



Structural and Optical Properties of PVA:Na₂S₂O₃ Polymer Electrolytes Films

KEYWORDS

optical energy band gap; optical conductance; dielectric constant; dielectric loss.

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ABSTRACT Polymer electrolytes films based on polyvinyl alcohol (PVA) with different concentrations of Sodium thiosulphate pentahydrate Na₂S₂O₃·5H₂O, were prepared by solution cast technique. The optical properties in the IR and UV-visible region of PVA polymer containing 0%, 2%, 4%, 6%, and 8% by weight Na₂S₂O₃·5H₂O are investigated. The optical absorption of the prepared films increases with increasing concentration of Na₂S₂O₃·5H₂O in UV region (190–280 nm). The optical results obtained were analyzed in terms of the absorption formula for non crystalline materials. The optical band energy gap (E_g) have been obtained from direct allowed transitions in k -space at room temperature. The width of the tail of localized states in the band gap E_u was evaluated using the Urbach-edges method. It was found that both E_g and E_u decrease as Na₂S₂O₃·5H₂O concentration increases in the polymer matrix. The optical conductance and band-gap indicated that the films are almost transmitting within the visible range. The single oscillator expression has been used to obtain the information about disorder degree. The real and imaginary parts of dielectric constant of the doped films increases with increasing Na₂S₂O₃·5H₂O concentration in the absorption edge (235-250) nm. The TGA and DTGA spectrum shows the thermal stability of polymer composite the increase with increasing Na₂S₂O₃·5H₂O content.

Introduction

In the recent years, studies on the solid polymer electrolytes have attracted much attention in view of their application in electronic and optical devices as well as for fundamental knowledge [1]. Solid polymer electrolytes have many advantages, such as no leakage, volumetric stability, ease of fabrication of thin films of desired size, and wide electrochemical stability windows [2]. Many studies have been made to enhance the room temperature ionic conductivities of polymer electrolytes [3]. The conduction in Polymer electrolytes takes place through two distinct events: the first is due to the charge migration of ions between the coordinate sites of the host polymer and the second is associated with the polymeric chain segmental motion [4]. The ionic conductivity of Polymer electrolytes is strongly affected by the degree of crystallinity, simultaneous cation and anion motions and the ion pair formation [5].

One of the important classes of polymer electrolytes is polar polymer, like polyvinyl alcohol (PVA) which is semi-crystalline polymer and has very important applications due to the role of OH group and hydrogen bonds [6].

In the present study polyvinyl alcohol (PVA) is incorporated that acts as host material. The concentration of the doping namely Sodium thiosulphate pentahydrate (Na₂S₂O₃·5H₂O) was varied in order to investigate the influence of doping compositions on structure, and optical properties of the composite polymer electrolytes, to better understanding the change in energy band diagram and other optical parameters.

Experimental

Two grams of polyvinyl alcohol (PVA) with MW = 7000, was dissolved completely in 40 ml distilled water under constant stirring. The mixture heated at 90 °C for 1 h and was left to cool down to room temperature. Extra pure Sodium thiosulphate pentahydrate (Na₂S₂O₃·5H₂O) provided by Merck company with M=248.18 gm/mol, were used as a doping in the mixture and stirred further for 10 min. Different amounts of salt (2, 4, 6, and 8 %) were added as stated above, the complete dissolution was obtained using a magnetic stirrer at temperature 60 °C for 10 min, these homogeneous solu-

tions were spread on a glass Petri dish and let to dry slowly at room temperature for 120 h, in a dust free chamber, after this time, the films were ready to cut into suitable pieces for characterization. The thickness of the films was in the range of (0.21 - 0.25) mm, it was determined using micrometer at different places in each film and an average was taken.

