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Physical, spectral and thermal properties of Mn^{2+} doped ZnO-PVA polymer

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Abstract

Mn^{2+} doped ZnO-PVA polymer is prepared via chemical method at 60 ^{0}C. The prepared polymer is characterized by physical, spectral and thermal techniques. Different physical parameters are evaluated using measured values of refractive index and density. The spectral characterizations like optical absorption and FT-IR techniques reveal band gap related information and functional groups present in the prepared polymer. TG-DTA reveals the thermal decomposition of Mn^{2+} doped ZnO-PVA polymer at different temperatures with relevant weight loss.

Keywords: ZnO-PVA polymers, Optical band gap, TG-DTA.

1 Introduction

Semiconductor oxide materials are of fundamental importance for the development of smart and functional devices and systems. Among these, zinc oxide is an important and attractive semiconducting material. It has drawn enormous research attention due to its useful properties in electronics, optics, photonics and extensive applications in diverse areas [1]. From application point of view, there is a need for these nanoparticles which can be coated to form thin films. As we have already seen that the key point of ZnO nanoparticles are the size uniformity, surface passivation and chemical stability, which remain to be a major interest. For this reason, many studies were dealing with the stabilization of composite by incorporation of ZnO nanoparticles in polymeric networks [2-6].

Polyvinyl alcohol (PVA) is well known for its use as a matrix material for various inorganic composites. PVA was chosen here as the polymer matrix for its aqueous solubility. It is highly soluble in water and alcohol. PVA is a potential semi-crystalline polar polymer having an excellent charge storage capacity, high dielectric strength, good mechanical stability, and it has dopant-dependent optical and electrical properties [7–8]. PVA has carbon chain backbone with hydroxyl (O–H) groups that can be a source of hydrogen bonding which assists the formation of polymer complexes [9]. So the ZnO-PVA composites are easier to fabricate through water, alcohol and surfactant medium. Also, it is a unique synthetic biocompatible polymer. Due to large range hydrogen bond formation

ability it is extensively used as a binder for the synthesis of composite materials [10]. Transition metal ions doped with II-VI semiconductor materials are of great interest in spintronic devices, sensors, and laser devices etc. Especially Mn^{2+} ions are excellent luminescence activators in thin film luminescent devices of next generation [11]. ZnO polymers has been prepared by various techniques, such as vapour-liquid–solid (VLS) process, chemical vapour deposition (MOCVD) and soft chemical methods [12-15]. Here Mn^{2+} doped ZnO- PVA polymer is prepared by chemical method. In the present investigation our aim is study to physical, spectral and thermal properties of Mn^{2+} doped ZnO- PVA polymer.

2 Experimental procedure

2.1 Materials

Sodium hydroxide (NaOH), Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Poly Vinyl Alcohol (CH_2CHOH), Manganese oxide (MnO) were used as starting materials and used without further purification. All the chemicals used were of analytical reagent (AR) grade. Double distilled water was used as solvent in the experiment.

2.2 Preparation of ZnO powder

ZnO powder was prepared by adding 200 mL of 0.1 M NaOH drop wise into 200 mL of 0.05 M zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) under continuous stirring of 2 hours and lead to the formation of white gel which was then kept at room temperature for 12 hours to complete precipitation. The precipitate was collected and dried in a hot air oven at 60 ^oC for 4 hours. This prepared powder was used for the polymer preparations.

2.3 Preparation of Mn^{2+} doped ZnO-PVA polymer

0.005 gms of ZnO was added to 1 gm of PVA and volume of the solution was completed to 20 ml by double distilled water. Then 0.01 mol % of MnO was added to the solution. After that the solution was warmed up to 50 ^oC and stirred for 2 hours until viscous transparent solution was obtained. Then the solution was poured in to a Petri dish and left for 1 or 2 days at room temperature to dry. After the solvent evaporation, a thin film containing Mn^{2+} doped ZnO-PVA polymer was obtained. Now the prepared polymers are ready for measurement of physical parameters and further characterizations like FT-IR, Optical absorption and TG-DTA etc.

