

EPR AND OPTICAL STUDIES OF VANADYL IONS IN ALKALI LEAD BOROTELLURITE GLASSES

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Electron Paramagnetic Resonance (EPR) and optical absorption spectra of VO^{2+} ions in different alkali lead borotellurite glasses have been studied. The spin-Hamiltonian parameters (g and A), bonding parameter β_2^{*2} and Fermi contact interaction parameter k have been calculated. The values of spin-Hamiltonian parameters confirm that the vanadyl ions are present in the glasses as VO^{2+} molecular ions in an octahedral site with a tetragonal compression. The number of spins (N) participating in resonance is calculated as a function of temperature (123–393 K) for 9 mol% of VO^{2+} ions in lithium lead borotellurite glass sample. It is observed that N obeys the Boltzmann law. From EPR data, the paramagnetic susceptibility (χ) is calculated at various temperatures and the Curie constant has been evaluated from $1/\chi$ - T graph. The optical absorption spectrum exhibits two bands characteristic of VO^{2+} ions in tetragonal symmetry. The band gap (E_{opt}) and the Urbach energies (ΔE) have been determined from the ultraviolet absorption edges and are found to be dependant on the size of the alkali ion. The theoretical values of optical basicity (Λ_{th}) of these glasses have also been evaluated.

Keywords: Alkali lead borotellurite glasses; EPR; optical absorption.

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1. Introduction

In recent years, tellurite based glasses are of scientific and technological importance because of their low melting temperature, high refractive indices and good infrared transmissions.^{1–3} These glasses are also characterized by low absorption ability in the visible region and therefore are suitable for lenses in photography.⁴ In addition TeO_2 based glass was recently recommended to be used as a candidate for new types of nonlinear optical glasses.^{5,6} TeO_2 itself is traditionally considered as a conditional glass former and it forms glasses in combination with a variety of other oxide materials such as B_2O_3 , V_2O_5 , PbO and alkalis. Tellurite vanadate glasses may also be suitable materials for applications in the field of solid state electrolytes.⁷

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On the other hand, borate glasses are also equally important and it is well-known that borate glasses exhibits unique structural features particularly in binary alkali borate glasses. In addition, borate glasses are of academic interest for many years because of the boron anomaly.⁸ The addition of transition-metal (TM) oxides to glasses, in general, permits the possibility for the glasses to exhibit semiconducting behavior. This electronic behavior as well as the optical, magnetic, and structural properties for these glasses depends upon the different valence states of the TM ions present.^{9–11}

Therefore we have made alkali lead borotellurite glasses, keeping in view of the possible applications. We are interested to study the structural evolution of these glasses using electron paramagnetic resonance (EPR). Structural investigations are worth being done in these glasses in order to know the nature of glassy state and its composition dependence. Recently, lead borate glasses containing TeO_2 as a network modifier with iron as an impurity ion has been investigated for their EPR and magnetic susceptibility studies.⁹ Cozar *et al.*¹⁰ studied the EPR and magnetic susceptibility investigations on some vanadate lithium–borate glasses.

In the present investigation, the authors systematically studied the EPR and optical absorption spectra of VO^{2+} ions in different alkali lead borotellurite glasses. The EPR spectra of vanadyl ions in glasses are very interesting because the valance state of vanadyl ions in glasses changes with the variation of glass composition and melting atmosphere.¹¹ We are also interested to know the effect of alkali ions on spin-Hamiltonian parameters in order to know the site symmetry around VO^{2+} ions in these glasses. The spin-Hamiltonian parameters are very sensitive to the ligands present around the transition metal ion and also the glass composition. The effect of temperature (123–393 K) on EPR signals has also been studied.

