PVA/Gd₂O₃@Zno Nanocomposite Films as New Uv-Blockers: Structure and Optical Revelations

H.S Vedhavathi

JSS Science and Technology University

Divya U S

JSS Science and Technology University

Madhukar B S

JSS Science and Technology University

Pradeep Reddy Vanga

Vel Tech Rangarajan Dr. Saguntala R & D Institute of Science and Technology

Kumara Swamy N (✉ kumaryagati@gmail.com)

JSS Science and Technology University

Research Article

Keywords: UV-blockers, optical conductivity, energy band gap, refractive index, finess coefficient, extinction coefficient

Posted Date: November 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1089043/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Journal of Inorganic and Organometallic Polymers and Materials on January 21st, 2022. See the published version at

<https://doi.org/10.1007/s10904-022-02231-1>.

PVA/Gd₂O₃@ZnO Nanocomposite Films as New UV-Blockers: Structure and Optical Revelations

Vedhavathi H.S¹ · Divya U S¹ · Madhukar B.S¹ · Pradeep Reddy Vanga² · Kumara Swamy N^{1,*}

¹Department of Chemistry, JSS Science and Technology University, Mysuru- 570 006, India

²Department of Physics, Vel Tech Rangarajan Dr. Saguntala R & D Institute of Science and Technology, Chennai-600 062, India

Corresponding Author:

E-mail:kumaryagati@gmail.com

Phone: +91-9741027970

Abstract

Herein we have synthesised Gadolinium oxide doped Zinc oxide (Gd₂O₃@ZnO) by solution combustion method and incorporated it as a nanofiller into Polyvinyl alcohol (PVA) polymer matrix using solution intercalation technique to get PVA/Gd₂O₃@ZnO nanocomposite film. The X-ray diffraction (XRD), Scanning electron microscopy (SEM), Differential scanning calorimetry (DSC) and UV-Vis spectroscopy were used to investigate the structural, morphological, glass transition temperature and optical properties of synthesized nanocomposites respectively. The optical properties of PVA/Gd₂O₃@ZnO film shows the interaction of –OH groups in PVA and dopant. From DSC, it is clear that T_g of prepared nano composites increases with increasing in dopant concentration. XRD analysis showed that the crystalline characteristics of the nanocomposites increases with increase in dopant concentration. The UV-Visible spectra reveals that there is decrease in indirect band gap of PVA from 4.94 eV to 3.12 eV and direct band gap from 4.90 eV to 3.03 eV compared to pristine PVA Gd₂O₃@ZnO doped nanocomposite films showed multifold enhancement in optical characteristics such as refractive index of PVA doped nanocomposites compared to pristine PVA, optical conductivity, finess coefficient, extinction coefficient on increasing in dopant concentration (0%, 2%, 4%, 6% and 8wt%). The optical characteristics of PVA/Gd₂O₃@ZnO nanocomposite films show excellent UV-blocking behaviour suggesting that, they are promising materials for optical devices.

Key words: UV-blockers · optical conductivity · energy band gap · refractive index · finess coefficient · extinction coefficient

1 Introduction

Polymer nanocomposites are of special interest in photonics and optoelectronics because of their superior potential to exploit unique material features resulting from the synergistic combination of nanoinclusions, opto-electrical effectiveness and amazing processability. The discovery of compounds with fascinating material properties frequently leads to new research paths and finally new technology. Polymer nanocomposite technology is one such area, which uses the unique material properties resulting from size-dependent material features to design/develop and produce materials with specific physicochemical qualities [1]. Polymer-encapsulated transparent semiconducting inorganic nanofillers have piqued scientists and engineers interest as sophisticated technological materials in recent years, particularly in the fields of photonics and optoelectronics [1–6]. Because of their outstanding heat stability and filler-dependent refractive index, polymer nanocomposites are widely used in optical storage applications. These multifunctional advanced materials make use of filler-specific optoelectrical characteristics as well as good matrix processability for photonics and optoelectronics applications. However, the size of the utilised filler and its uniform distribution inside the polymer matrix are the main aspects to be addressed for optimal harnessing of features coming from a synergistic combination of filler matrix interface. High dielectric polymeric materials with strong dispersion capacities have long been recognised as excellent host matrices for metallic and semiconductor materials [7–9].

PVA (polyvinyl alcohol) has been the most widely used water-soluble polymer in a variety of applications. PVA with high dielectric strength, great thermal stability, excellent chemical stability, hydrophilic, non-toxic, superior storage capacity, and dopant-dependent physical properties all have a significant impact [10]. The addition of a dopant to the polymer matrix can alter the characteristics of the polymer (PVA), allowing it to be employed for more advanced applications. PVA has a wide range of technological, pharmacological and biological uses. The selection of polymer-metal nanoparticles combinations, controlling particle size, concentration and distribution within the polymer matrix effectively protect the nanoparticles from aggregation and so on are key points for their application in optoelectronic, electrical and optical devices, biomedical science, sensors and so on [11].

