Synthesis and Characterization of ZnO and Fe Doped ZnO Photocatalytic Nanomaterial using Sol-Gel Method

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Abstract- In this research work, pure ZnO and Fe-doped ZnO photocatalytic nanomaterials were successfully synthesized by using sol-gel method. Characterizationof all synthesized samples were carried out using XRD, FTIR and UV techniques.Specifically, crystalline size and band gap studies are done using X-ray Diffraction (XRD) and UV-Vis spectroscopy techniquesrespectively. XRD study shows that, the samples possess hexagonal wurtzitetype structure having crystalline size is in the range of 23-24nm. FTIR studies shows theparticular molecular band is present in the synthesized samples. Here we also study the effect of iron as a doping material on optical band gap of pure ZnO.

Keywords: pure ZnO, Fe-doped ZnO, nanomaterial, photocatalytic, Sol-gel.

I. INTRODUCTION

In the research community, due to wide band gap[1-4], large excitation energy [1-5]and easy availability of ZnO makes it an important area for research. It has lot of applications such as photocatalyst [6], dye sensitized solar cell [7], gas sensors [8], optoelectronics [9-10], antibacterial material [11-13], etc. Simply it is a multifunctional material. Theunique feature of this material is that the physical and chemical properties of this material can be easily modified as per the demand of the device fabrication or application.It is a promising material in catalysis.

ZnO not only attracts attention of researchers in powder form [14-15] but also in thin film [16-17]form. We also extend our work in the next paper in the form of thin films of the same materials. ZnO has been synthesized using various techniques like, sol-gel process [18], wet chemical synthesis, precipitation [19], hydrothermal synthesis [20-22], SILAR [23], CVD [24-25], etc. In the present work we synthesizepure ZnO and Fe doped ZnO photocatalytic nanomaterial using sol-gel method and analyze the synthesized samples using various characterization parameters like XRD, FTIR and UV techniques [26].XRD is used to calculate crystalline size. Variation in the band gap as a function of size is determined using absorption spectra obtained by UV-Vis spectrophotometer (Shimadzu) 2450. FTIR studies show the particular molecular band present in the samplesindirectly it indicated the purity of synthesized material.

II. MATERIALS AND METHODS

ZnO and Fe doped ZnO photocatalytic nanomaterial was synthesized by using low cost sol-gel method.All the chemicals used in the present work were of analytical grade and all the solutions were prepared in distilled water. Chemicals used in this synthesis arezinc acetate dihydrate, sodium hydroxide, iron nitrate nona hydrate, ethanol and distilled water.

Zinc acetate dihydrate is used as a precursors and ethanol is used as a reagent. While sodium hydroxide is used as a source of oxygen. Iron nitrate nona hydrate is used as a source of iron for doping. Pure ZnO nanoparticles were prepared by sol-gel method. Initially,by dissolving 0.2M zinc acetate dihydrate in ethanol at room temperature and then stirring and mixing this solution using magnetic stirrer. Clear and transparent sol with no precipitate and turbidity was obtained. 0.02 M of NaOH was then added to the sol and stirred for 60 min. The sol was kept undisturbed till white precipitates settled down at the bottom of sol. After precipitation, the precipitates were filtered and washed with excess ethanol to remove starting material. Precipitates were dried at 50°C for 15 min on hot plate. Precipitates were then annealed at 50°C temperatures for 24hrs. [27]

Similarly, Fe doped ZnO nanoparticles were preparedby sol-gel method. Initially, by dissolving 0.2M zinc acetate dihydrate and 0.2M iron nitrate nona hydrate in ethanol at room temperature with different atomic % (2% and 4%) and then stirring and mixing this solution using magnetic stirrer. Clear and transparent sol with no precipitate and turbidity was obtained. 0.02 M of NaOH was then added to the sol and stirred for 60 min. The sol was kept undisturbed till white precipitates settled down at the bottom of sol. After precipitation, the precipitates were filtered and washed with excess ethanol to remove starting material. Precipitates were dried at 50°C for 15 min on hot plate. Precipitates were then annealed at 50°C temperatures for 24hrs each. [27]

