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A study of electron paramagnetic resonance and optical absorption spectra of VO^{2+} ions in alkali calcium borate glasses

R.P. Sreekanth Chakradhar*, A. Murali, J. Lakshmana Rao

Department of Physics, Sri Venkateswara University, Tirupati-517 502, India

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Abstract

Electron paramagnetic resonance (EPR) and optical absorption spectra of VO^{2+} ions in different alkali calcium borate glasses have been studied. The spin-Hamiltonian parameters (g and A), bonding parameter (β_2^{*2}), Fermi contact interaction parameter (k) and crystal field parameters have been evaluated. The values of spin-Hamiltonian parameters confirm that vanadyl ions are present in the glasses as VO^{2+} molecular ions in an octahedral site with a tetragonal compression. At high concentrations of vanadyl ions, the intensity of the EPR resonance signals decreases which has been attributed to the change of oxidation state from V^{4+} to V^{5+} . The EPR spectra have also been studied at different temperatures for VO^{2+} ions in sodium calcium borate glasses. The spin-Hamiltonian parameters are found to be independent of temperature. The magnetic susceptibility χ is calculated from the EPR data. It is observed that as the temperature is decreased the susceptibility increases in accordance with the Curie's law. The theoretical values of optical basicity (Λ_{th}) of glasses have been evaluated. The optical absorption spectrum exhibits two bands characteristic of VO^{2+} ions in tetragonal symmetry. The two bands have been assigned to the transitions ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$ in the decreasing order of energy. The octahedral field parameter (Dq) and the tetragonal field parameters Ds and Dt have been evaluated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: EPR; Optical absorption studies; VO^{2+} ions in glasses; Optical basicity; Crystalfield parameters

1. Introduction

In recent years, there has been a considerable interest in the study of glasses doped with transition metal ions because of their technological applications [1]. Transition metal ions can be used to probe the glass structure because their outer d electron orbital functions have rather broad dis-

tributions and their responses to the surrounding cations are very sensitive [2]. Also the study of transition metal ions in amorphous matrix is one of the interesting research subjects both from the theoretical and experimental points of view. The EPR spectra of VO^{2+} ions in glasses is an interesting research subject and affords a method to investigate the structure of glass. Various physical methods are used to obtain information on this matter. Electron paramagnetic resonance spectra of vanadyl ions in glasses are very interesting because the valence state of vanadyl ions in glasses change with variation of glass composition and melting

*Corresponding author. Tel.: + 91-8574-50666; fax: + 91-8574-27499.

E-mail address: jlrao@usa.net (R.P. Sreekanth Chakradhar).

Table 1
Composition of glasses studied in the present work (x in mol%)

| System | Composition |
|------------------------------------|--|
| 1. Alkali calcium borate | $20\text{M}_2\text{CO}_3 + (25 - x)\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + x\text{V}_2\text{O}_5$ ($\text{M} = \text{Li, Na and K and } x = 10$) |
| 2. Sodium calcium borate (Na Ca B) | $20\text{Na}_2\text{CO}_3 + (25 - x)\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + x\text{V}_2\text{O}_5$ ($x = 5, 10, 15, 20 \text{ and } 24$) |

atmosphere [3]. EPR spectra have been used to study the role of V_2O_5 in various glass systems [4–15] and it was reported that the spectral parameters show strong dependence on V_2O_5 content. In the present study, the EPR spectra of alkali calcium borate glasses containing vanadium were measured in order to examine the valence state of vanadium and also to know the influence of transition metal ion concentration on spectral parameters. The authors are also interested to know the effects of alkali ions on the spin-Hamiltonian parameters and also to know the site symmetries around VO^{2+} ions in these glasses.

2. Experimental

The starting materials M_2CO_3 ($\text{M} = \text{Li, Na and K}$), CaCO_3 , H_3BO_3 and V_2O_5 were used in the preparation of glasses. The chemicals were of Anala grade quality. Table 1 lists the batch composition in mol% of glasses studied in the present work. The chemicals were weighed accurately in an electrical balance and ground to fine powder and mixed thoroughly. The batches were placed in porcelain crucibles and then melted in an electrical furnace in air at 1248 K. The melt was then quenched at room temperature in air by pouring it onto a porcelain plate. The glasses thus obtained were brownish in colour.

