

Influence of mixed alkali on the spectral properties of vanadyl ions doped $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3$ glasses—an EPR and optical study

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Abstract

Electron paramagnetic resonance (EPR) and optical investigations have been performed in the mixed alkali borate $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3$ ($5 \leq x \leq 25$) glasses doped with 10 mol% of vanadyl ions in order to look for the effect of ‘mixed alkalis’ on the spectral properties of the glasses. The observed EPR spectra have structures for $x > 5$ mol% which are characteristic of a hyperfine interaction arising from an unpaired electron with the ^{51}V nucleus and it builds up in intensity as x increases. It is observed that the mixed alkali play a significant role in accommodating the vanadyl ions in these mixed alkali glasses and for $x > 5$ mol%, shows a well resolved hyperfine structure typical for isolated VO^{2+} ions. The spin-Hamiltonian parameters (g and A), the dipolar hyperfine coupling parameter (P) and Fermi contact interaction parameter (k) have been evaluated. It is observed that the spin-Hamiltonian parameters do not vary much with the change in composition. It is observed that with increase of x , an increase occurs in tetragonal distortion for VO^{2+} . The number of spins (N) participating in resonance and the paramagnetic susceptibility (χ) have been calculated. It is observed that N and χ increase with x . The optical bandgap energies evaluated for these glasses slightly increase with x and reach a maximum around $x = 20$ and thereafter decrease showing the mixed alkali effect. Optical band gap energies obtained in the present work vary from 2.73 to 3.10 eV for both the direct and indirect transitions. The physical parameters of the glasses are also determined with respect to the composition.

Keywords: A. Glasses; D. Electron paramagnetic resonance; D. Optical properties

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1. Introduction

The mixed alkali effect (MAE) is one of the classical ‘anomalies’ of glass science [1–6] and has been the subject of study over the years. Mixed alkali glasses exhibit a variety of interesting characteristics, in particular the non-linear dependence of their properties exhibiting a minimum or maximum on the relative concentration of the two network modifying alkali oxides [1]. Furthermore, one may investigate the cation dependent properties by systematically replacing one cation (R^I), with another cation (R^{II}), while the overall composition is held constant [2].

Properties associated with ionic mobility such as electrical conductivity, ionic diffusion, dielectric relaxation and internal friction exhibit most pronounced non-linear dependence on x in mixed alkali glasses. On the other hand, bulk properties such as density, refractive index and thermal expansion coefficient show only small deviations from linearity. Properties related to structural relaxation, such as viscosity and glass transition behavior usually exhibit negative deviation [1,3]. The mixed alkali effect is not much studied in borate glasses. Further, the spectroscopic investigations are very few but they would be important and useful to gain insight into the microscopic mechanisms responsible for the effect. As on today, there is no universal theory to explain this MAE, and more experimental studies have to be performed in different systems for better understanding of the phenomenon.

The present investigation is part of an ongoing program to study the MAE and in particular borate glasses viz. sodium potassium borate glasses (hereafter referred as NaKB) doped with V_2O_5 . Among the transition metal oxides V_2O_5 is of much interest in the contemporary and emerging technology, wherein it finds application in the fields like micro electronics, solid state ionics, opto-electronics, etc. [7]. Therefore, in this work we have concentrated on the influence of mixed alkalis on the spectral properties of NaKB glasses doped with V_2O_5 and are characterized by using electron paramagnetic resonance (EPR) and optical absorption techniques. The physical properties of the glasses have also been determined with respect to x .

2. Experimental

The starting materials M_2CO_3 ($M = Na$ or K), H_3BO_3 and V_2O_5 , used in the preparation of the glasses were of Analar grade quality. Table 1 lists the batch composition in mol% of glasses studied in the present work. The chemicals were weighed accurately in an electronic balance mixed thoroughly and ground to a fine powder. The batches were then placed in porcelain crucibles and melted in an electrical furnace in air

Table 1
Composition of glasses studied in the present work

Glass code (x in mol%)	Glass system
5	$5Na_2O-25K_2O-60B_2O_3-10V_2O_5$
10	$10Na_2O-20K_2O-60B_2O_3-10V_2O_5$
15	$15Na_2O-15K_2O-60B_2O_3-10V_2O_5$
20	$20Na_2O-10K_2O-60B_2O_3-10V_2O_5$
25	$25Na_2O-5K_2O-60B_2O_3-10V_2O_5$

at 1123 K for half-an-hour. The melt was then quenched to room temperature in air by pouring it onto a polished porcelain plate and pressing it with another porcelain plate. The glasses thus obtained were yellow in color. The glasses were then annealed at 423 K. The glass formation was confirmed by powder X-ray diffraction recorded with an X-ray diffractometer (Scintag USA) using copper $K\alpha$ radiation.

The EPR spectra were recorded on a EPR spectrometer (JEOL-FE-1X) operating in the X-band frequency (≈ 9.200 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 220 to 420 mT and the microwave power used was 20 mW. A powdered glass sample of 100 mg was taken in a quartz tube for EPR measurements. The optical absorption spectra of the glasses were recorded in the UV region in order to measure the optical absorption edges by using a Cintra (GBC40) spectrophotometer.

2.1. Physical properties of vanadyl doped mixed alkali borate glasses

The density (D) of the glass samples at room temperature was measured by the Archimedes' principle using a sensitive microbalance with xylene as the immersion liquid. The mean atomic volume (V) of each glass was obtained from the values of densities (D) and mean atomic weights. The number of vanadyl ions (N) was determined from the glass composition and its density value. The refractive index (n_d) of the glass was measured with an Abbe Refractometer at sodium wavelength ($\lambda = 5893 \text{ \AA}$). The dielectric constant (ϵ), the reflection loss from the glass surface (R), the molar refractivity (R_m), the electronic polarizability (α_e), the polaron radius and inter-ionic separation have been evaluated using the standard formulae explained in detail in our earlier paper [8]. The results thus obtained are tabulated in Table 2.

