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Study of EPR, optical properties and electrical conductivity of vanadyl doped $\text{Bi}_2\text{O}_3 \cdot \text{PbO} \cdot \text{B}_2\text{O}_3$ glasses

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Abstract

Heavy metal based oxide glasses having composition $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ have been prepared ($0.00 \leq x \leq 0.15$, mol%) containing 2.0 mol% of V_2O_5 by normal melt-quenching technique. Electron paramagnetic resonance (EPR), optical spectra and dc conductivity of these glasses have been studied. Spin Hamiltonian parameters (SHP) of VO^{2+} ions, dipolar hyperfine parameter, P and Fermi contact interaction parameter, K , molecular orbital coefficients (α^2 and γ^2) and optical band gap have been calculated. It is observed that in these glasses, the tetragonal nature of V^{4+}O_6 complex increases with Bi_2O_3 content. Increase in Bi_2O_3 : PbO ratio results in the contraction of $3d_{xy}$ orbit of the unpaired electron in the vanadium ion, and the SHP are dependent on the theoretical optical basicity, A_{th} . In present glasses, the conductivity (activation energy) first decreases (increases) with increase in mol% of Bi_2O_3 content upto $x = 0.08$ and then shows a maxima (minima) at $x = 0.10$ and then starts decreasing (increasing) upto $x \leq 0.15$ with mol% of Bi_2O_3 content.

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Keywords: EPR; Vanadyl ion; Heavy metal oxide glasses; Ionic conduction; Optical properties

1. Introduction

B_2O_3 is established as glass forming oxide whereas Bi_2O_3 is a conditional glass former. Growing attention has been given in the last two decades to glasses containing Bi_2O_3 [1–6]. There is considerable practical interest in these glasses due to their optical properties. It is known that Bi_2O_3 and PbO are not traditional glass formers, but Bi^{3+} and Pb^{2+} are highly polarizable ions and the asymmetry of their polyhedra inhibits the crystallization processes in the melts in which they participate. Several authors have compared glasses containing bismuth with those elements having similar outer electronic configuration. Bismuth glasses were also compared with lead glasses since both Bi and Pb are heavy elements with nearly same atomic weights, and their ions Bi^{3+} and Pb^{2+} are isoelectronic. Several authors have investigated some properties of bismuth glasses and different ideas were

presented for its role in glass structure [7–10]. EPR and optical spectra have been extensively used to obtain a detail information about some of the structural and dynamic phenomena of the material and to identify the site symmetry around the paramagnetic ions. The aim of the present investigation is to study the structure of vanadyl doped lead bismuth borate glasses through EPR, optical spectra and dc conductivity.

2. Experimental

For glass preparation analar grade reagents of Bi_2O_3 , PbO , H_3BO_3 and V_2O_5 were mixed in appropriate proportions to yield about 15 g in a porcelain crucible. The mixture was melted in an electrical muffle furnace at 1373 K in air for about 30 min and was stirred occasionally. The melts were poured onto a carbon plate and pressed with another plate quickly to get coin shaped samples of 1–2 mm thickness. A part of each sample was annealed at 473 K for 2 h. EPR

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spectra of annealed and unannealed glasses were recorded at room temperature (RT) using an EPR spectrometer (Varian E112) in the X-band (9.14 GHz) and using a magnetic field modulation of 100 kHz with peak to peak amplitude of 0.1 mT. Polycrystalline diphenyl picryl hydrazyl (DPPH) with $g = 2.0036 \pm 0.0002$ was used as a standard g reference. The optical transmission and absorption spectra of the polished glasses were recorded at RT using Perkin–Elmer UV–vis spectrometer (Lambda 20) in the wavelength region 400–1000 nm. To measure the dc conductivity, samples in the form of slices of nearly 1-mm uniform thickness were chosen. Colloidal silver paint was used as an electrode material. Conductivity measurements were made by the standard technique [11], i.e., two terminal method over a temperature range from about 373–573 K, first by increasing and then by decreasing the temperature. A constant voltage of 50 V was applied across the sample and the circulating current was measured by using a Keithley 617 programmable electrometer/source. To minimize the polarization effects the current was passed only for a very short period (less than 30 s at a time). The polarity of the applied voltage across the sample was also reversed.

