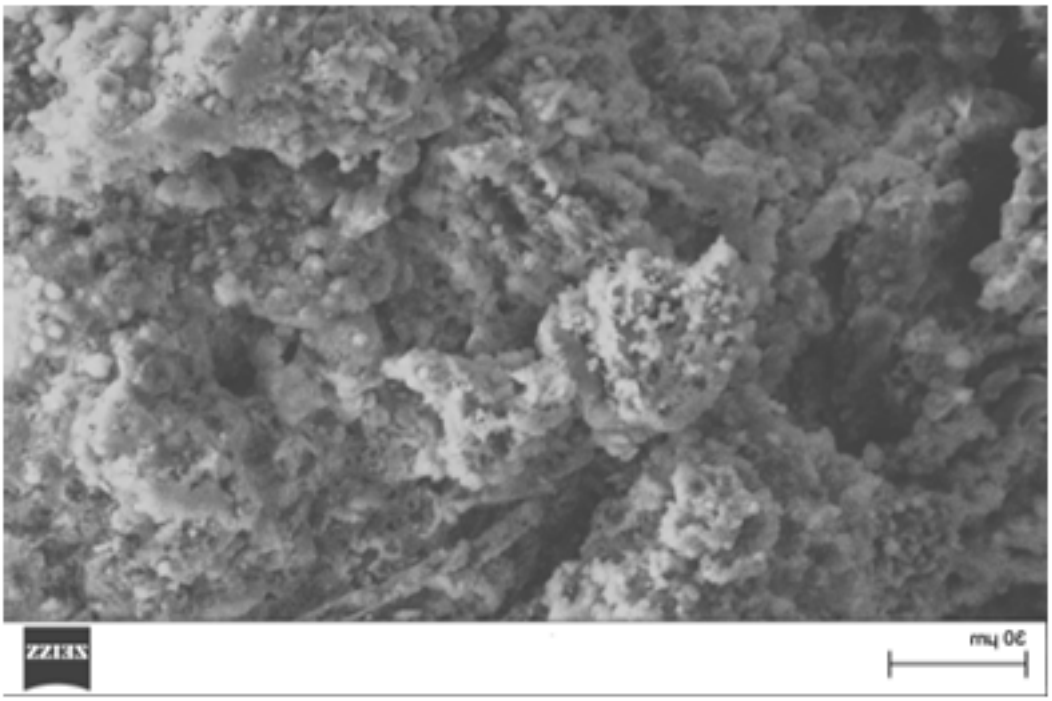

Fig. 2: The SEM Image of Zn(II) Complex

The elemental ratio in the complex was detected with energy dispersive spectrum and this corresponds to peaks shown in Figure 3. The experimentally found values for the elemental composition shows 80 % of Zn metal in the sample. This study shows that Zn^{2+} dominates in the complex.