Results and discussion

FTIR spectra of pure PVA and doped with Na₂S₂O₃·5H₂O salt range from (2, 4, 6, and 8 %) are shown in Fig. 1. The more relevant feature in the IR spectrum for all spectra, is the presence of a broad band at 3800–3200 cm⁻¹ which arises from O–H groups in several different H-bonding configurations of PVA [7, 8]. Several bands were observed at 2940–2820 cm⁻¹ due to CH₂ group vibration [9]. The characteristic absorption bands of PVA which are 1763, 1420, 1128, 917 and 820 cm⁻¹ were observed for all spectra with some shifts due to the doping with Na⁺. These bands are assigned to C–O, C–H band of CH₂ group, (CH–OH), C–O and CH rocking of PVA respectively [10]. The absorption band at 640 cm⁻¹ indicates the presence of hydroxyl group [11]. Further, the vibration peaks found in the range 2230-1950 cm⁻¹ for doped polymer can be attributed to (M–O) where M is, Na⁺ which indicated that the doping was complexes with polymer matrix [12].

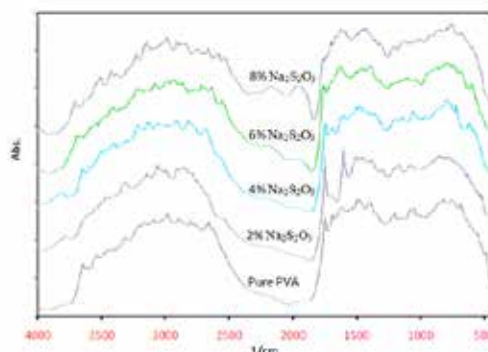


Fig.1. FTIR spectra of PVA composite and that doped with filler (2, 4, 6, and 8 % of Na₂S₂O₃·5H₂O).

The UV–VIS spectra of the sample under investigation were recorded, the spectra of pure PVA and that doped with different Sodium thiosulphate pentahydrate salt concentrations (2, 4, 6, and 8 %) is shown in Fig. 2. The optical absorption of the prepared films decreases with increasing concentration of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in UV region (190–340 nm). The intensity of the bands increases with increasing the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ contents providing an evidence for the incorporation of Na^+ into PVA matrix where as their positions are slightly shifted to higher wave length (red shift).

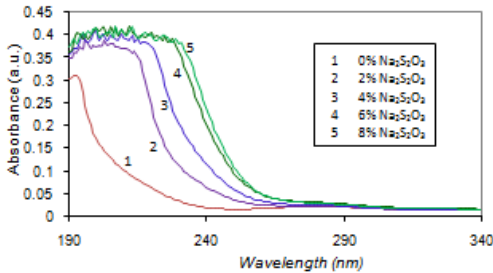


Fig.2. The absorption spectra in the UV–VIS region for films of pure PVA and that doped with (2, 4, 6, and 8) % of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

The absorption coefficient can be determined as a function of frequency using the formula[13]:

$$\alpha(\nu) = A/d \times 2.303 \tag{1}$$

where A is the absorbance at frequency ν and d is the thickness of the sample. The optical band gap for an direct allowed transition can be determined by using the relation [14].

$$E_g = h\nu - (\alpha h\nu / \beta)^2 \tag{2}$$

where β is a constant.

The energy band gap is calculated in the range near the absorption edge, as indicated in Table I. Fig. 3 illustrates the plots between $(\alpha h\nu)^2$ and $h\nu$ for pure PVA and that treated with $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ near the absorption edge produce a linear fit over a wider range of $h\nu$. This linearity indicates the existence of direct allowed transitions. The extrapolation of linear dependence to the abscissa yields the corresponding forbidden band width E_g . It is clear that E_g decreases with increasing $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ content. The variation of the calculated values of optical energy gaps may reflect the role of the doping in modifying the electronic structure of the PVA matrix due to appearance of various Polaroid and defect levels [15]. The decrease in optical energy gap E_g on doping may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix [16, 17]. These charge transfer complexes increase the conductivity by providing additional charges, this results in a decrease of the optical energy gap.