The EPR spectra were recorded at room temperature as well as at different temperatures on a EPR spectrometer (JEOL-FE-1X) operating in the X-band frequency (≈ 9.205 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 220 to 420 mT. The modulation

width was set at 0.1 mT and microwave power used was 10 mW. A powdered glass specimen 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 spectrum of $20\text{Na}_2\text{CO}_3 + 15\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + 10\text{V}_2\text{O}_5$ glass sample was recorded at different temperatures (123 to 423 K) using a variable temperature controller (JES-UCI-2AX). A temperature stability of ± 1 K was easily obtained by waiting approximately half an hour before recording a spectrum at each temperature.

The optical absorption spectra of $20\text{M}_2\text{CO}_3 + 15\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + 10\text{V}_2\text{O}_5$ ($\text{M} = \text{Li, Na and K}$) glass samples were recorded at 300 K using Hitachi spectrophotometer (model U-3400) in the wavelength region 330–1000 nm (30300 – 10000 cm^{-1}).

3. Results and analysis

No EPR signal was observed in the spectra of undoped glass samples indicating that no paramagnetic impurities were present in the starting materials. When various mol% of V_2O_5 ions were added to alkali calcium borate batches, the EPR spectra of all the investigated samples exhibit resonance signals. Fig. 1 shows the EPR spectra of 10 mol% of V_2O_5 ions in alkali calcium borate glasses. The EPR spectra of these samples showed a very similar pattern to those found for glasses containing vanadium [3–15]. The spectra have structures which are characteristic of a hyperfine interaction arising from an unpaired electron with a ^{51}V nucleus whose nuclear spin is $7/2$ and which is present in 99.76% abundance.

The EPR spectra were recorded for $20\text{Na}_2\text{CO}_3 + (25 - x)\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + x\text{V}_2\text{O}_5$ ($x = 5, 10, 15, 20$ and 24 mol%) glass samples (hereafter to be referred as NaCaB glasses) for different concentrations of vanadyl ion.

3.1. Calculation of number of spins

The number of spins of VO^{2+} ions participating in resonance can be calculated with a reference

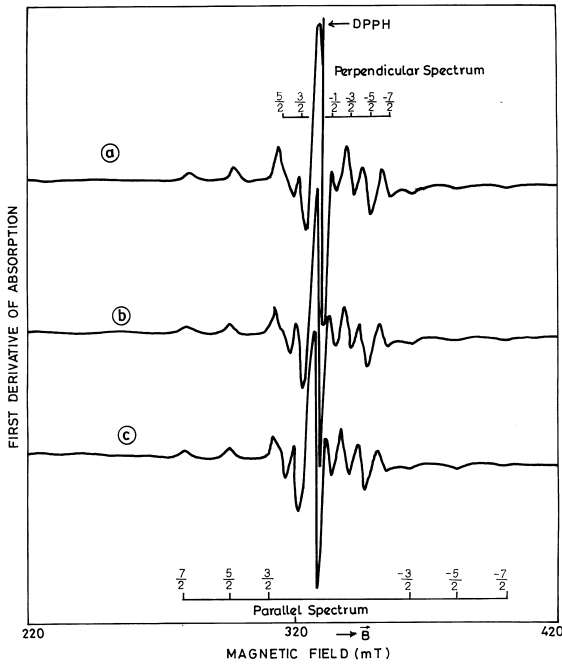


Fig. 1. EPR spectra of 10 mol% of vanadyl ions in various alkali calcium borate glasses $20 \text{ M}_2\text{CO}_3 + 15\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + 10\text{V}_2\text{O}_5$ at 300 K, (a) $M = \text{Li}$ (b) $M = \text{Na}$ and (c) $M = \text{K}$ [Microwave frequency = 9.205 GHz; Microwave power = 10 mW; Field modulation = 0.1 mT; Field sweep rate = 25 mT min^{-1} ; Recorder time constant = 0.1 s; Gain = 400].

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in this study) by using the formula given by Weil et al. [16]

$N =$

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

where A is the area under the absorption curve which can be obtained by double integrating the first derivative absorption curve, 'scan' is the magnetic field corresponding to the unit length of the chart; G is the gain, B_m is the modulation width; g is the g factor; S is the spin of the system in its ground state; P is the power of the microwave used. The subscripts x and std represent the corresponding quantities for the VO^{2+} : glass sample and [Std] is the number of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ molecules in the reference taken.

