

Research Article

Influence of Erbium Ions on the Optical and Structural Properties of Polyvinyl Alcohol

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Polyvinyl alcohol (PVA) films doped with erbium chloride (ErCl_3) have been prepared by casting from their aqueous solutions. The structure of the doped samples as well as the interactions between the host PVA and Er^{+3} was investigated using FTIR spectroscopy. The optical measurement was recorded at room temperature in the range from 200 nm to 2000 nm. FTIR measurements revealed that Er^{+3} forms complex configuration within the PVA structure. PVA doped with 9 wt% of ErCl_3 exhibits energy gap and refractive index of 5.1 eV and 1.72, respectively. The effect of the doping increment of ErCl_3 on the optical parameters has been discussed.

1. Introduction

Rare earth doped polymers are being widely used for many technological and biological applications. They have been greatly stimulated by their potential use as biosensors, bio-probes, electroluminescent displays, LED diodes, and lasers [1, 2]. Many attempts are being made to dope rare earth ions in polymeric materials and study their structural, dielectric, and optical properties. PVA is a semicrystalline polymer and its crystalline index depends on the synthetic process and physical aging [3, 4]. PVA is also a nontoxic and water soluble polymer. It has a strong film forming ability with very high dielectric strength, good charge storage capacity, high mechanical tensile strength, and optical properties [5, 6]. Doping of transition metal salts into permanently polarized vinyl polymers like PVA in a multiphase system can induce pronounced changes in various properties of complexes [7]. It is reported that Nd, Sm, Gd, and Er are monohydroxides which can form hydroxo complexes within the polymer solution [8]. The hydroxyl (OH) groups of PVA are attached to every second carbon atom in the carbon backbone of the long chain molecule. Hydroxyl functional groups can form

complexes with the lanthanides cations into their polymer network structure [9]. Rare earth complexes were integrated into polymer matrix with van der Waals force or weak static effects [10].

These complexes can be expected to exhibit more effective properties because each dispersed complex molecule is a luminescent unit. So the transparency interfacial interactions between the rare earth luminescent species and the polymer matrix are primary factors determining the total luminescent behavior of the rare earth polymer composites [11]. The most suitable molecular structures of the rare earth polymer complexes are shown in Figure 1. The refractive index of PVA is very useful in optics and photonics due to their ability to increase the light output and also reduce reflection loss [12]. The permanently polarized vinyl polymer will have various changes in its properties when it is doped with a rare earth salt like ErCl_3 [13, 14].

Moreover, rare earth salts have considerable effect on the structural, optical, and thermal properties of many types of polymer [15]. Er^{+3} doped material has attracted a lot of research interest due to its significant optical properties. In its trivalent state, at a wavelength of 1.52 μm , it exhibits

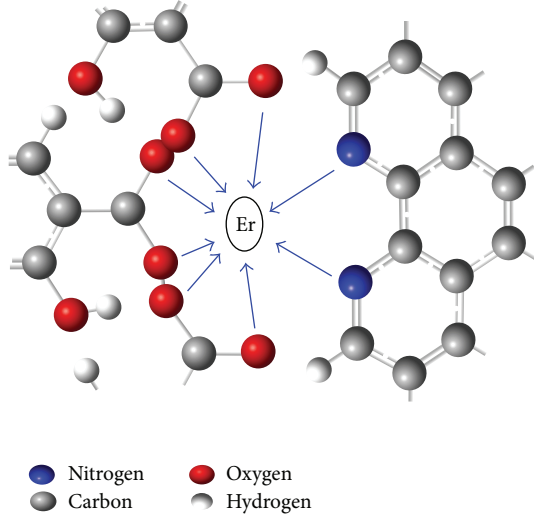


FIGURE 1: Molecular structure of Er-polymer complexes.

a transition from its first excite state $^4I_{13/2}$ to the ground state $^4I_{15/2}$ [16]. When Er^{+3} is mixed with a host solid material, it induces mixing of states. These states will lead to new transitions due to the fact that the partially filled 4f shell is shielded by filled 5s and 5p shell [17].