Due to their broad uses in opto-electronics and spintronics, zinc oxide materials have fascinated the whole world. Furthermore, the piezoelectric and crystal-clear conducting properties, ZnO member II–VI has an exclusive position among the semiconducting oxides. ZnO is a semiconductor with a wide bandwidth thickness of 3.37 eV at the room temperature and a large

exciton binding energy of ~60 meV. This extends the application from thermal energy (25 meV) to light-emitting and laser diode applications [12]. Doped ZnO, on the other hand, can have a wide range of characteristics when compared to pure ZnO. Group III elements, including as Ga, Al, and In, which can be utilised as n-type dopants in ZnO, have long been known to affect the material's optical and electrical properties [13]. Rare earth elements, such as Ce, Er, Eu, La, Tb, Tm, Yb, and Dy as p-type dopants in ZnO, have also piqued interest due to their distinctive optical properties, which result in high emission peaks in the visible and near infrared range [14]. As a result, doping can be used to change the electrical conductivity, type of conduction and band gap range of the nanomaterial, as well as its magnetic properties. As a result, the doping effect can improve ZnO's current qualities while also allowing for new uses. Several investigations of nanoparticles have recently been published using ions doped in various oxide matrices. In the visual range, these nanomaterials have a luminescence feature. Intra and inter electronic transitions were found to be responsible for the optical characteristics of nanoparticles [15].

The rare earth ion gadolinium (Gd) is the most common metal. Gd has the most effective paramagnetic property, which alters the properties of magnetic resonance imaging. However, MRI has not been used to its full potential in cancer treatment, maybe due to its small size (false-positive rate of 10% for breast cancer). The distinctive features, on the other hand, were corrected using a cell identifier to improve MRI detection in small numbers [16]. Due to emission quantum yields, the luminescence intensity is increased. In linked to a reduced crystal symmetry around the Gd ion, which is obtained through the use of nanoparticles or metal doping of the surface shell. The core of the doubly luminous nanoparticles is encased in a polysiloxane shell [17]. Compared to the covered or closed shell, nano-particles increase the luminescence properties. The doping of nano-grown ions in alkaline metals (Li, Na, K) increases luminescence over the quantifying ion level [18-19]. The intensity of the luminescence in the visible region increases by doping Zn ion.

In this study, we describe the synthesis of PVA/Gd₂O₃@ZnO nanocomposite films utilising the solution casting method, as well as several characterizations of these nanocomposite films for better understanding the changes in optical properties of the PVA after inclusion of nanoparticles.

2 Experimental section

2.1 Materials and Methods

The following materials were utilised to synthesize Gd₂O₃@ZnO nanoparticles: Gadolinium nitrate crystal [Gd(NO₃)₃] from Alfa Aesar, zinc nitrate [Zn(NO₃)₂] as a starting material, glycine [NH₂CH₂COOH] as a fuel, and PVA from S.D. fine chemicals. The compounds listed above are of

analytical grade and were used without being further purified, and all of the solutions were made with double distilled water. Solution combustion and solution intercalation methods are used to make Gd₂O₃@ZnO and PVA nanocomposites. Scanning electron microscope EM JSM-IT300LV (Japan), was used to analyse the morphological characteristics of the nano particles and nanocomposites. Powder X-ray diffractometer PROTO-AXRD, (Canada) is used to confirm the physical attributes of the synthesised Gd₂O₃@ZnO and PVA nanocomposite films, such as structure, crystallinity, and lattice planes.

2.2 Synthesis of Gd₂O₃@ZnO nanoparticles

The Gd₂O₃@ZnO was synthesised via eco-friendly solution combustion method. When compared to alternative ways, this strategy saves time and energy [1]. The stoichiometric amounts of respective metal nitrates (Gadolinium nitrate and Zinc nitrate) and fuel (glycine) were weighed and dissolved in required amount of distilled water on a magnetic stirrer with hot plate in an alkaline media [1]. The reaction mixture was continuously heated on hot plate, the water vapours and nitric gasses were discharged, and as a result the gel is formed. Reaction was completed by self-combustion, after few minutes, gel leaving behind fine powder. The powder was calcinated at 600°C using a muffle furnace to get nanoparticles.

The reactions involved in the formation of Gd₂O₃@ZnO is presented below [20]:

2.3 Fabrication of PVA/ Gd₂O₃@ZnO nano composite films

Fabrication of water-soluble polymer nano-composites by using environmental friendly solution intercalation method. 7.5 wt% of PVA solution was prepared by using calculated amount of PVA and distilled water under constant stirring for 2hr at 90°C [1]. The above prepared PVA solution were employed to fabricate films of various weight percentages Gd₂O₃@ZnO of PVA viz 0, 2, 4, 6 and 8 wt % of Gd₂O₃@ZnO. The various concentrations of Gd₂O₃@ZnO were dispersed in PVA solution by ultra-sonication at room temperature for 90 min to get uniform distribution in PVA matrix. The obtained uniformly distributed mixture were poured on clean mould of same dimension and dried at room temperature followed by annealing at 60°C for 2hr. The prepared films thickness varied from 0.27mm to 0.36mm.