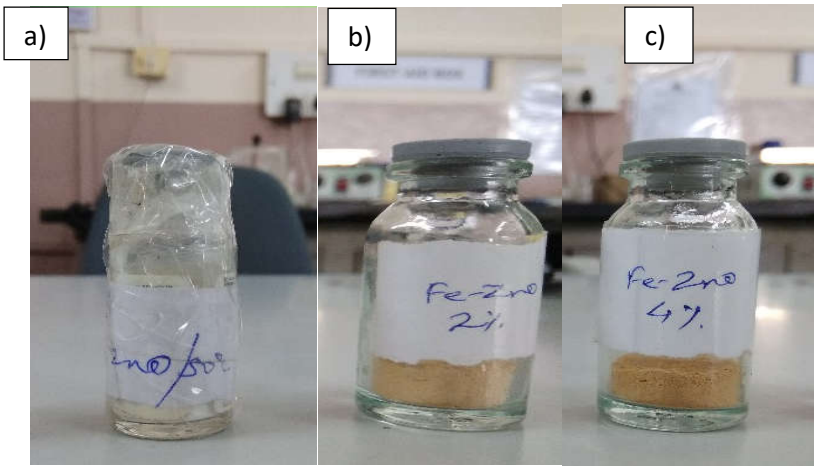

Fig.1a)Pure ZnO b) 2% Fe doped ZnO and c) 4% Fe doped ZnO synthesized at annealing temperature 50°C using Sol gel Method

III. RESULTS AND DISCUSSION

Characterization of synthesized nanoparticles

Characterization of all synthesized samples was carried out using XRD, FTIR and UV techniques. Generally structural properties include structure and crystal size of the samples. This structure and crystal size of the samples was determined by X-ray diffractometer (XRD). The powder x-ray diffraction (XRD) was performed using automated x-ray diffractometer (Rigaku MiniFlex-600) operating CuKα at wavelength 1.54056 Å. The average crystal size (D) has been calculated using the diffraction intensity of (101) peak from Debye -Sherrer relation [28-29] as shown in equation (1),

$$D = K\lambda/\beta\cos\theta \quad \ldots\ldots\ldots\ldots (1)$$

Where the constant K is taken to be 0.94, λ is the wavelength of x-ray used and β is the full width of half maximum (FWHM).

Here in this work all the peaks are indexed and found to be well matched withwurtzite structure of ZnO having hexagonal phase, which is in good agreement with the standard JCPDS (Card No. 36-1451).[30] UV-Vis spectrophotometer (Shimadzu) 2450 was used to record the UV-visible absorption spectra of the samples.

A.Crystal size and structure of the samples determination using -XRD Analysis

Figure 2(a) shows that the XRD pattern of ZnO nanoparticles prepared by sol-gel method.Eleven diffraction peaks are obtained at 2θ valuesand all were identified to originate from respective planes as given in Table-1. Based on the Scherrer equation the average crystal size of the nanoparticles is observed as 24.04 nm. All the peaks are indexed and found to be well matched to wurtzite structure of ZnO having hexagonal phase, which is in good agreement with the standard JCPDS (Card No. 36-1451).