In this paper, we have synthesized ErCl_3 (1, 3, 5, 7, or 9% wt) doped PVA polymers films. The effect of Er^{+3} ion concentration on the optical properties of PVA sample is investigated.

2. Theoretical Concept

To calculate the energy band gap (E_g) of the PVA samples, first the absorption coefficient (α) can be determined by

$$\alpha = \frac{1}{x} \ln \left(\frac{1-R}{T} \right), \quad (1)$$

where x is the sample thickness and R and T are the measured reflectance and transmittance, respectively. Then, the absorption constant k is given by $k = \lambda\alpha/4\pi$, where λ is the wavelength.

The refractive index n plays a vital role in the optical properties and it follows that [18]

$$n = \frac{(1+R) + \sqrt{4R - (1-R)^2} k}{(1-R)}. \quad (2)$$

To calculate the optical dispersion parameters, single oscillator energy (E_s), and dispersion energy (E_d), we use the proposed model of Wemple and DiDomenico (WDD) [19]. The refractive index is calculated using the single effective oscillator equation:

$$n^2 - 1 = \frac{E_d E_s}{E_s^2 - (h\nu)^2}, \quad (3)$$

where E_s is the single oscillator energy and E_d is the dispersion energy.

The optical parameters such as the refractive index (n_∞) at long wavelengths, the average interband oscillator wavelength (λ_o), and the average oscillator strength (S_o) are given by [20]

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o^2/\lambda^2)}. \quad (4)$$

Equation (4) can be rearranged as

$$\frac{1}{n^2 - 1} = \frac{1}{S_o \lambda_o^2} - \frac{1}{S_o \lambda^2}. \quad (5)$$

By plotting the relation between $1/n^2 - 1$ and $1/\lambda^2$, the slope of the straight line will be $-1/S_o$, while the intersection will be $1/S_o \lambda_o^2$.

Finally, the refractive index n_∞ at long wavelengths follows the relation

$$S_o = n_\infty^2 - \frac{1}{\lambda_o^2}. \quad (6)$$

3. Experimental Techniques

PVA material is obtained from Avondale Laboratories (Banbury, Oxon, England); it has an average molecular weight of 17 000 g/mole. Erbium chloride was obtained from Sigma-Aldrich (Steinheim, Germany). At 80°C with continuous stirring, PVA powder was dissolved in triple distilled water. We maintain the solution at 80°C for 30 min until a clear solution is obtained. At 50°C with continuous stirring, the solution was cooled slowly. ErCl_3 with different concentrations (1, 3, 5, 7, or 9% wt) was dissolved in 0.5–1 mL of concentrated HCl.

By addition of 10 mL of triple distilled water at 50°C, the mixture was diluted with continuous stirring. Then, the mixture was added to the PVA solution at 50°C with continuous stirring of the final mixture for 12 h. The aqueous solution of the mixture was cast into a Petri dish placed on a leveled plate at 35°C for 7 days until the solvent was completely evaporated. The obtained polymer film has 0.08 mm thickness. The optical transmittance and reflectance of the PVA samples have been measured by using a UV-Vis spectrophotometer model V-670 JASCO in the wavelength range of 200–2000 nm. Fourier transform infrared (FTIR) spectra of pure PVA and that doped with 1, 3, 5, 7, or 9 wt% of ErCl_3 were measured using IRPrestige-21 (Shimadzu, Japan). The FTIR spectral wavelength used is in the range from 400 cm^{-1} to 4000 cm^{-1} . The resolution for measuring the optical absorbance is 0.5 cm^{-1} .

