



Study of Electron Paramagnetic Resonance and Optical Absorption of Vanadyl ions in Sodium Fluoroborate Glasses

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Available online at: www.isca.in

Received 5th June 2013, revised 4th July 2013, accepted 2nd August 2013

Abstract

Sodium fluoroborate glasses were prepared using standard conventional melt-quench technique. Electron paramagnetic resonance (EPR) and optical absorption spectra of Vanadyl ions in different alkali fluoroborate glasses were studied. The spin-Hamiltonian parameters (g and A), Fermi contact interaction parameter (k) and crystal field parameters were 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. The optical properties of present glass system were studied from the optical absorption spectra recorded in the wavelength range 200-800 nm. The fundamental absorption edge was identified. The values of optical band gap for direct and indirect allowed transitions and Urbach energies were determined. The effect of alkaline-earth metal on these properties is discussed.

Keywords: EPR, Optical absorption spectra, Fluoroborate glass.

Introduction

The inorganic glasses containing transition metal ions have properties of technological importance in electronics, tunable solid state lasers and fiber optic communication systems. Transition metal ions (TMI) can be used to probe the glass structure because their outer d electron orbital functions have rather broad distributions and their responses to the surrounding cations are very sensitive. 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 view¹⁻³.

A number of papers have been published on alkali-fluoroborate glasses, for example Shelby and Ortolano⁴ prepared NaF-Na₂O-B₂O₃ glass system and studied the refractive index, density and glass transition temperature. Marimuthu et al.^{5,6} studied the structural and optical properties of alkali-fluoroborate glass system B₂O₃-XCO₃-NaF-Eu₂O₃ (X=Li, Na, Ca and Mg). El-Hofy and Hager et.al⁵ prepared B₂O₃-BaF-LiX (X=F, Cl, Br) glasses and investigated their IR and elastic moduli. Sumalatha et.al⁷ studied the EPR and optical absorption spectra of alkaline earth zinc borate glasses and found that the vanadyl ions are in +4 oxidation state⁴⁻⁷.

The addition of transition metal ions to the inorganic oxide glasses change them to exhibit the semiconducting behavior. Among the transition metal oxides, V₂O₅ is of much interest in the contemporary and emerging technology, wherein it finds applications in the fields like micro electronics, solid state ionics etc⁸⁻¹⁰.

In the present study, the EPR spectra of alkali fluoroborate glasses containing vanadium ions were measured in order to

examine the valance state of vanadium ions and also to know the effect of alkaline earth ions on the spin-Hamiltonian parameters and other optical properties of these glasses.

Material and Methods

Analytically pure grade chemicals were used to prepare the glass samples according to the molecular formula 30NaF-10AF₂-59B₂O₃-1 V₂O₅ (A= Ca, Sr and Ba). Analar grade reagents NaF, CaF₂, SrF₂, BaF₂, H₃BO₃, and V₂O₅ were taken in appropriate proportions in accordance with the above formula and ground together to constitute a 10g batch. The ground mixture was taken in porcelain crucibles. The melt was held at a temperature of 1000°C for 2 hours until homogeneous glasses were obtained and the melts were quenched in air by pouring on to a preheated steel mold plate to avoid breaking of the samples due to thermal strains and pressing it quickly with another steel plate. These glasses were then immediately transferred to another furnace kept at 300°C and annealed for 5 hours to remove thermal strains and then cooled to room temperature. The prepared glasses and their glass codes are given in Table-1.

Table-1
Chemical composition of prepared glasses

Sl. No.	Chemical Composition	Glass Code
1	30 NaF-10CaF ₂ -59B ₂ O ₃ -1V ₂ O ₅	NCB
2	30 NaF-10SrF ₂ -59B ₂ O ₃ -1V ₂ O ₅	NSB
3	30 NaF-10BaF ₂ -59B ₂ O ₃ -1V ₂ O ₅	NBB

The EPR spectra were recorded at room temperature on an EPR spectrometer (JOEL-FE-1X) operating in X-band frequency (9.153GHz) with a field modulation frequency of 100 Hz. The magnetic field was scanned from 200 to 500mT.

The optical absorption spectra of these glasses were recorded in the UV region to measure the optical absorption edges by using a UV Elmer Lambda 750 spectrophotometer in the wave length range 200-800 nm at room temperature.