2. Experimental

Glass systems of composition $80\text{R}_2\text{B}_4\text{O}_7 + 10\text{PbO} + (10 - x)\text{TeO}_2 + x\text{V}_2\text{O}_5$ ($\text{R} = \text{Li}, \text{Na}$ and K , $x = 9$ mol%) and $80\text{Li}_2\text{B}_4\text{O}_7 + 10\text{PbO} + (10 - x)\text{TeO}_2 + x\text{V}_2\text{O}_5$ ($x = 6, 7, 8, 8.5$ and 9 mol%) have been prepared by the melt quenching technique. The starting materials used in the present work were $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{K}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, PbO , TeO_2 and V_2O_5 . Vanadium was added to the batches as V_2O_5 . All the chemicals were weighed accurately in an electrical balance, ground to fine powder and mixed thoroughly. The batches were then placed in porcelain crucibles and melted in an electrical furnace in air at their respective melting temperatures. The melt was then quenched at room temperature in air by pouring it on to a polished porcelain plate and pressing it quickly with another porcelain plate. Care was taken to obtain glasses of uniform thickness for recording optical absorption spectra. Good quality glasses obtained after polishing were used for optical measurements.

The EPR spectra were recorded on a JEOL FE1X EPR spectrometer operating at the X-band microwave frequency equipped with TE_{011} cylindrical cavity with a

field modulation of 100 kHz. The room temperature EPR spectra were recorded for lithium lead borotellurite (LiPbBTe) glass samples with different concentrations of V_2O_5 and also for sodium lead borotellurite (NaPbBTe) and potassium lead borotellurite (KPbBTe) glass samples for one concentration (9 mol%) of V_2O_5 . A powdered glass sample of 100 mg was taken in a quartz tube for EPR measurements. Polycrystalline DPPH with an effective g value of 2.0036 was used as a standard field marker. The EPR spectra for lithium lead borotellurite glasses with 9 mol% of vanadyl ions (hereafter to be referred as LiPbBTe:9V) were recorded at different temperatures using a JES UCT 2AX variable temperature controller. A temperature stability of ± 1 K was easily obtained by waiting for about 30 minutes at the set temperature before recording a spectrum. The optical absorption spectra of the glass samples were recorded at room temperature on a JASCO UV/Vis/NIR spectrophotometer (model V-570) in the wavelength region 200–1200 nm.

3. Results and Discussion

3.1. Electron paramagnetic resonance studies

In undoped glasses, no EPR signal is observed confirming that the starting materials used in the present work were free from paramagnetic impurities or other centers (defects). When VO^{2+} ions are introduced into the glasses, all glass samples under investigation exhibit resonance signals characteristic of VO^{2+} ions. The V^{4+} ion belongs to $3d^1$ configuration, and the paramagnetism of the vanadyl ion arises from single unpaired electron as the orbital angular momentum is quenched by the crystalline fields. Figure 1 shows the EPR spectra of different alkali lead borotellurite glasses doped with 9 mol% of V_2O_5 . The observed resonance signals are due to the hyperfine interaction of an unpaired electron ($S = 1/2$) from VO^{2+} with its nuclear spin ($I = 7/2$). The EPR spectra of these samples showed a similar pattern to others reported for vanadyl ions in various glass systems.^{12–26}

Hecht and Johnston¹³ extensively studied the EPR and optical absorption spectra of V^{4+} ions in soda-boric oxide glasses and found that there are two possibilities either threefold or fourfold symmetry to describe the crystal field of V^{4+} ions in glasses. A detailed analysis of the g -tensor in the presence of trigonal symmetry has been given by Gladeny and Swalen.¹² For a trigonal distortion, either singlet or doublet is the ground state depending on whether the distortion is elongation or compression of the octahedron along the polar axis.

The spin-Hamiltonian parameters have been evaluated by using the standard procedure.²⁷ The iterative method for numerical analysis of the spectrum as suggested by Muncaster and Parke¹⁴ was used here to avoid the errors caused by certain amount of overlapping between hyperfine lines. Table 1 lists the spin-Hamiltonian parameters evaluated for different alkali lead borotellurite glasses.

