Electron paramagnetic resonance and optical absorption studies of chromium ions doped borophosphate glasses

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Abstract

Chromium (Cr^{3+}) ions doped borophosphate glasses was prepared by well known melt quenching technique and their Electron paramagnetic resonance (EPR), Optical absorption and FTIR spectra were investigated for application to various optical applications. The EPR spectra of the doped glasses exhibit two resonance signals at g=4.23 and g=1.96. The optical absorption spectrum shows bands corresponding to the presence of Cr^{3+} ions in octahedral symmetry. The crystal field parameters Dq, Racha parameter B and optical parameters like optical band gap, Urbach energy have been evaluated from the optical absorption spectra. The consequences supports the strong distorted Cr^{3+} ions in the present host environment with the craving of g values on crystal field parameters.

Keywords: borophosphate glass, Chromium ions, EPR studies, optical absorption

1. Introduction

The optical and spectroscopic studies of pure phosphate glasses is very limited due to its hygroscopic nature and low melting temperature. However, the hygroscopic nature can be reduced with the incorporation of baoron atoms into the network[1,2]. Addition of network modifiers (Li, Na and K) into the glass matrix helps in tailoring the properties of the glasses. Transition metal ions are the simplest and most well suited for applications due to partially filled d-shells. Thus, many researchers have used TM ions as a probing agent to study the structure of the glass and their ligands. Glasses doped with transition metal ions have greatly attracted researchers due to their potential applications in the field of construction of various optical devices like solid state lasesrs, solar energy concentrarors [3,4]. Transition metal ions are good coloring agents when doped in small quantities into the glasses. Each TM ion exhibits a specific color when doped in glasses and will have a strong influence on the optical properties of the glasses. Chromium exhibits two oxidation states Cr^{3+} and Cr^{6+}. Cr^{3+} acts as network

modifier and Cr^{6+} acts as network former [6-9]. In phosphate glasses the Cr^{3+} ions are exist in distorted octahedral sites and causes the emission property from Cr^{3+} in weak fields octaherdral sites [10].

The present work is to understand the influence of Chromium ions on the structure of lithium borophosphate glasses by studying the EPR, optical absorption, and FTIR.

2. Experiemntal

2.1 Preparation of Chromium ions doped glasses

The Cr^{3+} doped lithium borophosphate glasses samples glass samples (45-0.5x) B_2O_3 + (45-0.5x) P_2O_5 + 10 Li_2O + x Cr_2O_3 (where x = 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by melt quenching method and are presented in Table 1. The precuser materials were chemicals of analytical grade. The prepared glasses were labelled as Cr0(0), Cr1(0.1), Cr2(0.2), Cr3(0.3), Cr4(0.4) and Cr5(0.5) respectively as shown below:

Table 1: Glass Composition

Glass	B_2O_3	P_2O_5	Li_2O	Cr_2O_3
Cr0	45	45	10	0
Cr1	44.95	44.95	10	0.1
Cr2	44.90	44.90	10	0.2
Cr3	44.85	44.85	10	0.3
Cr4	44.80	44.80	10	0.4
Cr5	44.75	44.75	10	0.5

The above chemicals were thoroughly mixed in an agate mortar and taken in a silica crucible and heated at 1100^oC in temperature controlled furnace for around thirty five minutes until a buble free liquid was formed. Then melt was quenched to room temperature in air by pouring on pre heated brass mould and pressed with another brass plate and subsequently annealed at 250^oC for three hours. Finally, the glass samples were polished with emiri paper before sending spectroscopic regarding. The glasses show the typical green colour of the Cr_2O_3.

The densities of the prepared glass samples were measured using Archimede's principle with O-Xylene (99.99% pure) as the buoyant liquid. A digital balance of ESSAE, VIBRA model HTR-220E tuning-fork precision, direct reading balance (capacity 220g, readability 0.0001g) was used for weighing. With HT density measurement kit, the bulk glass is suspended on a measurement pan in air and then it is set in the immersion liquid container, densities of the samples are automatically measured by the instrument itself with an accuracy of ±0.0001. The Abbe refractometer was used to measure the refractive index (n_d) of the glasses.

