PROGRESS IN ELECTRICAL AND OPTICAL PROPERTIES OF VANADIUM IONS DOPED (PVA+ZnO) POLYMER FILMS

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ABSTRACT

The various concentrations of vanadium ions doped in (PVA+ZnO) polymer films prepared by the slow evaporation method and the electrical, optical, and structural properties of polymer films investigated by EPR, optical, and FTIR spectroscopy. The EPR spectrum exhibits lande g- factor $g_{||}=1.96$, $g_{\perp}=2.04$, and the hyperfine splitting constant values were $A_{||} \geq A_{\perp}$. The optical absorption spectrum shows three bands at 420nm, 692nm, and 832nm. The bandgap energy of polymer films decreased with increases in vanadium ions concentration. This change indicates that polymer films became more semiconducting. The (PVA+ZnO) polymer films show an evident change by the addition of vanadium ions and the structural peaks at 1003, 1079, 1142, 1271 cm^{-1} from the FTIR spectrum.

Keywords: Magnetic Stirrer, Distilled Water, Polyvinyl Alcohol, Zinc Oxide, Vanadium Sulphate.

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INTRODUCTION

Polymer-salt film compositions of vanadium and water-soluble polymers like PVA are the base for promising hybrid *polyfunctional* materials. Their properties are controlled to a great extent by complex formation between polymer and salt components. These films exhibit unique features, which are not intrinsic to either of the components. *Electrophysical* properties of PVA-Vanadium compositions are essential for both scientists and engineers¹. Organic polymers doped with transition metals oxides like V_2O_5 exhibits metallic and semiconductor conduction has attracted ever closer attention of researchers. The effect of V_2O_5 on polymeric materials proved by some experiments; these materials powerfully lean on the successes of improving their electrical and optical properties².

Scientists are continuously searching for effective new materials for *optoelectronics*, *microelectronics*, and *molecular electronics* all over the world. In the present work, we used polyvinyl alcohol (PVA) $(-\text{CH}_2-\text{CH}-\text{OH})_n$, which consists of hydroxyl groups bound to methane carbons with a carbon chain backbone. The formation of polymer films is due to the OH groups, which can be a source of hydrogen bonding. PVA used as a binder and *electrochemical* window due to its high tensile strength and excellent absorption resistance³⁻⁵. Zinc oxide is one of the most effective materials for the manufacture of future generation optoelectronic devices in the Ultra-Violet region and optical display devices. It has a high exciton binding energy (60 meV), much higher than that of Ge (25 meV) at room temperature. Zinc oxide shows much more resistant to radiation damage⁵. Vanadyl ion (VO^{2+}) is the most steady cation among a few molecular paramagnetic transition metal ions, which is used as an impurity probe extensively for EPR studies. Vanadium doped zinc polymer films attracted researchers because of improved electric, magnetic, optical, and semiconducting properties. Vanadium doped in zinc can abruptly increase its piezoelectric charge coefficient value and vary promising for the fabrication of high performance in nanogenerators⁶.

The present work focused on spectroscopic investigations of vanadyl doped (PVA+ZnO) polymer complexes. The effect of vanadyl ion on the (PVA+ZnO) complex is the main aim of the present study. The polymer films verified and studied with the EPR, optical absorption, and FTIR studies.

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EXPERIMENTAL

The high-quality chemicals Polyvinyl (alcohol) (PVA), zinc acetate ($(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$), Vanadium sulphate ($\text{V}_2\text{O}_5 \cdot \text{SO}_4$), and the double-distilled water used for the preparation of reactant solutions and collected by National scientific products Pvt. Ltd., Guntur, India.

5 mol% of each PVA and zinc acetate solutions were prepared separately by dissolving commercial AR grade chemicals using double distilled water as a solvent with gently heating in water bath. The two solutions stirred until the polymer wholly dissolved and forms a uniform, transparent, viscous solution. Then the two solutions were mixed and stirred for 30 min using a magnetic stirrer. The desired concentration of $\text{V}_2\text{O}_5 \cdot \text{SO}_4$ solutions were mixed with 5 mol% of (PVA+ZnO) solutions and stirred thoroughly with a magnetic stirrer. The final solution poured into the Petri dishes. The films were grown by slow evaporation in dry air and peeled off from the Petri dishes after seven days. The prepared films are light greenish color with a thickness of approximately 1mm. Hereafter the (PVA+ZnO) referred to as PVAZn films. The photographs of prepared samples shown in Fig.-1.