An octahedral site with a tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A_{\perp}$.^{14,15,27} The g and A values obtained in the present work agree with this relationship and are close to those vanadyl complexes reported in literature.^{17–22}

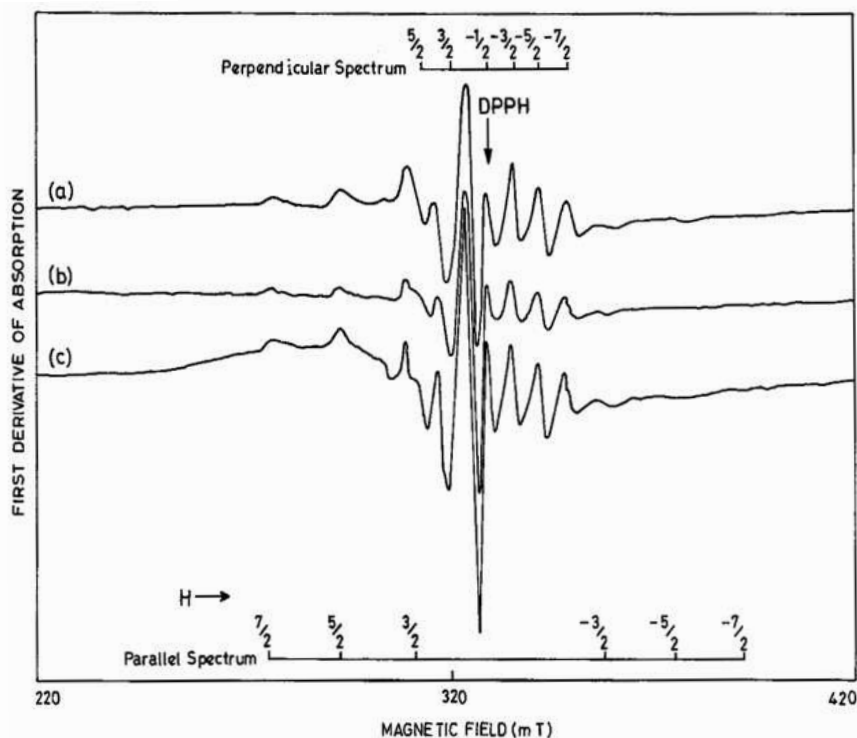


Fig. 1. EPR spectra for 9 mol% of vanadyl ions in different alkali lead borotellurite glasses: (a) LiPbBTe:9V, (b) NaPbBTe:9V, and (c) KPbBTe:9V at room temperature.

Table 1. The spin-Hamiltonian parameters, molecular orbital coefficients and theoretical optical basicity values for vanadyl ions in different alkali lead borotellurite glasses (the errors in g and A values are ± 0.001 and $2 \times 10^{-4} \text{ cm}^{-1}$).

Glass system	g_{\parallel}	g_{\perp}	$A_{\parallel} \times 10^{-4} \text{ cm}^{-1}$	$A_{\perp} \times 10^{-4} \text{ cm}^{-1}$	g_{\parallel}/g_{\perp}	β_2^2	k	$A_{\parallel}^1 \times 10^{-4} \text{ cm}^{-1}$	$A_{\perp}^1 \times 10^{-4} \text{ cm}^{-1}$	Λ_{th}
LiPbBTe:9V	1.940	1.953	164	59	1.256	0.895	0.757	62.0	42.0	0.5092
NaPbBTe:9V	1.950	1.954	153	64	1.065	0.727	0.969	64.0	41.0	0.5293
KPbBTe:9V	1.979	1.988	153	63	1.569	0.773	0.921	69.0	38.0	0.5370

It is therefore confirmed that the vanadyl ions in different alkali lead borotellurite glasses exist as VO^{2+} molecular ions in an octahedral coordination with a tetragonal compression and belongs to C_{4v} symmetry.