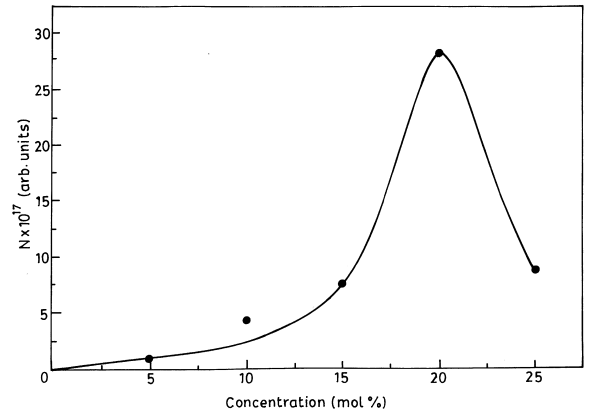


Fig. 2. Variation of the number of spins participating in the resonance for different mol% of vanadyl ions in NaCaB glass samples at room temperature.

Fig. 2 shows the number of spins participating in resonance in NaCaB glasses as a function of V_2O_5 content at room temperature. It is observed that the number of spins participating in resonance increases upto around 20 mol% of V_2O_5 content and afterwards it decreases.

The EPR spectra were recorded at different temperatures for 10 mol% of vanadyl ions in NaCaB glasses in order to measure the variation in intensities and the linewidths with temperature, and the EPR spectra are shown in Fig. 3. It is observed that the number of spins are increasing with decreasing temperature and the linewidths are found to be independent of temperature.

3.2. Magnetic susceptibility

The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula:

$$\chi = \frac{Ng^2\beta^2 J(J+1)}{3k_B T}, \quad (2)$$

where N is the number of spins per m^3 , the rest of the symbols have their usual meaning. N can be calculated from Eq. (1) and $g = (g_{\parallel} + 2g_{\perp})/3$ is taken from EPR data. Using the above equation, the paramagnetic susceptibility was calculated at

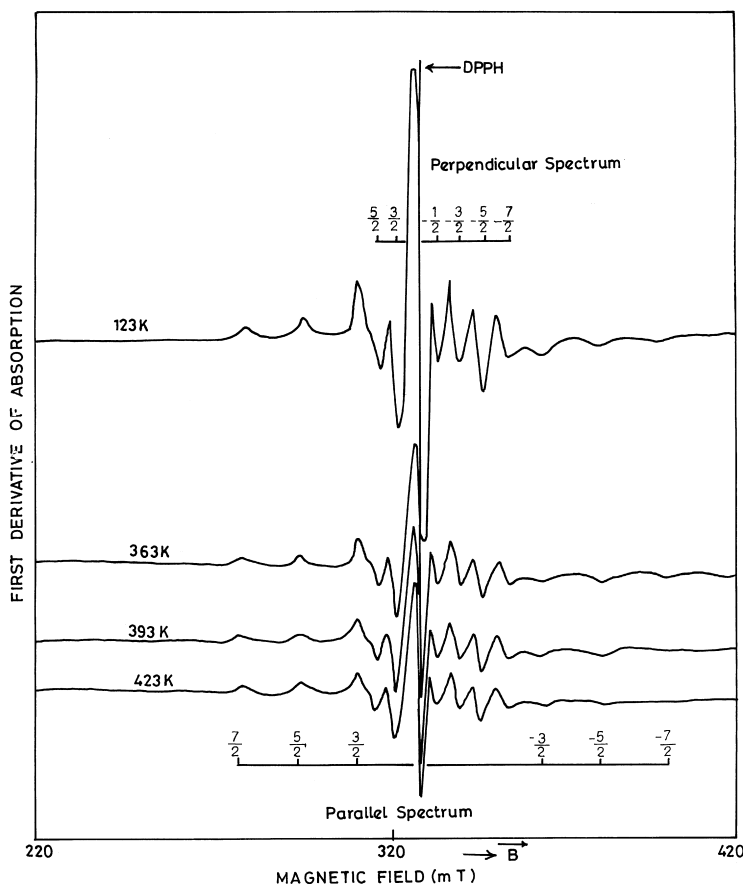


Fig. 3. EPR spectra of 10 mol% of vanadyl ions in NaCaB glass samples at different temperatures [Microwave frequency = 9.205 GHz; Microwave power = 10 mW; Field modulation = 0.1 mT; Field sweep rate = 25 mT min⁻¹; Recorder time constant = 0.1 s; Gain = 400].

various temperatures. Fig. 4 shows a plot of the reciprocal of paramagnetic susceptibility ($1/\chi$) of VO^{2+} ions in NaCaB glass sample as a function of absolute temperature (T). From the figure, it is clear that as the temperature is increased, the susceptibility of the sample decreases obeying Curie's law. Further, the slope of the line gives the Curie constant (244.49×10^{-3}) which is of the same order expected for a paramagnetic ion [17].

