Effect of Praseodymium Dopants on the Optical Properties of Polyvinyl alcohol (PVA) films

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ABSTRACT

Poly(vinylacohol) (PVA) films with different concentrations of with Praseodymium (Pr) ions were prepared using the method of a casting technique. Optical absorption and transmission measurements were performed on these samples. The UV-Vis absorption spectral of pure PVA shows absorption bands at 200, 275 and 325 nm, which were assigned to the presence of carbonyl groups. Four sharp absorption peaks at 435,460,474 and 587 nm were observed in the UV-Vis absorption spectral of the PVA doped samples. The intensity of such bands increases with increasing the concentration of Prcl₃ in PVA film. This is due to the link between the Praseodymium (Pr) metal ion and the polymer OH- groups. The dependence of the absorption coefficient, α , on the photon energy, hv, has been determined and energy gaps were calculated. It was found that the absorption coefficient and the absorption edge increase by increasing the Pr content for all the investigated samples. Optical energy gaps showed a decreasing trend with increasing Pr concentration. AC conductivity of prepared samples was automatically measured using an RLC Bridge at room temperature and it was found AC conductivity increases with increasing frequency. The obtained results illustrated that this material has promising applications in optical industries.

1. INTRODUCTION

Poly (vinly alcohol) (PVA) is one of the most important polymeric materials because of its unique chemical and physical properties [1,3]. There are a large number of reports on pure PVA with definite molecular weight [1] or on spectroscopic behavior of PVA film with different molecular weights [2,4,5] or on PVA with different additives[6-8], or on PVA doped with different types of lanthanides ions such as Ho^{+3} , Er^{+3} , Sm^{+3} . and Eu^{+3} [8].

Up to now there have been published many papers describing properties of Rare Earth (RE) doped with many different materials. Photonics materials such as glasses, optical crystals (LiNbO3, Al2O3, Y2O3) and semiconductors (Si, SiGe, SiC, GaN, etc.) are conventional materials for accomplishing lasing action [9-11] .The choice of host materials for RE ions hardly influences the energy levels of the RE ions. Therefore in principle any materials that have little absorption at the pump and emission wavelength

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can be used.

There is a number of properties make PVA attractive hosts for RE ions including high transparency in the visible and near-infrared spectra, well controlled refractive indices, offering simple fabrication process and low cost.

The purpose of the current investigation was to study the effect of Praseodymium Dopants on the Optical Properties of Polyvinyl alcohol (PVA) films.

2. EXPERIMENTAL

Polyvinyl alcohol (PVA) of molecular weight 17000gm/mole (Flucka) used as polymeric material and Praseodymium (III) chloride hydrate (99.9%) from Alfa Aesar Karlsruhe, Germany used as doping material in sample preparation.

Pure (undoped) and Prcl₃-doped PVA films with concentration range of 5-20% weight/weight (w/w) were prepared by the solution casting technique PVA solution were prepared by dissolving 1gm of PVA powder in 25ml of bidistilled water and thoroughly stirred using magnetic stirring at 60°C for about 4 hours till a transparent homogeneous solution is obtained. The mixture left for about 24 hours in room temperature to attain a homogenous and bubble free solution. The solution of Pure PVA is simply effused into a Petri-dish that a perfectly flat bottom. Subsequently, the solvent is allowed to evaporate for 3 days at room temperature. The film thickness can be controlled by the area of the dish that is used and by the volume and the concentration of the solution. PrCl₃-doped PVA doped samples were prepared by the same technique, by mixing a solutions of the desired concentrations (5%, 10%, 15%, and 20%) of PrCl₃ to the polymer solution and thoroughly stirred till attain a completely homogenous solutions then the mixtures are left for about 24 hours in the room temperature to obtain a bubble free solutions. The prepared films are then gently separated from the Petri dishes. Thickness of the prepared samples was measured using digital caliper. The optical absorption and transmission measurements of (a-d) samples were measured by using the JASSCO V-570 spectrophotometer in a range from 190 to 700 nm.

Samples of polyvinyl-alcohol; (PVA) mixed with granular praseodymium chloride (PrCl3) with different concentration ratios; were cut from the original sheets into disk shapes. The disks were coated very well by silver paint to confirm good electrical contact between the two electrodes of the sample. A cell consists of two stainless steel cylinders of lengths 10 and 6 cm, two copper disks in their shape as a top and a bottom bases is used for the electrical measurements, also many bulk rubber parts with different dimensions are used for insulating purposes. Very fine copper wires were well cemented on both surfaces of the sample holder. The cell including sample is put on a flat table at room temperatures. AC conductivity of prepared samples was measured at frequency range from 42HZ- 5MHZ in HIOKI LCR BRIDGE HITESTER 3532-50.

3. RESULTS AND DISCUSSIONS

3.1 UV-Visible characterization

Fig.1 shows optical transmission spectra of samples (a-e) in the region 190-700 nm.

One can observe for sample (a) nearly zero transmission in the wavelength range 190-220 nm, a sharp increase in the transmission intensity reach 60 % and is approximately constant in the visible region. For samples (b-e) the same trend is observed. Four sharp absorption peaks at 435,460,474 and 587 nm [11] were observed.



