

Optical properties of BaCl₂ doped poly (vinyl alcohol) films

Nadir Fadhil Habubi¹, Bashar Hatem Abed², Sami Salman Chiad¹

¹ Physics Department, College of Education, Al_Mustasiriyah University.

² Chemistry Department, College of Science, Al_Mustasiriyah University.

nadirfadhil@yahoo.com, bashar_hatem@yahoo.com, samichiad2003@yahoo.com

Abstract

The effects of BaCl₂ dopant on the optical properties of poly (vinyl alcohol) have been investigated. Pure and BaCl₂ doped PVA films were prepared using solvent casting method. These films were characterized using UV/VIS technique in order to estimate the kind of transition which was found to be indirect transition. The value of the optical energy gap was decrease with increasing dopant concentration.

Refractive index, extinction coefficient and Urbach tail have been also investigated; it was found that all the above parameters affects by doping.

Key words

PVA,
Doping,
Optical properties

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دراسة الخصائص البصرية لاغشية بولي فينايل الكحول المشوبة بكلوريد الباريوم

نادر فاضل حبوبي¹، بشار حاتم عبد²، سامي سلمان جيا¹

¹ قسم الفيزياء، كلية التربية، الجامعة المستنصرية

² قسم الكيمياء، كلية العلوم، الجامعة المستنصرية

الخلاصة

تم دراسة تأثير اضافة شائبة كلوريد الباريوم على الخواص البصرية لاغشية بولي فينايل الكحول. حضرت الاغشية غير المشوبة والمشوبة بكلوريد الباريوم لبولي فينايل الكحول بطريقة الصب. تم التحقق من خواص هذه الاغشية من خلال تقنية مطياف الاشعة فوق البنفسجية / المرئية وذلك لغرض تحديد نوع الانتقال والذي وجد بانه انتقال غير مباشر وان قيم فجوة الطاقة البصرية تقل بازدياد تركيز الشائبة. تم التحقق من قيم معامل الانكسار، معامل الخمود، ذيل اورباخ ووجد بان كافة هذه المعلمات قد تاترت بالتشويب.

Introduction

Doping of polymers attracted the scientific and technological researchers, because of their wide applications. The dopant in polymer can changes the molecular structure and hence the microstructure as well as macroscopic properties of the polymer. poly(vinyl alcohol) has been studied extensively due it several interesting properties such as water

soluble, semicrystalline, low electrical, conductivity polymer, relatively low cost in manufacture [1, 2]. Moreover this polymer is considered as an excellent host material for composites. Various research groups studied the effect of doping on optical, thermal, structural, and mechanical properties [3- 12]. These studies shows that the properties like crystallinity, structural order, thermal stability, electrical and optical

behavior of the polymer are affected by doping which depends on the interaction between the dopant and the polymer.

This material has potential applications in waveguides [13], nanofibrous composite membrane [14], solid polymer electrolyte [15], fuel cells [16], and integrated optics [17].

The purpose of the current investigation was to study the effect of BaCl₂ doping upon the optical properties of PVA.

Experimental procedure

Poly (vinyl alcohol) with molecular weight 10000 g/mol were used as a host polymeric material in this work. supplied by (BDH chemicals) with high purity, the aqueous solution of this polymer were prepared by dissolving PVA in a mixed of deionized water and ethanol and thoroughly stirred using a magnetic stirrer for about one hour until PVA was completely dissolved.

BaCl₂ solution was prepared by dissolving the salt in redistilled water. Appropriate mixtures of PVA and BaCl₂ solutions were mixed by a different concentration of salt (2%, 4%, 6%).

The solution was poured into flat glass plate dishes. Homogenous films were obtained after drying in an oven for 24 hours at 40°C. the film thickness was measured with the help of thickness gauge (indicating micrometer) and was found to be in the range of 20 ± 1 μm.

Absorbance and transmittance measurements were carried out using double beam UV/VIS spectrometer (shimadzu Japan) in the wavelength range (190-900) nm.

Results and discussion

The absorbance spectra of pure and BaCl₂ doped PVA is shown in Fig. (1), it is clearly seen that the absorbance increase as the doping percentage of BaCl₂

increased, the absorption in band at nearly 264 nm was assigned to π-π* transition. the absorption edge around 230 nm in pure PVA, it seems that the absorption in band and band edge shift to word higher wavelength as the doping percentage increase these shifts in bands indicate the formation of inter /intra molecular hydrogen bonding mainly between Ba²⁺ ions with the adjacent OH groups AS the BaCl₂ concentration increase inter/intra hydrogen bonding increases and hence absorption [18].