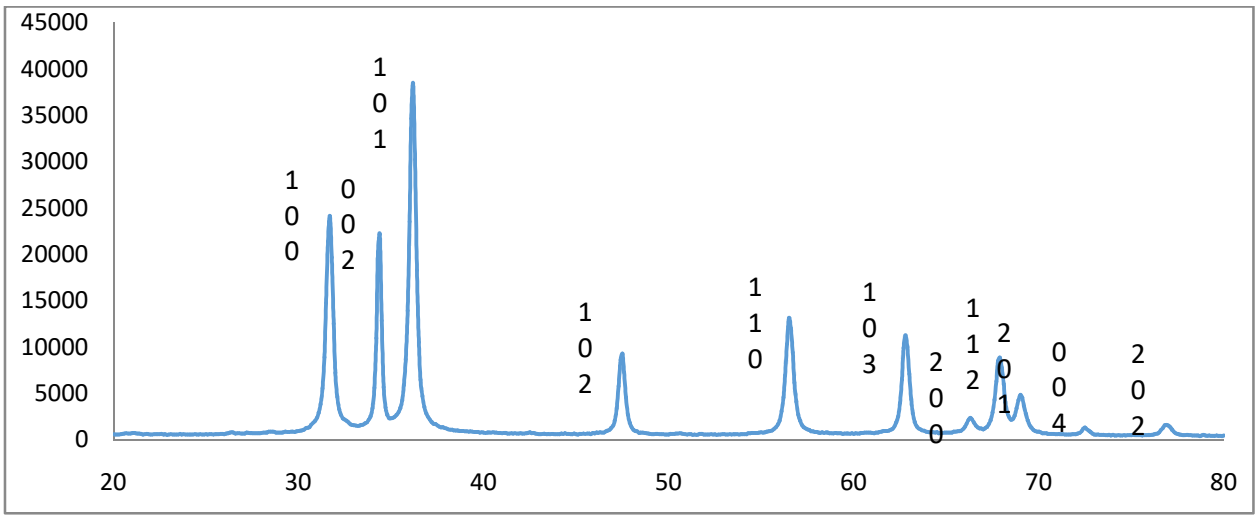

Fig.2(a) XRD pattern for Pure ZnO nanoparticles synthesized at 50^{0}C by sol-gel method

Table-1
Pure ZnO nanoparticles synthesized at 50^{0}C by sol-gel method

Observed			Standard	Planes			
Peak match	2Theta	d Observed	d Standard	h	k	l	Grain Size (nm)
1	31.66	2.8238	2.8143	1	0	0	
2	34.35	2.6086	2.6033	0	0	2	
3	36.155	2.4824	2.4759	1	0	1	
4	47.433	1.9151	1.9111	1	0	2	
5	56.503	1.6274	1.6247	1	1	0	
6	62.755	1.47943	1.4771	1	0	3	**24.04**
7	66.23	1.4099	1.4071	2	0	0	
8	67.818	1.3808	1.3781	1	1	2	
9	68.975	1.3604	1.3582	2	0	1	
10	72.483	1.303	1.3017	0	0	4	
11	76.82	1.2398	1.238	2	0	2	

Figure 2(b) shows the XRD patterns of 2%Fe doped ZnO nanoparticles prepared by sol-gel method. Eleven diffraction peaks areobtained at 2θ values and all peaks were identified to originate from respectiveplanes as given in Table-2.

Based on the Scherrer equation the average crystal size of the nanoparticles is observed as 23.38 nm. All the peaks are indexed and found to be well matched and is in good agreement with the standard JCPDS (Card No. 36-1451).