Fig.-1: A Photograph of Pure PVAZn and PVAZn:VO₂⁺ (0.8 mol%) Polymer Films.

RESULTS AND DISCUSSION

EPR Studies

Vanadyl ion has the electronic configuration $[\text{Ar}] 3d^1$, which thereby leads to paramagnetism in VO^{2+} . The ^{51}V nucleus (99.8%) abundant has a nuclear spin $I = 7/2$ and a massive magnetic moment. No Electron Paramagnetic Resonance signal observed in the spectra of undoped PVAZn polymer film, indicating that no paramagnetic signatures(EPR) were present in the starting materials. When various mol% of vanadyl ions added to the PVAZn complex, the EPR spectra of all the investigated samples exhibit well-resolved resonance signals. The Electron Paramagnetic Resonance Spectra of vanadyl ions doped PVAZn polymer films shown in Fig.-2. There is no specific effect of VO^{2+} ion concentration on the structure of the PVAZn: VO^{2+} polymer film except the variation in intensity.

Generally, an eight component *hyperfine* structure expected from the ^{51}V nucleus and the electronic moment of the paramagnetic V^{4+} ions. Due to the dipole-dipole interaction between them. An axial spin-Hamiltonian, which includes the hyperfine interaction, has been used to describe the EPR spectra of V^{4+} . The EPR spectra analyzed using the spin-Hamiltonian equation of the form⁷,

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

Where, β is the Bohr magneton. H_x , H_y , H_z are the static magnetic field components. S_x , S_y , and S_z are the spin operators of the electron. I_x , I_y , and I_z are the spin operators of the nucleus. $g_{\parallel}$ and $g_{\perp}$ are the parallel and perpendicular values of the anisotropic g tensor. Here $A_{\parallel}$ and $A_{\perp}$ are parallel and perpendicular hyperfine values of the hyperfine tensor 'A' and nuclear quadrupole contribution is neglected.

Fig.-2: EPR Spectra of PVAZn: VO²⁺ (0.2-0.8 mol%) Films at Room Temperature.

In order to describe the ⁵¹V in our EPR experiments, the magnetic field positions of the hf's lines expressed as,

$$H_{\parallel}(m_l) = (h\nu/g_{\parallel}\mu_B) - m_l A_{\parallel} - (63/4 - m_l^2) A_{\perp}^2 (g_{\parallel}\mu_B/h\nu) \quad (2)$$

$$H_{\perp}(m_l) = (h\nu/g_{\perp}\mu_B) - m_l A_{\perp} - (63/4 - m_l^2) (A_{\parallel}^2 + A_{\perp}^2) (g_{\perp}\mu_B/h\nu) \quad (3)$$

Where h is the Plank's constant, ν the microwave frequency, ' m_l ' is the magnetic quantum number of the vanadium nucleus, which takes the values $\pm 7/2$, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$. The spin-Hamiltonian parameters are calculated using Eqs.-2 and 3.

The two fundamental parameters derived from EPR spectral measurements, Lande g - factor and the electron-nuclear spin coupling constant (A) for the VO²⁺ ion-doped PVAZn polymer film, are evaluated and are given in Table-1. For VO²⁺ ions, the increase in values of $g_{\parallel}$ and $g_{\perp}$ depend on the vanadium-ligand distance, which is due to the shortening of V-O and V=O bond lengths. The experimentally obtained g values are more or less constant at $g_{\parallel} = 1.96$ and $g_{\perp} = 2.04$ for all the concentrations of vanadium ions and $A_{\parallel} > A_{\perp}$. The g and A values obtained in the present work are close to those vanadyl complexes reported in the literature⁸⁻¹⁰. Here the vanadyl ions in PVAZn polymers exist as VO²⁺ ions. The vanadium ions octahedral coordination with a tetragonal compression and has C_{4v} symmetry.