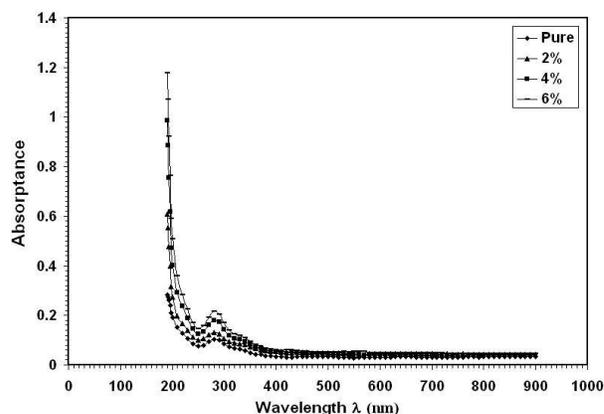


Fig. (1) Absorbance versus wavelength for the as deposited films.

The optical absorption coefficient of PVA and BaCl₂ doped PVA is very important because it provides information on the electronic transition by using the following equation [19]:

$$\alpha = B \frac{(h\nu - E_g)^2}{h\nu} \quad (1)$$

where α is the absorption coefficient, B a constant, $h\nu$ is the photon energy, E_g is the energy gap.

Figures (2), (3), (4) show the relationship between $(\alpha h\nu)^{1/2}$ and photon energy, as can be seen from the figures that the value of the energy gap was decrease as the doping percentage increased show an indirect allowed transition, these values were (5, 4.7, 4.6, 4.5) eV respectively. The existence and variation of optical energy gap may be

explained by invoking the occurrence of local cross linking within the amorphous phase of the polymer, in such a way as to increase the degree of ordering in these parts as a result of Ba²⁺ ion of BaCl₂ which interact with-OH group of PVA.

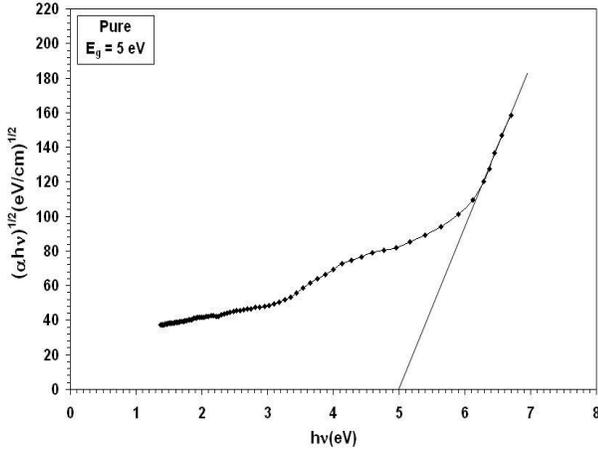


Fig. (2) $(\alpha h\nu)^{1/2}$ versus photon energy for pure PVA films.

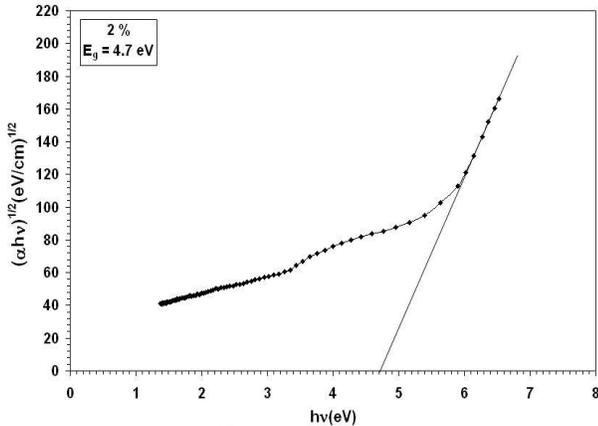


Fig. (3) $(\alpha h\nu)^{1/2}$ versus photon energy for BaCl₂ doped PVA films.

It is known that the absorption coefficient near the band edge shows an exponential dependence on photon energy [20]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \quad (2)$$

Where (α_0) is constant, $(h\nu)$ is the photon energy, and E_U is the Urbach energy which corresponds to the width of the band tail

and can be evaluated as the width of the localized state. Fig.(6) shows the dependence of $\ln(\alpha)$ on photon energy Urbach energy were calculated from the reciprocal gradient of these linear portion and found to be increase as the doping percentage increased, their values was (477, 510, 539, 567) meV respectively. The E_U value change inversely with the optical band gap, the decrease in E_g is attributed to the increase of disorder of the polymer occurred by doping.