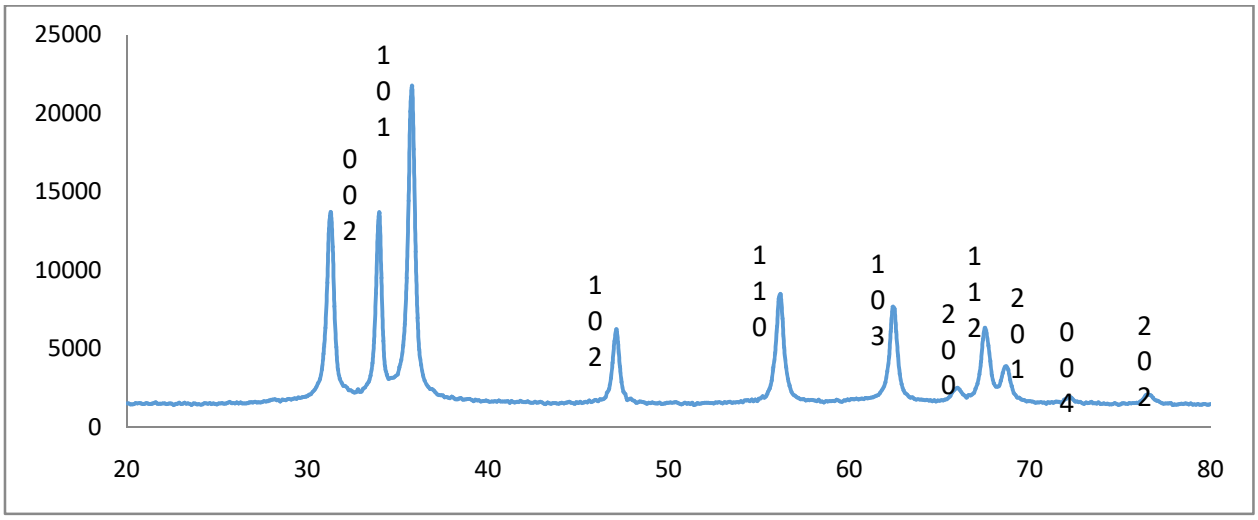

Fig. 2(b) XRD pattern for 2% Fe doped ZnO nanoparticles synthesized at 50^{0}C by sol-gel method

Table-2
2% Fe doped ZnO nanoparticles synthesized at 50^{0}C by sol-gel method

Observed			Standard	Planes			
Peak match	2Theta	d Observed	d Standard	h	k	l	Grain Size (nm)
1	31.259	2.8592	2.8143	1	0	0	
2	33.949	2.6384	2.6033	0	0	2	
3	35.755	2.5092	2.4759	1	0	1	
4	47.073	1.929	1.9111	1	0	2	
5	56.165	1.6363	1.6247	1	1	0	
6	62.451	1.48589	1.4771	1	0	3	**23.38**
7	65.84	1.4174	1.4071	2	0	0	
8	67.466	1.3871	1.3781	1	1	2	
9	68.621	1.3666	1.3582	2	0	1	
10	72.13	1.3084	1.3017	0	0	4	
11	76.45	1.2449	1.238	2	0	2	

Figure 2(c) shows the XRD patterns of 4% Fe doped ZnO nanoparticles prepared by sol-gel method. Eleven diffraction peaks are obtained at 2θ values and all peaks were identified to originate from respective planes as given in Table-3. Based on the Scherrer equation the average crystal size of the nanoparticles is observed as 23.44 nm. All the peaks are indexed and found to be well matched and is in good agreement with the standard JCPDS (Card No. 36-1451).

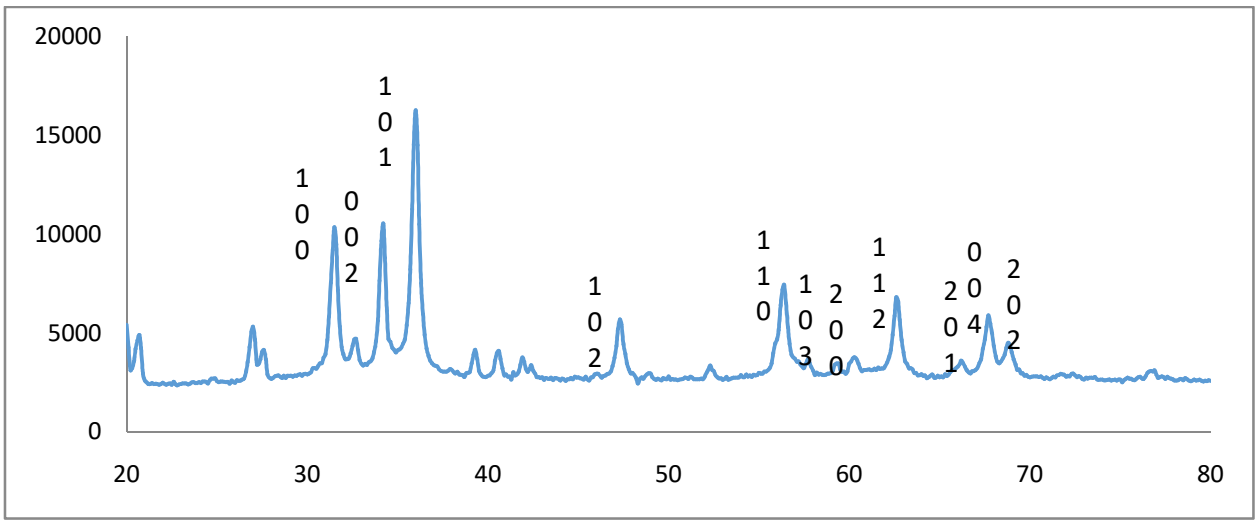

Fig.2(c) XRD pattern for 4% Fe doped ZnO nanoparticles synthesized at 50^{0}C by sol-gel method