The term $\Delta g_{\parallel}/\Delta g_{\perp}$ indicates the extent of tetragonal distortion, which relates to the bond strength of both V double bond oxygen (V=O) and V single bond oxygen (V-O) ligand. The values of $\Delta g_{\parallel}/\Delta g_{\perp}$ (where $\Delta g_{\parallel} = (2.0023 - g_{\parallel})$ and $\Delta g_{\perp} = (2.0023 - g_{\perp})$) is also calculated and are presented in Table 1. It observed that $\Delta g_{\parallel}/\Delta g_{\perp}$ value decreases with vanadyl content up to 0.6 mol%. This decrease indicates that the symmetry around VO²⁺ ions is improved. The vanadyl ions are in tetragonally less distorted octahedral sites. On the further increase of vanadyl content, the $\Delta g_{\parallel}/\Delta g_{\perp}$ increases. This change implies that as the concentration increases, the deviation from octahedral symmetry increases. So that the VO²⁺ ions are more tetragonally distorted¹¹.

In the absence of covalency, the parallel and perpendicular components of the hyperfine tensor can be written as¹²

$$A_{\parallel} = -P [(4/7) + (g_{\parallel} - 2.0023) + (3/7)(g_{\perp} - 2.0023) + k] \quad (4)$$

$$A_{\perp} = P [(2/7) + (11/14)(g_{\perp} - 2.0023) - k] \quad (5)$$

Where, ' P ' is the dipolar hyperfine coupling constant given by $P = 2\gamma\beta\beta_N \langle r^{-3} \rangle \geq 0.0128 \text{ cm}^{-1}$, where r^3 is the average size of the vanadium 3d orbital. It accounts for the dipole-dipole interaction of electron

moment with the nuclear moment. 'k' is the dimensionless Fermi contact interaction parameter, which constitute the quantity of unpaired electron density at the vanadium nucleus. In other words, it accounts for the contribution of an admixture of s-electrons to the value of hyperfine structure constant.

Bleaney and Stevens¹³ reported, the quantity Pk/γ_g (γ_g is the gyromagnetic ratio) is constant for iron group ions, and it takes the values 0.006, 0.0054, 0.0067 and 0.006 cm⁻¹ for Cu²⁺, Cr³⁺, Mn²⁺, and VO²⁺ ions respectively. To get this value, authors should take negative values for $A_{||}$ and $A_{\perp}$ and evaluated 'P' and 'k' values for the samples presented in Table-1. For the ⁵¹V nucleus, the value of the gyromagnetic ratio γ_g is 1.468.¹⁰ By using this value, the authors evaluated Pk/γ_g and obtained the value as 0.008, which is approximately equal to those vanadyl complexes reported in the literature^{14,15}. The parameter 'k' indicates extreme sensitivity to the distortion of the electron orbits of the central vanadium ion. The high values of 'k' indicate a significant contribution to the hyperfine constant by the unpaired 's' electron.

Spin Concentration

The concentration of V⁴⁺ centers was determined by double numerical integration of the EPR spectrum of V⁴⁺ signal and comparing with the reference sample. Here the copper is taken as a reference sample for the calculations. The formula is given by¹⁶,

$$N = [A_x(P_{std})^{1/2} (Scan_x)^2 G_{std} (B_m)_{std} (g_{std})^2 [S(S+1)]_{std}] / A_{std} (P_x)^{1/2} (scan_{std})^2 G_x (B_m)_x (g_x)^2 [S(S+1)]_x [Std] \quad (6)$$

Where, N is the number of spins participating in resonance, and A is the area under the absorption curve. 'Scan' is the magnetic field corresponding to the unit length of the chart, G is the gain, B_m is the modulation field width, g is the g- factor, S is the spin of the system in its ground state, P is the power of the microwaves. The subscripts 'x' and 'std' represents the corresponding quantities for the PVAZn: VO²⁺ polymer films and copper sample^{17,18}. A plot drawn between log N against different concentrations of VO²⁺ ions is shown in Fig.-3. From the graph, it observed that the no. of spins increases with VO²⁺ concentration except at 0.6 mol% of vanadium. At 0.6 mol% of VO²⁺ ions, the spin concentration decreases due to the dipolar interactions between the vanadyl ions¹¹.