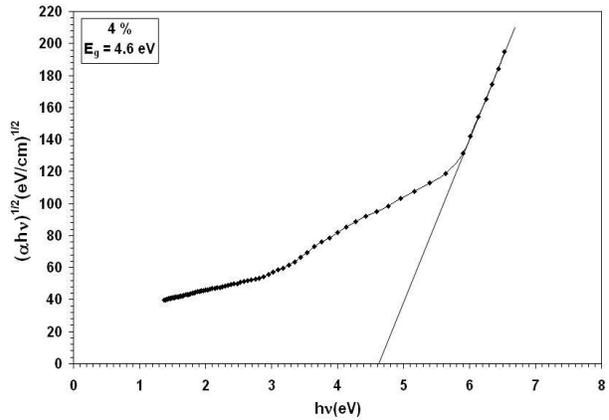


Fig. (4) $(\alpha h\nu)^{1/2}$ versus photon energy for BaCl₂ doped PVA films.

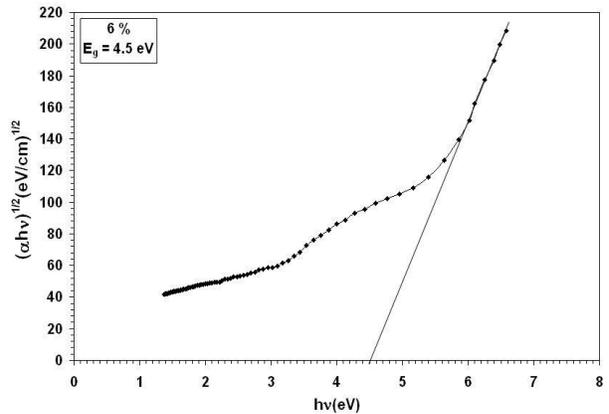


Fig. (5) $(\alpha h\nu)^{1/2}$ versus photon energy for BaCl₂ doped PVA films.

The refractive index (n) was determined from the reflectance (R) data using the relation [21]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

where k is the extinction coefficient and absorption coefficient can be related by [21]:

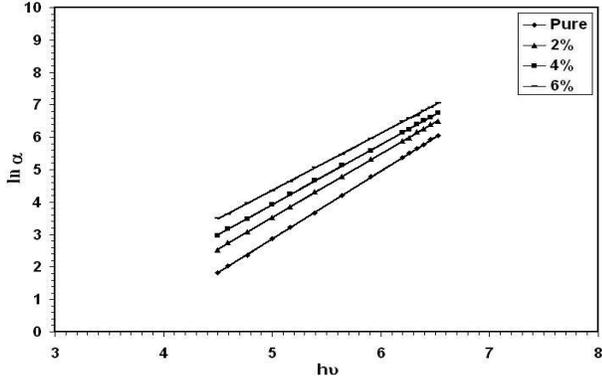


Fig. (6) $\ln \alpha$ as a function of $h\nu$.

$$k = \frac{\alpha \lambda}{4 \pi} \quad (4)$$

As shown from Fig. (7), the refractive index decreases as the wavelength increase until 400 nm and then become nearly constant with increasing wavelength, the value of refractive index within the constant range was varying from 1.5-1.65 as the doping percentage increase.

These values are in good agreement with the values obtained by other workers concerning PVA films [22,23].

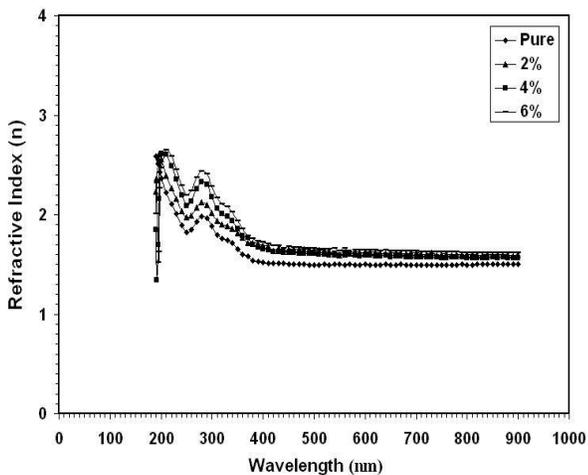


Fig. (7) Refractive index versus wavelength for the as deposited films.

Fig. (8) shows the dependence of the extinction coefficient on wavelength, it can be seen that extinction coefficient decrease until in 260 nm and then became to increase showing a noticable peak around 285 nm and then decrease again until 360 nm then became nearly constant, we can deuce from the graph that k increase as the doping percentage increased.