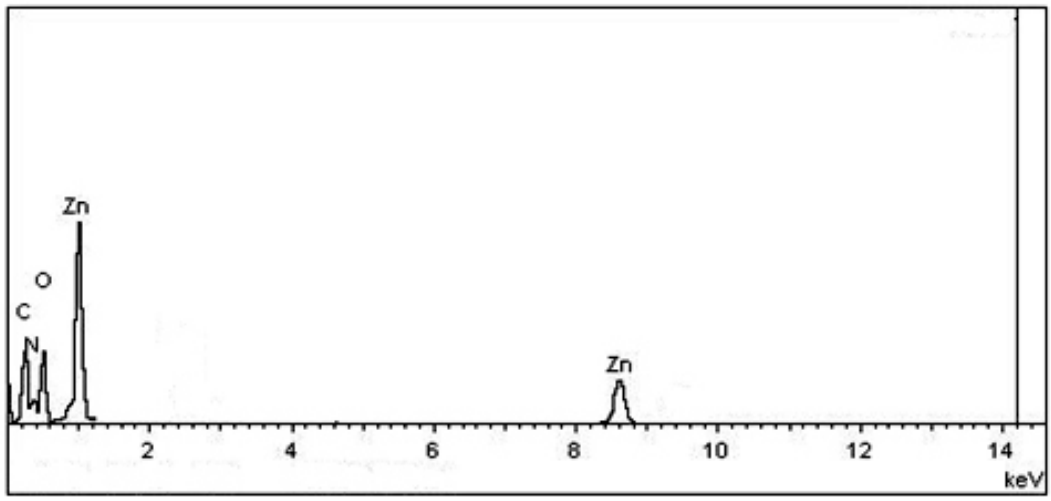

Fig.3: The EDAX Image of Zn(II) Complex

The FT-IR spectrum of the Zn(II) complex in Figure 4 shows characteristic bands of carboxylate groups at 1672–1539 cm^{-1} for asymmetric stretching and that at 1489 cm^{-1} for symmetric stretching, respectively. The shift in absorption bands of the ligands within the complex is an indication of coordination. In the title complex, the carboxylate exhibits the bidentate coordination mode which can also be seen from the separations between $\nu(COO^-)$ frequencies of 189 cm^{-1}, while the band at 3213 cm^{-1} assigned to $\tilde{o}_{as}$(N-H) stretching vibration appear almost at the same frequency in the complex as an indication of uncoordinated $\tilde{o}(NH_2)$ group showing a neutral bidentate coordination mode of the 4-1H- amino- 1,2,4-triazole via its two nitrogen atoms. The 4-1H-amino-1,2,4-triazole is acting as a neutral bridging ligand, coordinating as the 4-H tautomer through NI and N2. An important feature of infrared spectrum of the metal complex with these ligands is the absence of band at ~1701cm^{-1} due to the $\nu(COO^-)$ stretching vibration. These various assignments are in agreement with similar Zn(II) octahedral structured compounds reported in the literature (Nakamoto, 2009; Kani and Aksu, 2010). The infrared spectral analyses has been used to further confirm the proposed octahedral structure (Figure 5) for the zinc(II) complex.