2.2. Optical basicity of the glass (Λ_{th})

The optical basicity of an oxide glass will reflect the ability of the glass to donate negative charge to the probe ion [9]. Duffy and Ingram [10] reported that the optical basicity can be predicted from the

Table 2
Certain physical parameters of vanadyl ions doped in NaKB glasses studied in the present work at room temperature

S. No.	Physical property	Glass code				
		$x = 5$	$x = 10$	$x = 15$	$x = 20$	$x = 25$
1.	Average molecular weight	95.137	93.532	91.915	90.305	88.693
2.	Density, D (g/cm^3) (± 0.005)	2.773	2.756	2.721	2.586	2.727
3.	Refractive index, n_d (± 0.005)	1.519	1.516	1.512	1.505	1.502
4.	Molar refractivity, R_M (cm^{-3}) (± 0.005)	10.413	10.250	10.136	10.357	9.598
5.	Mean atomic volume, V (g/cm^3 per atom) (± 0.0025)	0.0745	0.0737	0.0734	0.0759	0.0707
6.	Optical dielectric constant, ϵ (± 0.005)	2.307	2.298	2.286	2.265	2.256
7.	Electronic polarizability, $\alpha_e \times 10^{-24}$ (ions/cm^3) (± 0.005)	4.128	4.063	4.018	4.106	3.805
8.	Concentration, $N \times 10^{23}$ (ions/cm^3) (± 0.005)	1.756	1.775	1.783	1.725	1.852
9.	Optical basicity, Λ_{th}	0.5509	0.5469	0.5427	0.5386	0.5345
10.	Polaron radius, r_p (\AA) (± 0.005)	0.719	0.716	0.715	0.723	0.706
11.	Inter-ionic distance, r_i (\AA) (± 0.005)	1.785	1.779	1.776	1.796	1.754

The errors in measurement are given in the parenthesis.

composition of the glass and the basicity moderating parameters of the various cations present. The theoretical values of optical basicity of the glass can be estimated using the formula [10]

$$\Lambda_{\text{th}} = \sum_{i=1}^n \frac{Z_i r_i}{2\gamma_i} \quad (1)$$

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 cations 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 [10] from the following equation

$$\gamma_i = 1.36(x_i - 0.26) \quad (2)$$

where x_i is the Pauling electronegativity [11] of the cation. The theoretical values of optical basicity (Λ_{th}) were calculated for all the glass samples and are listed in Table 2. The physical parameters like densities, molar volumes, number of vanadyl ions per unit volume, evaluated for the glasses studied in the present work is also included in Table 2. It is observed that the density initially decreases with x up to $x = 20$ and thereafter increases reaching a minimum at $x = 20$. With the increase of Na_2O content (keeping the B_2O_3 content constant at 60 mol%), the number of Na atoms increase and the number of K atoms decrease. As K atoms are heavier than Na, so the density should decrease continuously with increase of Na_2O content. But probably due to MAE we observe a rise in the density curve when the $x > 20$, reaching a minimum at $x = 20$ and thereafter increases. In addition to this the bond strengths of Na–O and K–O are different; the elastic moduli are directly influenced by the number of these bonds present in the glass sample.

The refractive index, optical dielectric constant decreases with x . The other parameters like molar refractivity, mean atomic volume, electronic polarizability, inter-ionic separation and ionic radius decreases with x up to $x = 15$, exhibiting a minimum and thereafter increases with x up to $x = 20$ exhibiting a maximum at $x = 20$ and thereafter decreases. However, it is observed that the average molecular weight and the theoretical values of optical basicity of the glass continuously decrease linearly with x . As the ability of equatorial ligands to donate the electron (Lewis basicity) decreases, σ -bonding between V^{4+} and ligands is reduced. This decrease in turn increases the positive charge on V^{4+} vanadyl oxygens. So the tetragonal distortion is increased and consequently the octahedral symmetry reduced.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction is a useful method to detect readily the presence of crystals in a glassy matrix if their dimensions are greater than typically 100 nm [12]. The X-ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material and consists of a few broad diffuse halos rather than sharp rings. All the samples were tested and the results showed the absence of crystalline characteristics. Fig. 1 shows the typical X-ray diffraction patterns for these compositions (see Table 1). The patterns obtained do not reveal any crystalline phase in the glass.

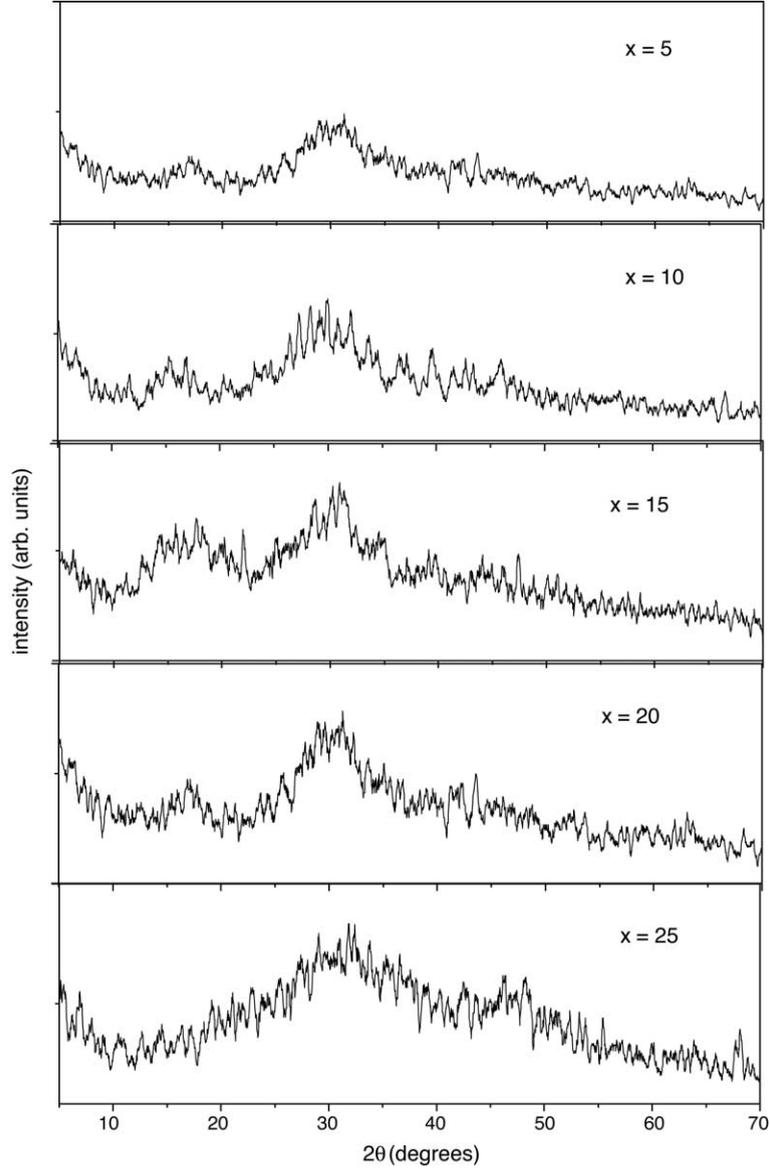


Fig. 1. X-ray diffraction pattern for different mixed alkali borate glasses: $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3-10\text{V}_2\text{O}_5$ ($5 \leq x \leq 25$), at room temperature.