3 Results and discussions

3.1 X-ray diffraction studies

Fig. 1 and 2 shows the XRD diffractograms of pristine PVA, Gd₂O₃@ZnO nanoparticle and PVA nanocomposites with 2, 4, 6 and 8 wt% of Gd₂O₃@ZnO. Fig. 1 indicates the hexagonal phase of Gd₂O₃ doped ZnO contains peaks centered at the 2θ values of 28.57, 31.80, 33.10, 34.45, 36.29, 42.64, 47.54, 56.55, 62.91, 67.96 corresponds to the (222), (100), (400), (002), (101), (521), (541), (640) and (200) planes respectively [JCPDS card no.36-1451] [21]. The XRD observation reveals diverse patterns of single phase PVA structure with successful Gd₂O₃@ZnO substitutes. Because of their high crystallinity, the produced nanoparticles showed a strong and sharp peak.

In Fig. 2, multiple strong peaks can be detected in the X-ray profile. All the graphs shows the intense peak around the 2θ =19.5° with d spacing at 4.49 Å [22, 23], which attributes for the amorphous nature of PVA coming from the intermolecular interaction between the PVA chains by hydrogen bonding [1]. When the PVA is doped with different concentration of Gd₂O₃@ZnO, the crystallinity increases with increasing in Gd₂O₃@ZnO concentration. Debye- Scherer's equation used to compute the average crystalline size [12].

$$L = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where L denotes the crystalline size, λ is incident wavelength, β is FWHM, and θ is glancing angle [13]. The computed crystalline size of all nanocomposites is displayed in the Table1. This table depicts that the introduction of Gd₂O₃@ZnO causes the formation of oxygen vacancies, which causes the lattice properties to decrease [12]. Incorporation of Gd₂O₃@ZnO into PVA also suppresses the agglomeration phenomena among Gd₂O₃@ZnO nanoparticles and results in increasing crystalline size.

3.2 Differential scanning calorimetry

The changes in melt properties of PVA caused by the addition of nanofiller were determined using DSC measurements. The DSC thermograms of fabricated PVA/Gd₂O₃@ZnO nanocomposite films are shown in Fig. 3a, and the melt properties upon addition of Gd₂O₃@ZnO and are listed in Table 2. The T_g value of pristine PVA increases from 93.1°C to 132.1°C (8 wt% of nanocomposite films) due to a significant interaction between the functional group of PVA and nano fillers, which restricts the polymer chains segmental mobility [1]. Fig. 3b reveals the inter correlation of the crystallinity and T_g values. When the concentration of dopants increases, the crystallinity and T_g values increases due to the interaction between –OH group of PVA and dopants.

3.3 Surface morphological studies

SEM was used to examine the degree of dispersion and compatibility of metallic nanofiller with PVA. SEM photomicrographs of PVA films with $\text{Gd}_2\text{O}_3@\text{ZnO}$ concentrations of 0, 2.0, 4.0, 6.0, and 8.0 wt% of PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films as shown in Fig. 4. Because of the aggregation of nanoparticles of varied sizes, SEM photomicrographs of nanocomposite films show that it has a porous agglomerated a spherical like structure. Which reduce individual nanoparticles high surface energy. The presence of -OH groups in the polymeric backbone may explain the good uniform dispersion of nanofillers in PVA matrix. Furthermore, the good adhesion and strong interfacial bonding between $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanofillers and PVA matrix OH groups allows for the improved physical interaction between the PVA matrix and filler $\text{Gd}_2\text{O}_3@\text{ZnO}$ interface, resulting in superior dispersion in the polymer matrix [1]. The nanoparticles are distributed equally throughout the PVA matrix, as seen in different resolutions of 20, 10, 3, 2, and 1 μm [22, 23].

Fig. 5 shows the EDAX spectra of PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films confirm the presence of proper ratio of dopant and sample chemical homogeneity [22, 23]. This spectra identifies the presence of all elemental components such as Zn, Gd, O in $\text{Gd}_2\text{O}_3@\text{ZnO}$ doped PVA films.