The physiochemical characteristics of Cr^{3+} ions doped lithium borophosphate glasss were studied by X-ray diffraction (XRD). This was performed using a Siemens D 5000 diffractometer with Cu-Kα radiation (λ= 1.5418Å). The FTIR spectra of the present prepared glasses were recorded by dispersing the glass powders in KBr with a BX Perkin Elmer FTIR spectrometer with a resolution of $0.1cm^{-1}$ in the range of $400\text{-}1400cm^{-1}$. The optical absorption spectra of the sample (thickness 1mm) were recorded in the wavelength range of 300-800nm up to a resolution of 0.1nm using JASCO V-670 UV-VIS-NIR Spectrophotometer. The EPR spectra were recorded on JEOL-FE_IX ESR Spectrometer operating at X-band frequency with a field modulation frequency of 100KHz. From 0 to 600mT magnitude of magnetic field applied to the present prepard samples and the microwave power 100mW was used. Glass sample in powder form of 100mg is taken in a quartz tube for EPR measurements.

3 Results and Discussion

3.1 Physical properties of Chromium ions doped glasses

The physical properties of the prepared samples like average molecular weight, molar volume and other properties have been calculated from the measured quantities like densities and refractiveindex using the relevant expressions [11] are tabulated in Table 2.

Table 2: Physical properties of Chroiumum ions doped borophosphate glasses

Physical properties	Symbol/ units	Cr³⁺ ions doped Borophosphate glasses						Formula/ Method
		Cr0	Cr1	Cr2	Cr3	Cr4	Cr5	
Density	ρ (g/cm³) (± 0.001)	2.564	2.572	2.573	2.579	2.580	2.583	Archimedes
Refractive Index	N (± 0.001)	-	2.251	2.264	2.282	2.274	2.269	Abbe-refractometer
Average Molecular Weight	$\overline{M}$ (g/mol) (± 0.001)	161.944	161.968	161.993	162.018	162.043	162.067	$\sum\limits_{i=1}^{4} y_i M_i$
Molar Volume	V_m (cm³/mol) (± 0.001)	63.161	62.974	62.959	62.822	62.807	62.744	$\overline{M}/\rho$
Chromium ion concentration	N_{Cr} (10^{21} ions cm⁻³) (± 0.001)	-	0.957	1.913	2.876	3.838	4.799	$N_A \times \dfrac{m\% \, N_{Cr}}{\overline{M}} \times d$
Polaron radius	$r_p \left(\overset{\circ}{A}\right)$ (± 0.001)	-	4.089	3.245	2.833	2.573	2.389	$\dfrac{1}{2}\left[\dfrac{\pi}{6N}\right]^{1/3}$
Interionic distance	$r_i \left(\overset{\circ}{A}\right)$ (± 0.001)	-	10.150	8.056	7.032	6.387	5.929	$\left[\dfrac{1}{N}\right]^{1/3}$
Field strength	F(10^{16}cm²) (± 0.001)	-	3.109	4.936	6.478	7.852	9.118	$\left[Z/r_p^2\right]$

Where NA= avogadro 's number; y_i = molar fraction of each compound; M% N_{Cr}= mole percent of chromium ion concentration; Z= atomic mass of chromium.

The density show increasing trend. Among all the prepared glass the maximum value of density is 2.583 gm/cm³ for Cr5 glass. The increase in density indicates that the glassy matrix becomes more rigid and strong. A similar trend in dopant ion concentration of glass samples is noticed. But, interionic distance and polaron radius of the prepared samples decreases with increase in concentration of chromium. The gradual decreases in inter ionic separation (Ri) with dopant concentration signifies the stipulation of the chromium ions coupled interactions.

3.2 XRD and Optical absorption spectra of Chromium ions doped glasses

The XRD spectra shown in Fig. 1 conforms the amorphous nature of the prepared glasses. The XRD spectra of anly three samples has been shown.
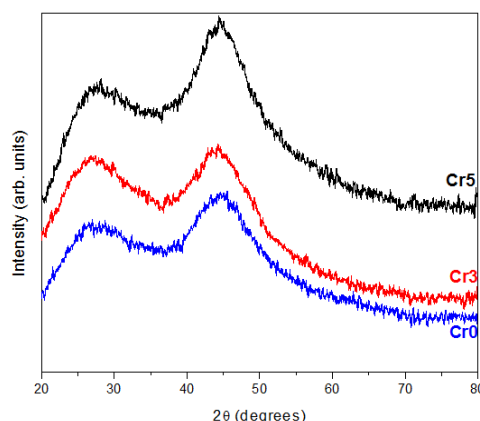
Fig 1: XRD Spectra of Chromium ions doped borophosphate glasses