The optical absorption spectra of VO^{2+} ions in different alkali calcium borate glass samples were recorded at room temperature and are shown in Fig. 5. The observed spectra consist of two bands and are assigned to d–d transitions ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$ in the decreasing order of energy.

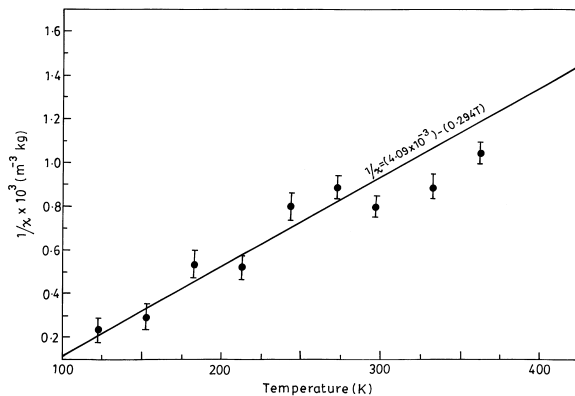


Fig. 4. A plot of the reciprocal of paramagnetic susceptibility ($1/\chi$) [calculated using Eq. (1)] for VO^{2+} ions in NaCaB glass against absolute temperature (T).

4. Discussion

4.1. EPR studies

The EPR spectra of VO^{2+} ions could be best analyzed by using a spin-Hamiltonian [18].

$$\mathcal{H} = g_{||}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + A_{||}S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (3)$$

where β is the Bohr magneton, $g_{||}$ and g_{\perp} are the parallel and perpendicular principal components of the g tensor, $A_{||}$ and A_{\perp} are the parallel and perpendicular principal components of the hyperfine coupling tensors, B_x , B_y and B_z are the components of the magnetic field and S_x , S_y and S_z and I_x , I_y and I_z are the components of the spin operators of the electron and nucleus, respectively.

The solution of the spin-Hamiltonian for the parallel and perpendicular hyperfine lines are

$$B_{||}(m_l) = B_{||}(0) - A_{||}m_l - (63/4 - m_l^2) \frac{A_{\perp}^2}{2B_{||}(0)} \quad (4)$$

$$B_{\perp}(m_l) = B_{\perp}(0) - A_{\perp}m_l - (63/4 - m_l^2) \frac{(A_{||}^2 + A_{\perp}^2)}{4B_{\perp}(0)} \quad (5)$$

where 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 $\pm 1/2$.

$$B_{||}(0) = \frac{h\nu}{g_{||}\beta} \quad \text{and} \quad B_{\perp}(0) = \frac{h\nu}{g_{\perp}\beta},$$

where the symbols have their usual meaning and ν is the microwave frequency.

The spin-Hamiltonian parameters are usually determined by using Eqs. (4) and (5). The iterative method for the numerical analysis of the spectrum as suggested by Muncaster and Parke [7] was used here to avoid the errors caused by certain amount of overlapping between hyperfine lines. Table 2 lists the spin-Hamiltonian parameters evaluated for different alkali calcium borate glasses.

Hecht and Johnston [5] 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

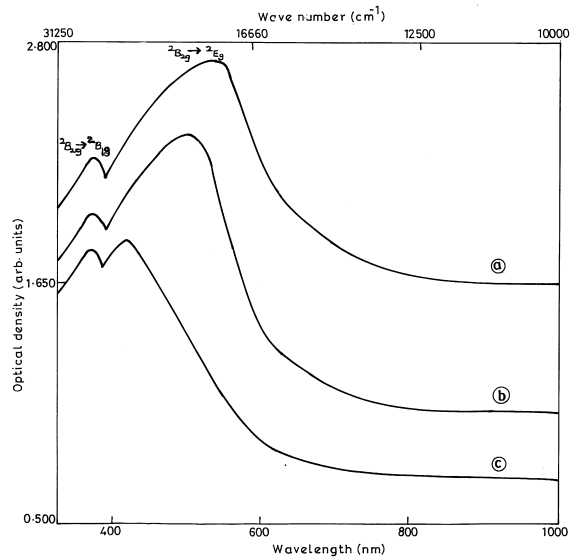


Fig. 5. Optical absorption spectra of vanadyl ions in different alkali calcium borate glasses $20\text{M}_2\text{CO}_3 + 15\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + 10\text{V}_2\text{O}_5$ at room temperature, (a) $\text{M} = \text{Li}$ (b) $\text{M} = \text{Na}$ and (c) $\text{M} = \text{K}$.