2.4 Characterization Techniques

In the present investigation Atago NAR-4T Abbe's Refractometer is used to measure the refractive index. Density values are observed with Vibra HT/HTR density measurement kit. JASCO V-670 UV-VIS-NIR Spectrophotometer is used to record optical absorption spectra for the prepared samples. Shimadzu IR Affinity 1S Spectrophotometer in the region 650-4000 cm^{-1} using HATR accessories is used for the FT-IR spectrum. TG-DTA analysis of the prepared polymer was recorded on Shimadzu DTG 60H instrument.

3 Results and Discussion

3.1 Physical Parameters

The physical properties of the Mn^{2+} doped ZnO-PVA polymer can be investigated by measuring their basic physical parameters like density and refractive index. The density and

refractive index are most important parameters for calculating the other parameters such as optical dielectric constant, electronic polarizability, elastic property, thermal conductivity, molar refractivity, ionic concentration, Inter-ionic distance and polaron radius etc. The physical transport properties of semi conducting materials are very interesting and provide useful information regarding the structure and conduction mechanism.

The dielectric constant (ε) can be calculated by knowing the refractive index [16]

$$\varepsilon = n_d^2 \quad (1)$$

The reflection loss can be computed from refractive index using Fresnel's formula [17]

$$R = [(n_d-1)/(n_d+1)]^2 \quad (2)$$

The molar refractivity R_m can be calculated by using [18]

$$R_m = [(n_d^2 - 1)/(n_d^2 + 2)]\ M/D \quad (3)$$

Where M is the average molecular weight and D is density in g/cc.

The electronic polarizability α_e can be expressed as [19]

$$\alpha_e = 3(n_d^2 - 1)/4\pi N\ (n_d^2 + 2) \quad (4)$$

Where N is the number of transition metal ions per unit volume.

The inter-ionic separation and polaron radius can be determined as [20]

$$r_i = (1/N)^{1/3} \quad (5)$$

$$r_p = (1/2)\ [\pi/6N]^{1/3} \quad (6)$$

using above equations different physical parameter values of the Mn^{2+} doped ZnO-PVA polymer are evaluated and tabulate in table 1.

Table.1 Physical parameters of Mn^{2+} doped ZnO-PVA polymer

S.No	Physical parameter (units)	Evaluated values
1.	Average molecular weight(gm/mol)	1.0049
2.	Density (ρ)(gm/cm^3)	1.4974
3.	Refractive index(μ)($\pm$0.001)	1.6485
4.	Optical dielectric constant(ε)($\pm$0.005)	2.7176
5.	Reflection loss	5.9000
6.	Molar refractivity(R_m) (cm^{-3})	0.2737
7.	Ion concentration (N) (10^{22} ions/cm^3)	1.4686
8.	Electronic polarizability (α_e) (10^{23} ions/cm^3)	1.4726
9.	Inter ionic distance(r_i)(Å)($\pm$0.005)	8.7976
10.	Polaron radius(r_p)(Å)($\pm$0.005)	90.5958

3.2 FT-IR studies: Fourier transform infrared spectroscopy (FT-IR) is one of the most powerful technique to investigate a multi-component system,

such as polymer film. FT-IR is used to characterize the functional groups of Mn^{2+} doped ZnO-PVA polymer. Fig. 1 shows FT-IR Spectrum of Mn^{2+} doped ZnO-PVA polymer in the range of 650-4000 cm^{-1}. The spectrum of the sample shows some strong bands in the region 700 to 1500 cm^{-1} (783, 973, 1212) corresponding to the characteristic peaks of PVA [21]. The band at 2343 cm^{-1} is due to C=O Stretching mode [22]. The band observed at 1361 cm^{-1} is assigned as CH_2 deformation [23]. In the spectrum of ZnO-PVA polymer, the broad band at 2945 and 1460 cm^{-1} are assigned to the stretching and bending vibrations of C-H group [24]. The peak at 1749 cm^{-1} arises from the OH stretching mode is due to H_2O on ZnO vibration while the band at 886 cm^{-1} results from CH_2 rocking vibration. The Peaks at 3801 and 3714 cm^{-1} may be attributing to stretching of O-H bonding.