The optical absorption spectra of the prepared glasses recorded at room temperature along with the assignment of bands is shown in Fig. 2. The sample Cr0 did not show any peak indicating the pure sample.
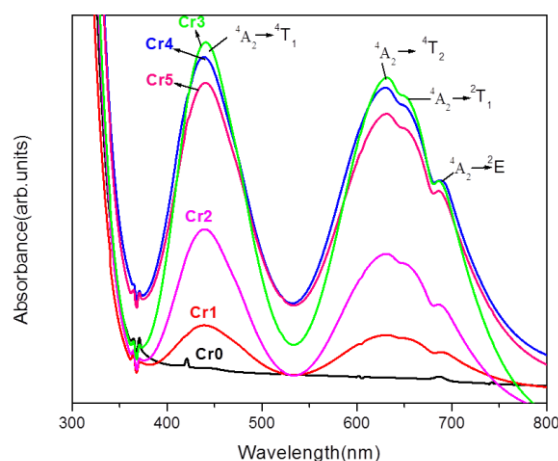

Fig 2: Opitcal absorption spectra of Chromium ions doped Borophosphate glasses

The optical absorption spectra for the Cr^{3+} doped borophosphate glass is shown in Fig. 2. The optical absorption spectra for prepared glasses are recorded in between 300–800 nm wavelength. Pure glass is colorless with no characteristic bands in both ultraviolet and visible regions. Cr_2O_3 doped glasses attained light green color and two bands appeared in the visible region at 440 nm (2.81 eV) and 627 nm (1.97 eV). These two bands are attributed to the spin allowed transitions $^4A_{2g}(F){\rightarrow}^4T_{1g}$ (F) and $^4A_{2g}(F){\rightarrow}^4T_{2g}$ (F) respectively. In addition two other feeble bands are identified at 651 nm (1.90 eV) and 690 nm (1.79 eV) respectively. These bands are assigned to transitions $^4A_{2g}(F){\rightarrow}^2T_{1g}(G)$ and $^4A_{2g}(F){\rightarrow}^2Eg(G)$ respectively. With the increase of the Cr ions (from 0.1 to 0.3 mol%) the intensities of the absorption band are observed to increase later with further increase of Cr ions the intensities are observed to

decrease. The optical band gap (E_g) of these glasses have been evaluated by drawing Tauc's plots between $h\upsilon$ (Photon energy) and $(\alpha h\upsilon)^{1/2}$ as per the equation $\alpha(\upsilon)h\upsilon=c(h\upsilon-E_g)^2$. The E_g values are obtained by extrapolation of the linear portion of the curve to the x-axis $[(\alpha h\upsilon)^{1/2}=0]$. Urbachenergy ($\Delta E$) which gives the crucial information about the density of energy states in the band gap is evaluated from the plots drawn between photon energy $h\upsilon$ versus $\ln\alpha(\upsilon)$ values. The relation between $\alpha(\upsilon)$ and Urbach energy (ΔE) is given by the Urbach law as follows [5].

$$\alpha(\upsilon)=C\exp(h\upsilon/\Delta E),$$

where C is constant and ΔE is the Urbach energy interpreted as the energy gap between localized tail states in the forbidden region. ΔE values are acquired by taking the reciprocals of the slopes of the linear region of the $\ln(\alpha)$ versus $h\upsilon$ plots as shown in Fig.3.
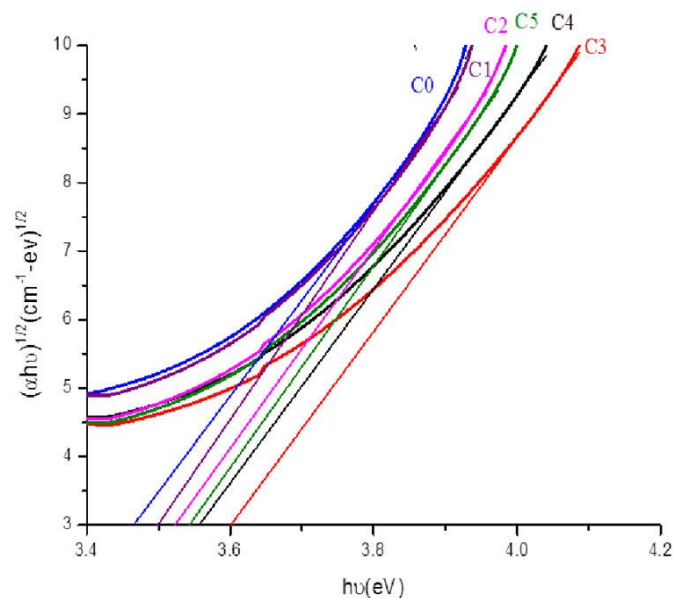