3.2. EPR studies

The EPR spectra of the investigated samples (see Table 1) exhibit resonance signals due to vanadyl ions entering the glass matrix as paramagnetic species VO^{2+} . Fig. 2 shows the EPR spectra of 10 mol% of V_2O_5 molecules in $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3$ ($5 \leq x \leq 25$) glasses as a function of x . From Fig. 2, it is clear that the EPR spectra have structures for $x > 5$ mol%, which are characteristic of a hyperfine interaction arising from an unpaired electron with a ^{51}V nucleus whose nuclear spin is $7/2$. However, we

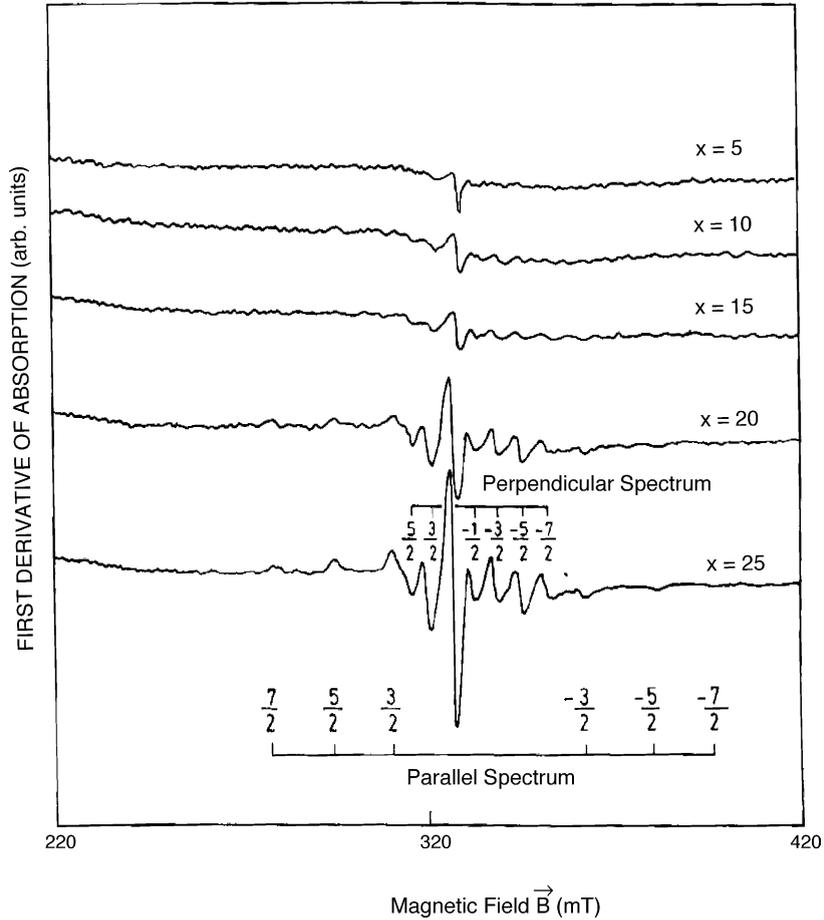


Fig. 2. EPR spectra of 10 mol% VO^{2+} ions doped in different mixed alkali borate glasses: $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3$ ($5 \leq x \leq 25$), at room temperature.

may notice from Fig. 2 that the EPR spectra exhibit marked composition dependence as a function of x , even though we have doped the glasses with a constant V_2O_5 content in this series. This change might be due to the mixed alkalis, which play a significant role in accommodating the vanadyl ions in the glass matrix. The EPR spectra of these samples showed a very similar pattern to others reported for vanadyl ions in various glass systems [13–43].

The EPR spectra for VO^{2+} ions in glasses could be best analyzed by using an axial spin-Hamiltonian [44].

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

where β is the Bohr magneton; g_{\parallel} and g_{\perp} are the parallel and perpendicular principal components of the g tensor; A_{\parallel} 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 , S_z and I_x , I_y , I_z are the components of the spin operators of the electron and nucleus, respectively.

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

$$B_{\parallel}(m_I) = B_{\parallel}(0) - A_{\parallel}(m_I) - \left(\frac{63}{4} - m_I^2\right) \frac{A_{\perp}^2}{2B_{\parallel}(0)} \quad (4)$$

$$B_{\perp}(m_I) = B_{\perp}(0) - A_{\perp}(m_I) - \left(\frac{63}{4} - m_I^2\right) \frac{(A_{\parallel}^2 + A_{\perp}^2)}{4B_{\perp}(0)} \quad (5)$$

where m_I is the magnetic quantum number of the vanadium nucleus, which takes the values $\pm 7/2$, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$.

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

where h is the Planck's constant, ν is the microwave frequency at resonance, β is the Bohr-magneton, B is the magnetic field, g and A are the spin-Hamiltonian parameters.

The spin-Hamiltonian parameters are usually determined by using Eqs. (4) and (5). Hecht and Johnston [14] 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 Gladney and Swalen [45]. An octahedral site with a tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$ and $|A_{\parallel}| > |A_{\perp}|$ [25,26].

The evaluated spin-Hamiltonian parameters (g and A) for NaKB ($10 \leq x \leq 25$) glasses with vanadyl ions, are presented in Table 3 and are compared with other systems. The uncertainties in measurement of g and A values are ± 0.001 and $\pm 0.5 \times 10^{-4} \text{ cm}^{-1}$, respectively. It is observed that spin-Hamiltonian parameters are in good agreement with those reported in literature. From Table 3, it is evident that the strength of hyperfine splitting constants A_{\parallel} and A_{\perp} in MAB glasses is small by about 12.5 and 25%, respectively, compared with binary borate glasses. For $x = 5$ glass, we did not observe the hyperfine structure (hfs) and also the intensity was very low compared to other glasses in this series. Therefore, the g value for $x = 5$ glass has been taken at the central resonance line. The hfs begins to appear for $x \geq 10$ mol% and it builds up in intensity as x increases. The appearance of hfs for $x \geq 10$ mol% is due to the interaction of electron spin of vanadyl ion with its nuclear spin, which increases with increasing x as evident from Fig. 2. The absence of hfs for $x = 5$, might be due to the absence of interaction between electron spin and nuclear spin or it may be considerably very weak.

So far, it is generally believed from the reports in the literature [21] that the intensity of the EPR signal increases with increase of vanadyl content whereas the hfs disappears with increase of V_2O_5 . The progressive disappearance of the vanadyl hfs with increase of V_2O_5 is due to the increase in dipolar interaction among the vanadyl ions themselves. However, in the present investigations, even though we are introducing constant V_2O_5 (10 mol%) in this series of mixed alkali glasses, the change in the ratio of the alkalis is able to change the structure significantly. The main features observed here are (1) the interaction between the electron and nuclear spin can be altered just by changing the alkali content (without changing the V_2O_5) (i.e., the interaction is more in $x = 25$ glass compared to $x = 5$, Fig. 2); (2) the intensity of the signal can also be altered by changing the alkali content (the intensity is more in $x = 25$). Therefore, the mixed alkali plays a significant role in accommodating the vanadyl ions in these mixed alkali glasses.