4. Results and Discussion

4.1. FTIR Analysis. Infrared spectroscopy is used to identify the interaction of polymer with filler material. It was found that FTIR spectroscopy is very sensitive to the formation of the hydrogen bond [20]. Figure 2 shows FTIR optical absorbance spectra for pure PVA, while Figures 3(a)–3(e) illustrate FTIR for PVA doped with 1, 3, 5, 7, or 9 wt% of ErCl_3 . It is observed that pure PVA undergoes strong bands

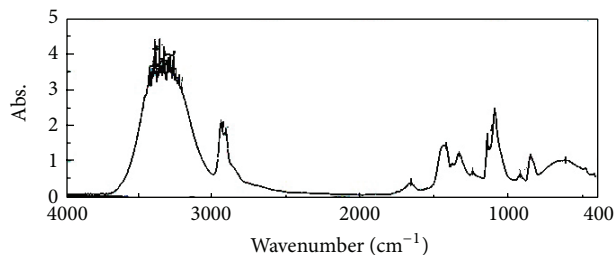


FIGURE 2: Absorption spectra of pure PVA obtained from FTIR in the range 4000–400 cm^{-1} recorded at room temperature. The peaks show the resonance wavenumber of pure PVA.

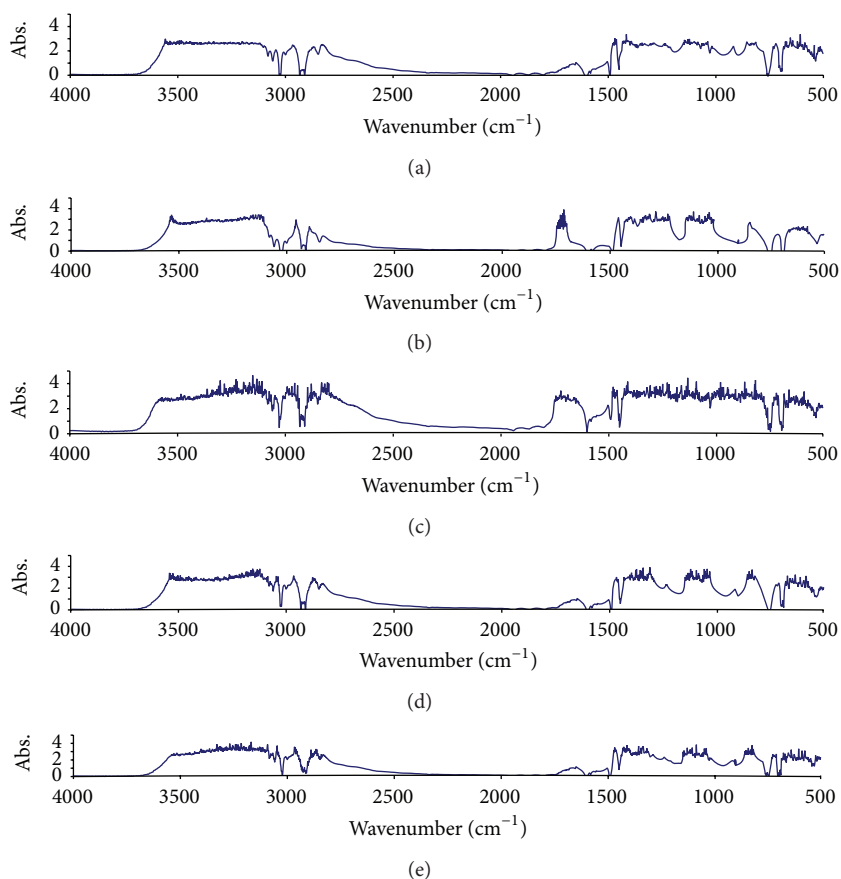


FIGURE 3: (a–e) Absorption spectra of pure PVA obtained from FTIR for PVA doped with ErCl_3 of concentrations 1, 3, 5, 7, or 9 wt%, respectively.

at 3430–3244 cm^{-1} . This band is attributed to OH stretching vibration of OH groups of PVA structure. The bands at 2941 cm^{-1} and 2855 cm^{-1} correspond to asymmetric and symmetric stretching vibration of C–H bond of PVA main chain, respectively. The band corresponding to stretching vibration of the carbonyl groups C=O of PVA ester occurs at 1735 cm^{-1} . The band at 1568 cm^{-1} is assigned to O–H and C–H bending vibrations. The bending wagging of CH_2 vibrations is observed at 1433 cm^{-1} and 1375 cm^{-1} , respectively. Also, C–H wagging is obtained at 1256 cm^{-1} . The band at about 1095 cm^{-1} is due to C–O stretching of acetyl

groups of PVA and the band which is observed at 945 cm^{-1} is assigned to C–O symmetric stretching.