The values of $\Delta g_{\parallel}/\Delta g_{\perp}$ (where $\Delta g_{\parallel} = g_e - g_{\parallel}$ and $\Delta g_{\perp} = g_e - g_{\perp}$, with g_e representing the g -factor of a free electron) are calculated for different alkali lead borotellurite glass samples and are presented in Table 1. A decrease in $\Delta g_{\parallel}/\Delta g_{\perp}$ values suggests that the octahedral symmetry around VO^{2+} ion is improved.²⁸ From Table 1, it is also observed that the $\Delta g_{\parallel}/\Delta g_{\perp}$ value is less in sodium lead

borotellurite glasses when compared to lithium lead borotellurite and potassium lead borotellurite glasses. Thus, it is evident that the vanadyl ions in sodium lead borotellurite glasses are in tetragonally less-distorted octahedral site than those in lithium lead borotellurite and potassium lead borotellurite glasses. In lithium lead borotellurite glasses, it is observed that with the increase of mol% of V_2O_5 the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ increases asserting that the deviation from octahedral symmetry increases and the VO^{2+} ions are in more tetragonally distorted sites.

Molecular orbital theory shows that the hyperfine constants A_{\parallel} and A_{\perp} consist of the contributions from $A_{\parallel}^{\downarrow}$ and A_{\perp}^{\downarrow} of the $3d_{xy}$ electron to the hyperfine structure and the term $P\beta_2^{*2}k$ arises due to the anomalous contribution of the s-electron. Kivelson and Lee²⁹ gave the following relations

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

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

where

$$A_{\parallel}^{\downarrow} = P[-\beta_2^{*2}(4/7) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + D_{\parallel} + 3/7D_{\perp}] \quad (3)$$

$$A_{\perp}^{\downarrow} = P[\beta_2^{*2}(2/7) + 11/14(g_{\perp} - 2.0023) + 11/14D_{\perp}]. \quad (4)$$

Here P is the dipolar hyperfine coupling parameter ($P = 2\gamma\beta\beta_N\langle r^{-3} \rangle = 0.0128 \text{ cm}^{-1}$) and k is a dimensionless Fermi contact interaction parameter,³⁰ which represents the amount of unpaired electron density at the vanadium nucleus; $D_{\parallel} = 0.0125 \text{ cm}^{-1}$ and $D_{\perp} = 0.0015 \text{ cm}^{-1}$ are small corrections. Using the values of A_{\parallel} , A_{\perp} , g_{\parallel} and g_{\perp} , the values of $A_{\parallel}^{\downarrow}$ and A_{\perp}^{\downarrow} have been calculated and are also presented in Table 1.

The molecular orbital coefficients β_2^{*2} and k are determined from the spin-Hamiltonian parameters, i.e. using Eqs. (1), (2), (3) and (4). The parameter β_2^{*2} is a measure of out-of-plane π -bonding with the equatorial ligands and is assumed to be equal to one for many oxide glasses.³¹ The value of β_2^{*2} (see Table 1) in the present work obtained indicates that the V = O out-of-plane π -bonding is significantly ionic ($\beta_2^{*2} = 1$ for ionic) and the covalency is independent of the alkali metal ion present in the glasses.

k represents the amount of unpaired electron density at the vanadium nucleus. However, the unpaired electron present in d-orbital causes a zero Fermi contact interaction. Because of the spin polarization of inner s-electrons, there exists a nonzero value of k . The large value of k indicates a large contribution to hyperfine constant by the unpaired s-electrons. The values calculated for β_2^{*2} and k (see Table 1) for different alkali lead borotellurite glasses are in good agreement with the values reported in the literature.³²

The EPR spectra were also recorded at different temperatures from 123 to 393 K for LiPbBTe:9V glass sample. From the temperature variation spectra, it is observed that the intensity of the spectral lines decreases with increasing temper-

ature following the usual Boltzmann law. It is also observed that the number of spins decreases with increasing temperature and the line widths are found to be independent of temperature.