Fig 3: Urbach plot for evaluating optical band gap of Chromium ions doped borophosphate glasses

The evaluated ΔE values for different concentration of chromium ions are mentioned in Table 3. The minimum and maximum values of ΔE for the prepared glasses are 0.23 eV and 0.35 eV respectively. The crystal field (Dq) and the Racah (B) parameters were estimated from the spectral positions of the absorption bands as [6,8,13–16].

$$\upsilon_1=10Dq$$
$$B=(X_2-10X)Dq/15(X-8)$$
$$X=(\upsilon_2-\upsilon_1)/Dq$$

where υ_1, υ_2, υ_3 are the peak position in cm^{-1} that correspond to $^4A_{2g}(F)\rightarrow^4T_{1g}$ (F), $^4A_{2g}\rightarrow^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow^2T_{1g}(G)$ transitions respectively as shown in Fig. 2. The calculated value of Dq

and B were presented in table 3. From the knowledge of the optical band gap (E_g), refractive index (n) can be estimated from the simple equation [17,18]. $(n_2-1)/(n_2+2)=1-sqrt(E_g/20)$. The estimated values of refractive index (n) are presented in the Table 2 above.

The observed optical bands for the prepared samples at 440nm, 627nm, 651nm, 690nm are the characteristic of $Cr^{3+}(d^3)$ ions in an octahedral symmetry. In the weak crystal fields in an octahedral coordinated system, the ground state term ^4F of Cr^{3+} ions splits as $^4A_{2g}(F)$, $^4T_{2g}(F)$ and $^4T_{1g}(F)$, whereas ^4P transforms as $^4T_{1g}(P)$. The weak field terms $^4A_{2g}(F)$, $^2E_g(G)$, $^2T_{1g}(G)$ and $^2T_{2g}(G)$ correspond to the lowest strong field. From the observed optical absorption band positions, the crystal field parameters D_q and Racah inter electronic repulsion parameter B is evaluated using the relations given by Casalboni et al. [19]. The values are tabulated in Table 3.

Table 3: Optical absorption data of Chromium ions doped borophosphate glasses

Sample	Optical band gap E_g (eV)	Urbach Energy ΔE	Dq (cm^{-1})	B (cm^{-1})	Dq/B
Cr(0.0)	3.5575	0.3515	---	---	---
Cr(0.1)	3.6026	0.2370	1596.6	442.0760	3.6110
Cr(0.2)	3.5446	0.2740	1590.1	448.2090	3.5476
Cr(0.3)	3.4657	0.3252	1587.6	460.6655	3.4463
Cr(0.4)	3.4995	0.2897	1589.9	390.9122	4.0672
Cr(0.5)	3.5220	0.2421	1592.3	360.9360	4.4115