Results and Discussion

EPR studies: Figure-1 shows the EPR spectra of 1 mole % of V₂O₅ ions in sodiimi fluoroborate glasses. The spectra have structures which are characteristic of a hyperfine interaction arising from an unpaired electron with a ⁵¹V nucleus (Its nuclear spin is 7/2 and is present in 99.76% abundance). These spectra were analyzed by assuming that vanadium is present as vanadyl ion in ligand field of C_{4v} symmetry¹¹⁻¹³.

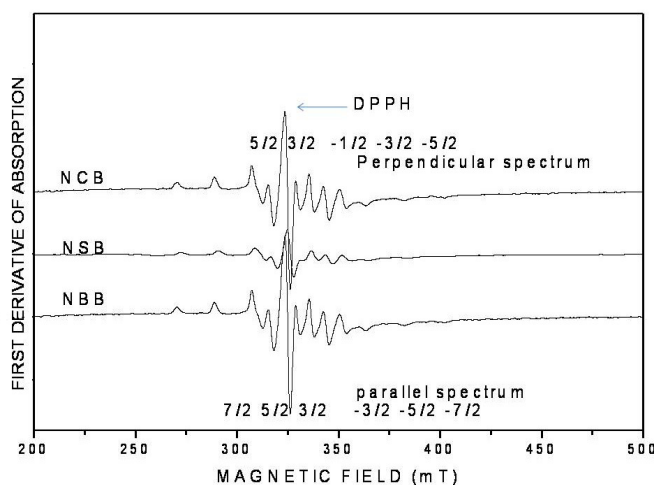


Figure-1
EPR Spectra of 1 mole% of vanadyl ions in various sodium alkaline earth fluoroborate glasses at room temperature

The EPR spectra of VO²⁺ ions could be analyzed by using a spin-Hamiltonian¹⁴

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

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 tensor, B_x , B_y and B_z are the components of the magnetic field, 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 given by

$$B_{\parallel}(m_1) = B_{\parallel}(0) - A_{\parallel} m_1 - (63/4 - m_1^2) \frac{A_{\perp}^2}{2B_{\parallel}(0)} \quad (2)$$

$$B_{\perp}(m_1) = B_{\perp}(0) - A_{\perp} m_1 - (63/4 - m_1^2) \frac{(A_{\parallel}^2 + A_{\perp}^2)}{4B_{\perp}(0)} \quad (3)$$

where m_1 is the magnetic nuclear quantum number of the vanadium nucleus, which takes the values $\pm 7/2$, $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$;

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

here ν is the microwave frequency.

The spin-Hamiltonian parameters are usually determined by using equations (2) and (3). The iterative method for the numerical analysis of the spectrum as suggested by Muncaster and Parke was used to avoid the errors caused by certain amount of overlapping between hyperfine lines. Table-2 lists the spin-Hamiltonian parameters evaluated for different sodiimi fluoroborate glasses. The paramagnetism of the vanadyl ion (V⁴⁺) arises from a single unpaired electron, as the crystalline fields quench the orbital angular momentum. The crystal fields of V⁴⁺ ions in glasses can be described either by threefold or fourfold symmetries¹⁵.

The variation of g_{\parallel} and g_{\perp} depend critically on the local symmetry of the field. Although the V⁴⁺ ion is present usually in six-fold coordination, its local symmetry is generally a distorted octahedron of oxygen ions in many complexes. An octahedral site with a tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A_{\perp}$ ^{14, 16}. The g and A values obtained in the present work agree with this relationship and are close to those of other vanadyl complexes reported in the literature¹⁷⁻²¹. It is, therefore, confirmed that the vanadyle ions in the present glass system exist as VO²⁺ ions in octahedral coordination with a tetragonal compression and have a C_{4v} symmetry.

The value of $(\Delta g_{\parallel} / \Delta g_{\perp})$ where $\Delta g_{\parallel} = (g_e - g_{\parallel})$ and $\Delta g_{\perp} = (g_e - g_{\perp})$ which measures the tetragonality of the VO²⁺ site are also calculated and are presented in table-3. A decrease in the value of $(\Delta g_{\parallel} / \Delta g_{\perp})$ shows that the octahedral symmetry around VO²⁺ ion is improved from NCB to NBB glass. It is seen from the table that $(\Delta g_{\parallel} / \Delta g_{\perp})$ value decreases with increase in atomic radii of alkaline earth metal ions, the deviation from octahedral symmetry increases and the VO²⁺ ions are less tetragonally distorted²².