3. Results

3.1. EPR

Fig. 1 illustrates hyperfine spectra of VO^{2+} ion of glass samples Pb1, Pb3, Pb5, Pb7 and Pb8 at 300 K. Hyperfine spectra of VO^{2+} ion in the annealed samples reveal that there is no change in the EPR spectra on annealing. The spectra of these glasses show patterns very similar to those found in various alkali borate glasses containing vanadium [12,13] and have structures which are characteristic of a hyperfine interaction arising between an unpaired electron with the ^{51}V nucleus whose spin is $7/2$ and which is present in 99.75% abundance [14]. These spectra were analyzed by assuming [15,16] that the vanadium is present as a vanadyl ion in a ligand field of C_{4v} symmetry. The spin Hamiltonian used is of the form [12]:

$$H = \beta g_{\parallel} B_z S_z + \beta g_{\perp} (B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

where the symbols have their usual meaning. Quadrupole and nuclear Zeeman interaction terms are ignored. The solutions [17] of the spin Hamiltonian are given in Eqs. (2) and (3) for the parallel and perpendicular orientations, respectively:

$$B_{\parallel}(m) = B_{\parallel}(o) - mA_{\parallel} - \left\{ \left(\frac{63}{4} \right) - m^2 \right\} \frac{A_{\perp}^2}{2B_{\parallel}(o)} \quad (2)$$

$$B_{\perp}(m) = B_{\perp}(o) - mA_{\perp} - \left\{ \left(\frac{63}{4} \right) - m^2 \right\} \frac{A_{\parallel}^2 + A_{\perp}^2}{4B_{\perp}(o)} \quad (3)$$

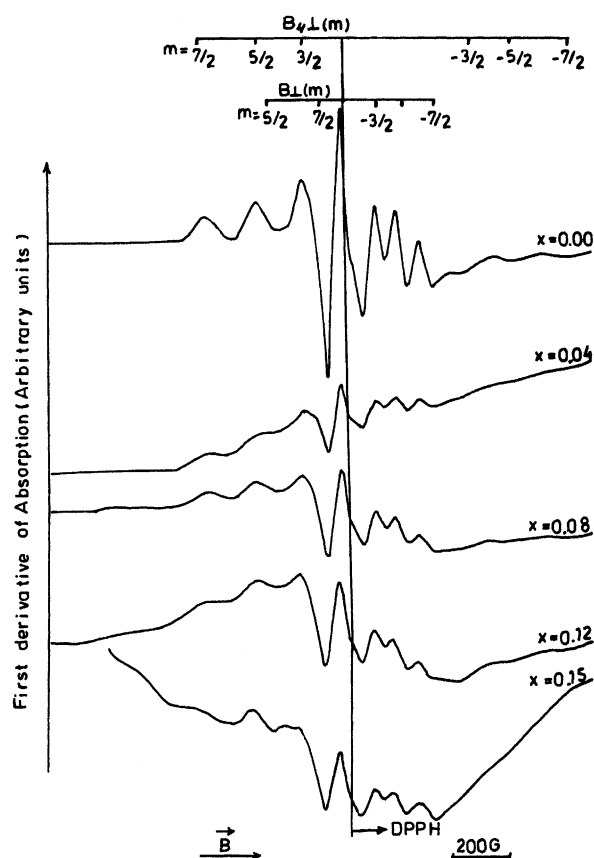


Fig. 1. The X-band EPR spectra of VO^{2+} ions in unannealed $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses at room temperature.

where m is the magnetic quantum number of the vanadium nucleus having values $\pm 7/2, \pm 5/2, \pm 3/2$ and $\pm 1/2$; $B_{\parallel}(o) = h\nu/g_{\parallel}\beta$ and $B_{\perp}(o) = h\nu/g_{\perp}\beta$ where ' h ' is the Planck constant, ν is the frequency of the spectrometer and β is the Bohr magneton. The measurements for the B_{\parallel} position were taken which correspond to a maximum in the first derivative curve of the parallel hyperfine structure (hfs) component for a given m value, whereas the B_{\perp} position is enclosed between the first derivative perpendicular peak and its "zero" [12]. Spin-Hamiltonian parameters of VO^{2+} ion determined from the observed positions of spectral lines and using Eqs. (2) and (3) are given in Tables 1 and 2.