3.2. Calculation of number of spins (N) participating in resonance

The number of spins participating in resonance can be calculated by comparing the area under the absorption curve with that of a standard ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in this study) of known concentration. Weil *et al.*³³ gave the following expression which includes the experimental parameters of both sample and standard.

$$N = \frac{A_x(\text{scan}_x)^2 G_{\text{std}}(B_m)_{\text{std}}(g_{\text{std}})^2 [S(S+1)]_{\text{std}} (P_{\text{std}})^{1/2}}{A_{\text{std}}(\text{scan}_{\text{std}})^2 G_x(B_m)_x (g_x)^2 [S(S+1)]_x (P_x)^{1/2}} \quad (5)$$

where A is the area under the absorption curve which can be obtained by double integrating the first derivative EPR absorption curve, “scan” is the magnetic field corresponding to unit length of the chart, G is the gain, B_m is the modulation field width, g is the g-factor, and S is the spin of the system in its ground state. P is the power of the microwave source. Subscripts “ x ” and “std” represent the corresponding quantities for VO^{2+} glass sample and the reference ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) respectively. Figure 2 shows the number of spins participating in resonance in LiPbBTe glass samples as a function of different mol% of V_2O_5 content at room temperature. From the figure, it is observed that the number of spins participating in resonance increases with the increase of V_2O_5 content.

3.3. Calculation of paramagnetic susceptibility (χ) from EPR data

The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the standard formula.³⁴ A graph between the reciprocal of susceptibility ($1/\chi$) and the absolute temperature (T) is fit to a straight line as shown in Fig. 3. It is interesting to observe that it obeys Curie–Weiss law. From the slope of the graph, the Curie constant is evaluated and it is found to be 16.66×10^{-3} , which is of the same order as expected for a paramagnetic ion reported earlier.³⁵

4. Optical Absorption Studies

The ground state term for VO^{2+} ion is ${}^2\text{D}$. In an octahedral symmetry, the d-electron occupies t_{2g} orbital and gives rise to ${}^2\text{T}_{2g}$ ground state. On excitation, the d-electron occupies e_g orbital and gives rise to ${}^2\text{E}_g$ state. Thus, only single transition ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ and correspondingly single band is expected for VO^{2+} ions in an octahedral symmetry. However, due to non-symmetrical alignment of the $\text{V} = \text{O}$ bond, VO^{2+} site symmetry lowers to tetragonal or rhombic. In a tetragonal symmetry, the lower ${}^2\text{T}_{2g}$ level splits into ${}^2\text{B}_{2g}$ and ${}^2\text{E}_g$ levels. The upper level ${}^2\text{E}_g$ splits into ${}^2\text{B}_{1g}$ and ${}^2\text{A}_{1g}$ levels. Therefore one can expect three bands corresponding to

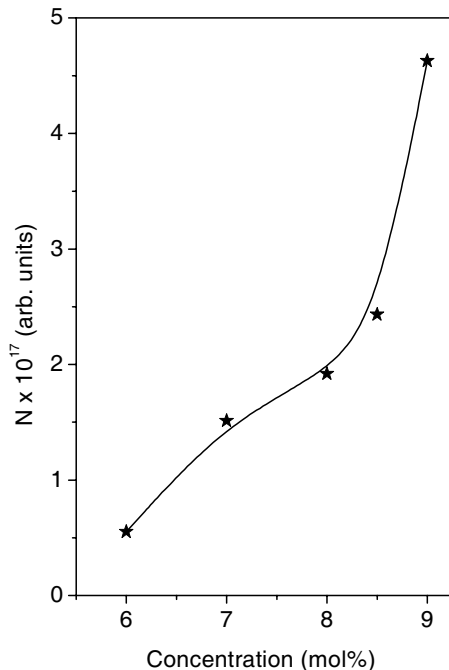


Fig. 2. A plot of variation of number of spins (N) participating in $80\text{Li}_2\text{B}_4\text{O}_7 + 10\text{PbO} + (10 - x)\text{TeO}_2 + x\text{V}_2\text{O}_5$ ($x = 6, 7, 8, 8.5$ and 9 mol%) glass samples at room temperature.