From Figures 3(a)–3(e) it is clear that FTIR bands for lanthanides chlorides doped PVA are not modified drastically. However, it can be observed that the intensity of the peak of C=O band (1735 cm^{-1}) is increased with the increase in ErCl_3 within PVA structure from 1 wt% up to 5 wt%. This can be attributed to the formation of new carbonyl groups within the doped PVA samples. These groups (C=O) are responsible for the degradation and the increase in the amorphous phases within the investigated PVA samples.

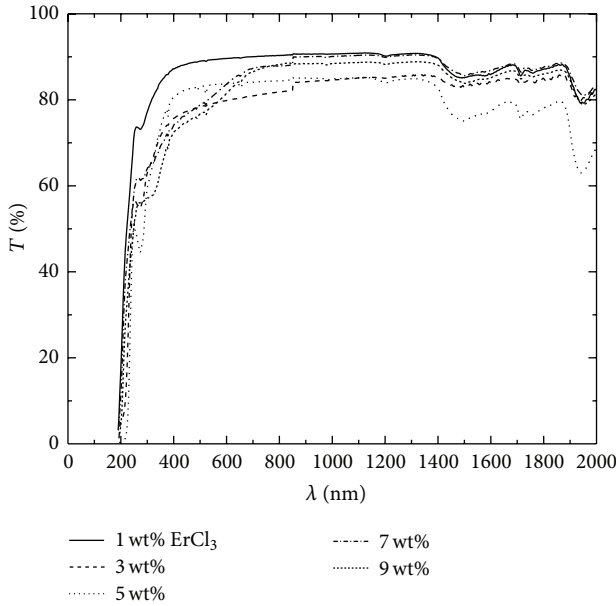


FIGURE 4: Transmission spectra for PVA contain different doping concentrations of ErCl_3 .

In addition, the observed band of O–H groups at $3430\text{--}3244\text{ cm}^{-1}$ exhibits a decrease in the intensity for all doped PVA samples. So the decrease in the intensity of this band indicates that there is a decrease in the number of free OH groups of the PVA main chain. This can be attributed to the complexes formation between Er^{+3} ions with OH groups of PVA skeleton [21]. Consequently, it can be concluded that the presence of Er^{+3} ions within PVA sample leads to the main chain degradation and the increase of the amorphous phases within the investigated sample. So the decrease in the hydrogen bonds along the PVA main chain can be expected.

4.2. Optical Properties Analysis. Figure 4 shows the optical transmission variation versus the wavelength from 200 nm to 2000 nm. Different doping ratio of ErCl_3 (1, 3, 5, 7, or 9 wt%) within PVA has been considered. The transmission of the PVA samples decreased by the increase in the doping ratio of ErCl_3 within the PVA samples. The decrease in the transmission of all doped PVA samples with the increase in ErCl_3 concentration can be assigned to the increase of the disorder within the polymeric samples. It was previously reported that rare earth ions within the polymer structure decrease the ordering character in the crystalline phases of PVA as well as polyvinylidene fluoride (PVFD) [13]. This is due to the complexes formation between rare earth ions and cations of the polymer main chain.