Table-3
4% Fe doped ZnO nanoparticles synthesized at 50^{0}C by sol-gel method

Observed			Standard	Planes			
Peak match	2Theta	d Observed	d Standard	h	k	l	Grain Size (nm)
1	31.498	2.838	2.8143	1	0	0	
2	34.184	2.6209	2.6033	0	0	2	
3	35.968	2.4949	2.4759	1	0	1	
4	47.26	1.9217	1.9111	1	0	2	
5	56.295	1.6329	1.6247	1	1	0	
6	57.6	1.599	1.4771	1	0	3	**23.44**
7	60.22	1.535	1.4071	2	0	0	
8	62.643	1.4818	1.3781	1	1	2	
9	66.2	1.4106	1.3582	2	0	1	
10	67.746	1.382	1.3017	0	0	4	
11	68.849	1.3626	1.238	2	0	2	

B.Optical band gap determination using-UV-Visible spectroscopy

The UV-visible absorption spectrum of pure ZnO and Fe doped ZnOnanoparticles was shown in Figure3(a).The optical absorption spectra was studied in the range of 200-800 nm using UV-Vis spectrophotometer (Shimadzu) 2450. The absorption edge takes the value around 375 nm for pure ZnO, 376 nm for 2% Fe doped ZnO nanoparticles and 377 nm for 4% Fe doped ZnO nanoparticles. The Tauc Plot of $(\alpha h\nu)^2$ *vs* hν is plotted from UV-vis-Spectrum for band gap determination[31].The energy gap (Eg) of synthesized nanomaterial was determined by using Tauc formula as shown in equation (2)

$$\alpha h\nu = A\,(h\nu - Eg)^m \qquad \text{……..(2)}$$

Where, α = Absorption coefficient, hν = Photon energy, Eg = Optical band gap

A=Constant which is related to effective masses associated with V.B. and C.B.

m = Assume value of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transition, respectively.

Such as, for allowed direct type of transition following equation (3) is used.

$$\alpha h\nu = A\,(h\nu - Eg)^{1/2} \qquad \text{……..(3)}$$

The band gap of the pure ZnO, 2% Fe doped ZnO and 4% Fe doped ZnO nanomaterial is 3.08 eV, 3.12 eV and 3.2 eVrespectively. Also it is indicated that by increasing the concentration of doping metal that is iron band gap increases [32-34] and it is useful to use the synthesized material as a photocatalyst due to wide band gap.

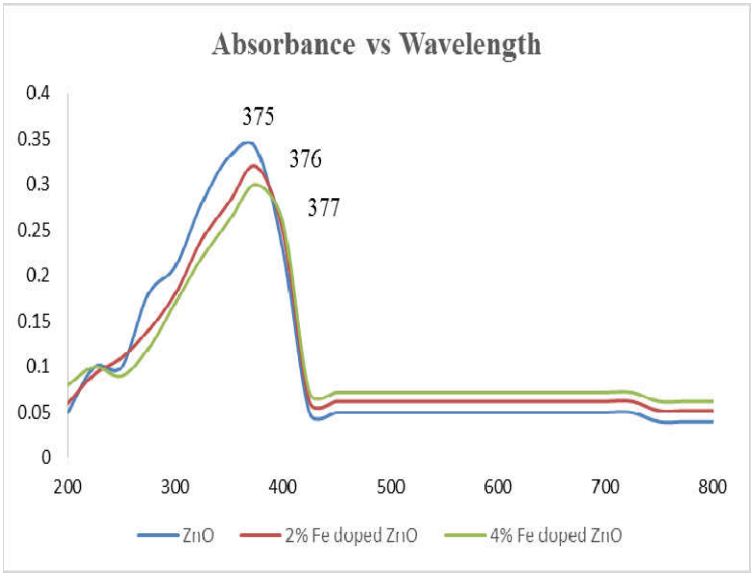

Fig.3(a) UV spectrum of ZnO, 2% Fe doped ZnO and 4% Fe doped ZnO nanoparticles synthesized at 50^0C by sol-gel method