3.3 FTIR spectra of Chromium ions doped borophosphate glasses

The structural analysis of the prepared glasses are studied by infrared spectroscopy in the wavenumber range 400-1400 cm^{-1}. The vibrational bands observed from the above spectra and their corresponding assignments are presented in the Table 3. Due to the existence of similar bands in all the spectra, The only infrared spectrum of the Cr5 sample is shown in the Fig.4.
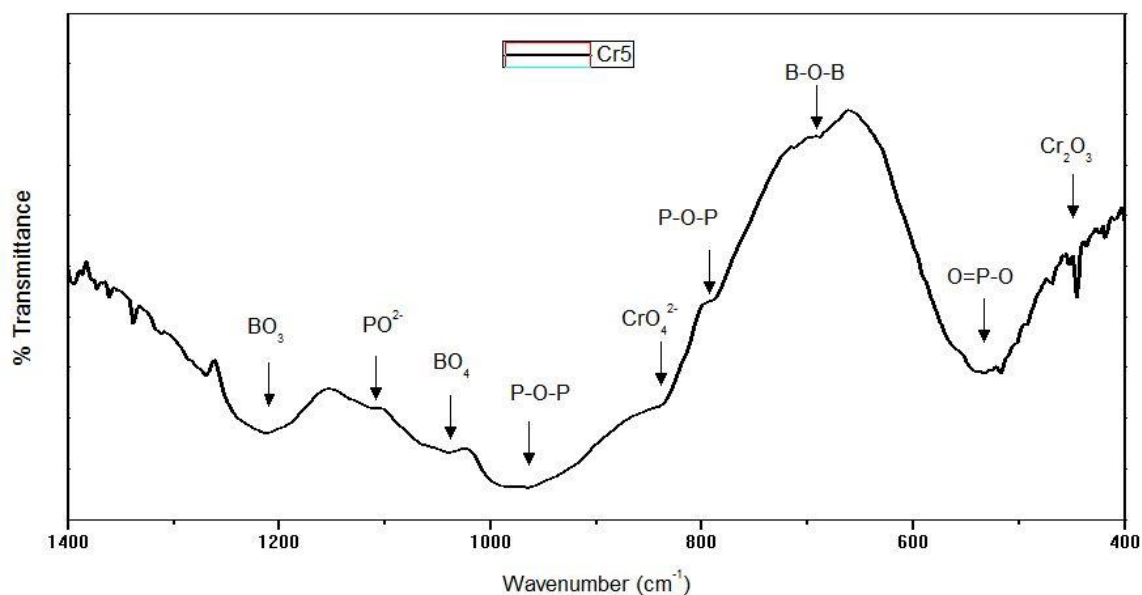
Fig 4: FTIR spectra of Cr5 glass

Table 4: Various band positions in the FTIR spectra of Chroiumum doped borophosphate glasses

Wave number (cm^{-1})	IR band assignments
1198	B-O stretch in BO_3 units from pyro & ortho borate
1102	PO^{2-} symmetric stretching
1029	Stretching vibration of B-O bonds in BO_4 units
927	P-O-P asymmetric stretching vibrations
859	υ_4-vibrational mode of CrO_4^{2-} units
780	P-O-P symmetric vibrations
690	B-O-B bending vibrations
543	O=P-O
436	υ_4-Cr_2O_3 structural units

The spectrum of pure sample shows the absorption bands at 1198 cm^{-1} (identified due to the stretching vibrations of triangular BO_3 structural units), 1102 cm^{-1} (assigned to PO^{2-} symmetrical stretching vibrations), 1029 cm^{-1} (due to stretching vibrations of B-O bonds in BO_4 units, 927 cm^{-1} (assigned to P-O-P asymmetric vibrations), 780 cm^{-1} (due to P-O-P symmetric vibrations), 690 cm^{-1} (attributed to B-O-B bending vibrations) and 543 cm^{-1} (due to O=P-O vibrations). Due to the addition of chromium ions to the pure glass matrix, two new bands are identified at 859 cm^{-1} and 436 cm^{-1} due to CrO_4^{2-} structural units and Cr_2O_3 units respectively [20–22]. When Li_2O is incorporated in B_2O_3 it leads to conversion of sp^2 planar BO_3 units into more sp^3 tetrahedral BO_4 units. Long tetrahedral chains of BO_4 areformed when each BO_4 unit is bonded with two other similar units. When the pure glass is doped with Cr_2O_3, it will twist or distort the interconnected chains of BO_4 units and enhance the randomness of

glass network. The intensity of bands due to BO_4 units is observed to decrease with the shifting of meta-center towards a slightly higher wavenumber, whereas the intensity of the bands due to the BO_3 structural units is observed to increase. With the increasing concentration of Cr_2O_3 the intensity of vibration band corresponding to BO_3 units, P-O-P asymmetric vibrations and B-O-B bending vibrations increases. This clearly suggests the escalating modifying action of Cr^{3+}. The intensity of the banddue to υ_4 vibrations of Cr_2O_3 with CrO_6 octahedral units increases whereas theintensity of the band due to Cr_2O^{4-}tetrahedral units follows reverse trend. These features confirm the raise of CrO_6 octahedral units at the expense of CrO_4^{2-} tetrahedral units.