Table 3
Comparison of spin-Hamiltonian parameters for VO²⁺ ions in different glass systems

System with VO ²⁺	$g_{ }$	g_{\perp}	$ A_{ } $ (10 ⁻⁴ cm ⁻¹)	$ A_{\perp} $ (10 ⁻⁴ cm ⁻¹)	Reference
Na ₂ O–4SiO ₄	1.938	1.993	166	62	[19]
K ₂ O–4SiO ₄	1.939	1.995	167	62	[19]
Cs ₂ O–4SiO ₄	1.936	1.995	166	62	[19]
Li ₂ O–B ₂ O ₃	1.935	1.987	174	64	[15]
Na ₂ O–B ₂ O ₃	1.943	1.980	168	61	[15]
K ₂ O–B ₂ O ₃	1.933	1.987	174	62	[15]
Cs ₂ O–B ₂ O ₃	1.934	1.988	173	62	[15]
Li ₂ O–BaO–B ₂ O ₃	1.937	1.971	167	59	[22]
Li ₂ O–CaO–B ₂ O ₃	1.937	1.972	169	61	[22]
Li ₂ O–MgO–B ₂ O ₃	1.939	1.970	180	72	[22]
Li ₂ O–Na ₂ O–B ₂ O ₃	1.931	1.956	171	51	[24]
ZnO–B ₂ O ₃	1.929	1.961	165	59	[16]
PbO–B ₂ O ₃	1.919	1.960	166	57	[16]
Li ₂ SO ₄ –CdSO ₄ –B ₂ O ₃	1.928	1.989	187	66	[27]
Na ₂ SO ₄ –CdSO ₄ –B ₂ O ₃	1.928	1.989	187	67	[27]
K ₂ SO ₄ –CdSO ₄ –B ₂ O ₃	1.928	1.988	188	67	[27]
Na ₂ SO ₄ –ZnSO ₄ –B ₂ O ₃	1.936	1.982	181	73	[27]
Cs ₂ SO ₄ –ZnSO ₄ –B ₂ O ₃	1.934	1.984	180	72	[27]
Na ₂ SO ₄ –ZnSO ₄	1.936	1.982	175	65	[26]
K ₂ SO ₄ –ZnSO ₄	1.922	1.970	180	68	[20]
K ₂ SO ₄ –Na ₂ SO ₄ –ZnSO ₄	1.927	1.977	181	71	[36]
Na ₂ O–P ₂ O ₅	1.937	1.979	175	59	[41]
10Na ₂ O–20K ₂ O–60B ₂ O ₃	1.941	1.966	157.7	48	Present work
15Na ₂ O–15K ₂ O–60B ₂ O ₃	1.940	1.965	157.4	47	Present work
20Na ₂ O–10K ₂ O–60B ₂ O ₃	1.941	1.966	157.6	48	Present work
25Na ₂ O–5K ₂ O–60B ₂ O ₃	1.942	1.966	157.7	48	Present work

The reason to choose 10 mol% of V₂O₅ content as optimum in this series is due to, at lower V₂O₅ content <10 mol% the EPR signal intensity is very low, as evident from $x = 5$ glass. Since the V₂O₅ is also a network former, at high concentrations (V₂O₅ > 20 mol%), there is a possibility that V₂O₅ along with B₂O₃ becomes a glass network former [42]. However, in the present study we used V₂O₅ = 10 mol% in this series and we strongly believe that the vanadyl ions enter the glass matrix only as an EPR probe and not as a network former.

It is observed that the spin-Hamiltonian parameters (g and A) do not vary much with the change in composition in this series of mixed alkali borate glasses. The g and A values obtained in the present work agree with the relationship $g_{||} < g_{\perp} < g_e$ and $|A_{||}| > |A_{\perp}|$ and are close to those vanadyl complexes as reported by others [13–43]. It is therefore confirmed that the vanadyl ions in NaKB glasses exist as VO²⁺ ions in octahedral coordination with a tetragonal compression and have a C_{4v} symmetry. The bonding of the vanadyl ion in ligand field of octahedral symmetry has been well characterized by earlier workers [25,28,29]. The V⁴⁺ site in the VO²⁺ ion forms coplanar bonds with each of the four oxygen ligands. The vanadyl oxygen is attached axially above the V⁴⁺ site along the z -axis while the sixth oxygen forming the octahedral O–VO₄–O unit lies axially below the V⁴⁺ site. The vanadyl ion (VO²⁺) is known to form an octahedral oxygen complex and V=O direction will be predominant axial distortion.

The values of spin-Hamiltonian parameter g and A were used to calculate the dipolar hyperfine coupling parameter (P) and the Fermi contact interaction parameter (k) values. Hyperfine coupling terms A_{\parallel} and A_{\perp} may be expressed by the relations developed by Kivelson and Lee [46].

$$A_{\parallel} = -P \left[\beta^2 \left(k + \frac{4}{7} \right) - \Delta g_{\parallel} - \frac{3}{7} \Delta g_{\perp} \right] \quad (6)$$

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

where k represents the contribution to hyperfine coupling due to isotropic Fermi contact interaction.

$$k \propto \left\langle \phi_{b_2}^* \left| \sum_K \delta(r_K) S_K \right| \phi_{b_2}^* \right\rangle \quad (8)$$

here $\phi_{b_2}^*$ is the ground state wavefunction for unpaired electron, δ is the delta function operator evaluated in the ground state and S_k is the spin operator for the k th electron the term β^2 is a measure of the degree of π bonding with the equatorial ligands and may be taken as equal to unity for vanadium [17]. $P = 2\gamma\beta_0\beta_N\langle r^{-3} \rangle = 0.0128 \text{ cm}^{-1}$ is the dipolar hyperfine coupling parameter, where β_N is the nuclear magneton, γ is the gyromagnetic ratio and r is the distance joining V^{51} nucleus and the unpaired electron. $\Delta g_{\parallel} = g_{\parallel} - 2.0023$ and $\Delta g_{\perp} = g_{\perp} - 2.0023$.

Molecular orbital theory shows that the hyperfine components A_{\parallel} and A_{\perp} consists of the contributions $A_{\parallel}^{\downarrow}$ and A_{\perp}^{\downarrow} of the $3d_{xy}$ electron to the hyperfine structure and the $P\beta^2k$ term arising due to the anomalous contribution of the s-electrons [17]. Eqs. (6) and (7) can be written in terms of component parts as

$$A_{\parallel} = -P \left[\frac{4}{7} \beta^2 - \Delta g_{\parallel} - \frac{3}{7} \Delta g_{\perp} \right] - P\beta^2k = A_{\parallel}^{\downarrow} - P\beta^2k \quad (9)$$

$$A_{\perp} = P \left[\frac{2}{7} \beta^2 + \frac{11}{14} \Delta g_{\perp} \right] - P\beta^2k = A_{\perp}^{\downarrow} - P\beta^2k \quad (10)$$

The values of $A_{\parallel}^{\downarrow}$ and A_{\perp}^{\downarrow} are calculated using Eqs. (9) and (10) and are given in Table 4.