From the EPR spectral information, the magnetic susceptibilities calculated for different concentrations of VO²⁺ ions using the formula¹⁹,

$$\chi = [Ng^2 \beta^2 J(J+1)] / 3K_B (T) \quad (7)$$

Where, 'N' is the spin concentration per kg, 'J' is the total angular momentum, ' β ' is the Bohr magneton, ' k_B ' is the Boltzmann constant, and 'T' is the absolute temperature. The concentrations of spins 'N' can be calculated by double integrating the first derivative EPR spectrum by using Eq.-6, $g = [(g_{||} + 2g_{\perp})/3]$ taken from EPR data. By using the above equation, the paramagnetic susceptibilities calculated as a function of VO²⁺ ion concentration. Fig.-4 shows a plot of $1/\chi$ as a function of different concentrations of VO²⁺ ions in PVAZn:VO²⁺ polymer film.

Fig.-3: A Plot of log N against VO²⁺ Ion Concentrations in PVAZn Films at Room Temperature.

Table-1: The Spin-Hamiltonian Parameters, Molecular Orbital Bonding Coefficients for PVAZn: VO²⁺ Polymer Films.

VO ²⁺ (mol%)	g	g _⊥	A x 10 ⁻⁴ (cm ⁻¹)	A _⊥ x 10 ⁻⁴ (cm ⁻¹)	Δ g /Δ g _⊥	A ¹ x 10 ⁻⁴ (cm ⁻¹)	A _⊥ ¹ x 10 ⁻⁴ (cm ⁻¹)	P x 10 ⁻⁴ (cm ⁻¹)	K	α ²	β ^{2*}
0.2	1.96	2.04	177	100	1.12	55	28	93	1.39	1.042	1.02
0.4	1.96	2.04	173	111	1.09	42	23	71	1.87	1.085	1.06
0.6	1.96	2.06	175	102	1.02	50	28	86	1.51	1.056	1.02
0.8	1.95	2.04	179	102	1.39	43	22	70	1.76	1.390	1.16

Fig.-4: A Plot is drawn between the Reciprocal of Susceptibility against Different Concentrations of Vanadyl Ions in PVAZn: VO²⁺ Polymer Films at Room Temperature.

Optical Absorption Studies

The optical absorption spectra of different concentrations (0.2-0.8 mol %) of vanadyl ions doped in PVAZn polymer films shown in Fig.-5(a)

Fig.-5(a): Optical Absorption Spectrum of PVAZn:VO²⁺ (0.2-0.8 mol%) Polymer Films.

The absorption spectra consist of three bands, centered at 420 nm, 692 nm, and 832 nm and are assigned to ${}^2B_{2g} \rightarrow {}^2E_g$, ${}^2B_{2g} \rightarrow {}^2B_{1g}$ and ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transitions, respectively shown in Fig.-5(b, c & d)²⁰. VO²⁺ ion belongs to d¹ configuration and will have a ground state of 2D . In octahedral symmetry, the d electron occupies the t_{2g} orbital and gives rise to a ${}^2T_{2g}$ ground state. On excitation, the electron occupies E_g orbital and gives rise to 2E_g state. Thus only one single transition ${}^2T_{2g} \rightarrow {}^2E_g$, and correspondingly a single band is expected for VO²⁺ ions in octahedral symmetry. However, due to non-symmetrical alignment of the V=O bond along the axis, VO²⁺ site symmetry lowers to tetragonal or rhombic. In a tetragonal symmetry, the ${}^2T_{2g}$ level splits into ${}^2B_{1g}$ and ${}^2A_{1g}$ levels. Accordingly, the optical absorption spectra of VO²⁺ ions in

tetragonal symmetry mostly consist of three bands corresponding to the transitions ${}^2B_{2g} \rightarrow {}^2B_{1g}$, ${}^2B_{2g} \rightarrow {}^2E_g$, and ${}^2B_{2g} \rightarrow {}^2A_{1g}$.²¹ In the present study, there is no considerable change in the band positions of the all-polymer films with different concentrations of vanadyl ions.