3.4 Optical properties

3.4.1 Uv-visible spectral studies

Diffused reflectance spectroscopy is employed to investigate the optical properties of fabricated pristine PVA and PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films. In the range of 200-800nm, Fig. 6a displays the optical absorbance of pristine PVA and PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films. The absorption maxima for PVA are at 230-250nm in this diagram which illustrates the electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ for the presence of functional groups such as -OH and -CH=CH- groups which are related with ethylene unsaturation [24-27]. In the presence of conjugated polyene double bonds, it functions as an indicator [1]. Doping different concentrations of $\text{Gd}_2\text{O}_3@\text{ZnO}$ (0, 2, 4, 6, 8wt%) with PVA results in additional peaks around 360nm, indicating the formation of charge transfer complexes between the hydroxyls group of PVA and $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanoparticles [28, 29], but no additional peaks between 370nm and 800nm for all nanocomposite films, where absorption gradually decreases and becomes constant due to decrease in incident light energy at higher wavelengths. The absorption spectra of PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films reveal that absorption rises as the concentration of $\text{Gd}_2\text{O}_3@\text{ZnO}$ in the nanocomposite film increases, and it

exhibits red shift when compared to PVA. However, the location of absorption peaks does not change significantly. It is apparent that the PVA matrix has a superior dispersion of all various concentrations of Gd₂O₃@ZnO nanoparticles. The visible area showed good transparency and low absorbance, whereas the UV zone showed strong absorption, indicating that PVA/Gd₂O₃@ZnO nanocomposite films can also be used as UV protective materials.

Fig. 6b illustrates the optical transmittance spectra of PVA/Gd₂O₃@ZnO nanocomposite films with various Gd₂O₃@ZnO nanoparticle concentrations. The transmittance increases as the wavelength increases, but decreases as the concentration of Gd₂O₃@ZnO nanoparticle increases. Because of the layer structure of covalent connections between polymer chains and additives, nanoparticles absorb and scatter incident light, reducing incident light transmission, especially at short wavelengths [30]. The electrons on the outer orbits have migrated up to higher energy levels, taking up positions in vacant energy bands. As a result, it does not allow all of the incident light to pass through. Pure PVA, on the other hand, has no free electron and requires a high-energy photon to enter the conduction band, after which it has a high transmittance [30].

3.4.2 Effect of nano fillers on the absorption coefficient of PVA

Absorption edge is a vital parameter in the fabrication of photo detector. To evaluate the efficacy of employing the PVA/Gd₂O₃@ZnO nanocomposites in photo detectors, absorption co-efficient was calculated which inturn was used to calculate the absorption edge. Fig. 7 shows that absorption coefficient (α) of PVA/Gd₂O₃@ZnO nanocomposites. It was computed using the formula with the values of absorbance (A).

$$\alpha = \frac{2.303}{d} \cdot \log \frac{1}{I_0} = \left(\frac{2.303}{d} \right) A \quad (2)$$

where α is absorption coefficient, A is absorbance and d is thickness of the film. The absorption edge was derived from the plot of absorption coefficient against photon energy by extrapolating the linear portions of the plotted curves. Table 3 shows the absorption edge values for PVA films with varied dopant content concentrations. The absorption edge of pure PVA films is 4.90eV, while for doped PVA films shifted toward lower energy values, with a minimum value of 3.01eV for 8wt % PVA/Gd₂O₃@ZnO nanocomposite films. The shifting of absorption edge from higher wavelength or lower energy may be attributed to the effective dispersion of nanofillers in the PVA matrix [1]. The rise in absorbance towards the absorption edge is obvious, suggesting that the films are of good crystalline quality and therefore more important in the development and design of photo-detectors [31].

3.4.3 Evaluation of optical energy band gap of PVA/Gd₂O₃@ZnO nanocomposites

Using the Wood and Tauc equation [23], one can calculate the optical energy band gap (E_g) of the nanocomposite films from the observed UV retention data.

$$(\alpha h\nu)^{1/m} = B(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical energy band gap, B is proportionality constant, m is used to determine the type of electronic transition and is associated with the appropriation of the thickness of states. The values of m for direct transition are $1/2$ or $3/2$, whereas for indirect transition, m is equivalent to 2 or 3 [32]. From high photon energy to low photon energy, the absorption coefficient varies. Because the energy necessary to transport an electron from the valence band to the conduction band ($h\nu < E_g$) is inadequate, electron transitions are uncommon [30]. The relationship between photon energy and the absorption edge $(\alpha h\nu)^{1/2}$ for casted material is shown in Fig. 9a. The curve is extrapolated to values of $(\alpha h\nu)^{1/2} = 0$ to get indirect allowable gap transition. Table 3 shows the calculated values of the energy band gap of synthesized nanocomposite films.