Bleaney and Stevens [47] reported that the quantity Pk/γ (γ is the gyromagnetic ratio 1.468 for ^{51}V [17]) is constant for iron group of ions and it takes the values 0.0060, 0.0067 and 0.0060 for Cu^{2+} , Mn^{2+} and VO^{2+} ions, respectively. In order to get this value, one should take negative values for A_{\parallel} and A_{\perp} [17]. Thus, taking negative values for A_{\parallel} and A_{\perp} , we have evaluated Pk/γ values for the samples and are presented in Table 4.

The calculated values of Pk/γ are close to the values reported by Bleaney and Stevens [47]. It is observed that k and P did not reflect clear trends with variation of x . However, $P\beta^2k$ (where $\beta^2 = 1$ has been used) increases with increase of x indicating an increase in tetragonal distortion for VO^{2+} [35]. $P\beta^2k$ is evaluated which is a measure of 's' character of the spin of the vanadium and also the tetragonal distortion.

3.3. Calculation of number of spins 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.

Table 4

$A_{||}^{|}$, $A_{\perp}^{|}$, molecular orbital coefficients, number of spins participating in resonance (N), paramagnetic susceptibility (χ) and Urbach energies for VO^{2+} ions in NaKB glass matrices with x

Glass system	$ A_{ }^{ } $ (10^{-4} cm^{-1})	$ A_{\perp}^{ } $ (10^{-4} cm^{-1})	P (10^{-4} cm^{-1})	k	$P\beta^2 k$ (cm^{-1})	Pk/γ (cm^{-1})	$N \times 10^{20}$ (arb. units)	$\chi \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$	Urbach energy ΔE (eV) (± 0.002)
$x = 5$	–	–	–	–	–	–	5.8	0.135	0.297
$x = 10$	79.88	29.82	121.6	0.64	77.82	0.0054	6.3	0.147	0.265
$x = 15$	79.45	30.95	121.8	0.64	77.95	0.0053	7.0	0.163	0.249
$x = 20$	78.89	30.71	121.1	0.65	78.71	0.0053	7.2	0.168	0.241
$x = 25$	78.86	30.84	121.3	0.65	78.84	0.0054	9.8	0.230	0.283

[48] gave the following expression, which includes the experimental parameters of both sample and standard.

$$N = \frac{A_x(\text{Scan}_x)^2 G_{\text{std}}(B_m)_{\text{std}}(g_{\text{std}})^2 [S(S+1)]_{\text{std}} (P_{\text{std}})^{1/2}}{A_{\text{std}}(\text{Scan}_{\text{std}})^2 G_x(B_m)_x (g_x)^2 [S(S+1)]_x (P_x)^{1/2}} [\text{Std}] \quad (11)$$

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, S is the spin of the system in its ground state and P is the power of the microwave source. The subscripts 'x' and 'std' represent the corresponding quantities for VO²⁺ glass sample and the reference (CuSO₄·5H₂O), respectively. By using Eq. (11), the number of spins participating in resonance has been evaluated. It is observed that the number of spins participating in resonance increases with increasing x in these glasses and is listed in Table 4. The increase in spins is due to more number of vanadyl ions entering the matrix as paramagnetic species.

3.4. Calculation of paramagnetic susceptibility from EPR data

The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula [49]

$$\chi = \frac{Ng^2\beta^2J(J+1)}{3k_B T} \quad (12)$$

where N is the number of spins per m³ and the other symbols have their usual meaning. N can be calculated from Eq. (11) and $g = (g_{||} + 2g_{\perp})/3$ is taken from EPR data. The paramagnetic susceptibility has been evaluated as function of x and is presented in Table 4. It is observed that χ increases with x .

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

The optical band gap and Urbach energy of NaKB glasses were obtained from their ultraviolet absorption edges. The study of the fundamental absorption edge in the UV-region is a useful method for the investigation of optical transitions, electronic band structure in crystalline and non-crystalline materials. There are two types of optical transitions, which can occur at the fundamental absorption edge of crystalline and non-crystalline semiconductors. They are direct and indirect transitions. In both the cases, electromagnetic waves interact with the electron in the valence band, which are raised across the fundamental gap to the conduction band. In glasses, the glass forming anions influences the conduction band; the cations play an indirect but significant role [50,51]. 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 excitation levels due to the lack of long-range order or presence of defects [50,52]. The least ΔE , i.e., sharp absorption edge, suggests that defects are the minimum facilitating long-range order.

A main feature of absorption edge of amorphous semiconductors, particularly at the lower values of absorption coefficient, is the exponential increase of the absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$ in accordance with an empirical relation [53]

$$\alpha(\nu) = \alpha_0 \exp\left(\frac{h\nu}{\Delta E}\right) \quad (13)$$

where α_0 is a constant, ΔE is the Urbach energy and ν is the frequency of radiation.

The absorption coefficient $\alpha(\nu)$ can be determined near the edge using the formula

$$\alpha(\nu) = \left(\frac{1}{d}\right) \ln \left(\frac{I_0}{I}\right) = 2.303 \frac{A}{d} \quad (14)$$

where A is the absorbance at frequency ν and d is the thickness of the sample. For an absorption by indirect transitions, the equation takes the form:

$$E_{\text{opt}} = h\nu - \left(\frac{h\nu}{B}\right)^{1/2} \quad (15)$$

Using the above equations, by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, one can find the optical energy band gaps (E_{opt}) for indirect and direct transitions respectively by extrapolating the linear region of the curve to the $h\nu$ axis and are shown in Figs. 3 and 4, respectively. Plots were also