Fig.-5(b, c and d): The Three Optical Absorption Bands for VAZn: VO²⁺(0.2 mol%) Polymer Film.

The absorption bands assigned to the d – d transitions corresponding to VO²⁺ ions. The octahedral and tetragonal crystal field parameters calculated using the expressions,

$${}^2B_{2g} \rightarrow {}^2E_g = E_1 = -3D_S + 5D_t \quad (8)$$

$${}^2B_{2g} \rightarrow {}^2B_{1g} = E_2 = 10D_q \quad (9)$$

$${}^2B_{2g} \rightarrow {}^2A_{1g} = E_3 = 10D_q - 4D_s - 5D_t \quad (10)$$

The above three equations were solved and the parameters $D_q=1445 \text{ cm}^{-1}$, $D_s= -3064 \text{ cm}^{-1}$ and $D_t= 590 \text{ cm}^{-1}$ are obtained.

The fundamental absorption edge studied in the UV region, which is a useful technique to study the optical transitions and electronic band structure in crystalline and non-crystalline material. The main factor of the absorption edge is an exponential increase in the absorption coefficient ' α ' with photon energy $h\nu$. The absorption coefficient ' α ' can be determined as a function of frequency by using the relation,

$$\alpha(\nu) = (A/d) \times 2.303 \quad (11)$$

Where 'A' is the absorbance at frequency ' ν ' and 'd' is the width of the sample. The optical band gap for a direct and indirect transition can be calculated using the relation,

$$E_{\text{opt}} = h\nu - (\alpha h\nu / B)^n \quad (12)$$

The direct bandgap energies (E_{opt}) of the VO^{2+} :PVAZn polymers obtained from their ultraviolet absorption by plotting $(\alpha h\nu)^2$ as a function of photon energy $h\nu$ and shown in Fig.-6.

Fig.-6: A Plot between $(\alpha h\nu)^2$ and $h\nu$ for PVAZn: VO^{2+} (0.2-0.8 mol%) Polymer Films.

The indirect bandgap energies (E_{opt}) of the PVAZn: VO^{2+} polymer films calculated from their ultraviolet absorption graphs. The graph by plotting $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$. It shows Fig.-7.

The respective values of E_{opt} obtained by extrapolating the linear region of the graph towards the X-axis to meet at $(\alpha h\nu)^2 = 0$ and $(\alpha h\nu)^{1/2} = 0$ for direct and indirect transitions respectively.

The absorption coefficients in Urbach's tail region given as a function of photon energy by the Eq.-13,

$$\alpha = \alpha_0 \exp(h\nu/\Delta E) \quad (13)$$

Here α_0 is a constant, ΔE is the Urbach energy explains the energy gap between localized tails in the forbidden region. Urbach plots are the natural logarithm of the absorption coefficient $\ln(\alpha)$ plotted against photon energy ($h\nu$). In the present study, such an Urbach plots for VO^{2+} : PVAZn polymer films shown in Fig.-8.

All the direct, indirect optical band gaps and Urbach energy values of PVAZn: VO^{2+} polymer films calculated. These values tabulated in Table-2.

The direct, indirect and Urbach energies of the PVAZn: VO^{2+} polymer samples decrease with an increase of vanadyl ion concentration. This increase indicates that with an increase in the strength of VO^{2+} ions, PVAZn polymer film becomes more semiconducting.

Fig.-7: A Plot Drawn between $(\alpha hv)^{1/2}$ and $h\nu$ for PVAZn: VO^{2+} (0.2-0.8 mol%) Polymer Films.

Fig.-8: A Plot between $\ln(\alpha)$ and $h\nu$ for PVAZn: VO^{2+} (0.2-0.8 mol%) Polymer Films.