In Fig. 9a and 9b, it is observed that when the concentration of dopant increases, the optical energy band gap of nanocomposite films decreases, relative to pure PVA. Pure PVA has an energy band gap of 4.90eV and 4.94eV, whereas doped PVA/Gd₂O₃@ZnO nanocomposite films of various concentrations had energy band gaps of 3.12, 3.10, 3.09, 3.03eV and 3.20, 3.17, 3.16, 3.12eV for 2, 4, 6 and 8wt % of films for both direct and indirect allowed transition, respectively (Fig. 8). The shift in band gap toward lower values allows for possible charge transfer coupling between the dopant and polymeric host, resulting in new energy states inside the polymeric band gap and lower energy electronic transitions as shown in Fig. 8 [33]. As shown by decreasing in their electronic band structure and, as a result, enhanced charge conduction, the decreased optical energy band gap also implies increased energy transformation efficiency in fabricated nanocomposite films [33].

3.4.4 Effect of nanofillers on refractive index of PVA

Refractive index [RI] of semiconducting materials has been revealed to have an important influence in both optical and electrical characteristics [34]. High refractive index materials have been shown to capture incident rays which falls on them [35, 36]. Organic solar cells are becoming increasingly important in recent years. The refractive index is crucial in determining how effective solar cells are followed by its efficiency [37]. Organic solar cells on a large scale require a high refractive index, which is well understood. The Fresnel formula was used to determine the RI [32].

$$n = \left(\frac{1+R}{1-R} \right) + \left[\frac{4R}{(1-R)^2} - K^2 \right]^{1/2} \quad (4)$$

where, n is refractive index, R is reflectance, K is extinction coefficient it is calculated by following equation.

$$K = \frac{\alpha\lambda}{4n} \quad (5)$$

The plot of refractive index variation as a function of wavelength is shown in Fig. 10a. Due to net atomic refractions, low density, large surface area, and high absorption co-efficient, the n values increase with increasing nano filler concentration, according to Bhar and Pinto models [1]. High refractive index materials are ideal for optical communication, sophisticated multifunctional applications, and spectrum dispersion device design [32].

3.4.5 Effect of nanofillers on optical conductivity of PVA

Optical conductivity (σ_{opt}) is a characteristic that indicates how electromagnetic waves affect the flow of charge carriers in a substance. This can be accessed from the following equation [38-40]

$$\sigma_{\text{opt}} = \frac{\alpha n c}{4n} \quad (6)$$

where c is the speed of light in a vacuum. The optical conductivity of PVA/Gd₂O₃@ZnO nanocomposite films is shown in Fig. 10b as a function of incident photon energy. Optical conductivity increases as Gd₂O₃@ZnO concentration in the PVA matrix increases, as demonstrated, with a high optical conductivity value for 8 wt%. At lower photon energies, optical conductivity increases somewhat, and at higher photon energies, there is a progressive increase in optical conductivity, followed by a rapid increase in the absorption edge area at $h > 3.5\text{eV}$. This is due to the overabundance of free charge carriers released by the polymer surface [41].

3.4.6 Effect of nanofillers on extinction coefficient of PVA

The extinction coefficient (K) indicates how much energy is lost as an electromagnetic wave travels through a material. It can be calculated using the equation below [39, 40].

$$K = \frac{\alpha\lambda}{4n} \quad (7)$$

where, λ is the wavelength of the incident light. Fig. 11a shows how the extinction coefficient varies with wavelength for different concentrations of PVA/Gd₂O₃@ZnO nanocomposite films. The extinction coefficient is found to drop dramatically in the UV area, especially around 375-475nm due to the absorption of free carriers. The optical loss owing to little absorption or scattering is shown by low extinction coefficient values, which also shows that the

fabricated films have high surface homogeneity [1]. The extinction coefficient increased in the high wavelength area when the $\text{Gd}_2\text{O}_3@\text{ZnO}$ content in the polymer matrix increased due to the increased packing density of the polymer film. This shows that as $\text{Gd}_2\text{O}_3@\text{ZnO}$ concentration rises, the proportion of light lost increases [38]. Low extinction coefficient values indicate that optical loss due to absorption or scattering is minimal, and they also indicate that manufactured films have superior surface uniformity. PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films have a dopant-content-dependent RI, which supports their optoelectronics applications.

3.4.7 Influence of nanofillers on finesse coefficient of PVA

Fig. 11b illustrates the finesse coefficient values against wavelengths at varied concentrations of PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films. F values appear to decline from 280 to 320nm wavelengths before becoming constant. Peak signal position is somewhat altered at the greatest concentration of doping. It denotes that doping causes a little change in the structure of the polymer, and that the finesse coefficient rises as the quantity of doping concentration increases, and that F is dependent on R, as stated in the below equation [30].