Fig.1 Transmission spectra of (a-e) PVA samples



Fig. 2 The absorption spectrum of sample (b-e) samples. The inset shows the absorption spectrum of sample (a)

Fig. 2 shows the absorption spectra of samples (b-e) in the wavelength 400-700 nm. Four sharp absorption peaks were observed at 445, 470, 484 and 591 nm due to the transitions from ${}^{3}H_{4}$ to ${}^{3}P_{2}$, ${}^{3}P_{0}$, ${}^{3}P_{1}$ and ${}^{1}D_{2}$, respectively [11-13]. Table I gives the energy level transitions responsible for those observed peaks. There is observable change in the band position and with filling levels (Table I). This is due to the link between the praseodymium metal ion and the polymer OH- groups. The dependence of the intensity of the bands on the filling level provides an evidence for the incroporation of the complex into PVA matrix. Three of these absorption peaks are situated in blue region with different wavelengths due to different atomic transitions and the other peak is in yellow region [10]. The absorption spectrum of the sample (a) under investigation in the range 190-700 nm (see inset of Fig. 2). The spectrum of the sample (a) contains three absorption bands (200, 275 and 325 nm) and it shows high transparency in the wavelength range 400-700 nm. The three absorption bands identify carbonyl groups of the type $-(CH = CH)_n - C = O -$ where n =1,2 and 3, which arises from the presence of acetaldehyde in vinyl acetate monomer during polymerization [3].

Band (nm)	samples	Abcorption	Transition
Ballu (IIII)	samples	Absolption	Transmon
		(a.u)x10 °	
	b	1.4	_
435	С	3.7	
	d	4.7	$^{3}H_{4} \rightarrow ^{3}P_{2}$
	е	6.9	_
	b	0.5	
460	С	1	_
	d	1.6	$^{-3}H_4 \rightarrow ^{3}P_o$
	е	2.3	_
	b	0.3	
574	С	1.6	$^{-3}H_4 \rightarrow {}^{3}P_1$
	d	2.3	_
	е	2.3	_
	b	0.3	
587	С	0.9	$^{-3}H_4 \rightarrow ^{1}D_2$
	d	0.9	_
	е	1.5	

Table 1 Transition levels of Pr in PVA matrix

3.2 Dependence of optical absorption coefficient on the concentrations of Pr ion

Fig. 3 illustrates the dependence of the optical absorption coefficient (α) on the photon energy for samples (b-e). The inset shows the absorption coefficient of sample (a). For the sample (a) one can observe slight increase up to approximately 2.71 eV which may be attributed to electronic transitions from the bonding molecular orbital to nonbonding molecular orbital. The marked increase of the absorption coefficient at higher energies may be attributed to extra transition from the bonding molecular orbital to nonbonding molecular orbital.



Fig. 3 Absorption coefficient versus photon energy for (a-e) samples. The inset shows the absorption coefficient of sample (a)

The fundamental absorption edge can be determined by plotting a relation between the photon energy (*hv*) and absorption coefficient α . for all samples under consideration (Fig.3).



Fig.4 The dependence of absorption coefficient on the sample concentration

It is clear from the calculated values of the Absorption edges for samples

that absorption edge increases as a result of increasing Pr doping.

The absorption edge in many disorder materials follow two apporaches, one of them given by Mott and Davis [14]. Mott and Davis suggested that the expression for direct transition can be written as

$$\alpha(\omega) = \beta \frac{(\hbar \omega - E_{op})^n}{\hbar \omega}$$
(1)

where α is the absorption coefficient, β is a constant, E _{op} is the band gap and n is an index determined by the nature of the electronic transition during the absorption process. The most satisfactory results were obtained by plotting the quantity (α hu)^{1/2} as a function of photon energy, as shown in Fig. 5.



Fig. 5 (α hu) ^{1/2} versus photon energy for (a-e) samples and the inset shows the spectrum of sample (a)

The values of E _{op} can obtain by extrapolating the linear parts of the curves to $(\alpha h \upsilon)^{1/2}$ =0 and the results are presented in Fig. 6.





From the Fig. 6, it is observed that optical band gap values decreased with increasing concentration of Pr ions.

3.3 Electrical properties

Electrical conductivity is a prominent factor which reveals reliable information about the transport phenomenon in materials.



Fig. 7 illustrates the variation of the natural logarithm of AC conductivity versus the natural logarithm of frequency ($Ln\sigma_{ac}$ versus $Ln\omega$) at room temperatures for (a-d) samples. AC conductivity increases with increasing frequency. The ac conductivity component is the result of the charge carriers that trapped in PVA and hopping between the sites over a potential barrier separating them

CONCLUSIONS

Absorption spectra of pure PVA and Pr doped PVA films in the visible range of wavelength from 400-700 nm showed four sharp absorption peaks were observed in the mentioned wavelength range. Such peaks were assigned to the ${}^{3}H_{4} \rightarrow {}^{3}P_{2}$, ${}^{3}H_{4}$ \rightarrow ³P₀, ³H₄ \rightarrow ³P₁ and ³H₄ \rightarrow ¹D₂ transitions for Pr. Optical energy gaps showed a decreasing trend with increasing Pr concentration. The intensity of such bands increases with increasing the concentration of Prcl₃ in PVA film. This is due to the link between the Praseodymium (Pr) metal ion and the polymer OH- groups. The dependence of the absorption coefficient, α , on the photon energy, hv, has been determined and energy gaps were calculated. It was found that the absorption coefficient and the absorption edge increase by increasing the Pr content for all the investigated samples. The energy gap of the prepared samples were calculated. It was found that the optical gaps decrease as Pr concentration is increased. Increasing the degree of disorder causes the band tail to increase, which according to the electronic structure of amorphous materials will lead to a decrease of the estimated optical band gap. The Ac electrical conductivity was measured as a function of frequency for the prepared samples at room temperature. The obtained results illustrated that this material has promising applications in optical industries.

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