EPR and optical data can be correlated and the molecular orbital theory shows that the components $A_{\parallel}$ and $A_{\perp}$ consists of the contribution from $A_{\parallel}^1$ and $A_{\perp}^1$ of the $3d_{xy}$ electron to the hyperfine structure and the $P\beta_2^{*2}k$ term arising due to the anomalous contribution of the s-electrons. The modified form of the equations (1.14) & (1.15) can be written as²²,

$$A_{\parallel} = A_{\parallel}^1 - P\beta_2^{*2}k \quad (14)$$

$$A_{\perp} = A_{\perp}^1 - P\beta_2^{*2}k \quad (15)$$

Where, $A_{\parallel}^1 = P[-\beta_2^{*2}(4/7) + (g_{\parallel} - 2.0023) + (3/7)(g_{\perp} - 2.0023) + D_{\parallel} + (3/7)D_{\perp}]$
and $A_{\perp}^1 = P[\beta_2^{*2}(2/7) + (11/4)(g_{\parallel} - 2.0023) + (11/4)D_{\perp}]$.

Here $D_{\parallel} = -0.0125$ and $D_{\perp} = -0.0015$ are small corrections²³ and other symbols have their usual meanings. Using the EPR data, the molecular orbital coefficients α^2 and β_2^{*2} evaluated, where β_2^{*2} is a measure of the degree of π bonding with the equatorial ligands. α^2 represent the in-plane σ -bonding⁹, which are obtained

from a suitable linear combination of the $g_{\parallel}$ and $g_{\perp}$ and also $A_{\parallel}$ and $A_{\perp}$ which are defined by the following equations^{24,25},

$$\alpha^2 = (7/4) [(A_{\parallel} - A)/P + (2/3)g_{\parallel} - (5/21)g_{\perp} - (6/7)] \quad (16)$$

Where 'P' is a term, which takes into account the dipole-dipole interaction of the electron moment with the nuclear moment. A_0 is the isotropic hyperfine interaction factor obtained from the equation $A = (A_{\parallel} + 2 A_{\perp})/3$.²⁶

The molecular orbital coefficient is represented by,

$$\beta_2^{*2} = (-7/6)\Delta g_{\parallel} + (5/12)\Delta g_{\perp} + (7/6) [(A_{\parallel} - A_{\perp})/P] \quad (17)$$

Where $\Delta g_{\parallel} = 2.0023 - g_{\parallel}$, $\Delta g_{\perp} = 2.0023 - g_{\perp}$. β_2^{*2} represents the axial ligand π -bonding. The evaluated values of β_2^{*2} show that the electrons in the in-plane vanadium ligand π bonding orbitals are ionic in nature. The calculated values of α^2 , β_2^{*2} , k , $A_{\parallel}$, $A_{\perp}$, $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}^1$ and $A_{\perp}^1$ are depict in Table-1.

The term $C = 1 - \beta_2^{*2}$ represents the fraction of the delocalization of the unpaired 'd' electrons over ligand orbitals. The average value of $C = 0.024$ indicates the delocalization of the unpaired d-electrons over ligand orbital²⁷.

Table - 2: The Values of Direct, Indirect Bandgaps and Urbach Energies of VO^{2+} Ions doped in PVAZn Polymer Films.

VO^{2+} mol%	Optical Bandgap Energy (Eopt)		Urbach Energy (eV)
	Direct(eV)	Indirect (eV)	
0.2	3.12	3.67	3.15
0.4	2.95	3.10	2.15
0.6	2.61	2.61	2.07
0.8	2.53	2.53	1.25

FT-IR

FT-IR spectroscopy used to identify the structural bonds present in the polymer matrix. The FTIR spectra of PVAZn and PVAZn: VO^{2+} polymer films recorded at room temperature in the wavenumber range 600-2000 cm^{-1} and shown in Fig.-9(a and b).