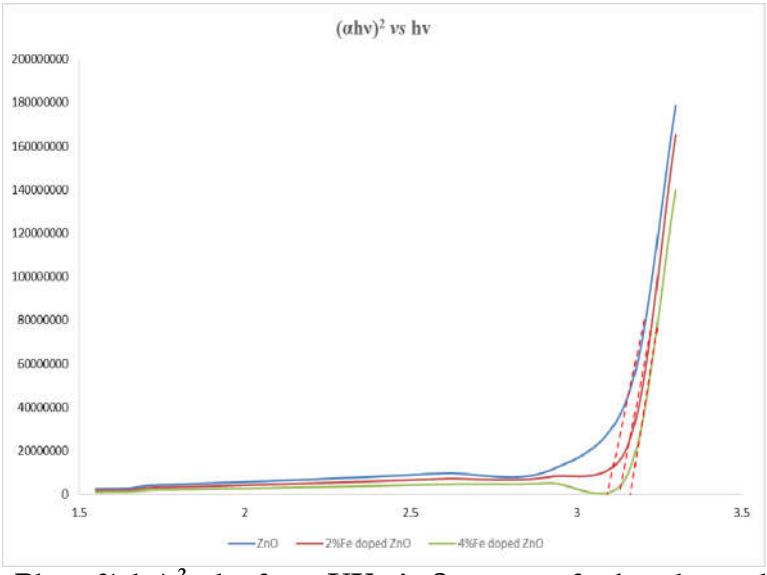

Fig. 3(b)Tauc Plot of$(\alpha h\nu)^2$ *vs*hν from UV-vis-Spectrum for band gap determination

C.Determination of purity of the synthesized material using-FTIR analysis

It is one of the most effective characterization technique to confirm purity and characterization behavior of oxide molecules.[35]The FTIR spectra was studied in the range of 500-4000cm^{-1}using FTIR (Shimadzu) 8400-S.Generally metal oxides shows absorption band in the fingerprint region i.e. below 1000 cm^{-1}. FTIR spectra for pure ZnO and Fe doped ZnO is shown in figure 4(a), 4(b), 4(c).The significant band at 543 cm^{-1}, 532 cm^{-1}, and 482.22$cm^{-1}$are the characteristics absorption bandsof Zn-O stretching mode[36].This shift in peaks is due to the variation in the concentration of dopant. Also the peak at 3527.92cm^{-1}, 3385.18 cm^{-1}, 3246.31 $cm^{-1}$and 1408.08 cm^{-1}, 1383.01 cm^{-1}, 1479.75cm^{-1}may be due to water O-H , C-H and C-O stretching it shows the purity of molecule. The obtained data is identical with previously reported results. [31,37-39].

