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RESEARCH ARTICLE

EPR and Optical Studies of SrO-Li₂O-CaO-B₂O₃ (SLCB) glasses doped with Chromium ions.

M.Ratna Raju

Department of Physics, Andhra Christian College, Guntur- 522 001

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Abstract

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*Corresponding Author

M.Ratna Raju

The Electron Paramagnetic Resonance (EPR) and optical absorption spectral studies of Chromium ions doped xSrO-(20-x)Li₂O-(10-y)CaO-70B₂O₃-y, (x=5, 10, 15 mol %) and y=0.1mol% (SLCB) glasses have been studied. The optical absorption spectra have shown the characteristic spectra of Cr^{3+} ions in octahedral symmetry. The crystal field parameter (D_q), Racah parameters B and C are evaluated from the optical absorption spectra. The optical band gap energies (E_g) and Urbach energies (E_g) are also evaluated. The results assert that the optical band gap energy values are depended quite sensitively on added chromium content.

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INTRODUCTION

Glasses are important optical materials. Transparency is an important property for any glass. Glasses are amorphous materials and hence do not show optical anisotropy. Among all the classical network formers boric acid (B_2O_3) is one of the important glasses former. Glasses based on borates have special features like high thermal stability, good solubility making them promising candidates for a vast amount technological applications [1-2]. Glasses containing transition metal ions have attracted a great interest for their use as photo-conducting devices, magnetic material, etc. Oxide glasses containing transition metal oxides possess both scientific and technological interest because of their wide range optical properties depending on the presence of such transition metal (TM) ions in varying valences or coordination's and with respective different colors [3–5]. Also, semiconducting properties are expected from these glasses which arise from the electron hopping process between TM ions having at least two valence states [6, 7]. Glasses containing Cr_2O_3 have interesting optical properties due to the presence of chromium ions in two possible oxidation states, namely trivalent and hexavalent forms [8]. The optical properties of Cr^{3+} ions can be tuned by the random disordered structural units of glasses, since the environment of each Cr^{3+} ion in the glass network varies due to differences in bonding to nearest-neighbor ions [9]. Among the different transition metal ions one of the most investigated transition metal ions is chromium. Chromium is a low cost activator. In glass phases chromium ions occupy a variety of sites with different crystal field strengths due to site variability and compositional disorder; further the efficiency of the most common lasing transition ${}^{4}T_{2} \rightarrow {}^{4}A_{2}$ of Cr³⁺ ion is found to be very sensitive to its chemical environment. Broad investigations on the optical absorption and EPR spectroscopy of Cr^{3+} ion a variety of inorganic glasses have been investigated in the recent years due to their technological importance in the development of tunable solid state laser, electro optic modulators, electro-optic switches, non-liner optical and parametric converters and also new luminescence materials [10-12].

2. Experimental

2.1. Glass preparation

A Series of chromium doped SLCB glasses are prepared by using analar grade (AR) chemicals of SrCO₃, Li₂CO₃, CaO, H₃BO₃ and Cr₂O₃ as starting materials with 99.9% purity. The compositions of all the glass samples are given in **Table1**. For the preparation of about 10 g of each batch appropriate amounts in wt. % of chemicals in powder form are weighed using digital balance having sensitivity of ± 0.00001 g, grounded until a fine powder is obtained, and mixed thoroughly in mortar and pestle. The batches are transferred to silica crucibles and kept in an electrical furnace for a time of 20 min. maintained at a temperature 950^oC. The melts are poured on the surface of a plane brass plate and pressed quickly with another brass plate. The thin glasses formed are annealed for about 1 hr to relieve from mechanical stress. The glasses thus obtained are cut, polished and made suitable for optical measurement.

3. Results and Discussion

3.1 EPR studies

Absence of EPR signal is observed in the undoped glass. When Cr^{3+} ions are doped into the SLCB glasses, all samples exhibit absorption lines as shown in **fig. 1**. The EPR spectrum exhibits two resonance signals. The first band at low magnetic field with an effective g value of ~ 5. The second is a band at high magnetic field with an effective g value of ~ 5. The second is a band at high magnetic field with an effective g value of ~ chromium doped glasses [13–17]. No important modifications are observed, except the signal intensity variation.