$$F = \frac{4R}{(1-R)^2} \quad (8)$$

3.4.8 Evaluation of Urbach energy of PVA nanocomposites

Photon absorption in solids may occur at photon energies less than or equal to the energy gap, $h\nu < E_{\text{opt}}$, due to the presence of tail states in the forbidden gap. The photon energy is related to the absorption coefficient below the optical gap (tail absorption), which follows the Urbach relation, which is calculated by following relationship [1]

$$\alpha = \alpha_0 \exp(E - E_u) \quad (9)$$

where, α_0 is a constant and E_u is Urbach energy is the width of the tails of localized states corresponding to the optical transition between the localized state near to the valence band and the extended state of the conduction band, which is found to be above the mobility edge, is interpreted as the slope of the absorption edge defines the breadth of the localized state, which eventually reveals the structure's ordering. It is often assumed that increasing the concentration of nanofillers bridges the gap between localized states by decreasing the potential barrier and promoting charge carrier transmission. The reciprocal gradient of the linear part of the plot of $\ln(\alpha)$ vs E (Fig. 12) was used to determine the Urbach's energy (E_u) values of PVA nanocomposites, which provides a quantitative measure of defect states. Nanometal oxides cause structural changes in the host PVA matrix when they are incorporated. E_u values are shown to be monotonic with dopant content (Table

4), with a steady increase with dopant level, showing molecular ordering of nanocomposites leading to an increase in the number of charge trapping centers.

4 Conclusion

By using an environmentally friendly solution intercalation method, the $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanofillers were effectively incorporated into a transparent, particle-stabilizing PVA matrix. The XRD studies show a strong connection between the inorganic nano filler and the organic polymeric host, resulting in stable nanoparticle dispersions in hydrophilic polymers and transparent nanocomposites. The DSC studies reveal that the T_g value of pristine PVA increases from 93.1°C to 132.1°C when it incorporated into different concentrations of dopant. The SEM images indicated a homogeneous presence of nanoparticles with some aggregation in the films at higher dopant concentration. The existence of atoms in the right ratios gave additional proof for the sample's purity via the EDAX. The UV-visible absorption studies show a steep absorption in the entire UV region, with absorption maxima ranging from 300-350nm with high transparency in the visible spectrum, indicating that PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ films might be utilized as UV shields. The energy requirements for optical transitions were found to decrease as filler content increased, with a minimum of 3.01 eV for PVA@8 wt % $\text{Gd}_2\text{O}_3@\text{ZnO}$ film. The optical band gap decreases from 4.90eV to 3.01eV and 4.94 to 3.12eV for PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ (0, 2, 4, 6, 8 wt%) reinforcing nanocomposite films for indirect and direct allowed transition, but the refractive index displays typical dispersion behavior, as predicted by Bhar and Pinto. The Refractive index increased as a result of the incorporated fillers Except for the transmittance, the absorbance, absorption coefficient, extinction coefficient, finesse coefficient, refractive index, and reflectance, optical conductivity of $\text{Gd}_2\text{O}_3@\text{ZnO}$ doped PVA films rise as the doping percentages increase. Thus, the opto-electronic characteristics of nanocomposite films may be properly tailored to achieve innovative capabilities by intercalating optimal quantities of metallic and mixed metallic nanofillers without affecting the processing, scalability, or mechanical flexibility of PVA composites and can be applied for various applications. From all the above optical investigations, it was observed that the PVA matrix exhibited improved optical absorption characteristics as well as optical conductivity upon the incorporation of $\text{Gd}_2\text{O}_3@\text{ZnO}$ as a filler. The optical properties of PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ films can easily be tailored to achieve the optical characteristics desired in optical or optoelectronic applications such as UV-blocker material.