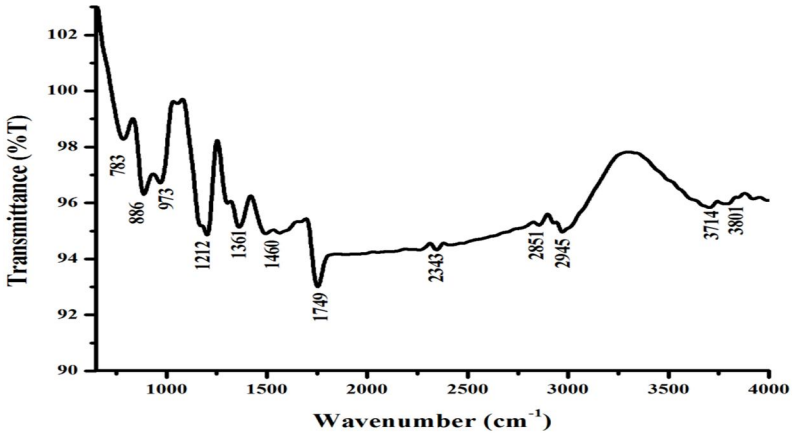

Fig. 1 FT-IR spectrum of Mn^{2+} doped ZnO-PVA polymer

Table 2 FT-IR Band assignments of Mn^{2+} doped ZnO-PVA polymer

Vibrational Frequency (cm^{-1})	Band assignment
3801, 3714	stretching of O-H bonding
2945	stretching mode of C-H
2343	C=O Stretching mode
1749	OH stretching mode is due to H2O
1460	bending vibrations of C-H group
1361	deformation of CH_2
886	CH_2 rocking vibration
1212, 973, 783	characteristic PVA bands

3.3 UV-Vis absorption studies

UV–Visible absorption spectroscopy is a widely used technique to examine the optical transitions, electronic band structures of Mn^{2+} doped ZnO-PVA polymer were recorded over the range 200–1000 nm as shown in Fig. 2.

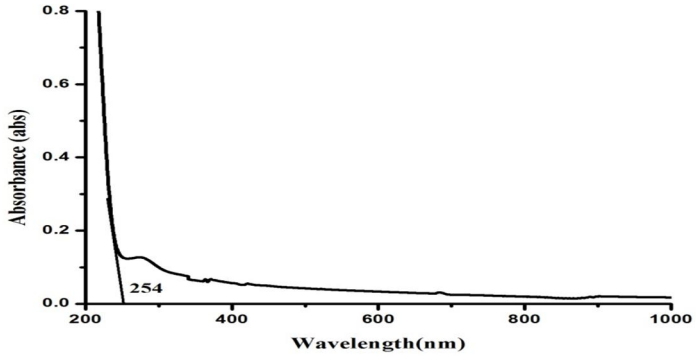

Fig. 2 Optical absorption spectrum of Mn^{2+} doped ZnO-PVA polymer

The absorption coefficient $\alpha(\nu)$ is a function of photon energy for direct and indirect transitions can be defined as [25]

$$\alpha(\nu) = B(h\nu - E_{opt})^n / h\nu \quad (7)$$

Here n = ½ for spin allowed transitions, B is a constant and E_{opt} is direct optical band gap. Here n = 2 for spin allowed transitions and E_{opt} is the indirect optical band gap. Here n = 3/2 for spin forbidden transitions, B is a constant and E_{opt} is direct optical band gap. Here n = 3 for spin forbidden transitions and E_{opt} is the indirect optical band gap. Fig. 2 shows optical absorption spectrum of Mn^{2+} doped ZnO-PVA polymer. Here the absorption edge is found at 254 nm. Plots drawn for $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$ vs $h\nu$ are shown in Fig. 3 and Fig. 4. The optical band gap energy is obtained by extrapolating the linear region of the curve to the $h\nu$ axis.