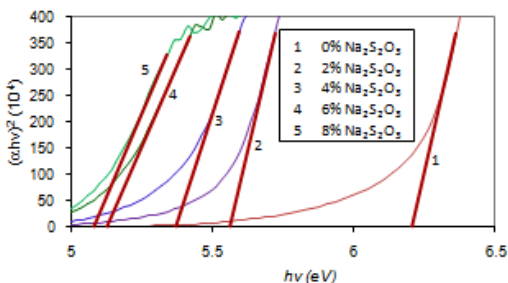


Fig.3. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for films of pure PVA and that doped with different $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

The optical absorption coefficient near the band edge for many amorphous and crystalline materials obeys an empirical relation given by Urbach [18]

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_u) \tag{3}$$

where α_0 is a constant and E_u is Urbach energy related to width of the band tails of localized states in the normally forbidden band gap that associated with the amorphous nature of the material. it should be mentioned that this equation is applicable only in the low absorption region ([15])

The tail of localized state of the films was calculated from the slope of the Urbach plot, in which the natural logarithm of absorption coefficient $\ln \alpha$ is plotted as a function of photon energy $h\nu$. The band tails of the localized state of the samples are tabulated in Table I.

Table I. The variation of energy band gap E_g , tale of localized state, and constants (β, α_0) versus $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration.

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ %	E_g (eV)	E_u (eV)	$\beta(\text{cm}^{-1} \text{eV}^{1/2} \times 10^3)$	α_0
0%	6.2148	0.47687	4.9543	8.1417
2%	5.5511	0.38008	4.5573	13.8877
4%	5.4074	0.34293	4.0452	18.4673
6%	5.1282	0.29146	3.8623	30.9075
8%	5.0740	0.26610	3.5645	42.8626

The absorption coefficient α , and the refractive index n , were used to obtain the optical conductivity σ , using the relation [19],

$$\sigma = \alpha n c / 4\pi \tag{4}$$

where c is the velocity of light in the space.

Fig.4 shows the variation of optical conductivity with the incident photon energy. The optical conductivity is constant up to 4.5 eV of photon energy after that it increases with increase in photon energy. The increased optical conductivity at high photon energies is due to high absorbance of film in that region. The optical conductance spectra indicated that the films are transmittance within the visible range.

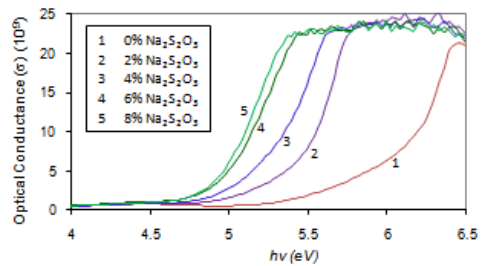


Fig.4. Optical conductivity of $\text{PVA}:\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ electrolytes films.

The dispersion data of the refractive index can be calculated by single-oscillator model. Which developed by Wemple and Didomenico [20]:

$$(\eta^2 - 1)^{-1} = \frac{E_g^2 - (h\nu)^2}{E_d E_o} \tag{5}$$

where η is the average values of the single oscillator energy, and E_d is the dispersion energy, which measures the average strength of inter band transitions [21].

According to equation (5), plotting $(\eta^2 - 1)^{-1}$ versus $h\nu$ near the absorption edge, as shown in Fig.5, allows one to determine the oscillating parameters E_d and E_o , by fitting a linear function to

the data, the slope of the line represented ϵ_2 and determined from intercept on the vertical axis. The values obtained for the oscillating parameters are listed in Table II.

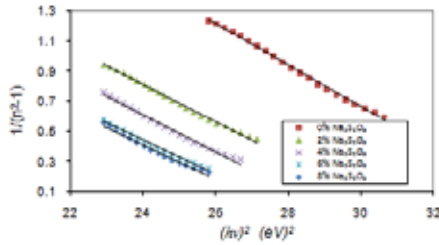


Fig.5. Plots of $1/(\epsilon^2-1)$ versus $(h\nu)^2$ for different $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration.

The single-oscillator energy E_o and dispersion energy E_d are related to the optical energy band gap, they are decreases as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration increase. Since the dispersion energy E_d measures the average strength of inter-band optical transitions [22], we expect the decrease of bound strength by increasing the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration, which lead to increases in degree of disorder.