The uncertainty in the value of g is ± 0.0010 and in the value of A , it is $\pm 1.0 \times 10^{-4} \text{ cm}^{-1}$. From the values of these parameters the dipolar hyperfine coupling parameter, $P = 2\gamma\beta_e\beta_N\langle r^{-3} \rangle$ and Fermi contact interaction term, K , are evaluated by using the expressions developed by Kivelson and Lee [17]:

$$A_{\parallel} = -P \left[K + \frac{4}{7} - \Delta g_{\parallel} - \frac{3}{7} \Delta g_{\perp} \right] \quad (4)$$

$$A_{\perp} = -P \left[K - \frac{2}{7} - \frac{11}{14} \Delta g_{\perp} \right] \quad (5)$$

where $\Delta g_{\parallel} = g_{\parallel} - g_e$; $\Delta g_{\perp} = g_{\perp} - g_e$ and $g_e (= 2.0023)$ is the g factor of free electron. Both A_{\parallel} and A_{\perp} are found to

Table 1

Spin Hamiltonian parameters^a of VO²⁺ ions at room temperature and A_{th} in unannealed $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses

Glass number	x	V_2O_5 (mol%)	$g_{ }$ (± 0.0010)	g_{\perp} (± 0.0010)	$ A_{ } $ (10^{-4} cm^{-1}) (± 1.0)	$ A_{\perp} $ (10^{-4} cm^{-1}) (± 1.0)	A_{th}
Pb1	0.00	2.0	1.9361	1.9772	168.6	64.6	0.4294
Pb2	0.02	2.0	1.9365	1.9780	168.6	64.6	0.4295
Pb3	0.04	2.0	1.9371	1.9783	168.7	64.6	0.4296
Pb4	0.06	2.0	1.9377	1.9789	168.7	64.7	0.4297
Pb5	0.08	2.0	1.9382	1.9794	168.8	64.7	0.4297
Pb6	0.10	2.0	1.9391	1.9797	168.8	64.7	0.4298
Pb7	0.12	2.0	1.9397	1.9806	168.9	64.7	0.4298
Pb8	0.15	2.0	1.9399	1.9815	169.9	64.8	0.4299

^a $A_{||}$ and A_{\perp} are negative.

Table 2

 P , K , $|A'_{||}|$, $|A'_{\perp}|$, and $\Delta g_{||}/\Delta g_{\perp}$, of VO²⁺ ions in unannealed $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses at room temperature

Glass number	P (10^{-4} cm^{-1})	K	$ A'_{ } $ (10^{-4} cm^{-1})	$ A'_{\perp} $ (10^{-4} cm^{-1})	$\Delta g_{ }/\Delta g_{\perp}$
Pb1	113.7	0.834	73.7	30.2	2.6401
Pb2	113.7	0.835	73.6	30.3	2.7029
Pb3	113.8	0.835	73.6	30.4	2.7126
Pb4	113.9	0.835	73.6	30.4	2.7569
Pb5	114.0	0.835	73.5	30.5	2.8035
Pb6	114.2	0.835	73.5	30.6	2.8025
Pb7	114.2	0.835	73.5	30.7	2.8914
Pb8	114.2	0.836	73.4	30.8	3.0016

be negative [18]. The term $-PK$ in Eqs. (4) and (5) is due to the s-character of the magnetic spin of the vanadium. This s-character arises due to partial unpairing or polarization of the s electrons as a result of an interaction with the unpaired d electrons [19]. The effect of polarization on the hyperfine coupling was determined by Heine [19] and is included as $-PK$ in the expression for hyperfine coupling. For transition metal ions K is found to be positive [20]. From the molecular orbital theory it is shown [21] that the components $A_{||}$ and A_{\perp} consist of the contributions $A'_{||}$ and A'_{\perp} of the $3d_{xy}$ electron to the hyperfine structure and the $-PK$ term arising due to the anomalous contribution of the s-electrons. Eqs. (4) and (5) can be rewritten in the following form:

$$A_{||} = -PK - P \left[\frac{4}{7} - \Delta g_{||} - \frac{3}{7} \Delta g_{\perp} \right] = -PK + A'_{||} \quad (6)$$

$$A_{\perp} = -PK + P \left[\frac{2}{7} + \frac{11}{14} \Delta g_{\perp} \right] = -PK + A'_{\perp} \quad (7)$$

Calculated values of $A'_{||}$ and A'_{\perp} are given in Table 2.