Several reports confirmed that the optical absorption of PVA sample is increased with the increase in Eu^{+3} , Sm^{+3} , and Ce^{+3} within PVA structure [13, 22, 23]. This is due to the presence of the amorphous phases that is constructed by the interaction between these ions and OH groups of PVA samples. Consequently, the decrease in the optical transmission of PVA with the increase in the doping ratio of Er^{+3} within PVA structure is expected. The presence of

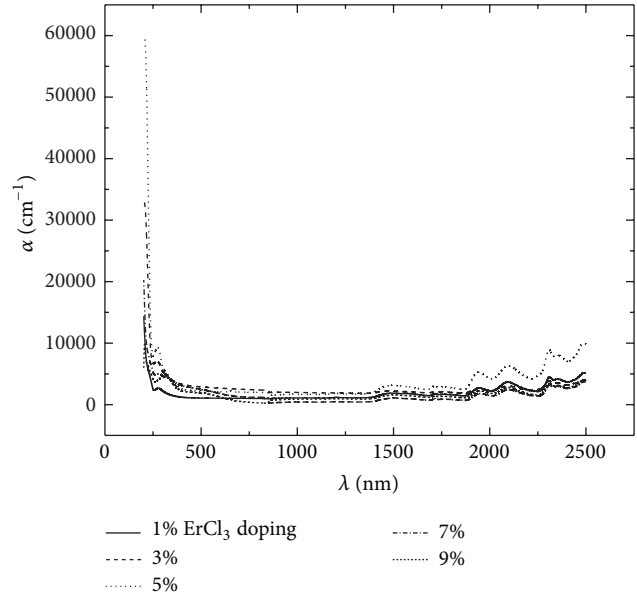


FIGURE 5: Absorbance of the wavelength for PVA contains different doping concentrations of ErCl_3 .

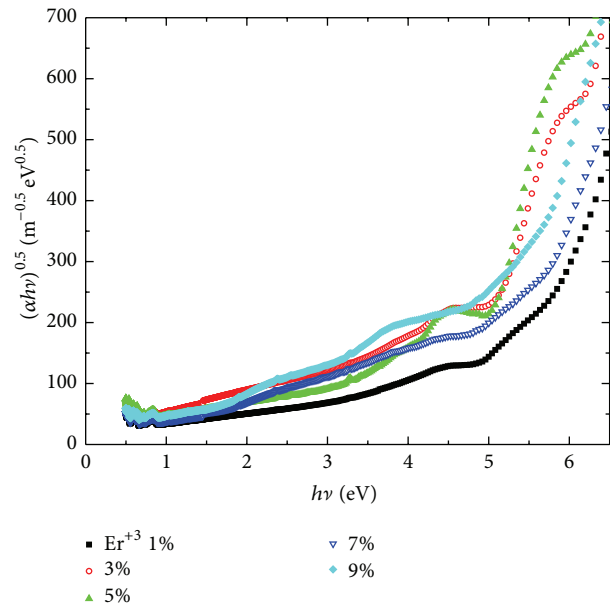


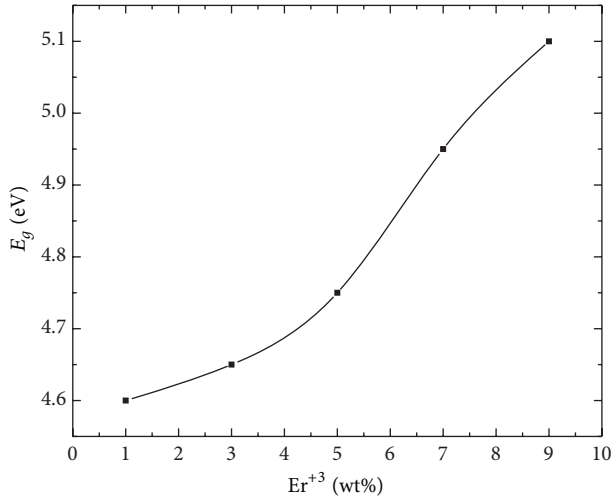
FIGURE 6: The plot of $(\alpha h\nu)^{0.5}$ versus $h\nu$ for PVA : ErCl_3 .

these complexes decreases the free hydrogen bonds of the main chain of the doped PVA samples. Consequently, it is suggested that the decrease in the hydrogen bonds may lead to the decrease in the transmission of all the PVA samples. Figure 5 displays the relation between the absorbance of the PVA with different ErCl_3 concentrations mentioned above and the wavelength. It is found that the absorption coefficient will increase by the increment of the filler concentration.