The theoretical band gap energy can be calculated using the formula

$$E_{opt} = hc / \lambda \quad (8)$$

From the above expressions the theoretical bandgap energy of Mn^{2+} doped ZnO-PVA polymer is determined to be 4.88 eV which lies between pure PVA (6.27eV) and ZnO (3.23 eV). From the graphs the direct optical band gap is evaluated to be 5.31 eV while in indirect optical band gap it is 4.74 eV. The absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$ in accordance with the empirical relation [26].

$$\alpha(\nu) = \alpha_0 \exp(h\nu / \Delta E) \quad (9)$$

Here α_0 is a constant, ΔE is Urbach Energy, which indicates the width of the band tails of the localized states and ν is the frequency of the radiation. Urbach energies (ΔE) are calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy regions of the curves.

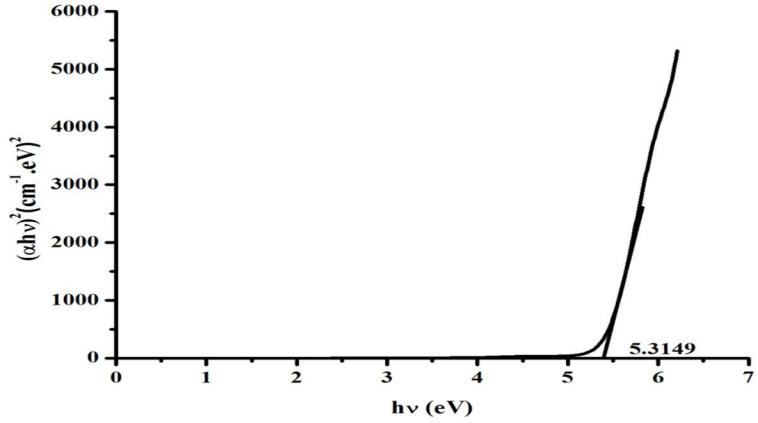

Fig.3 Direct band gap energy plots of the Mn^{2+} doped ZnO-PVA polymer

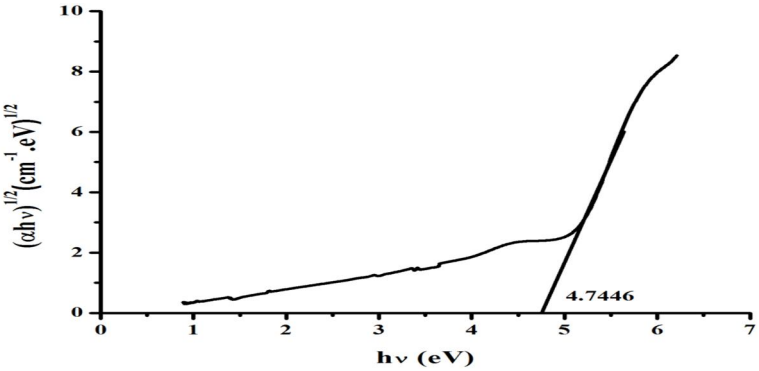

Fig.4 Indirect band gap energy plots of Mn^{2+} doped ZnO-PVA polymer

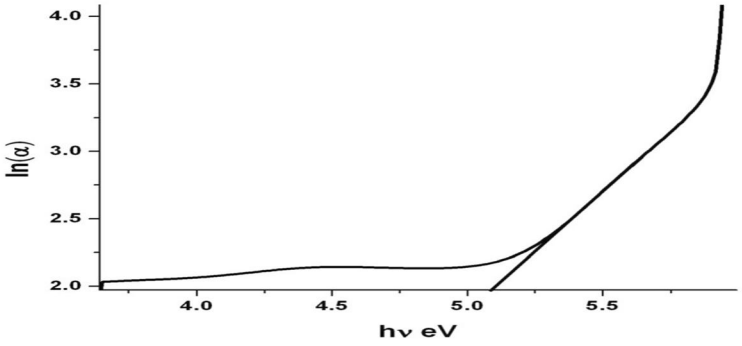

Fig.5 Urbach Energy plots of Mn^{2+} doped ZnO-PVA polymer

Optical band gap energy of a system is maximum, where its Urbach energy is minimum and vice versa. Smaller is the value of Urbach energy greater the structural stability of the polymer system. It also shows the structural disorder of the system.

From the graph (Fig. 5) the Urbach energy ΔE is evaluated as 0.1966 eV which is small means it has greater stability.

3.4. TGDTA analysis

Thermal behavior of Mn^{2+} doped ZnO-PVA polymer was performed at a heating rate of 10 ºC min^{-1} under nitrogen atmosphere, the possible gravimetric and thermal changes were investigated by TGA and DTA as shown Fig. 6.