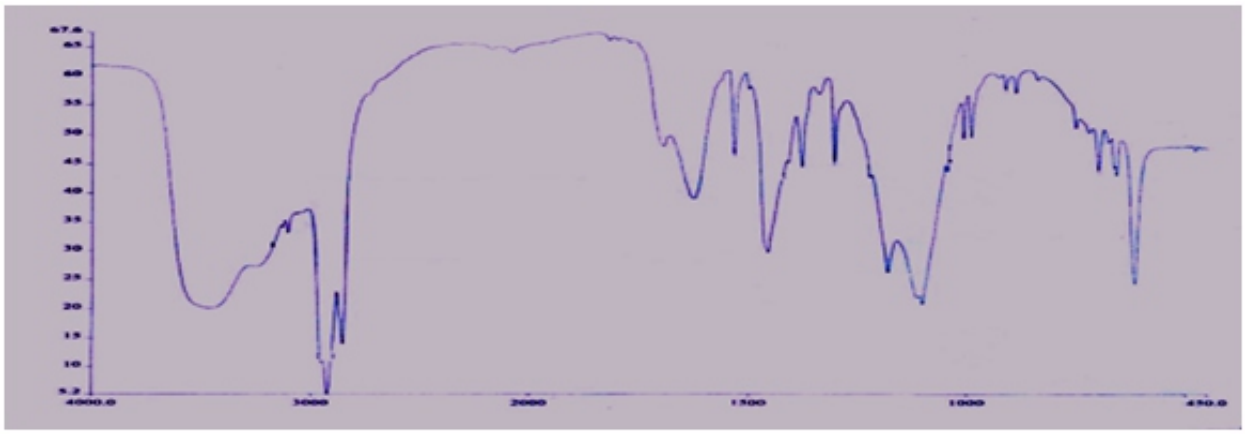

Fig. 4: FT-IR Spectrum of Zn(II) Complex

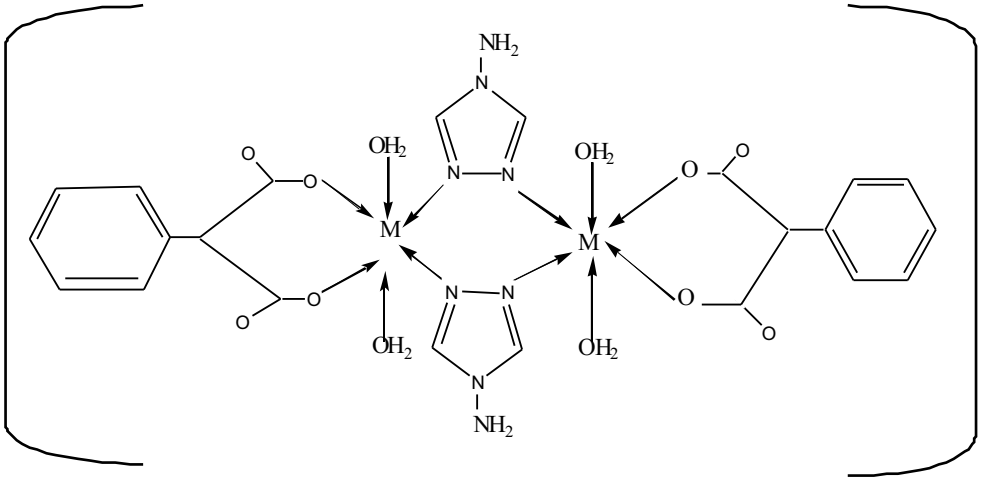

Fig. 5: Proposed Octahedral Structure of Zn(II) Complex (M = Zn)

Figures 6 and 7 show the spectral distributions of absorbance (A) and transmittance (T), respectively for the Zn(II) complex. The observed electronic spectral data is as shown in Table 2. The UV absorption spectrum in Figure 6 shows broad absorption band of λ_{max} at 239 nm. This is attributed to incorporation of the ligands (Kumar and Rao, 2011). The ultraviolet radiation is the main source of energy needed in photovoltaic devices for the conversion of solar energy to electricity (Fultz and Howe, 2013). The characteristic absorption of Zn(II) complex crystal is found between 231-252 nm and a highly transparent nature of the complex after the wavelength at 252 nm, which is one of the important characteristic properties of a material suitable for optical applications (Pandian and Anbusrinivasan, 2014).

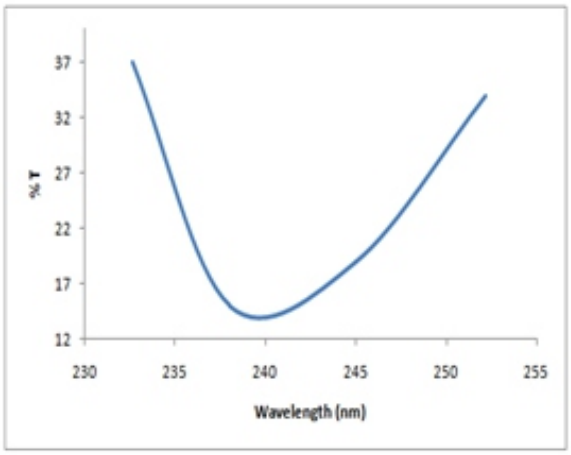

Fig.6: UV- Spectrum of Zn(II) Complex

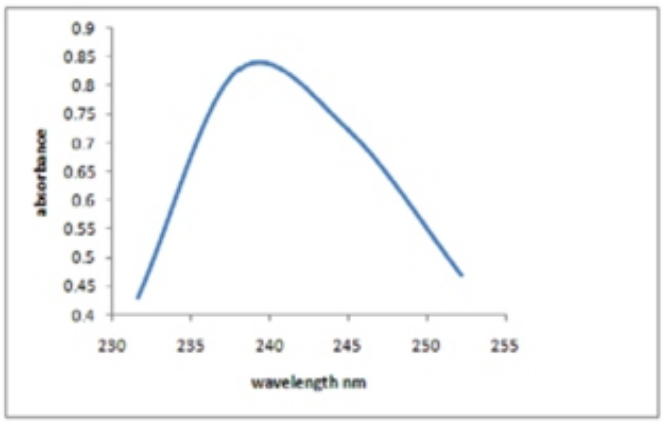

Fig. 7: Plot of Transmittance Versus Wavelength for Zn(II) Complex

Table 2: Observed Electronic Spectral Data and Optical Parameters of the Zn(II) Complex Recorded in Dimethylsulfoxide