Table 2

Spin-Hamiltonian parameters, molecular orbital coefficients and optical basicity values for vanadyl ions in alkali calcium borate glasses (The errors in g and A values are ± 0.002 and $\pm 3 \times 10^{-4} \text{ cm}^{-1}$, respectively)

| Glass system | $g_{ }$ | g_{\perp} | $ A_{ } \times 10^{-4} (\text{cm}^{-1})$ | $ A_{\perp} \times 10^{-4} (\text{cm}^{-1})$ | $\Delta g_{ }/\Delta g_{\perp}$ | β_2^{*2} | k | $Pk/\gamma (\text{cm}^{-1})$ | Λ_{th} |
|--------------|----------|-------------|--|---|----------------------------------|----------------|------|------------------------------|-----------------------|
| LiCa B | 1.941 | 1.966 | 158 | 54 | 1.688 | 0.98 | 0.69 | 0.0060 | 0.5277 |
| NaCaB | 1.935 | 1.963 | 161 | 53 | 1.721 | 0.91 | 0.71 | 0.0061 | 0.5401 |
| KCaB | 1.939 | 1.969 | 161 | 50 | 1.900 | 0.94 | 0.68 | 0.0059 | 0.5571 |

glasses. A detailed analysis of the g -tensor in the presence of trigonal symmetry has been given by Gladney and Swalen [19]. An octahedral site with a tetragonal compression would give $g_{||} < g_{\perp} < g_e$ and $|A_{||}| > |A_{\perp}|$ [8,18]. The g and A values obtained in the present work agree with this relationship and are close to those vanadyl complexes reported in literature [11,20–27]. It is, therefore, confirmed that the vanadyl ions in alkali calcium borate glasses exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and have a C_{4v} symmetry.

The variation of g values with different concentrations of vanadyl ions is shown in Fig. 6. The spin-Hamiltonian parameters evaluated for different concentrations of vanadyl ions are presented in

Table 3. Fig. 6 shows the variation of $g_{||}$ and g_{\perp} with concentration of V_2O_5 in NaCaB glasses. As the concentration of V_2O_5 increases $g_{||}$ value decreases and g_{\perp} value increases. A similar behaviour was observed by Bandyopadhyay in barium borate glasses [28]. This is due to the structural changes in NaCaB glasses with increasing concentration of V_2O_5 .

The value of $\Delta g_{||}/\Delta g_{\perp}$ where $\Delta g_{||} = (g_e - g_{||})$ and $\Delta g_{\perp} = (g_e - g_{\perp})$ which measures the tetragonality of the VO^{2+} site are also calculated and are presented in Tables 2 and 3. A decrease in $\Delta g_{||}/\Delta g_{\perp}$ shows that the octahedral symmetry around VO^{2+} ion is improved [25]. From Table 2, we can observe that $\Delta g_{||}/\Delta g_{\perp}$ value is less in lithium calcium borate glass (LiCaB) compared to potassium calcium borate glass (KCaB). Thus we can assert that the vanadyl ions in LiCaB glass are in tetragonally less distorted octahedral sites than those in KCaB glass samples. It is seen from Table 3, that $\Delta g_{||}/\Delta g_{\perp}$ values increase with concentration of V_2O_5 in NaCaB glass. This implies that as the concentration increases, the deviation from octahedral symmetry increases and the VO^{2+} ions are more tetragonally distorted.

Hochstrasser [4] reported that an increase in g_{\perp} value is an indicative of increasing tetragonality of the vanadium site. It is clear from Table 2, that with increasing vanadium content in NaCaB glass, the g_{\perp} values also increase. This confirms that the symmetry around VO^{2+} ions are more tetragonally distorted as the concentration of vanadyl ions are increased.