3.4 Electron Paramagnetic Resonance (EPR) spectra of Chromium doped glasses

Fig. 5. Shows the EPR spectra of Cr doped lithium borophosphate glasses. No EPR signal was detected in the spectra of undoped glasses, confirming that the starting materials used in the present work were free from paramagnetic impurities. All the lithium borophosphate glasses when doped with Cr^{3+} ions exhibited two resonance signals as shown in Fig. 5. Which is an indicative of the presence of Cr^{3+} ions, with its three unpaired electrons in distorted octahedral sites.
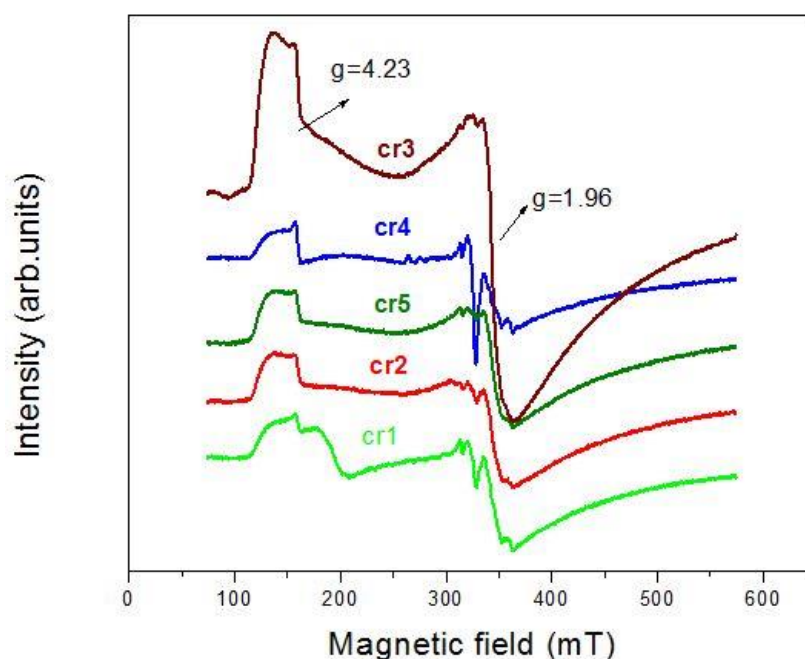

Fig 5: EPR spectra of Chromium ions doped borophosphate glasses

The first is a broad asymmetric resonance at low magnetic field with an effective g value at g=4.23. The second is an intense and symmetric resonance at high magnetic field with

an effective g value at g=1.96. According to Landry, the low field line (at g=4.23) of the spectrum is ascribed to the isolated Cr^{3+} ions and the high field portion (g=1.96) mainly belongs to the exchange coupled pairs Cr^{3+}-Cr^{3+} [23–25]. The fall in intensity of g=4.23 line with increase in the content of chromium beyond 0.3% indicates a decrease in the concentration of isolated Cr^{3+} ions. Such a decrease suggests the conversion of some of the Cr^{3+} ions into Cr^{6+} ions that take part network forming positions with CrO_4^{2-} structural units as is also observed in optical absorption spectra. From the EPR spectra it can be understood that beyond 0.3 mol% the intensity of the EPR signal g=1.96 decreases with the increase in Cr2O3 concentration. This decrease in intensity can be predicated because of the two reasons: Such a decrease may be attributed to the following reasons: The presence of Cr_2O_3 microcrystalline which exhibits antiferromagnetic interactions at room temperature [26] and due to the presence of large concentration of chromium ions in Cr^{6+} state. The kink observed at g=4.23 may be attributed to the presence of Fe^{3+} ion impurity [27,28].

4. Conclusions

In the present work chromium ions doped lithium borophosphate glasses have been prepared with with different concentrations of chromium oxide. The EPR and optical absorption studies were reported. The EPR spectrum of Cr^{3+} doped glasses exhibits two resonance signals. The first is a broad asymmetric resonance at low magnetic field with an effective g value at g=4.23 and the other at g=1.96 which is an intense and symmetric at a high magnetic field. The optical band gap (E_{opt}) and the Urbach energy (ΔE) were calculated from the ultraviolet absorption edges. The evaluated Urbach energy (ΔE) values for different concentration of chromium ions were reported. The minimum and maximum values of ΔE for the prepared glasses are 0.23eV and 0.32eV respectively. These results shows the strong correlation between the EPR and optical studies. The effective g value variation with the crystal filed suggests the strong distorted octahedral symmetry in the present borophosphate glass host. Among the different concentrations of chromium doped glasses, Cr3 glass is optimised and has suitable environment for the desired optical applications.

5 Acknowledgements

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