Figure 6 depicts the relation between $(\alpha h\nu)^{0.5}$ and photon energy ($h\nu$). The relation governing the straight line partition in the curve is $(\alpha h\nu)^{0.5} = A(h\nu - E_g^{\text{opt}})$, where A is

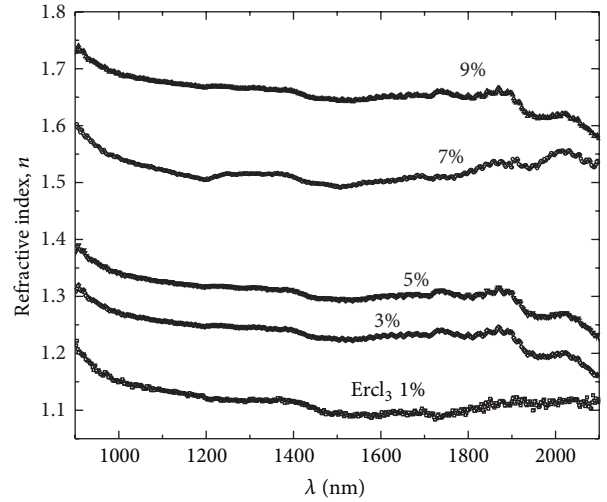
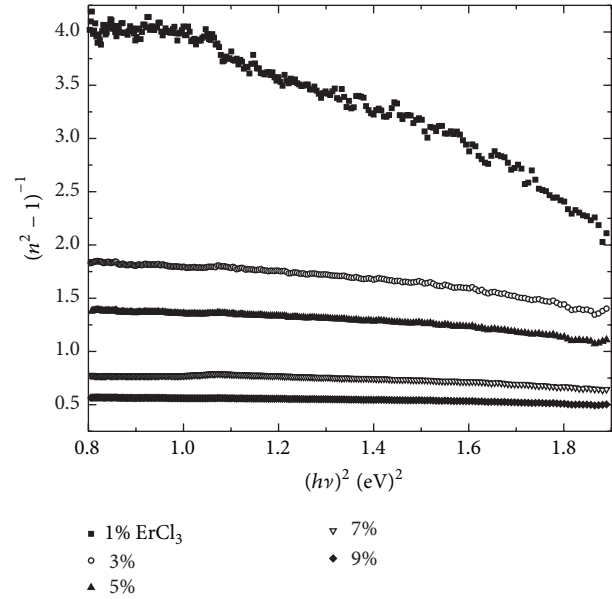
TABLE 1: The optical parameters for PVA doped with different concentration of ErCl_3 .

	PVA/ ErCl_3 wt 1%	Wt 3%	Wt 5%	Wt 7%	Wt 9%
E_s (eV)	2.25	1.96	1.63	1.52	1.48
E_d (eV)	1.30	1.50	1.82	2.10	2.60
S_o (10^{-7} nm^{-2})	26.00	51.00	62.00	69.00	74.00
n_{∞}	1.40	1.43	1.50	1.52	1.59
λ_o (nm)	296.00	330.00	338.00	442.00	519.00

FIGURE 7: Energy gap variation in eV with the doping concentrations of ErCl_3 within PVA samples.

a constant. So the extrapolation to the abscissa yields to the corresponding forbidden band width energy (E_g). The slope of the straight line gives us the constant A . The values of A are scheduled in Table 1 and they increase with the increase of ErCl_3 . Figure 7 shows the relation between the energy gap of PVA samples and the ErCl_3 doping concentrations. It is indicated that the energy gap increases with the increase of ErCl_3 doping. The increment of E_g for all doped PVA samples can be discussed as follows. The increase of ErCl_3 ratio within the skeleton of PVA leads to the decrease in the intensity of the OH groups of the main PVA chains. This is due to the formation of noncovalent bonds between Er^{+3} and OH groups of the PVA backbone.