Based on single-oscillator model the moment of optical spectra M_{-1} and M_{-3} can be determined from the following relations [21]:

$$E_o = \sqrt{\frac{M_{-1}}{M_{-3}}} ; E_d = \sqrt{\frac{(M_{-1})^3}{M_{-3}}} \quad (6)$$

The obtained E_o and E_d are both increases as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration increased as shown in Table II. The optical moments are related to the macroscopic quantities like dielectric constants, effective number of valence electrons in the investigated material [21, 23].

Table II. The Wemple-Didomenico oscillating parameters.

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ %	E_o (eV)	E_d (eV)	M_{-1} (eV) ²	M_{-3} (eV) ²
0	1.2251	5.9149	0.2071	0.0059
2	1.4767	5.5508	0.2660	0.0086
4	1.5305	5.3997	0.2834	0.0097
6	1.6711	5.2957	0.3156	0.0113
8	1.6664	5.2641	0.3166	0.0114

The complex dielectric constant can be obtained theoretically, since it was related to the absorption coefficient. The real part ϵ_1 and the imaginary part ϵ_2 of the dielectric constant, was obtained using relation [24]:

$$\epsilon_1 = n^2 - k^2 ; \epsilon_2 = 2nk \quad (7)$$

where n is the refractive index of the films and k is the extinction coefficient, they can be calculated by [24]:

$$n = \sqrt{\frac{4R - R^2}{(R-1)^2} \frac{(R+1)}{(R-1)}} ; k = \frac{R-1}{4n} \quad (8)$$

where R is reflectivity, and λ is the wavelength of the incident light. The imaginary part of dielectric constant, represents loss factor or energy absorbed.

Fig.6(a,b) illustrate the variation of real part and imaginary part of the dielectric constant as a function of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration for different frequency, near absorption edge region. The real and imaginary part of the dielectric constant increases slowly with salt concentration, while they decrease with increase of wavelength, and they are almost constant in the visible region.

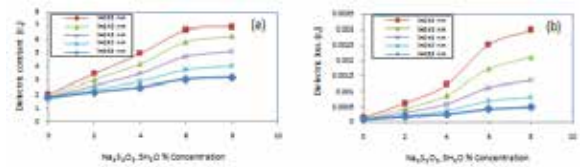


Fig.6. (a) Real part and (b) Imaginary part of dielectric constant as a function of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ concentration.

Thermal Gravimetric Analysis (TGA) and Derivative Thermal Gravimetric Analysis (DTGA) of PVA: $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ polymer electrolyte films, are shown in Fig.(7) and Fig.(8) respectively. The TGA and DTGA curves have been summarized in Table III, which is divided to two main temperature regions and the final decomposition process represented by the percentage of ash left. The temperature at which weight loss is reaching 70% is also tabulated.

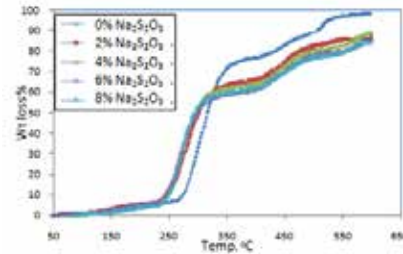


Fig.7. Weight loss from Thermal Gravimetric Analysis TGA curves of PVA: $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ polymer electrolyte films.

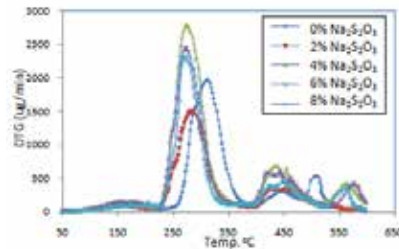


Fig.8. Derivative Thermal Gravimetric Analysis DTGA curves of PVA: $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ polymer electrolyte films.

The gradual decrease in the % of Wt loss with the increase of $\text{Na}_2\text{S}_2\text{O}_3$ contents, for both temperature regions (230-380 and 380-520 oC) indicate there is an increase in the thermal stability of the polymer.