Theoretical optical basicity A_{th} , has been calculated [22] by using the expression:

$$A_{th} = \sum_i \frac{Z_i r_i}{2\gamma_i} \quad (8)$$

where Z_i is the oxidation number of the cation i , r_i is the ratio of the cation i with respect to the total number of oxides and γ_i is the basicity moderating parameter. γ_i for the cation is given by:

$$\gamma_i = 1.36(x_i - 0.26) \quad (9)$$

where x_i is the Pauling electronegativity [23] of the cation. Calculated value of A_{th} of glasses is given in Table 1.

3.2. Optical spectra

The optical transmission spectra of sample were recorded at room temperature. For all the glasses only two transmission bands are observed. These bands are at about 785 and 560 nm. Spectra for sample nos. Pb1 and Pb7 are shown in Fig. 2. These two bands are typical for VO²⁺ and can be assigned to $b_2 \rightarrow e_{\pi}^*$ and $b_2 \rightarrow b_1^*$ transitions. The values of $g_{||}$ and g_{\perp}

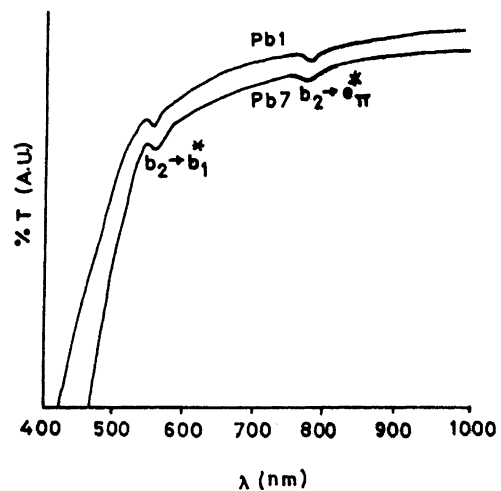


Fig. 2. The optical transmission spectra of VO²⁺ ions $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses at room temperature for glass nos. Pb1 and Pb7.

Table 3

Cutoff wavelength, λ_c (nm), optical band gap, E_{opt} (eV) and molecular orbital coefficients, α^2 , γ^2 for $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses

Glass number	λ_c (nm)	E_{opt} (eV)	α^2	γ^2
Pb1	441	2.34	0.593	0.649
Pb2	451	2.30	0.589	0.628
Pb3	459	2.29	0.584	0.620
Pb4	463	2.24	0.578	0.605
Pb5	466	2.23	0.574	0.592
Pb6	471	2.22	0.566	0.584
Pb7	479	2.21	0.561	0.561
Pb8	483	2.16	0.559	0.538

are related to bonding parameters by the following equations [21]:

$$\alpha^2 = \left[1 - \frac{g_{||}}{g_e} \right] \frac{E_2}{4\lambda\beta^2} \quad (10)$$

$$\gamma^2 = \left[1 - \frac{g_{\perp}}{g_e} \right] \frac{E_1}{\lambda\beta^2} \quad (11)$$

where E_1 and E_2 are the energies of transitions ($b_2 \rightarrow e_{\pi^*}$) and ($b_2 \rightarrow b_1^*$), respectively. β^2 is a measure of the in-plane π bonding with the equilateral ligands and is assumed [22] to be equal to 1 for many glasses containing VO^{2+} ion. λ is the spin orbit coupling constant and is equal to 249 cm^{-1} [14]. $(1 - \alpha^2)$ and $(1 - \gamma^2)$ indicate the covalency rates. Using Eqs. (10) and (11) the values of α^2 and γ^2 were calculated and are given in Table 3.

The optical absorption spectra of the samples Pb1, Pb2, Pb4, Pb5, and Pb8 are shown in Fig. 3. The absorption coefficient $\alpha(\nu)$, near the edge of each curve in Fig. 3 were