Table-2
Spin-Hamiltonian parameters of VO²⁺ ion in the present glasses

Glass	g_{\parallel}	g_{\perp}	Δg_{\parallel}	Δg_{\perp}	$ A_{\parallel} \times 10^{-4}$ (cm ⁻¹)	$ A_{\perp} \times 10^{-4}$ (cm ⁻¹)
NCB	1.956	1.987	0.0463	0.0153	195	62
NSB	1.950	1.985	0.0523	0.0173	182	62
NBB	1.947	1.978	0.0553	0.0243	162	64

Table-3
Tetragonality and covalency rates of V⁴⁺ ion in the present glasses

Glass	$\Delta g / \Delta g_{\perp}$	$ A'_{\parallel} \times 10^{-4}$ (cm ⁻¹)	$ A'_{\perp} \times 10^{-4}$ (cm ⁻¹)	$(1 - \alpha^2)$	$(1 - \nu)$	k	Pk/γ (cm ⁻¹)
NCB	3.026	81.5	34.9	0.628	0.616	0.89	0.0077
NSB	3.023	80.8	34.7	0.580	0.566	0.71	0.0061
NBB	2.275	79.9	34.0	0.556	0.390	0.65	0.0056

Molecular orbital theory shows that the hyperfine components A_{\parallel} and A_{\perp} consist of the contributions of A_{\parallel}' 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-electrons.

Kivelson and Lee²³ gave the following relations
 $A_{\parallel} = A_{\parallel}' - P\beta_2^{*2}k$ (4)

$A_{\perp} = A_{\perp}' - P\beta_2^{*2}k$ (5)

where

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

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

Here $P = 2\gamma\beta\beta_N \langle r^{-3} \rangle = 0.0128 \text{ cm}^{-1}$ is the dipolar hyperfine coupling parameter, r^{-3} is the average size of the vanadium 3d orbital and k is dimensionless Fermi contact interaction parameter, which represents the amount of unpaired electron density at the vanadium nucleus. The Fermi contact interaction term k , Pk/γ representing the s-character of the spin of vanadium and the covalency rates $(1 - \alpha^2)$ and $(1 - \nu^2)$ were calculated and are given in Table- 3. The high values of k indicate a large contribution to the hyperfine constant by the s-electron. The $(1 - \alpha^2)$ and $(1 - \nu^2)$ values indicate moderate covalency for σ and π -bonds respectively²³⁻²⁴.

Optical absorption studies: The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and for the provision of information about the band structure and energy gap in both crystalline and non crystalline materials.

Figure-2 shows the optical absorption spectra of all the prepared glasses in the wavelength region of 200–800 nm and exhibit one band characteristic of V⁴⁺ ions in the tetragonal symmetry.

For V⁴⁺ ion in tetragonal symmetry, we expect three bands corresponding to the transitions ${}^2B_{2g} \rightarrow {}^2E_g$, ${}^2B_{2g} \rightarrow {}^2B_{1g}$ and ${}^2B_{2g} \rightarrow {}^2A_{1g}$. In the present case, for all the glass samples only the first band is observed. The band has been assigned to the transition ${}^2B_{2g} \rightarrow {}^2E_g$ at 377nm, 374 nm and 367 nm wave length of NCB, NSB and NBB glasses respectively.

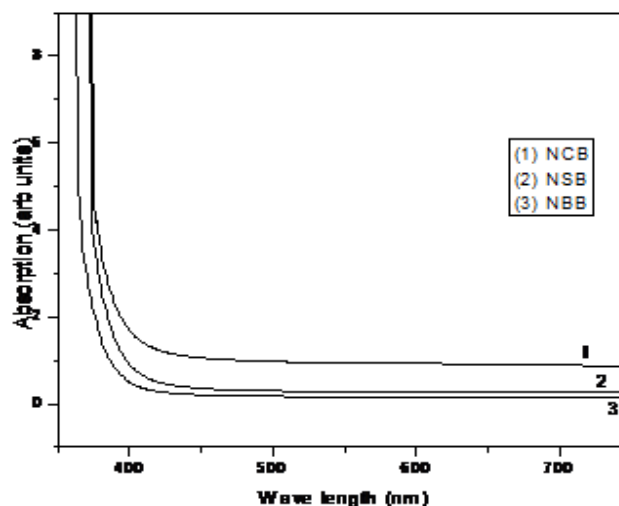


Figure-2
Optical absorption spectra of present glasses

The absorption peak is characteristic of V⁴⁺ ions with a distorted octahedral site. Assignment of the absorption bands are made in the light of energy level scheme for molecular orbitals of the VO²⁺ ions in a ligand field of C_{4v} symmetry²⁵.