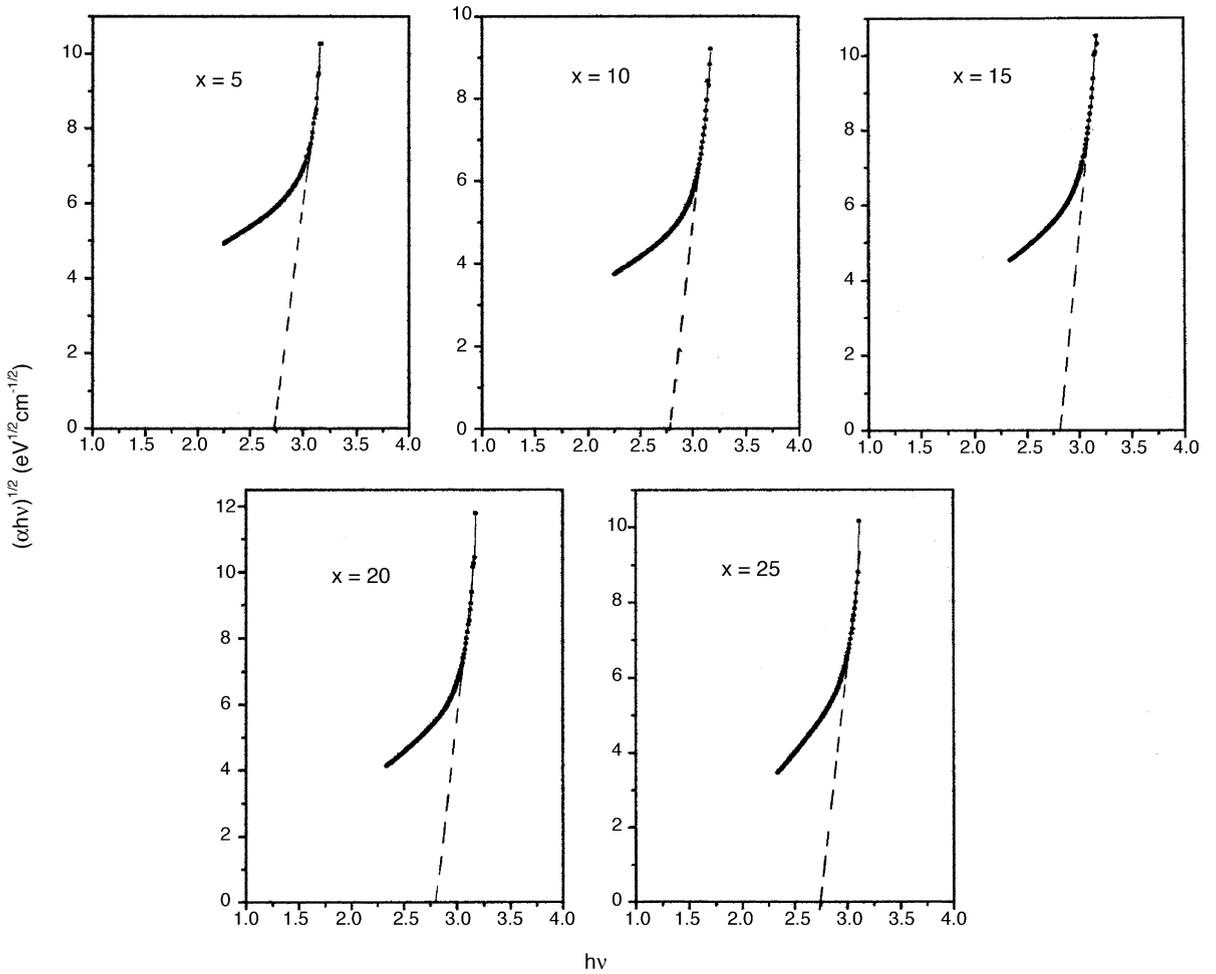


Fig. 3. Plots corresponding to $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for different mixed alkali borate glasses: $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3-10\text{V}_2\text{O}_5$ ($5 \leq x \leq 25$), at room temperature.

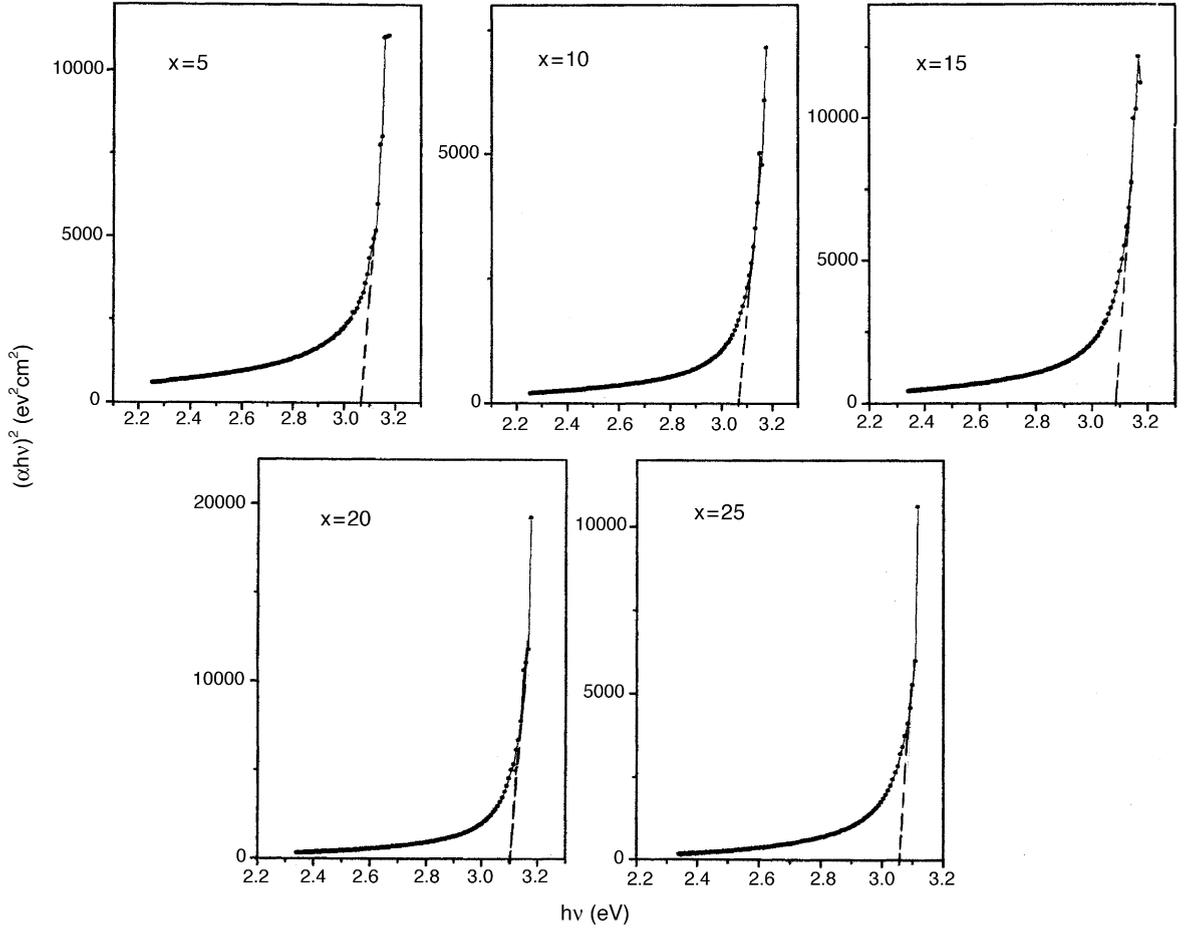


Fig. 4. Plots corresponding to $(\alpha hv)^2$ vs. $h\nu$ for different mixed alkali borate glasses: $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3-10\text{V}_2\text{O}_5$ ($5 \leq x \leq 25$), at room temperature.