λ	A	T %	$\log \frac{1}{T}$	α (m^{-1})	K	E (eV)	$(\alpha h\nu)^2$
231.60	0.429	37.3	2.6853	6.18	113.87	5.35	10.93
238.00	0.828	14.9	6.7298	15.50	293.48	5.21	65.21
245.00	0.723	18.9	5.2845	12.17	237.20	5.06	37.92
252.20	0.468	34.0	2.9376	6.77	135.83	4.92	11.09

The analysis of data from transmittance spectra can be used to determine optical properties for applications in integrated optic devices such as switches, filters and modulators, etc., where the optical properties of the material is the key parameter for device design. The optical molar absorption coefficient (α) was calculated from the transmission data using this relation (Antoine *et al.*, 2006; Hussain and Shabeeb, 2014):

$$\alpha = \frac{2.303 \log \frac{1}{T}}{d} \qquad (2)$$

Where *d* is the optical path length of the complex (1 cm).

The molar absorption coefficient and optical band gap *Eg* were determined for the Zn(II) nano particles, and shown as a function of photon energy in Figure 8. This analysis reveals that the absorption coefficient increases gradually to the point where the photon energy is 5.19 eV and thereafter decreases steadily. The sharp increase in molar extinction coefficient is as a result of the enhanced optical properties afforded by the substitution of carboxy groups of phenylmalonic acid and the nitrogen groups of the 4-1H-amino-1,2,4-triazole to the back bone of the Zn(II) ion through π -bond elongation. The role of these substituents on the ligands are expected to tune and enhance stability of the synthesized complex (Kumar and Rao, 2011; Hussain and Shabeeb, 2014).

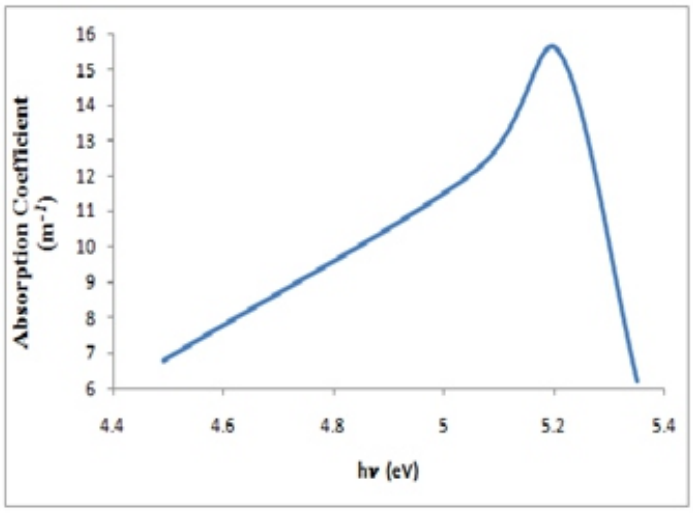

Fig. 8: Plot of Absorption Coefficient Versus Photon Energy for Zn(II) Complex

The electronic spectral data of the synthesized Zn(II) complex crystal was used to evaluated its band gaps energy from the relation between molar absorption coefficient α and photon energy *hν* (Metha *et al.,* 2005; Kumar and Rao, 2011):

$$(\alpha h\nu)^2 = A(Eg - h\nu) \qquad (3)$$

Where α is molar absorption coefficient, *Eg* is the optical band gap energy of the material, *A* is a constant related to the effective masses associated with the bands, h is Planck's constant and *ν* is the frequency. The optical band gap has been calculated from the relation in equation 3. Figure 9 shows the plot between $(\alpha h\nu)^2$ and *hν* of the synthesized Zn(II) complex crystal. The extrapolation of linear portion of the curves on *hν* axis gives the direct band gap energy. The value of band gap energy for the prepared Zn(II) crystal is 4.49 and 5.35 eV, which reveals the Zn(II) complex crystal has semi conducting property (Pandian and Anbusrinivasan, 2014).