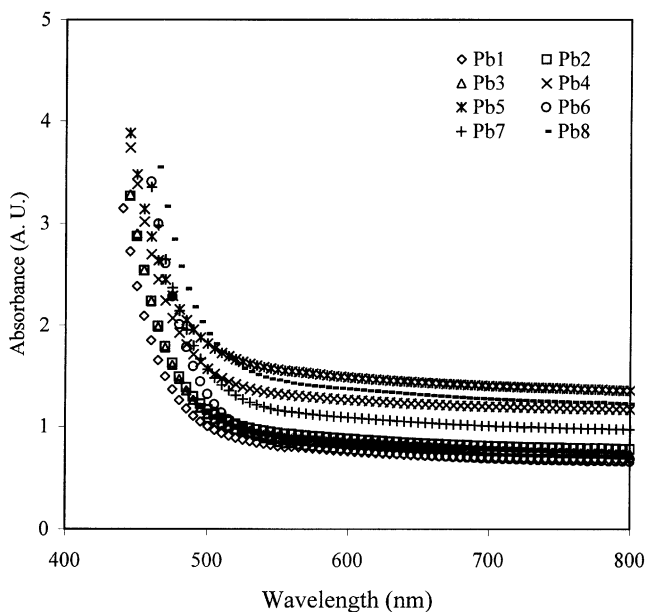


Fig. 3. The optical absorption spectra for $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses.

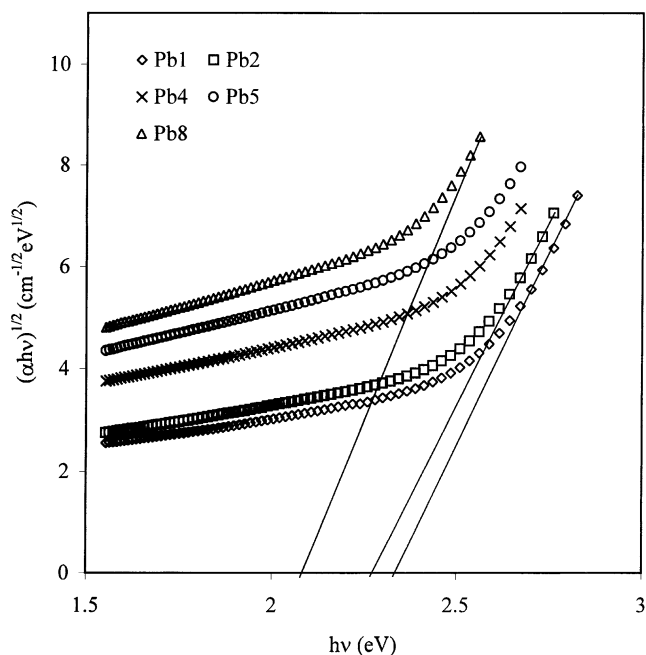


Fig. 4. Tauc's plots for glass nos. Pb1, Pb2, Pb4, Pb5 and Pb8.

determined at wavelength interval of 5 nm for linear region from the relation

$$\alpha(\nu) = \frac{1}{d} \ln \frac{I_0}{I_t} \quad (12)$$

where d is the thickness of sample, I_0 and I_t are the intensities of the incident and transmitted beams respectively, and $\ln(I_0/I_t)$ corresponds to absorbance in Fig. 3. The data for Fig. 4 (Tauc's plots) were obtained from the relation [24]:

$$\alpha(\nu) = B \frac{(h\nu - E_{opt})^2}{h\nu} \quad (13)$$

where B is constant, E_{opt} is the optical band gap and $h\nu$ is the photon energy of the incident radiation. Since the Eq. (13) can be readjusted to represent the linearity between $(\alpha h\nu)^{1/2}$ and $h\nu$, one can determine the optical band gap from the curve representing $(\alpha h\nu)^{1/2}$ as a function of photon energy, $h\nu$ as shown for the linear curves in Fig. 4 by the method of least square fitting.

3.3. DC conductivity

Fig. 5 shows the temperature dependence of the dc conductivity of the $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ ($0.00 \leq x \leq 0.15$) glasses. The linear relationship between the logarithm of the dc conductivity ($\log \sigma$, σ measured in $\Omega^{-1} \text{ m}^{-1}$) and inverse of temperature ($1000/T$, T measured in Kelvin), with a negative slope indicates that ionic conductivity is satisfied by the following relation developed by Rasch–Hinrichsen:

$$\sigma = \sigma_0 \exp \left(-\frac{W}{kT} \right) \quad (14)$$

Table 4
DC conductivity σ , $\log \sigma_0$ and activation energy W of $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses

Glass number	x	V_2O_5 (mol%)	$\sigma_{\text{at } 573\text{K}} (\Omega^{-1} \text{ m}^{-1})$	$\sigma_{\text{at } 533\text{K}} (\Omega^{-1} \text{ m}^{-1})$	$\log \sigma_0 (\Omega^{-1} \text{ m}^{-1})$	W (eV)
Pb1	0.00	2.0	7.05×10^{-8}	4.67×10^{-8}	4.73	0.301
Pb2	0.02	2.0	6.73×10^{-8}	4.37×10^{-8}	4.67	0.302
Pb3	0.04	2.0	6.05×10^{-8}	3.78×10^{-8}	4.52	0.308
Pb4	0.06	2.0	5.28×10^{-8}	3.29×10^{-8}	4.53	0.313
Pb5	0.08	2.0	4.92×10^{-8}	3.04×10^{-8}	4.53	0.317
Pb6	0.10	2.0	7.77×10^{-8}	5.18×10^{-8}	4.49	0.298
Pb7	0.12	2.0	6.48×10^{-8}	4.26×10^{-8}	4.79	0.305
Pb8	0.15	2.0	5.50×10^{-8}	3.43×10^{-8}	4.53	0.311

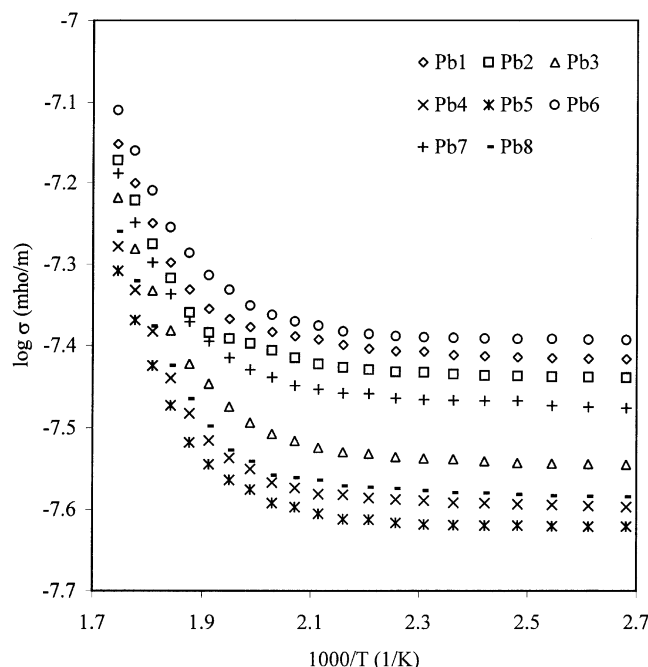


Fig. 5. Variation of $\log \sigma$ as a function of $1/T$ for $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ glasses.

where ' σ_0 ' is a constant for a given glass, ' k ' the Boltzmann constant and W the activation energy for conduction. The calculated values of W and $\log \sigma_0$ are presented in Table 4. The values of the conductivity at 573 and 533 K are included in Table 4. From the Table 4 and Fig. 5, it is observed that the dc conductivity increases with increase in temperature. It is also observed that the dc conductivity decreases when PbO is replaced by Bi_2O_3 in $x\text{Bi}_2\text{O}_3 \cdot (0.30 - x)\text{PbO} \cdot 0.70\text{B}_2\text{O}_3$ samples and activation energy increases upto $x = 0.08$. At $x = 0.10$, the activation energy shows minima and conductivity shows maxima. On further increasing Bi_2O_3 :PbO ratio, dc conductivity decreases, and the activation energy increases. Since the vanadium ions in these glasses may exist in more than one valence states, e.g., V^{4+} and V^{5+} , so conduction could also take place by transfer of electrons from low to high valence states. Decrease in conductivity with time reveals that the electronic conductivity due to hopping of electrons between V^{4+} and V^{5+} does not play an important part in total conductivity of present glass system.

4. Discussion

4.1. EPR

Tables 1 and 2 show that $g_{||}$, g_{\perp} , $A_{||}$, A_{\perp} , A'_{\perp} , K and $\Delta g_{||}/\Delta g_{\perp}$ increase with mol% of Bi_2O_3 in the glass. Increase in value of K suggests [25–28] an increase in the tetragonal nature of the V^{4+}O_6 complex because of a strongly bonded oxygen atom at V^{4+} ion, in the site opposite to the vanadyl oxygen atom. However the increase in $\Delta g_{||}/\Delta g_{\perp}$ with Bi_2O_3 content in the unannealed glasses suggests that the tetragonal nature of the V^{4+}O_6 complex is enhanced with increase in the concentration of Bi_2O_3 . The increase of the anisotropic contribution $|A'_{\perp}|$ of the $3d_{xy}$ electron of the hyperfine splitting is brought about by decreasing screening of the $3d_{xy}$ orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This produces a contraction of the $3d_{xy}$ orbital, resulting in an increased interaction between electron and the vanadium nucleus. The increase in the value of P also support the argument that $3d_{xy}$ orbit contracts in the system.