drawn between $\ln \alpha$ and $h\nu$ (not shown here) and from these plots, the slopes and thereby Urbach energies were calculated. The variation of optical band gap energies with x is shown in Fig. 5. It is interesting to note that the optical band gap energies for these glasses slightly increase with x and reach a maximum around $x = 20$ and thereafter decrease showing the mixed alkali effect. The optical band gap obtained in the present work varies from 2.73 to 3.10 eV for both the direct and indirect transitions, which is of the same order expected for borate glasses. This non-linear variation of E_{opt} with x indicates the existence of MAE in optical properties of the NaKB glass system. In single alkali borate glasses, the E_{opt} decreases monotonically with the content of alkali ions and has been attributed to the formation and increase in the non-bridging oxygens [54,55]. However, the existence of minima/maxima in E_{opt} at around $x = 20$ may be due to the formation of a large number of non-bridging oxygens at around this composition compared to dilute foreign alkali regions [56]. The Urbach energies have also been evaluated in the present work and are listed in Table 4. It is also interesting to observe that the Urbach energy decrease with x and reach a minimum around $x = 20$ and thereafter increase showing the mixed alkali effect.

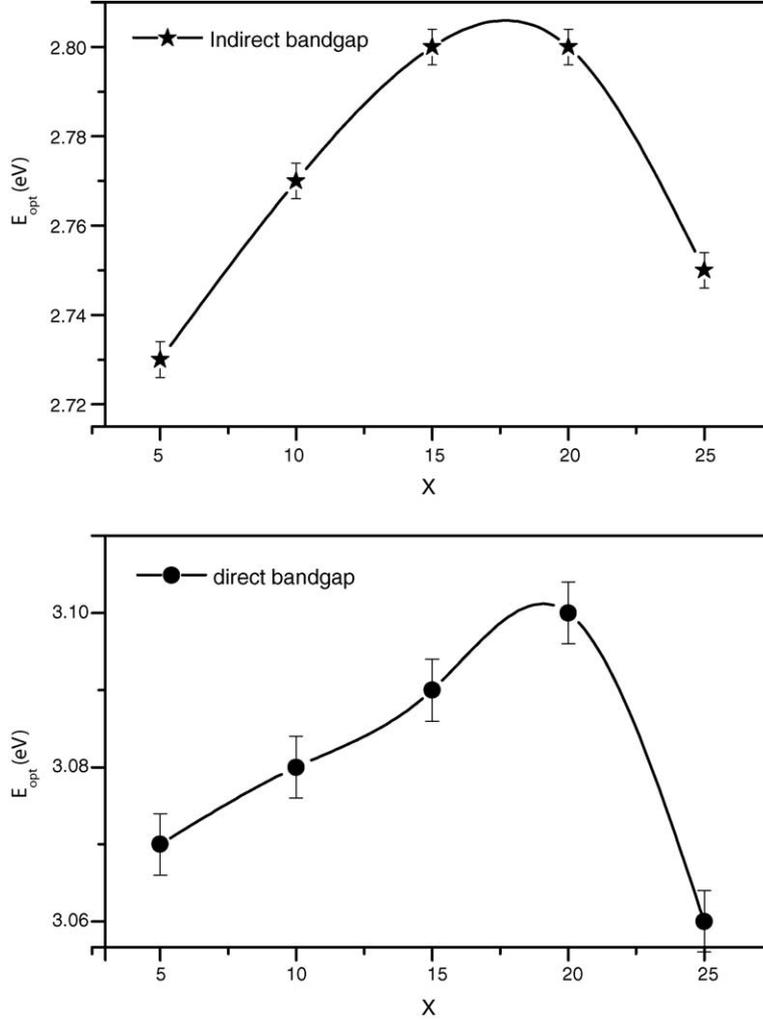


Fig. 5. The variation of optical bandgap energies in the mixed alkali borate glasses: $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3-10\text{V}_2\text{O}_5$ ($5 \leq x \leq 25$) as a function of x at room temperature.

5. Conclusions

The EPR spectra of VO^{2+} ions doped mixed alkali borate $x\text{Na}_2\text{O}-(30-x)\text{K}_2\text{O}-60\text{B}_2\text{O}_3$ glasses have structures for $x > 5$ mol% which are characteristic of a hyperfine interaction arising from an unpaired electron with the ^{51}V nucleus whose nuclear spin is $7/2$. It is observed that the mixed alkalis play a significant role in accommodating the vanadyl ions in the glass matrix and for $x > 5$ mol%, shows a well-resolved hyperfine structure. The spin-Hamiltonian parameters (g and A), the dipolar hyperfine coupling parameter (P) and Fermi contact interaction parameter (k) have been evaluated. The spin-Hamiltonian parameters in NaKB glasses indicates that the VO^{2+} ions are in octahedral coordination with a tetragonal compression and have a C_{4v} symmetry. The strength of the hyperfine splitting constants $A_{||}$ and A_{\perp} in MAB glasses is small by about 12.5 and 25%, respectively, compared with binary borate glasses. It is

observed that the spin-Hamiltonian parameters (g and A) do not vary much with the change in composition. It is observed that with increase of x , $P\beta^2k$ increases indicating an increase in tetragonal distortion for VO^{2+} . The number of spins (N) participating in resonance and the paramagnetic susceptibility (χ) have been calculated. It is observed that N and χ increases with x . From ultraviolet absorption edges, the optical bandgap energies have been evaluated. It is interesting to observe that the optical bandgap energies for these glasses slightly increase with x and reach a maximum around $x = 20$ mol% and thereafter decrease showing the mixed alkali effect. Optical band gaps obtained in the present work vary from 2.73 to 3.10 eV for both the direct and indirect transitions. It is also interesting to observe that the Urbach energy decrease with x and reach a minimum around $x = 20$ and thereafter increase showing the mixed alkali effect.