3.2 Optical absorption Spectral studies

The optical absorption spectra of all SLCB glasses doped with Cr^{3+} ions are shown in **Fig.2.** 2(a), 2(b), 2(c) representing three absorption bands. These transitions are assigned as ${}^{4}A_{2g}$ (F) $\rightarrow {}^{4}T_{1g}$ (F), ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ (F), ${}^{4}A_{2g}$ (F) $\rightarrow {}^{2}E_{g}$ (G). The electronic configuration of Cr^{3+} ions gives rise to the free ion terms ${}^{4}F$, ${}^{4}P$, ${}^{2}G$, where ${}^{4}F$ is the ground state. The wide absorption band observed at 605nm, 606nm and 611nm have been credited to Cr^{3+} ions in octahedral symmetry. In octahedral symmetry, usually the optical absorption spectra of Cr^{3+} ions show two strong broad bands in the visible region corresponding to the transitions ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ and the third broad band in the ultraviolet region corresponding to ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$ transition is less intense due to double electron jump ($t^{3}_{2g} \rightarrow t^{1}_{2g}e^{2}_{g}$). In the present study, one broad band is observed. The intensity and position of this main band around 600 nm suggest that this band to be related to d-d electronic transition and is assigned to the transition ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ of Cr^{3+} ions in octahedral symmetry. The transition corresponding to ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ gives the value of 10D_q, the wavenumber corresponding is v₁, the wavenumber corresponding to ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ gives the v₂. The Racah parameter can be calculated by the equation

=
$$(2v_1^2 + v_2^2 - 3v_1v_2)/(15v_2 - 27v_1)$$

(1)

The value of B is a measure of inter-electronic repulsion in the d-shell and is useful in discussing the ionic/covalent properties of Cr–O ligand bonding. The values of B obtained are 683cm^{-1} , 681 cm^{-1} and 693 cm^{-1} which are lower than for Cr³⁺ free ion i.e. the value of B_{free} is 918 cm⁻¹. The Racah parameter C can be calculated from the position of the ${}^{4}\text{A}_{2g}(F) \rightarrow {}^{2}\text{E}_{g}(G)$ absorption peak using the equation [18].

 $C/B=1/3.05[E(^{2}E)/B-7.9+1.8(B/D_q)]$ (2) The obtained values of C are 3133 cm⁻¹, 3130 cm⁻¹ and 3099 cm⁻¹. The values obtained for crystal field, Racah parameters and D_q/B are in agreement with previous reported values of Cr_2O_3 doped glasses in the literature [19, 20]. There is a good agreement between the observed and calculated positions of the bands. The values obtained are given in **Table 2**.

3.3 Optical Band gap and Urbach Energies

B

Two types of optical transitions occur at the fundamental absorption edge of crystalline and non-crystalline materials, which direct and indirect transitions. In these cases, when electromagnetic waves interact with the electrons in the valence band electrons jumps up to the conduction band. In case of glasses, conduction band is influenced by the anions, but the cations play an indirect major role. The absorption co-efficient α (v) is a function of photon energy for direct and indirect transitions [21] can be written as

$\alpha(v) = A(hv - E_g)^n / hv$

(3)

Here n = 1/2 for allowed transitions, A is constant and E_g is direct optical band gap. For indirect allowed transition n=2. A is constant and E_g is indirect optical band gap. The plots are drawn for $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ as a function of photon energy 'hv' with respect to the equation (3). The direct and indirect band gaps are shown in **Fig.3** and **Fig.4**. The respective values of E_g for direct and indirect transitions are obtained by extrapolating to $(\alpha hv)^2 = 0$ for direct and $(\alpha hv)^{1/2} = 0$ for indirect transitions. The optical band gap energy values are obtained by extrapolating the linear region of the curve to hv- axis. The optical band gap energies obtained are given in the **Table 3**. The theoretical value can be obtained by using the following formula

$$E_g = hc/\lambda$$

(4)

The optical band gap energies are found to decrease with increase of SrO mol%. For amorphous materials absorption coefficient α (v) increases exponentially with increase of photon energy hv in accordance with the empirical relation [22]

 $\alpha(v)=\alpha_0 exp(hv/\Delta E) \tag{5}$ where α_0 is constant v is the frequency of radiation and E_g is the Urbach energy which indicates the width of band tails of localized states and depends on temperature, static disorder, induced disorder and average photon energies. Hence Urbach energy is used to measure disorder in amorphous and crystalline materials [23, 24]. The static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygen's in glasses [25]. Urbach energies (Eg) are calculated by taking the reciprocals of slopes of linear proportion in the lower photon energy regions of these curves are shown in **Fig. 5.** The values are given in **Table 3.** They are found to increase with increase of SrO mol%. Smaller is the value of Urbach energy, greater is the structural stability of glasses.