The structural change was assumed to explain the variation in $g_{||}$ and g_{\perp} values with

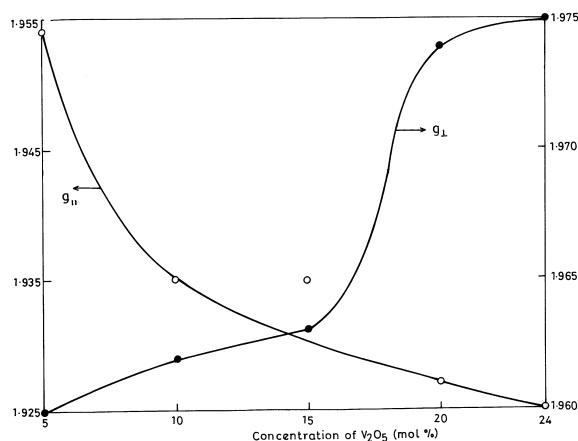


Fig. 6. The variation of $g_{||}$ and g_{\perp} as a function of V_2O_5 in $20\text{Na}_2\text{CO}_3 + (25 - x)\text{CaCO}_3 + 55\text{H}_3\text{BO}_3 + x\text{V}_2\text{O}_5$ glasses at room temperature ($x = 5, 10, 15, 20$ and 24 mol%).

Table 3

Spin-Hamiltonian parameters, molecular orbital coefficients and optical basicity values for vanadyl ions in sodium calcium borate glass samples with increase of V_2O_5 content (The errors in g and A values are ± 0.002 and $\pm 3 \times 10^{-4} \text{ cm}^{-1}$, respectively)

| V_2O_5 content (mol%) | $g_{ }$ | g_{\perp} | $ A_{ } \times 10^{-4} (\text{cm}^{-1})$ | $ A_{\perp} \times 10^{-4} (\text{cm}^{-1})$ | $\Delta g_{ }/\Delta g_{\perp}$ | β_2^* | k | $Pk/\gamma (\text{cm}^{-1})$ | $ A'_{ } \times 10^{-4} (\text{cm}^{-1})$ | $ A'_{\perp} \times 10^{-4} (\text{cm}^{-1})$ | A_{th} |
|---------------------------------------|----------|-------------|--|---|----------------------------------|-------------|------|------------------------------|---|--|----------|
| 5 | 1.954 | 1.960 | 153 | 51 | 1.142 | 0.92 | 0.69 | 0.0060 | 71 | 30 | 0.5492 |
| 10 | 1.935 | 1.962 | 161 | 53 | 1.669 | 0.91 | 0.71 | 0.0061 | 79 | 29 | 0.5401 |
| 15 | 1.935 | 1.963 | 161 | 53 | 1.712 | 0.91 | 0.71 | 0.0061 | 79 | 29 | 0.5325 |
| 20 | 1.927 | 1.974 | 160 | 59 | 2.660 | 0.83 | 0.82 | 0.0071 | 73 | 28 | 0.5259 |
| 24 | 1.925 | 1.975 | 158 | 59 | 2.831 | 0.81 | 0.83 | 0.0072 | 72 | 27 | 0.5214 |

concentration. Such a change is not related to the concentration of paramagnetic ion. The reason for such structural change is not known.

In general, when the symmetry around a paramagnetic ion lowers, one expects a change in optical properties. However, in the present case no significant changes are observed even though the structure appears to be changing.

Molecular orbital theory shows that the hyperfine components $A_{||}$ and A_{\perp} consists the contributions of $A'_{||}$ and A'_{\perp} 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-electron.

Kivelson and Lee [29] gave the following relations:

$$A_{||} = A'_{||} - P\beta_2^{*2}k, \quad (6)$$

$$A_{\perp} = A'_{\perp} - P\beta_2^{*2}k, \quad (7)$$

where

$$A'_{||} = P[-\beta_2^{*2}(4/7) + (g_{||} - 2.0023) + 3/7(g_{\perp} - 2.0023) + D_{||} + 3/7D_{\perp}],$$

$$A'_{\perp} = P[\beta_2^{*2}(2/7) + 11/14(g_{\perp} - 2.0023) + 11/14D_{\perp}].$$

Here $P = 2\gamma\beta\beta_N\langle r^{-3} \rangle = 0.0128 \text{ cm}^{-1}$ is the dipolar hyperfine coupling parameter and k is dimensionless Fermi contact interaction parameter [30] which represents the amount of unpaired electron density at the vanadium nucleus. $D_{||} = -0.0125$ and $D_{\perp} = -0.0015$ are small corrections [31].

From Table 3, it is evident that $A_{||}$ and A_{\perp} increases slowly with increasing V_2O_5 content and at higher concentrations of V_2O_5 both $A_{||}$ and A_{\perp} decrease; and A_{\perp} slightly increases whereas much difference is not observed in $A_{||}$. These changes are associated with the change in the environment of VO^{2+} ion (i.e., in the ligand field at the site of VO^{2+}). A similar change in $g_{||}$ and $A_{||}$ values have also been reported by several research workers [32,33] in the systems showing boron anomaly.