From the pure spectra, the bands at 617-738 cm^{-1} have assigned to Zn-O stretching of the polymer complex. The band at 838 cm^{-1} has assigned to C-C, which arises from the stretching mode of the host polymer. The bands observed at 1000-1142 cm^{-1} has assigned to the C-O-C stretching mode formed by the cross-linking of PVA with Zn-O.^{28,29} The bands at 1396 cm^{-1} , 1457 cm^{-1} , 1520 cm^{-1} , 1541 cm^{-1} has assigned to bending vibrations of the CH_2 group. The bands at 1649-1741 cm^{-1} have attributed to the C=O stretching mode. The band at 738 cm^{-1} splits into 713 and 766 cm^{-1} due to the addition of vanadium into (PVA+ZnO) matrix. An apparent shifting was observed for 1003, 1079, 1142, 1271, 1396, and 1457 cm^{-1} bands when vanadium added to the polymer matrix. The shifting of the bands is the clear evidence of vanadium enters into the (PVA+ZnO) complex. The shifting of these bands in the polymer matrix correlated to the charge transfer reaction between the polymer chain and the dopant.

(a)

(b)
Fig.-9: FT-IR Spectrum of (a) Pure PVAZn and (b) PVAZn:VO²⁺ (0.2-0.8mol%) Polymer Films recorded at Room Temperature.

The remaining bands are broadened and slowly disappeared after 1142 cm⁻¹ when increasing of vanadium content in PVAZn. All the IR band positions and their corresponding band assignments presented in Table-3.

Table - 3: The IR Band Positions and Their Corresponding Band Assignments of PVAZn and VO²⁺:PVAZn Polymer Films.

Pure (PVAZn)	PVAZn:VO ²⁺ (x mol%)				Band Assignment
	0.2mol%	0.4mol%	0.6mol%	0.8mol%	
617					Zn-O
667	662	659	657	657	
738	713	713	714	714	
	766	767	766	767	C-C
838	840	840	840	840	
1003	947	949	949	949	
1079	1015	1015	1015	1015	C-O-C
1142	1107	1107	1107	1103	
1271	1190	1195	1195	1195	
1396	1337	1337	1337	1337	CH ₂
1457	1491	1491	1491	1491	
1541					
1649					C=O
1702					
1741					
1838					

CONCLUSION

- From the EPR spectra of PVAZn: VO²⁺ polymer films, the VO²⁺ ions are in tetragonally compressed octahedral sites.
- The spin-Hamiltonian parameters g & A were calculated. The variation of N values with the increase of VO²⁺ ion concentration gives non-monotonic behavior due to the dipole interactions between the vanadyl ions.
- The optical absorption spectra of polymer films exhibit three absorption bands at 421, 692, 832 nm. These bands give characteristics of VO²⁺ ions in tetragonally distorted octahedral sites.
- From the ultra-violet absorption edges, the optical band gap energies (E_{opt}) calculated. It stimulates to observe that the optical band gap energies for these polymers decrease with increases of vanadium content were found. This change indicates that the polymer films turn into more semiconducting.

- The FTIR spectra exhibit stretching and bending vibration modes of Zn-O, C-H, C=C, CH₂, and C-O groups.