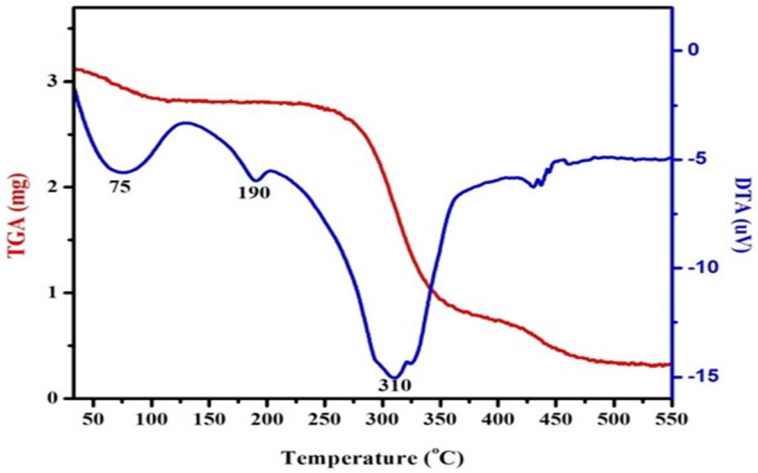

Fig.6 TG-DTA of Mn^{2+} doped ZnO-PVA polymer

On the DTA curve there are four endothermic peaks were observed. The first endothermic peak is at 75 ºC due to the evaporation of water and corresponding weight loss is 10%. On the DTA curve the second endothermic peak at 190 ºC and the corresponding weight loss is 1% is due to the melting of substance. The major weight loss (61%) is observed between 274 to 352 ºC is due to the surface hydroxyl groups on the ZnO surface that catalyze the thermal degradation of polyvinyl alcohol.

4. Conclusion

In summary, Mn^{2+} doped ZnO-PVA polymer was synthesized by chemical method. The various physical parameters like density, refractive index, Molar volume, Average molecular weight, molar refractivity of the Mn^{2+} doped ZnO-PVA polymer were evaluated. From optical absorption edge, optical bandgap energies both direct and indirect band gap energies and Urbach values are evaluated. The direct and indirect bandgap energy values are well agreed with the theoretical value obtained from absorption edge. The Urbach energy value confirms the structural stability of the Mn^{2+} doped ZnO-PVA polymer. FT-IR spectrum exhibited different bands related to the presence of functional vibrational bands of carbo hydroxyl groups, OH stretching mode due to H_2O vibrational modes and characteristic PVA bands. TG-DTA analysis gives the weight loss of Mn^{2+} doped ZnO-PVA polymer with respective to temperature and its thermal decomposition.

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