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References

- [1] D.E. Day, *J. Non-Cryst. Solids* 21 (1976) 343.
- [2] W.M. Risen Jr., G.B. Rouse, J.M. Gordon, in: G.H. Frischat (Ed.), *J. Non-Cryst. Solids*, Trans. Tech. Publications (1977) 473.
- [3] G.B. Rouse, J.M. Gordon, W.M. Risen Jr., *J. Non-Cryst. Solids* 33 (1979) 83.
- [4] M.D. Ingram, *Glasstech. Ber.* 67 (1994) 151.
- [5] A. Bunde, M.D. Ingram, P. Maass, *J. Non-Cryst. Solids* 172–174 (1994) 1222.
- [6] J.E. Shelby, *Introduction to Glass Science and Technology*, Royal Society of Chemistry, Cambridge, 1997.
- [7] A. Talledo, C.G. Granqvist, *J. Appl. Phys.* 77 (1995) 4655.
- [8] R.P. Sreekanth Chakradhar, K.P. Ramesh, J.L. Rao, J. Ramakrishna, *J. Phys. Chem. Solids* 64 (2003) 641.
- [9] E. Guedes de Sousa, S.K. Mendiratta, J.M. Machado da Silva, *Portugal Phys.* 17 (1986) 203.
- [10] J.A. Duffly, M.D. Ingram, *J. Inorg. Nucl. Chem.* 37 (1975) 1203.
- [11] L. Pauling, *The Nature of Chemical Bond*, third ed., Cornell University Press, New York, 1960, p. 93.
- [12] G.W. Anderson, W.D. Luehrs, *J. Appl. Phys.* 39 (1969) 1634.
- [13] G. Hochstrasser, *Phys. Chem. Glasses* 7 (1966) 178.
- [14] H.G. Hecht, T.S. Johnston, *J. Chem. Phys.* 46 (1967) 23.
- [15] H. Toyuki, S. Akagi, *Phys. Chem. Glasses* 13 (1972) 15.
- [16] H. Toyuki, S. Akagi, *Phys. Chem. Glasses* 15 (1974) 1.
- [17] R. Muncaster, S. Parke, *J. Non-Cryst. Solids* 24 (1977) 399.
- [18] A.K. Bandyopadhyay, J.O. Isard, S. Parke, *J. Phys. D: Appl. Phys.* 11 (1978) 2559.
- [19] H. Hosono, H. Kawazoe, T. Kanazawa, *J. Non-Cryst. Solids* 33 (1979) 125.
- [20] A. Klonkowski, *Phys. Chem. Glasses* 22 (1981) 170.
- [21] A. Yadav, V.P. Seth, *Phys. Chem. Glasses* 27 (1986) 182.
- [22] V.P. Seth, A. Yadav, P. Chand, *J. Non-Cryst. Solids* 89 (1987) 75.
- [23] A. Yadav, V.P. Seth, S.K. Gupta, *J. Non-Cryst. Solids* 101 (1988) 1.
- [24] D. Suresh Babu, M.V. Ramana, S.G. Satyanarayana, G.S. Sastry, *Phys. Chem. Glasses* 31 (1990) 80.
- [25] B. Sreedhar, J. Lakshmana Rao, S.V.J. Lakshman, *J. Non-Cryst. Solids* 116 (1990) 111.
- [26] G.L. Narendra, J. Lakshmana Rao, S.V.J. Lakshman, *Solid State Commun.* 77 (1991) 235.

- [27] A.S. Rao, J.L. Rao, S.V.J. Lakshman, *Phys. Chem. Glasses* 33 (1992) 1.
- [28] R.V. Anavekar, N. Devaraj, K.P. Ramesh, J. Ramakrishna, *Phys. Chem. Glasses* 33 (1992) 116.
- [29] V.P. Seth, S. Gupta, A. Jindal, S.K. Gupta, *J. Non-Cryst. Solids* 162 (1993) 263.
- [30] B. Sreedhar, P. Indira, A.K. Bhatnagar, K. Kazuo, *J. Non-Cryst. Solids* 167 (1994) 106.
- [31] N.C. Biswas, R. Dayal, P. Chand, *Phys. Chem. Glasses* 37 (1996) 62.
- [32] S. Khasa, D. Prakash, V.P. Seth, S.K. Gupta, R.M. Krishna, *Philos. Mag. B. Phys. Condens. Matter* 76 (1997) 859.
- [33] A. Murali, J. Lakshmana Rao, A. Venkata Subbaiah, *J. Alloys Compd.* 257 (1997) 96.
- [34] L.D. Bogomolova, V.A. Jachkin, N.A. Krasilnikova, *J. Non-Cryst. Solids* 241 (1998) 13.
- [35] H. Farah, M.P. Brungs, D.J. Miller, G.R. Belton, *Phys. Chem. Glasses* 39 (1998) 318.
- [36] Md. Shareefuddin, Md. Jamal, G. Ramadevudu, M. Lakshmi Rao, M. Narasimha Chary, *J. Non-Cryst. Solids* 255 (2–3) (1999) 228.
- [37] I. Ardelean, O. Cozar, G. Ilonca, V. Simon, V. Mih, C. Craciun, S. Simon, *J. Mater. Sci. – Mater. Electron.* 11 (2000) 401.
- [38] R.P. Sreekanth Chakradhar, A. Murali, J. Lakshmana Rao, *Physica B* 293 (2000) 108.
- [39] J.E. Garbacz, L. Tykarski, P. Machowski, M. Wasiucinek, *Solid State Ions-Diffu. React.* 140 (2001) 141.
- [40] O. Cozar, I. Ardelean, I. Bratu, S. Simon, C. Craciun, L. David, C. Cefan, *J. Mol. Struct.* 563–564 (2001) 421.
- [41] I. Ardelean, O. Cozar, C. Craciun, C. Cefan, *Int. J. Mod. Phys. B* 16 (2002) 2807.
- [42] A. Garwal, V.P. Seth, P.S. Gahlot, S. Khasa, P. Chand, *J. Phys. Chem. Solids* 64 (2003) 2281.
- [43] A. Agarwal, V.P. Seth, P.S. Gahlot, S. Khasa, P. Chand, *Mater. Chem. Phys.* 85 (2004) 215.
- [44] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970, p. 175.
- [45] H.M. Gladney, J.D. Swalen, *J. Chem. Phys.* 42 (1965) 1999.
- [46] D. Kivelson, S. Lee, *J. Chem. Phys.* 41 (1964) 1896.
- [47] B. Bleaney, K.W.H. Stevens, *Rep. Progr. Phys.* 16 (1953) 108.
- [48] J.A. Weil, J.R. Bolton, J.E. Wertz, *Electron Paramagnetic Resonance—Elementary Theory and Practical Applications*, Wiley, New York, 1994, p. 498.
- [49] N.W. Aschcroft, N.D. Mermin, *Solid State Physics*, Harcourt College Publishers, 2001, p. 656.
- [50] G. Fuxi, *Optical and Spectroscopic Properties of Glasses*, Springer, Berlin, 1992, p. 62.
- [51] P. Nachimuthu, P. Harikrishnan, R. Jagannatha, *Phys. Chem. Glasses* 38 (1996) 59.
- [52] E.A. Davis, N.F. Mott, *Philos. Mag.* 22 (1970) 903.
- [53] M.A. Hassan, C.A. Hogarth, *J. Mater. Sci.* 23 (1988) 2500.
- [54] R. Sheibani, C.A. Hogarth, *J. Mater. Sci.* 26 (1991) 429.
- [55] T. Suzuki, M. Hirano, H. Hosono, *J. Appl. Phys.* 91 (2002) 4149.
- [56] W. Soppe, J. Kleerebezem, H.W. den Hartog, *J. Non-Cryst. Solids* 93 (1987) 142.