The lower values of percentage mass loss in the first decomposition step may be due to splitting or volatilization of small molecule, and/or the evaporation of residual absorbed water which indicate the presence of physical transition [25]. The latter process in TGA curves covers a temperature range (380-520 oC), as physical transition and the thermal degradation of the samples. Therefore the higher values of mass loss in second decomposition step indicate the existence of chemical degradation process resulting from bond scission in the polymeric backbone. The increase in T70 oC and Ash % with the increasing of % $\text{Na}_2\text{S}_2\text{O}_3$ also indicates the increase in the thermal stability of the polymer films by addition of $\text{Na}_2\text{S}_2\text{O}_3$.

Table III: TGA and DTGA data for PVA: $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte polymer films.

Polymer film	Temp. range	Mass loss %	DTG peak oC	T70 oC	Ash %
Pure PVA	230-380	71.1	308	345	1.98
	380-520	21.25	447		

2% Na ₂ S ₂ O ₃	230-380	60	280	429	13.7
	380-520	20.5	438		
4% Na ₂ S ₂ O ₃	230-380	58.4	274	436	11.04
	380-520	19.6	436		
6% Na ₂ S ₂ O ₃	230-380	56.0	268	451	14.5
	380-520	19.6	441		
8% Na ₂ S ₂ O ₃	230-380	56.4	270	454	16.2
	380-520	18.0	450		

T70 oC Temperature corresponding to 70% weight loss

Conclusions

The polymer electrolyte films of PVA:Na₂S₂O₃·5H₂O are prepared by solution caste technique. The IR spectra showed vibration peaks in the range 2230-1950 cm⁻¹ which indi-

cated that the doping was complexed with polymer matrix. The IR-UV-VIS spectra provide evidence for the formation of polymer composite. The optical behavior of the samples shows that the films almost transmitting in the visible region. The Na₂S₂O₃·5H₂O content caused increase in the absorbance at the near infrared domain. The real and imaginary parts of dielectric constants are investigated near absorption edge region. Information about disorder degree and optical band gap of the films has been obtained from Wemple-DiDomenico model. The results have shown that the single oscillator energy and the dispersion energy, of the samples are dependent on the Na₂S₂O₃·5H₂O concentrations. The TGA and DTGA spectrum analysis shows the addition of Na₂S₂O₃·5H₂O to PVA films increase the thermal stability of the polymer.