The theoretical optical basicity serves in the first approximation as a measure [28] of the ability of oxygen to donate a negative charge in the glass. In other words, the optical basicity reflects the Lewis basicity of the oxide glasses. As the ability of the equatorial ligands to donate the electron (i.e., Lewis basicity) decreases, σ bondings between V^{4+} and the ligands reduces [29]. This reduction, in turn, increases the positive charge on V^{4+} and increases the π bonding between V^{4+} and vanadyl oxygen. This increase, decreases the bond length of V^{4+} -(vanadyl oxygen). Consequently, the tetragonal nature of the V^{4+}O_6 complex is enhanced.

Calculated values of the theoretical optical basicity, Λ_{th} is included in Table 1. Value of Λ_{th} increases with increase in the mol% of Bi_2O_3 . This behavior suggests that the tetragonal nature of the V^{4+}O_6 complex should increase with increase in the concentration of Bi_2O_3 in the system. EPR measurements also reveal this behavior. Thus the variation in theoretical value of Λ_{th} is in agreement with the experimental findings.

4.2. Optical studies

$(1 - \alpha^2)$ gives an indication of the effect of σ bonding among the vanadium atom and the equatorial ligands, while

$(1 - \gamma^2)$ indicates the effect of the π bonding with the vanadyl oxygen. From Table 3, the decrease in α^2 and γ^2 indicates that the covalency of the vanadium oxygen bonds increases when Bi_2O_3 replaces PbO . This is also supported by the increasing value of $\Delta g_{\parallel}/\Delta g_{\perp}$. From Fig. 3, it is observed that the samples have a distinct cutoff. The values of the cutoff wavelength (λ_c) are different for the samples and are shown in Table 3. The values of E_{opt} were obtained from the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves and are listed in Table 3. These are found to be dependent in a systematic manner on the glass composition. The addition of Bi_2O_3 to the glass leads to an effective reduction in E_{opt} , which may be attributed to the increases of nonbridging oxygens [30].

4.3. DC conductivity

From Fig. 5 and Table 4 it is observed that the dc conductivity measured in present samples decreases with a small increase in the concentration of Bi_2O_3 in the range $0.00 \leq x \leq 0.08$. In binary $\text{PbO-Bi}_2\text{O}_3$ glasses, modifying Pb^{2+} cations are assumed to be the charge carriers [31]. As the concentration of the charge carrier decreases, conductivity also decreases, but shows a maxima at $x = 0.10$. At this value of x , the content of PbO is just twice of Bi_2O_3 . At this value of x , probably the glass structure expands through which lead ions pass and at this particular value, the number of nonbridging oxygen ions formed in the network may also be maximum and therefore, dc conductivity is maximum. The similar results were also observed by Chowdari et al [32] in $\text{Bi}_2\text{O}_3\text{-Li}_2\text{O-B}_2\text{O}_3$ glass samples.

5. Conclusions

The site symmetry around V^{4+} ion in $\text{Bi}_2\text{O}_3\text{-PbO-B}_2\text{O}_3$ glasses is octahedral with tetragonal enhancement (C_{4v} symmetry). In $\text{Bi}_2\text{O}_3\text{-PbO-B}_2\text{O}_3$ samples, the $3d_{xy}$ orbital in the vanadium ion contracts with increase in $\text{Bi}_2\text{O}_3\text{:PbO}$ ratio. Variation in the theoretical optical basicity in $\text{Bi}_2\text{O}_3\text{-PbO-B}_2\text{O}_3$ glasses is in agreement with variation in SHP. α^2 and γ^2 decrease in $\text{Bi}_2\text{O}_3\text{-PbO-B}_2\text{O}_3$ glasses with increase in Bi_2O_3 , which indicate that the covalency of the vanadium oxygen bonds increases. The optical band gap decreases with increase in Bi_2O_3 content. The dc conductivity is maximum at $x = 0.10$ when PbO is replaced by Bi_2O_3 keeping B_2O_3 constant. Activation energy is maximum at $x = 0.08$.

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