REFERENCES

1. M. I. Abd-Elrahman, *Nanoscale and Microscale Thermophysical Engineering*, **17**, 194(2013), DOI:10.1080/15567265.2013.776152
2. Nabil Shash, *Ionics*, **19**, 1825(2013), DOI:10.1007/s11581-013-0923-0
3. Ch. Liga Raju, K.V.Narasimhulu, N.O.Gopal, J.L. Rao, B.C.V.Reddy, *Journal of Molecular Structure*, **754**, 100(2005), DOI:10.1016/j.molstruc.2005.07.006
4. A.S. Kutsenk, S.M. Maloletor, S.Y.A. Kuchmiletal, *Ukrainian Journal of Physics*, **49(12A)**, A34(2004).
5. A. A. Ostroushko, M.Yu. Sennikov, *Russian Journal of Inorganic Chemistry* **54**, 115(2009), DOI:10.1134/S0036023609010185
6. Manoj Kumar Gupta, Ju-Hyuck Lee, Keun Young Lee, Sang-Woo Kim, *American Chemical Society Nano*, **7(10)**, 8932(2013), DOI:10.1021/nn403428m
7. A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 175(1970).
8. S. Khasa, V. P. Seth, Ashish Agarwal, R. Murali Krishna, S. K. Guptha, Prem Chand, *Journal of Material Chemistry and Physics*, **72(3)**, 366(2001), DOI: 10.1016/S0254-0584(01)00317-0
9. O. Cozar, I. Ardelean, V. Simon, L. David, V. Mih, N. Vedeian, *Applied Magnetic Resonance*, **16**, 529(1999), DOI:10.1007/BF03161948
10. O. Cozar, I. Ardelean, V. Simon, G. Ilonca, C. Cracium, C. Cefan, *Journal of alloys and Compounds*, **326**, 124(2001), DOI:10.1016/S0925-8388(01)01247-6
11. I. Omkaram, R. P. Sreekanth Chakradhar, J. Lakshmana Rao, *Physica B*, **388**, 318(2007), DOI: 10.1016/j.physb.2006.06.134
12. R. Muncaster, S. Parke, *Journal of Non-Crystalline Solids*, **24**, 399(1977), DOI:10.1016/0022-3093(77)90107-7
13. B. Bleaney, K.W.H. Stevens, *Reports on Progress in Physics*, **16**, 108(1953), DOI:10.1088/0034-4885/16/1/304/pdf
14. B. Yasoda, R. P. Sreekanth Chakradhar, J. L. Rao, N. O. Gopal, *Material Chemistry Physics*, **106**, 33(2007), DOI: 10.1063/1.5130252
15. N. Kerkouri, M. Haddad, M. Et. Tabirou, A. Chahine, L. Laanab, *Physica B*, **406**, 3142(2011), DOI: 10.1016/j.physb.2011.04.057
16. J. A. Weil, J. R. Bolton, J. E. Wertz, *Electron paramagnetic Resonance- Elementary Theory and Practical Applications Wiley, New York*, 498(1994), DOI:10.1002/recl.19951140115
17. Ch. Liga Raju, J. L. Rao, N. O. Gopal, K.V. Narasimhulu, B. C. V. Reddy, *Material Chemistry and Physics*, **101**, 423(2007), DOI:10.1016/j.matchemphys.2006.08.001
18. M. A. Hassan, C. A. Hogarth, *Journal of Material Science*, **23**, 2500(1988), DOI:10.1007/BF01111908
19. N.W. Aschcroft, N. N. Mermin, *Solid State Physics, Harcourt, Fort worth, TX*, 656(2001).
20. R. Kripal, S. Shukla, *Spectroscopy Letters*, **44**, 235(2011), DOI:10.1080/00387010.2010.506905
21. Ballhausen, 'Introduction to Ligand Field Theory', *Mc Graw Hill, New York* (1962).
22. D. Kivelson. S.Lee, *Journal of Chemical Physics*, **41**,1896(1964), DOI:10.1063/1.1726180
23. C. M. Brodbeck, L. E. Iton, *Journal of Chemical Physics*, **83**, 4285(1958), DOI:10.1063/1.449041
24. B. Sumalatha, I. Omkaram, T. Rajavardhanarao, Ch. Linga Raju, *Non- Crystalline Solids*, **357**, 3143(2011), DOI:10.1016/j.jnoncrysol.2011.05.005
25. T. Blasco, L. Fernandez, A. Martinez-Arias, M. Sanchez- Sanchez, P. Concepcion, J. M. L. Nieto, *Mesopor, Microporous Mesoporous Materials*, **39**, 219(2000), DOI:10.1023/A:1016605916860
26. J. A. McMillan, T. Halpern, *Journal of Chemical Physics*, **55**, 33(1971).
27. K. V. Narayana, B. David Raju, S. Khaja Martin, V. Venkat Rao, P. Kantha Rao, R. Subrahmanian, A. Martin, *Catalysts Catalysis Communications*, **5**, 457(2004), DOI:10.1016/j.catcom.2004.05.012
28. Ibrahim Uslu, Burcu Baser, Ahmet Yayli, Mehmet Levent Aksu, *e-Polymers*, **145**,(2007), DOI:10.1515/epoly.2007.7.1.1699
29. E. M. Abdelrazek, A. M. Abdelghany, A. H. Oraby, G. M. Asnag, *IJET- International Journals of Engineering & Technology*, **12(4)**, 4343(2012).

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