References

1. K.S. Nithin, Siddaramaiah., J. Phys. Chem. C 119.35, 20244-20255 (2015).
2. N. Aleshin, Andrey N, L. Elena, Alexandrova, P. Igor, Shcherbakov. J. Phys. D. Appl. Phys. 42.10, 105108 (2009).
3. Beek, J.E. Waldo, M.M. Wienk, A.J. Janssen, Adv Funct Mater 16.8, 1112-1116 (2006).
4. Ma, Wanli, Cuiying Yang, Xiong Gong, Kwanghee Lee, J. Alan. Heeger, Adv Funct Mater. 10, 1617-1622 (2005).
5. S. Sachhidananda, K.S. Nithin, Kumara Swamy, K.N. Shilpa, Jagajeevan Raj Balasamudra Muthuraj, Siddaramaiah, J Lumin . 208, 488-494 (2019):.
6. Wang, Hongmei, Pengfei Fang, Zhe Chen, Shaojie Wang, Appl Surf Sci. 253, 20 8495-8499 (2007).
7. Sun, Yugang, Younan Xia. Adv Mater. 14.11: 833-837 (2002).
8. Z. M. Mbhele, M.G. Salemane, C.G.C.E. Van Sittert, J.M. Nedeljkovic, V. Djokovic, A.S. Luyt, Chem. Mater. 15, 5019–5024 (2003).
9. P. Bhargav, Balaji, B. A. Sarada, A. K. Sharma, VVR Narasimaha Rao, J. Macromol Sci A. 47, 2, 131-137(2009).
10. N. Che Ani, M.Z. Sahdan, N. Nafarizal, S.N. Mohd Tawil, Adv Mat Res. 1133, 424-428 (2016).
11. Cheng, Peng, Lei Fang, Huan Yang, Xiyu Zhu, Gang Mu, Huiqian Luo, Zhaosheng Wang, HaiHu Wen, Sci China Ser G. 51, 6, 719-722(2008).
12. Aggarwal, Nupur, Kamaldeep Kaur, Ajay Vasishth, N. K. Verma, J Mater Sci-Mater El. 27, 12 13006-13011(2016).
13. Kajal, Priyanka, D. Pooja, Neena Jaggi, Mater Res Express. 6, 065011 (2016).
14. N. Sarip, A.L. Nordin, M.S. Sam, S.A. Kamaruddin, F. Mahmud, S.N. Tawil, M.Z. Sahdan, Appl Mech Mater. 773, 734-738 (2015).
15. A.A. Dakhel, M. El-Hilo, Jpn J Appl Phys. 107.12, 123905 (2010).
16. D.M. Fernandes, J.L. Andrade, M.K. Lima, M.F. Silva, L.H.C. Andrade, S.M. Lima, A.A. Winkler Hechenleitner, E.A. Gómez Pineda, Polym Degrad Stabil. 98, 9, 1862-1868 (2013).
17. T.E. Somesh, M.Q. Al-Gunaid, B.S. Madhukar, Siddaramaiah Basavarajaiah, J. Mater Sci-Mater El, 30(1), 37-49 (2019).
18. Gong, Xinghou, Chak Yin Tang, Ling Pan, Zhonghua Hao, Chi Pong Tsui. Compos Part B-Eng. 60, 144-149 (2014).

19. K. S Hemalatha., K. Rukmani, N. Suriyamurthy, B. M. Nagabhushana. *Mater Res Bull.* 51, 438-446 (2014).
20. Varma, Arvind, Mukasyan, S. Alexander, Rogachev, V. Khachatur, Manukyan. *Chemical reviews.* 116, 23, 14493-14586 (2016).
21. Aggarwal, Nupur, Kamaldeep Kaur, Ajay Vasishth, N.K. Verma, J. *Mater Sci-Mater El.* 27. 12 13006-13011 (2016).
22. Al-Gunaid, Q.A. Murad, M.N. Adel Saeed, Nithin Kundachira Subramani, B. S. Madhukar, Siddaramaiah Basavarajaiah, *J. Mater Sci-Mater El.* 11, 8074-8086 (2017).
23. S.N. Madhuri, K. S. Hemalatha, K. Rukmani. *J. Mater Sci-Mater El.* 30.9, 9051-9063 (2019).
24. Al-Gunaid, Q.A. Murad, M.N. Adel Saeed, H.M. Gayitri, Siddaramaiah Basavarajaiah, *Poly-Plast. Tech. Maters.* 59, 5, 469-483 (2020).
25. Al-Gunaid, Q.A. Murad, M.N. Adel Saeed, Siddaramaiah Basavarajaiah, *J. Appl Polym Sci* 135.8, 45852 (2018).
26. Roohani, Mehdi, Youssef Habibi, M. Naceur . Belgacem, Ghanbar Ebrahim, Ali Naghi Karimi, Alain Dufresne *Eur, Polym, J.* 44, 8, 2489-2498 (2008).
27. Samir, My Ahmed Said Azizi, *Polym,* 45.12, 4149-4157 (2004).
28. Rao, Chintamani Nagesa Ramachandra. *Ultra-violet and visible spectroscopy.* Butterworth, 1975.
29. A. Wasan, T, Mohammed, K. Tagreed, *J. Baghdad Sci.* 8, 543–550 (2011).
30. Mustafa, A. Faisal, *Phys Sci Res. Int* 1. 1, 1-9 (2013).
31. S. Shivanna, N.K. Subramani, K. Swamy, S.K. Nagaraj, J.R. Muthuraj, H. Siddaramaiah, *J. Lumin.* 208, 488-494 (2019).
32. O.G. Abdullah, S.B. Aziz, K.M. Omer, Y.M. Salih, *J. Mater Sci-Mater El.* 26(7), 5303-5309 (2015).
33. H.Wang, P. Fang, Z. Chen, S. Wang, *Appl. Surf. Sci.* 253, 8495–8499 (2007).
34. H.S. Bolarinwa, M.U. Onuu, A.Y. Fasasi, S.O. Alayande, L.O. Animasahun, I.O. Abdulsalami, O.G. Fadodun, I.A. Egunjobi, *Journal of Taibah University for Science.* 1;11(6),1245-58 (2017).
35. N. Baydogan, T. Ozdurmusoglu, H. Cimenoglu, A.B. Tugrul, *Defect Diffus Forum.* 334, 290-293 (2013).
36. M Ma, F.W. Mont, X. Yan, J. Cho, E.F. Schubert, G.B. Kim, C. Sone, *Opt Express,* 12,19(105), A1135-40 (2011).