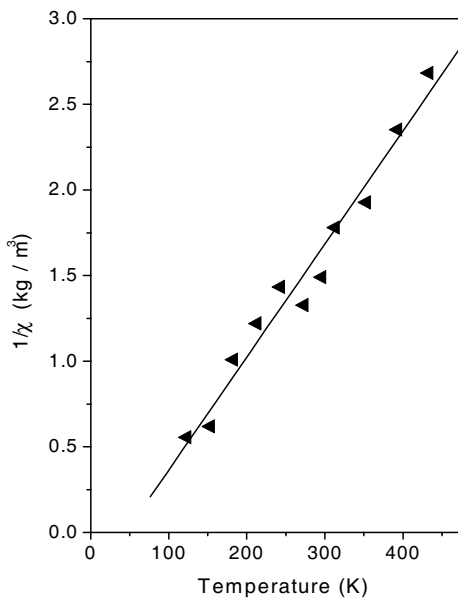


Fig. 3. A plot of reciprocal of susceptibility ($1/\chi$) as a function of absolute temperature (T) for LiPbBTe:9V glass sample.

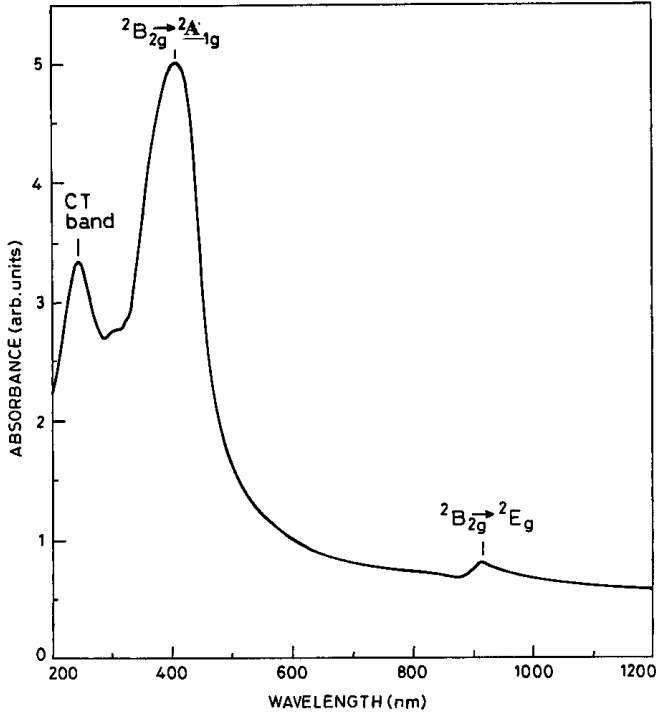


Fig. 4. Optical absorption spectrum of LiPbBTe:9V glass sample at room temperature.

${}^2B_{2g} \rightarrow {}^2E_g$, ${}^2B_{2g} \rightarrow {}^2B_{1g}$, and ${}^2B_{2g} \rightarrow {}^2A_{1g}$ in the region $10000\text{--}11400\text{ cm}^{-1}$, $14000\text{--}17000\text{ cm}^{-1}$ and $23000\text{--}26700\text{ cm}^{-1}$ respectively.^{36,37} Figure 4 shows the optical absorption spectrum of LiPbBTe:9 V glass sample and it exhibits bands centered at 24445 cm^{-1} (413 nm) and 11320 cm^{-1} (913 nm) assigned to the transitions ${}^2B_{2g} \rightarrow {}^2A_{1g}$ and ${}^2B_{2g} \rightarrow {}^2E_g$ in the decreasing order of energy respectively. The optical absorption spectrum also exhibits a band at 40640 cm^{-1} (246 nm) and this band has been attributed to charge transfer band.