REFERENCE

- [1] P. Sharma, D. K. Kanchan, N. Gondaliya, "Effect of Nano-Filler on Structural and Ionic Transport Properties of Plasticized Polymer Electrolyte", *Open Journal of Organic Polymer Materials*, 2012, 2, 38-44, (2012). | [2] P. C. Sekhar, P. N. Kumar, A. K. Sharma, "Effect of plasticizer on conductivity and cell parameters of (PMMA+NaClO₄) polymer electrolyte system", *IOSR Journal of Applied Physics*, 2 (4), 1-6, 2012. | [3] A. Tawansi, A.H. Oraby, H.M. Zidan, M.E. Dorgham, "Effect of one-dimensional phenomena on electrical, magnetic and ESR properties of MnCl₂-filled PVA films", *Physica B* 254 (1-2), 126-133, (1998). | [4] D. K. Pradhan, R.N.P. Choudhary, and B.K. Samantaray, "Studies of dielectric and electrical properties of plasticized polymer nanocomposite electrolytes", *Materials Chemistry and Physics* 115, 557-561 (2009). | [5] D. K. Pradhan, R.N.P. Choudhary, and B.K. Samantaray "Studies of Dielectric Relaxation and AC Conductivity Behavior of Plasticized Polymer Nanocomposite Electrolytes", *Int. J. Electrochem. Sci.*, 3, 597-608 (2008). | [6] A. Tawansi, A. El-Khodary, and M.M. Abdelnaby, "A study of the physical properties of FeCl₃ filled PVA", *Current Applied Physics*, 5, 572-578 (2005). | [7] S. Rajendran, M. Sivakumar, R. Subadevi, "Investigations on the effect of various plasticizers in PVA-PMMA solid polymer blend electrolytes", *Mater. Lett.* 58, 641-649, (2004). | [8] Hew-Der Wu, Peter P. Chu, Chen-Chi M. Ma, and Feng-Chih Chang, "Effects of Molecular Structure of Modifiers on the Thermodynamics of Phenolic Blends: An Entropic Factor Complementing PCAM", *Macromolecules* 32, 3097-3105, (1999). | [9] H. Eisazadeh, "Studying the Characteristics of Polypyrrole and its Composites", *World Journal of Chemistry* 2 (2), 67-74, (2007). | [10] S. Rajendran, M. Sivakumar, R. Subadevi, "Effect of salt concentration in poly(vinyl alcohol)-based solid polymer electrolytes", *Journal of Power Sources* 124 (1), 225-230, (2003). | [11] O.J. Sweeting, *The Science and Technology of Polymer Films*, Vol.2, Interscience Publishers, New York, (1968). | [12] A.A. El-Zahhar, M. Ismail, H.A. El-Naggar, Seventh Aaab International Conference on Polymer Science & Technology, Cairo, Egypt, 5-9, (2003). | [13] O. Gh. Abdullah, and D. R. Saber, "Optical absorption of polyvinyl alcohol films doped with Nickel Chloride", *Applied Mechanics and Materials* 110-116, 177-182, (2012). | [14] A. Deronzier, and J.C. Moutet, "Functionalized polypyrroles. New molecular materials for electrocatalysis and related applications", *Acc. Chem. Res.* 22 (7), 249-255, (1989). | [15] O. Gh. Abdullah, and S. A. Hussen, "Variation of Optical Band Gap Width of PVA films Doped with Aluminum Iodide", *Advanced Materials Research* 383-390, 3257-3263, (2012). | [16] C. Uma Devi, A.K. Sharma, and V.V.R.N. Rao, "Electrical and optical properties of pure and silver nitrate-doped polyvinyl alcohol films", *Material Letters* 56, 167-174 (2002). | [17] V. Raja, A.K. Sarma, and V.V.R. Narasimha Rao, "Optical properties of pure and doped PMMA-CO-P4VPNO polymer films", *Materials Letters* 57 (30), 4678-4683 (2003). | [18] F. Urbach, "The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids", *Phys. Rev.* 92, 1324 (1953). | [19] R. Das, and S. Pandey, "Comparison of optical properties of bulk and nano crystalline thin films of CdS using different precursors", *International Journal of Material Science* 1 (1), 35-40, (2011). | [20] S.H. Wemple, M. DiDomenico, "Behavior of the Electronic Dielectric Constant in Covalent and Ionic Materials", *Phys. Rev. B* 3 (4), 1338-1351, (1971). | [21] M.A. Mahdi, and S.K.J. Al-Ani, "Optical characterization of chemical bath deposition Cd_{1-x}Zn_xS thin films", *Int. J. Nanoelectronics and Materials* 5, 11-24, (2012). | [22] M. Modreanu, M. Gartner, N. Tomozeiu, "Optical characterization of LPCVD SiO_xNy thin films", *Proceedings-Electrochemical Society*, 1, 118-129, (2003). | [23] A.H. Ammar, "Studies on some structural and optical properties of ZnxCd1-xTe thin films", *Applied Surface Science*, 201, 9-19, (2002). | [24] F.I. Ezema, P.U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke, and R.U. Osuji, "Growth and optical properties of Ag₂S thin films deposited by chemical bath deposition technique", *Journal of the University of Chemical Technology and Metallurgy* 42 (2), 217-222, (2007). | [25] A. M. Shehap, "Thermal and Spectroscopic Studies of Polyvinyl Alcohol/Sodium Carboxy Methyl Cellulose Blends", *Egypt. J. Solids*, 31 (1), 75-91, (2008). |