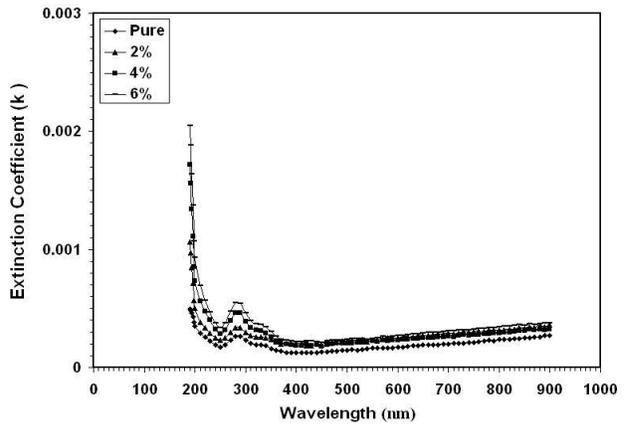


Fig. (8) Extinction coefficient versus wavelength for the as deposited films.

Conclusions

PVA and BaCl₂ doped were prepared by casting technique. The constant transparency in the visible and near IR region revealed that this polymer can be used as an optical window within this spectral region.

The optical energy gap Urbach tail assures that the crosslink is increased as the doping percentage increase. The optical energy gap was found to be indirect, and all the value of the optical parameters under consideration was increased by doping.

References

[1] A. Tawansi, M. D. Migahed and M. I. A. El-Hamid: Journal of Polymer Science Part B: Polymer Physics, 24,12 (1986) 2631.
 [2] K. M. Abd El-Kader and A. S. Orabi: Polymer Testing, 21 (2002) 591.

- [3] H. R. Yang, E. J. Kim, S. J. Lee, G. Y. Kim, C. H. Kwak: Optics Communications, 282,9 (2009) 1902.
- [4] M. V. Fake, P. V. Adhyapak, V. P. Mulik, D. P. Amalnerkar and R. C. Alyer, 78,2 (2009) 590.
- [5] M. Andelaziz and M. M. Ghannam: Physica B. Condensed Matter, 405, 3 (2010) 958.
- [6] S. Y. El-Zaiat, H. El-Ghandoor and F. Sharaf: Optics & Laser Technology, 29, 2 (1997) 117.
- [7] F. Sharaf, S. A. Mansour and A. M. Y. El-Lawindy: Polymer Degradation and Stability, 66, 2 (1999) 173.
- [8] A. Tawansi, A. El- Khodary and M. M. Abdeinaby: Current Applied Physics, 5, 6 (2005) 572.
- [9] C. W. Lin, R. Thangamuthu and C. J. Yang; Journal of Membrane Science, 253, 1-2 (2005) 23.
- [10] C. U. Devi, A. K. Sharma and V. V. R. N. Rao: Materials Letters, 56, 31 (2002) 167.
- [11] G. V. Kumar and R. Chandramani: Applied Surface Science, 255, 15 (2009) 7047.
- [12] G. N. H. Kumor, J. Lakshmana Rao, N. O. Gopal, K. V. Narasimhulu, R. P. S. Chakradhar and A.V. Rajulu: Polymer, 45,16 (2004) 5407.
- [13] R. Kumar, A. P. Singh, A. Kapoor and K. N. Tripathi: Optik, 119 (2008) 553.
- [14] B. Duan, X. Yuan, Y. Zhu, Y. Zharg, X. Li, Y. Zhang and K. Yao: European Polymer Journal, 42 (2006) 2013.
- [15] P. R. Samani, R. Marimuthu, A. K. Viswanath and S. Radhakrishnan: Polymer Degradation And Stability, 79 (2003) 77.
- [16] J. Qiao, T. Hamaya and T. Okada: Polymer, 46 (2005) 10809.
- [17] M. Bulinski, V. Kuncser, D. Cristea, C. Plapcianu, S. Krautwald, H. Franke, F. E. Wanger and G. Filoti, Journal of Optoelectronic and Advanced Materials, 5, 1 (2003) 331.
- [18] R. F. Bhajantri, V. Ravindrachary, A. Harisha, V. Crasta, S.P. Nayak and B. Poojary:, Polymer, 47 (2006) 3591.
- [19] K. A. M. Abd El- Karder, S.F. Abdel Hamied, A. B. Man Sour, A. M. Y. El-Lawindy and F. El-Tantaway: Polymer Testing, 21 (2002) 847.
- [20] S. W. Xue, X. T. Zu, W. L. Zhou, H. X. Deng, X. Xiang, L. Zhqng, L. Zhang and H. Deng: Journal of Alloys and Compounds, 448 (2008) 21.
- [21] N. A. Subrahmanyam: A Text Book of Optics, Ninth ed., BRJ Laboratoray Delhi, India 1977.
- [22] A. N. Krkljes, M. T. M. Cincovic, Z. M. K. Popovic and J. M. Nedeljkovic: European Polymer Journal, 43 (2007) 2171.
- [23] S. Yano, K. Kurita, K. Iwata, T. Furukawa and Kodomari: Polymer, 44 (2003) 3515.