4.1. Optical basicity (Λ_{th})

The optical basicity of an oxide glass can be measured in terms of the ability to donate negative charge to the ion.³⁸ Duffy and Ingram³⁹ proposed that the ideal values of optical basicity can be predicted from the composition of the glass and basicity moderating parameters of various cations present. In the present study, the optical basicity (Λ_{th}) of the glass is estimated by using the formula given by Duffy and Ingram.³⁹ The theoretical values of the optical basicity (Λ_{th}) can be used to classify the covalent/ionic ratios of the glasses since an increasing value of Λ_{th} indicates decreasing covalency. In the present study, the Λ_{th} values are increasing from lithium lead borotellurite glass to potassium lead borotellurite glass. Hence

the covalency between V^{4+} and oxygen ion should decrease as one can move from lithium lead borotellurite to potassium lead borotellurite glasses.

4.2. Optical band gap energy (E_{opt}) and Urbach energy (ΔE)

The optical band gap and Urbach energies for 9 mol% of V_2O_5 doped in different alkali lead borotellurite glass samples were obtained from their ultraviolet absorption edges. The optical band gap in the amorphous system is closely related to the energy gap between valence and conduction bands.^{40,41} In glasses, the conduction band is influenced by the glass forming anions, the cations play an indirect but significant role.⁴⁰ The Urbach energy gives the width of the tails of localized states within the optical band gap. At the absorption edge, random internal electric fields will dominate the broadening of the exciton levels due to the lack of long range order or presence of defects.^{40,42} The least ΔE , i.e. sharp absorption edge, suggests that the defects are minimum facilitating long range order.

The optical band gap energies calculated for lithium lead borotellurite, sodium lead borotellurite and potassium lead borotellurite glasses are found to be 2.98 eV, 3.05 eV and 3.18 eV respectively. The values obtained in the present work are of the same order reported in the literature for borate glasses.^{43,44} The widths ΔE of the tails of the localized states within the optical band gap for the present glasses lie in the same range as reported for tellurite glasses.⁴⁵ The Urbach energies calculated for 9 mol% of V_2O_5 doped lithium lead borotellurite, sodium lead borotellurite and potassium lead borotellurite glass samples are found to be 0.18 eV, 0.16 eV and 0.17 eV, respectively. The small value of Urbach energy in the present study suggests that the defects are minimum in this glass sample.

5. Conclusions

From the EPR and optical absorption spectra of vanadyl ions in alkali lead borotellurite glasses, it is observed that the vanadyl ions exist as VO^{2+} molecular ions in an octahedral symmetry with a tetragonal compression. It is observed that the vanadyl ions in sodium lead borotellurite glasses are in tetragonally less distorted octahedral site than those in lithium lead borotellurite and potassium lead borotellurite glasses. In lithium lead borotellurite glasses, it is observed that with increase of V_2O_5 content in the glass, the deviation from octahedral symmetry increases and the VO^{2+} ions are in more tetragonally distorted sites. The paramagnetic susceptibilities are calculated for VO^{2+} ions in lithium lead borotellurite glasses as a function of temperature from EPR data. The linear dependence between $1/\chi$ and T is used to evaluate the Curie constant and is found to be in good agreement with the value reported in literature for vanadyl ions in glasses. The theoretical values of optical basicities are calculated for different alkali lead borotellurite glasses. The optical basicities are increasing from lithium lead borotellurite to potassium lead borotellurite glasses, as the alkali size increases. The optical absorption spectrum of vanadyl ions in alkali lead borotellurite glasses exhibit two bands characteristic

of VO^{2+} molecular ions in tetragonal symmetry. The optical band gap (E_{opt}) and Urbach energies (ΔE) are found to be dependent on the size of the alkali ions.

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