37. S.B. Aziz, H.M. Ahmed, A.M. Hussein, A.B. Fathulla, R.M. Wsw, R.T. Hussein, J. Mater. Sci. Mater. Electron. 26(10), 8022-8 (2015).
38. O.G. Abdullah, S.B. Aziz, K.M. Omer, Y.M. Salih, J. Mater Sci-Mater El, 1, 26(7), 5303-38 (2015).
39. Abdullah, Omed Gh, B. Shujahadeen. Aziz, M. Khalid . Omer, M. Yousif. Salih, J. Mater Sci-Mater El. 26, 7, 5303-5309 (2015).
40. Soliman, S. Tarek, A.M. Rashad, A. Ismail Ali, I. Sabah, Khater, I. Shimaa . Elkalashy, Phys Status Solidi. 217, 19, 2000321 (2020).
41. M.B Mohamed, M.H. Abdel-Kader, Appl. Phys. A. 125(3):1-1 (2019).

Figure Legends

Fig. 1 XRD spectra of pure $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanoparticles

Fig. 2 a XRD spectra of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite with different composition,

b XRD spectra of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite with different compositions from 2θ 15 to 24°

Fig. 3 a DSC thermograms of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films, **b** Plot of crystallinity and $T_g(^{\circ}\text{C})$ vs wt% of $\text{Gd}_2\text{O}_3@ \text{ZnO}$ in PVA nanocomposite films

Fig. 4 SEM image of (a) $\text{Gd}_2\text{O}_3@ \text{ZnO}$, PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films with 0 (b), 2 (c), 4 (d), 6 (e) and 8 (f) wt% of $\text{Gd}_2\text{O}_3@ \text{ZnO}$.

Fig. 5 EDAX of (a) PVA & (b) 8 wt % PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite film

Fig. 6 a UV-Vis absorbance spectra, **b** Transition spectra of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films (0, 2, 4, 6, 8 wt%)

Fig. 7 Absorption coefficient as a function of photon energy of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films

Fig. 8 Energy (E)-Wave vector (k) diagram showing variation in optical band gap energies of PVA and PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$

Fig. 9 a Allowed direct band transitions, **b** Allowed Indirect band transitions for PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films (0, 2, 4, 6 and 8 wt%)

Fig. 10 a Refractive index dispersion and **b** Optical conductivity of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films

Fig. 11 a Extinction coefficient and **b** Finess coefficient of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films

Fig. 12 Urbach energy of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films

Title of Tables

Table 1 The structural parameters of PVA/Gd₂O₃@ZnO nanocomposite films at corresponding to 2θ max

Table 2 Thermal functionalities of PVA/Gd₂O₃@ZnO nanocomposite films obtained from DSC thermograms

Table 3 Calculated optical energy

Table 4 Calculated optical parameters

Figures

Figure 1

XRD spectra of pure Gd₂O₃@ZnO nanoparticles

Figure 3

a DSC thermograms of PVA/Gd₂O₃@ZnO nanocomposite films, b Plot of crystallinity and Tg(°C) vs wt% of Gd₂O₃@ZnO in PVA nanocomposite films

Figure 4

SEM image of (a) Gd₂O₃@ZnO, PVA/Gd₂O₃@ZnO nanocomposite films with 0 (b), 2 (c), 4 (d), 6 (e) and 8 (f) wt% of Gd₂O₃@ZnO.

Figure 5

EDAX of (a) PVA & (b) 8 wt % PVA/Gd₂O₃@ZnO nanocomposite film

Figure 6

6 a UV-Vis absorbance spectra, b Transmittance spectra of PVA/Gd₂O₃@ZnO nanocomposite films (0, 2, 4, 6, 8 wt%)

Figure 7

Absorption coefficient as a function of photon energy of PVA/ $\text{Gd}_2\text{O}_3@\text{ZnO}$ nanocomposite films

Figure 8

Energy (E)-Wave vector (k) diagram showing variation in optical band gap energies of PVA and PVA/Gd₂O₃@ZnO

Figure 9

a Allowed direct band transitions, b Allowed Indirect band transitions for PVA/Gd₂O₃@ZnO nanocomposite films (0, 2, 4, 6 and 8 wt%)

Figure 10

a Refractive index dispersion and b Optical conductivity of PVA/Gd₂O₃@ZnO nanocomposite films

Figure 11

a Extinction coefficient and b Finess coefficient of PVA/Gd₂O₃@ZnO nanocomposite films

Figure 12

Urbach energy of PVA/ $\text{Gd}_2\text{O}_3@ \text{ZnO}$ nanocomposite films