The absorption coefficient $\alpha(\nu)$ can be determined near the edge using the relation²⁶

$$\alpha(\nu) = (1/d) \ln(I_0/I) = 2.303 \frac{A}{d} \quad (6)$$

where the factor $\ln(I_0/I)$ is the absorbance (A) at a frequency ν and d is the thickness of the sample. According to Davis and Mott's relation²⁶

$$\alpha(\nu) = B(h\nu - E_{opt})^n/h\nu \quad (7)$$

where B is an energy independent constant, $n=2$ is indirect allowed transition, $n=3$ is indirect forbidden transition, $n=1/2$ is direct allowed transition and $n=1/3$ is direct forbidden transition.

According to Tauc's picture, generally indirect transitions are favored in amorphous materials²⁷. In this case the value of n is 2 and equation-7 after re-arrangement becomes

$$E_{opt} = h\nu - (\alpha h\nu / B)^{1/2} \quad (8)$$

The values of indirect optical band gap energy can be obtained from equation- 8 by extrapolating the absorption coefficient to zero absorption in $(\alpha hv)^{1/2}$ vs. hv plot (figure-3).

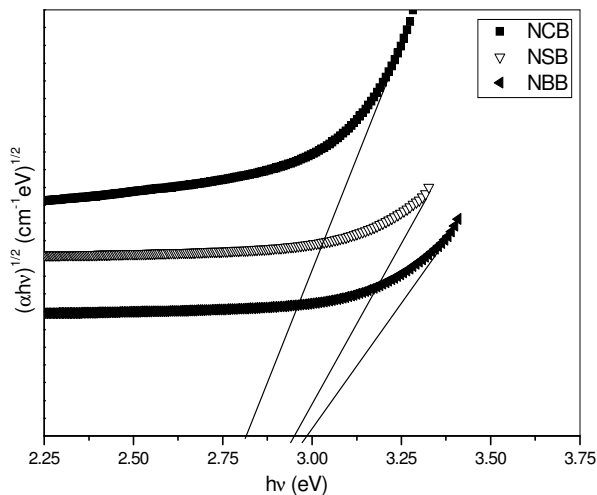


Figure-3
 $(\alpha hv)^{1/2}$ vs. hv of present glasses (Tauc's plots)

The variation of $\ln \alpha$ with hv is found to be non-linear near UV absorption edge. This shows that the absorption coefficient near the edge has an exponential behavior and obeys the empirical Urbach rule²⁸ given by

$$\alpha(v) = B \exp(hv / \Delta E) \quad (9)$$

where ΔE is the Urbach energy and is found as the inverse slope of the $\ln \alpha$ vs. hv plot²⁸. The cut off wavelengths, Urbach energy and the optical band gap energy for allowed indirect and direct transitions are calculated in the present glass system and the values are given in Table-4.

Table-4
Optical parameters of present glasses

Glass	λ_c (nm)	Urbach energy (eV)	Band gap energy (eV)	
			indirect	direct
NCB	388	0.69	2.82	3.10
NSB	381	0.64	2.92	3.12
NBB	364	0.54	2.98	3.18

Conclusion

i. It is observed that $S_{||}$ and S_{\perp} values are decreasing with alkaline earth metals from calcium to barium. The decrease in $S_{||}$ and S_{\perp} values are attributed to the increasing tetragonality at the vanadium site. ii. It is noticed that as the alkaline earth metal content is changed from calcium to barium, the deviation from octahedral symmetry increases and the symmetry around VO^{2+} ions is less tetragonally distorted. iii. The EPR and optical absorption studies show that the vanadium ions (V^{4+}) exist as

VO^{2+} ions in octahedral coordination with tetragonal compression. iv. The optical energy gap and the Urbach energy values are found to vary linearly with atomic radii of alkaline earth metal ions.

Acknowledgements

One of the authors V.R. Reddy thanks Dr. Sreepathi, UGC-DAE Centre, Indore for providing experimental facilities.

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