Table.1

Composition of the glasses studied and their corresponding codes

Glass	Glass	Glass chemical Composition
System	Code	
SLCB 0	Cr 0	10 SrO - 10 Li O - 10 CaO -70 B O 2 3
SLCB 1	Cr 1	5 SrO - 15 Li O - 9.9 CaO -70 B O - 0.1 Cr O 2 3 2 3
SLCB 2	Cr 2	10 SrO - 10 Li O - 9.9 CaO -70 B O - 0.1 Cr O 2 3 2 3
SLCB 3	Cr 3	15 SrO - 5 Li O - 9.9 CaO - 70 B O - 0.1 Cr O 2 3 2 3

Table.2

Optical absorption band positions and their assignments of Cr³⁺ ions doped SLCB glasse

Glass Code	Transitions ${}^{4}A_{2} \rightarrow$	Wavelength (nm)	Wavenumber		D _q cm ⁻¹	$\operatorname{B}_{1} \operatorname{cm}^{-}$	C cm ⁻¹	D _q /B
coue	1 Lg	(iiiii)	Obs	Cal			UIII	
Cr ₁	${}^{4}T_{1g}$	429	23310	23303	1652	683	3133	2.4
	${}^{4}T_{2g}(F)$	605	16528	16524				
	$^{4}E_{g}(G)$	692	14450	14447				
Cr ₂	${}^{4}T_{1g}$	430	23255	23249	1649	681	3130	2.4
	${}^{4}T_{2g}(F)$	606	16501	16497				
	${}^{4}E_{g}(G)$	693	14430	14426				
Cr ₃	${}^{4}T_{1g}$	431	23201	23195	1636	693	3099	2.3
	${}^{4}T_{2g}(F)$	611	16366	16362				
	$^{4}E_{g}(G)$	694	14409	14405				

Table.3

Optical band gap energies (E_g), Urbach energies (E_g) of Cr^{3+} ions doped SLCB glasses

Glass	Direct band gap	Indirect band gap	Urbach
Code	$E_{g} (eV)(\pm 0.001)$	Eg	$Energy(E_g)$
	0	(eV)(±0.001)	eV(±0.001)

Cr.	3 7 7 7	2 713	0 3608			
Cr ₂	3.812	3.006	0.3243			
Cr ₁	3.871	3.271	0.2976			
Cr ₀	3.962	3.591	0.2815			



Fig.1. EPR spectra of Cr³⁺ ions doped SLCB glasses



Fig.2. 2(a)Optical absorption bands for Cr^{3+} ions doped SLCB glass (Cr_1)



Fig.2. 2(b).Optical absorption bands for Cr^{3+} ions doped SLCB glass (Cr_2)



Fig.2. 2(c). Optical absorption bands for Cr^{3+} ions doped SLCB glass (Cr_3).



Fig.3. Direct bands of Cr^{3+} ions doped SLCB glasses.



Fig.4. Indirect bands of Cr^{3+} ions doped SLCB glasses.



Fig.5. Urbach energy plots of Cr^{3+} ions doped SLCB glasses.

Conclusion

From the optical and EPR spectral studies of 0.1 mol% of Cr^{3+} ions doped xSrO-(20x)Li²O-(10-y)CaO-70B²O³-y (SLCB) glasses with ($5 \le x \le 15$ mol%) the following conclusions are drawn.

- (i) The EPR spectra of Cr^{3+} ions doped SLCB glasses resemble the characteristic spectra of other chromium doped glasses.
- (ii) The optical absorption spectra have shown the characteristic spectra of Cr3+ ions in octahedral symmetry
- (iii) The evaluated crystal field parameter (D_q) , the Racah parameters B and C for all the SLCB glasses are in good agreement with the literature values.
- (iv) From optical absorption edges, the direct and indirect optical band gap energies (Eg) and Urbach energies (Eg) evaluated, and found to be in good agreement with the previous reported values.

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