The values of spin-Hamiltonian parameters g and A were used to calculate the molecular orbital coefficient (β_2^{*2}) and k values, where β_2^{*2} is a measure of the degree of Π bonding with the

equatorial ligands and k is the Fermi contact interaction parameter. The values of β_2^{*2} show that the electrons in the inplane vanadium ligand Π bonding orbitals are almost localized on the ligand atoms and the ionic character in the bonds decreases at concentrations greater than 15 mol% of V_2O_5 . The present results can also be interpreted as the V^{4+} ion being complexed as VO^{2+} ion with a tetragonally distorted octahedral site, which is consistent with the results of the absorption spectra and the V^{4+} -O bonding becomes less ionic with the concentrations greater than 15 mol% of V_2O_5 content. The large values of k indicates a large contribution to hyperfine constant by the unpaired s-electron. Using the calculated values of β_2^{*2} , k , $A_{||}$, A_{\perp} , $g_{||}$ and g_{\perp} , the values of $A'_{||}$ and A'_{\perp} are calculated and are also given in Table 3.

Bleaney and Stevens [34] reported that the quantity Pk/γ (γ is the gyromagnetic ratio 1.468 for ^{51}V [7]) is constant for iron group of ions and it takes values 0.0060, 0.0067, 0.0054 and 0.0060 of Cu^{2+} , Mn^{2+} , Co^{2+} and VO^{2+} ions, respectively. In order to get this value one should take negative values for $A_{||}$ and A_{\perp} [7]. Thus, taking negative values for $A_{||}$ and A_{\perp} , the authors have evaluated Pk/γ values for the samples and are presented in Tables 1 and 2. The calculated values of Pk/γ are close to the values reported by Bleaney and Stevens [34].

From Fig. 2, it is observed that the number of spins participating in resonance increases up to 20 mol% of V_2O_5 and afterwards it decreases. In general, the EPR technique is sensitive to the vanadium ion in its + 4 oxidation state (d^1 configuration) rather + 5 oxidation state (d^0 configuration). In the present work, the vanadium ion in + 5 state (in the form of V_2O_5) was used as a dopant and in the melting process of preparing the glass samples, there may be a conversion of a part of vanadium ions in + 5 oxidation state to those in + 4 state. These vanadium ions in + 4 state are responsible for the EPR spectrum observed in the present work. At higher concentrations, there will be a possibility that the ratio of the number of V^{4+} ions (N_4) to the number of V^{5+} ions (N_5) may decrease with increase in concentration. This will cause a decrease in the intensity of the EPR signal. Hence, in the present work, the decrease in number

of spins above 20 mol% of V_2O_5 may be attributed to a fall in the ratio N_4/N_5 .

The optical basicity of an oxide glass can be conveniently measured in terms of the ability of the glass to donate negative charge to the probe ion [35]. Duffy and Ingram [36] reported that the ideal values of optical basicity can be predicted from the composition of the glass and basicity moderating parameters of various cations present. The theoretical values of optical basicity of the glass can be estimated using the formula:

$$A_{th} = \sum_{i=1}^n \frac{Z_i r_i}{2\gamma_i}, \quad (8)$$

where n is the total number of cations present, Z_i is the oxidation number of the i th cation, r_i is the ratio of number of i th cation to the number of oxides present and γ_i is the basicity moderating parameter of the i th cation. The basicity moderating parameter γ_i can be calculated [36] from the following equation:

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

where x_i is Pauling electronegativity [37] of the cation. The theoretical values of optical basicity (A_{th}) calculated for glass samples are presented in Tables 2 and 3. From these tables, it is evident that the changes in optical basicity are independent of the changes in spin-Hamiltonian parameters. Further, it is observed that the theoretical values of A_{th} increases from LiCaB to KCaB glass. Similar observations have been reported earlier by Rao et al. [23].