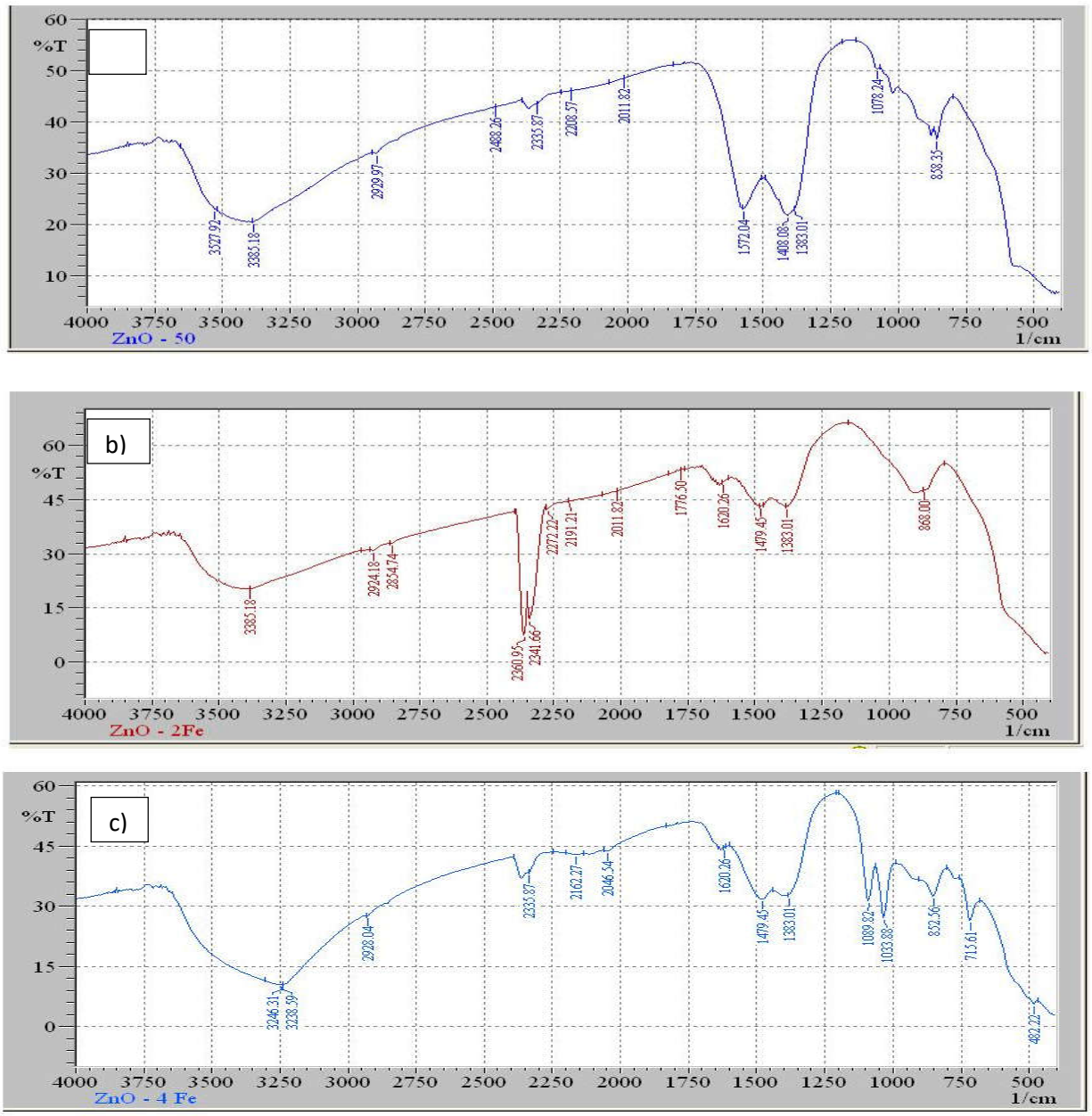

Fig.4 FTIR spectrum of a) Pure ZnO, b) 2% Fe doped ZnO and c) 4% Fe doped ZnO nanoparticles synthesized at 50^0C by sol-gel method

IV. CONCLUSIONS

Pure ZnO and Fe doped ZnO nanoparticles were synthesized by sol-gel method and the prepared nanoparticles were characterized by XRD, UV-Visible and FTIR analysis. The crystal size of the prepared nanoparticles were determined by Debye-Scherer equation and it was found to be in the nanometer range 24.04nm , 23.384nm and 23.44nm respectively for the Pure ZnO,2% Fe doped ZnO and 4% Fe doped ZnO nanoparticles and show preferred growth orientation along (101) plane. All the prepared nanoparticles showed hexagonal wurtzite structure. From UV-Visible spectrum the optical band gap of the synthesized nanomaterial is obtained as 3.08 eV, 3.12 eV and 3.2 eV respectively. UV study of these materials indicating that by increasing the concentration of doping metal that is iron, band gap increases. Finally the FTIR analysis confirms the purity at unique band frequency.

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