Figure 8 shows the relation between the refractive index (n) of PVA samples and wavelength. The refractive index dispersion is a significant factor in optical communication and in designing devices for spectral dispersion. It is clear that the increase in doping ratio of ErCl_3 inside the PVA samples will increase the refractive index of PVA. The maximum value of refractive index (1.72) was achieved for the PVA samples containing 9 wt% of ErCl_3 at 1000 nm. This can be attributed to the highest electronegative value of Er (1.24 eV) [24]. As a result, Er^{+3} ions can form metal-ligand complexes inside the polymer matrix. These complexes can be bounded via coordination and ionic bonds with OH groups of the next layer of PVA. Consequently, Er^{+3} ions act as structure

FIGURE 8: Relation between the refractive index and the wavelength for PVA : ErCl_3 .FIGURE 9: Variation between $(n^2 - 1)^{-1}$ and $(h\nu)^2$ in eV for PVA doped with different ErCl_3 concentrations.

forming linking components for polymeric material and the multiple salt bridge results in the formation of a condensed structure.

The relation between $(n^2 - 1)^{-1}$ and $(h\nu)^2$ is displayed in Figure 9. Using (3), the slope of the linear part of this relation determines E_d , while the intercept with y -axis determines E_s . From Table 1 it is clear that the values of E_s decrease with the increase in ErCl_3 ratio within PVA structure. On the contrary, E_d increases with the increase in ErCl_3 . Figure 10 shows that the relation between $(n^2 - 1)^{-1}$ and λ^{-2} for PVA contains different concentrations of ErCl_3 mentioned before. Using (5) and (6), we could calculate n_{∞} , λ_o , and S_o , for each doped PVA sample. We expect that the results of this work will help

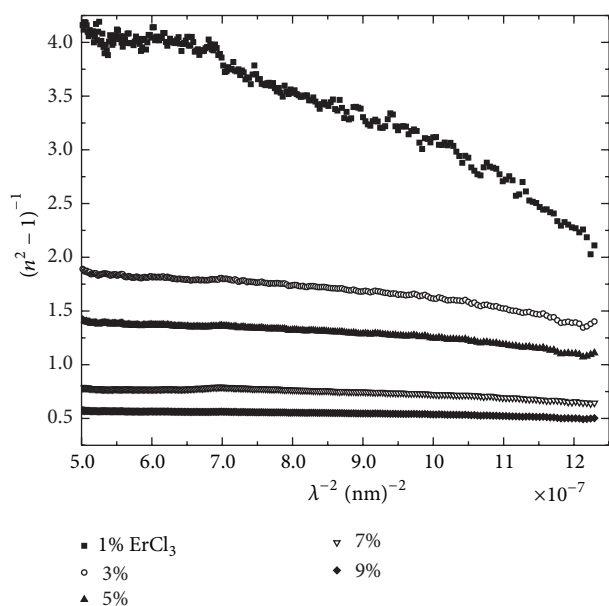


FIGURE 10: Variation between $(n^2 - 1)^{-1}$ and λ^2 in nm^{-2} for PVA doped with different concentrations of ErCl_3 .

the future research works in exploring the use of ErCl_3 doped PVA for many optical applications.

5. Conclusion

The optical properties of PVA doped with different ErCl_3 have been investigated. All doped PVA samples exhibit an apparent change in the optical transmittance and reflectance. The drastic change in the energy gap $E_g = 0.5$ eV and the refractive index $n = 1.72$ is achieved for PVA containing 9 wt% of ErCl_3 . This was attributed to the complexes formation between Er^{+3} ions and OH groups of PVA structure. The formation of complexes within PVA sample affects all optical parameters of the investigated sample. We have seen a drastic change in E_s and E_d , due to the presence of Er^{+3} within PVA sample. PVA doped with 9 wt% of ErCl_3 could be utilized as a new material for many optical applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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