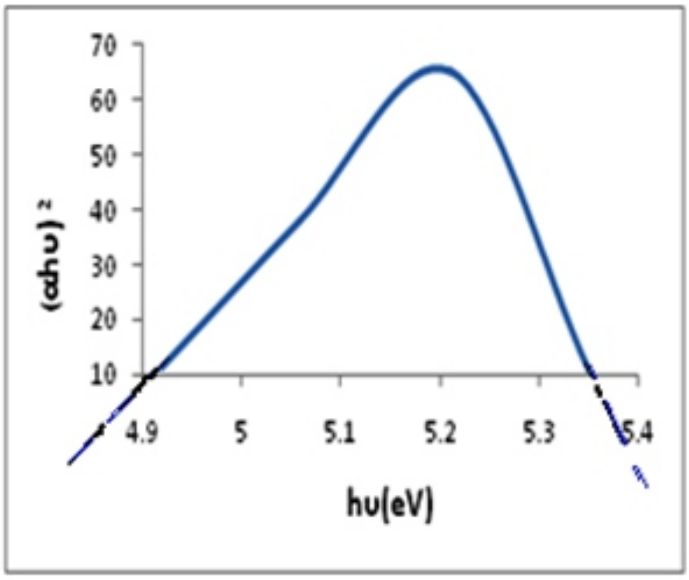

Fig. 9: Dependence of $(\alpha h\upsilon)^2$ on the Photon Energy hυ for Zn(II) Complex

The extinction coefficient (K) was obtained from the relationship [10]:

$$K = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

Where, λ is the wavelength.

From the plot of extinction coefficient vs wavelength (Figure 10) the highest value of K was found to be 300. This is ideal for photovoltaic devices as such; value shows that the complex absorbs more than 90 % of the incident photons at the peak maximum 239 nm.

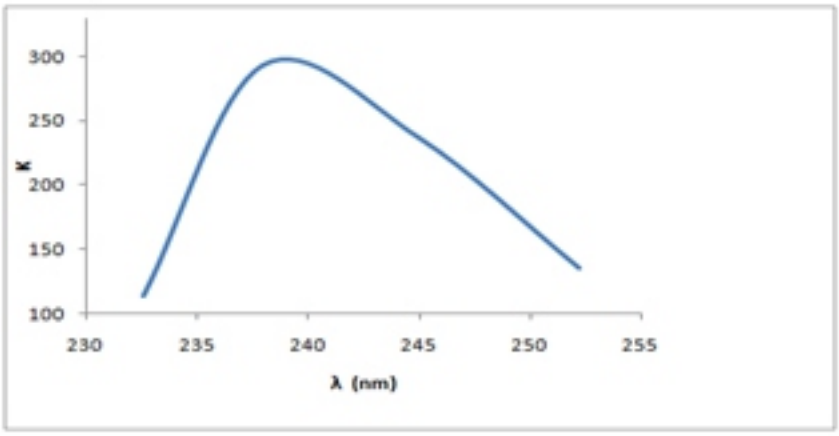

Fig.10: Dependence of *k* on the Wavelength λ for Zn(II) Complex.

CONCLUSION

This study investigated the optical properties of the nanocrystalline particles of Zn^{2+} synthesized by slow evaporation method. The powder X- ray analysis confirmed the nanoparticle size and the fundamental diffraction patterns of the compound. The scanning electron microscopy and EDAX analysis revealed the structure, morphology and elemental composition of the synthesized compound. FT-IR spectrum gave the different vibrations frequencies of the functional groups present in the synthesized compound. The value of wavelength of maximum absorption for this complex 239 nm showed that the compound absorbs in the ultraviolet region

suggesting high energy content of the synthesized complex compound. An octahedral structure had been proposed for the synthesized Zn(II) complex. The optical property studied by UV absorption spectrum and high value of and gap energy revealed large transmittance in ultraviolet region for application towards optoelectronic devices.

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