4.2. Optical absorption studies

For V^{4+} ion in tetragonal symmetry, we expect three bands corresponding to the transitions

${}^2B_{2g} \rightarrow {}^2E_g$, ${}^2B_{2g} \rightarrow {}^2B_{1g}$, and ${}^2B_{2g} \rightarrow {}^2A_{1g}$ [38]. In the present case, for all the glass samples only the first two bands are observed. Su Fang and Hou Bihui [39] also observed only two bands nearly about the same position. The two absorption peaks are characteristic of V^{4+} ion with a distorted octahedral site. The observed band positions and their assignments are given in Table 4. Assignment of the absorption bands are made in the light of energy level scheme for molecular orbitals of the VO^{2+} ion in a ligand field of C_{4v} symmetry [40]. Ballhausen and Gray [40] obtained the Dq value of 1600 cm^{-1} for VO^{2+} in $VOSO_4 \cdot 5H_2O$ on the basis of crystal field theory. They pointed out that this value is very much smaller than that expected (2600 cm^{-1}) by an extrapolation of the Dq values found for $V(H_2O)_6^{2+}$ (1220 cm^{-1}) and $V(H_2O)_6^{3+}$ (1900 cm^{-1}) ions. In the present study, the authors obtained the Dq value of 2685 cm^{-1} which is very close to the expected value. The authors also calculated the tetragonal (C_{4v}) field parameters (Ds and Dt) assuming the probable occurrence of the third band at around 35000 cm^{-1} [40]. The crystal field parameters are found to be in the same range reported for V^{4+} complexes [41].

It is interesting to note that the band ${}^2B_{2g} \rightarrow {}^2E_g$ shifts towards lower wavelength side as the alkali content is changed from lithium to potassium while the ${}^2B_{2g} \rightarrow {}^2B_{1g}$ band showed no such shift. From the energy level diagram given for d^1 configuration [41], it is seen that the band ${}^2B_{2g} \rightarrow {}^2B_{1g}$ is independent of the tetragonal field parameters (Ds and Dt) but it is dependent only on the octahedral field parameter Dq. The octahedral (Dq) and tetragonal (Ds and Dt) field parameters derived from the observed and expected band positions are presented in Table 4. These values suggest that the crystal field of the vanadyl complexes is rather a highly

Table 4

Observed band positions and their assignments, octahedral and tetragonal field parameters for 10 mol% of vanadyl ions in alkali calcium borate glass samples at room temperature

| Glass system | Transition from ${}^2B_{1g}$ (cm^{-1}) ($\Delta_{ }$) | ${}^2B_{2g}$ to 2E_g (cm^{-1}) (Δ_{\perp}) | Dq (cm^{-1}) | Ds (cm^{-1}) | Dt (cm^{-1}) | $\Delta_{ }/\Delta_{\perp}$ |
|--------------|---|---|-------------------------|-------------------------|-------------------------|------------------------------|
| LiCaB | 26 850 | 18 830 | 2685 | − 3854 | 1453 | 1.4 |
| NaCaB | 26 850 | 20 425 | 2685 | − 4082 | 1636 | 1.3 |
| KCaB | 26 850 | 24 170 | 2685 | − 4616 | 2064 | 1.1 |

distorted tetragonal [41]. $\Delta_{||}$ and Δ_{\perp} are the crystal field splitting energies of the transitions ${}^2B_{2g} \rightarrow {}^2B_{1g}$ and ${}^2B_{2g} \rightarrow {}^2E_g$, respectively. Table 4 also includes the ratio of $\Delta_{||}$ and Δ_{\perp} obtained in the present work which are in good agreement with the value (1.3) reported for V^{4+} ion by Baugher and Parke [42].

5. Conclusions

- (1) The EPR and optical absorption spectra of vanadyl ions doped in alkali calcium borate glasses have been successfully interpreted as being due to the presence of six coordinated tetravalent vanadium existing as a vanadyl complex with a tetragonally compressed octahedral site.
- (2) It is observed that $g_{||}$ value decreases with increasing V_2O_5 content whereas g_{\perp} value increases. The increase in g_{\perp} value is attributed to the increasing tetragonality at the vanadium site.
- (3) It is noticed that as the alkali content is changed from lithium to potassium, the deviation from octahedral symmetry increases and the symmetry around VO^{2+} ions are more tetragonally distorted.
- (4) It is also observed that as the concentration of V_2O_5 increases, the number of spins participating in resonance increases upto around 20 mol% and afterwards it decreases. This decrease in intensity may be due to the fall in the ratio of number of vanadyl ions in + 4 oxidation to those in + 5 oxidation state.
- (5) The magnetic susceptibilities were calculated for VO^{2+} ions at room and various temperatures from the EPR data. The linear dependence between $(1/\chi)$ and T was used to calculate the Curie constant and found to be in good agreement with the value reported in literature.
- (6) From molecular orbital coefficients, it is concluded that the V^{4+} –O bonding becomes increasingly covalent with the concentrations greater than 15 mol% of V_2O_5 .
- (7) The spin-Hamiltonian parameters are found to be independent of temperature.

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