



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

KEYWORDS

Optical absorption spectra, crystal field parameter, the Racah parameters, optical band gap energies and Urbach energy.

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ABSTRACT

The EPR and optical absorption spectra of 0.1 mol% MnO doped x SrO-(20-x)Li₂O-(10-y)CaO - 70B₂O₃ - y, (5 ≤ x ≤ 15) mol% (SLCB) glasses are synthesized and studied. The EPR spectra of all Mn²⁺ ions doped SLCB glasses have exhibited resonance signals around g ≈ 4.2 at low magnetic field with a shoulder around g ≈ 3.0 at a medium value of magnetic field and a well resolved hyperfine sextet around g ≈ 2.0 at high magnetic field, which is the characteristic of Mn²⁺ ions in a close environment to octahedral symmetry. The optical absorption spectra has shown four transitions which are 6A_{1g}→4T_{1g}, 6A_{1g}→(4E_g+4A_{1g}) [G], 6A_{1g}→4T_{2g}, 6A_{1g}→4T_{1g} (D) in the increasing order of energy. From these transitions the crystal field parameter Dq, the Racah parameters B, C are evaluated for all the SLCB glasses. From the values obtained it is concluded that the site symmetry is octahedral. The optical band gap energies and Urbach energy values are obtained from the direct, indirect and Urbach plots

1. INTRODUCTION

Transition metal ions doped glasses have attracted the attention many researchers because of their interesting properties related to spectroscopy and many other practical applications like fiber optical communication, memory devices, and photo-conducting properties [1], luminescent solar concentrators (LSCs). Borate glasses provide an ideal case to demonstrate the effectiveness in optical and EPR spectroscopy in glass science in comparison with the other oxide glass forming systems. Borate glasses (B₂O₃) are easily melted and are good hosts for transition metal ions. Hence when glasses are doped with transition metal ions, they will become suitable for many practical applications. These properties can change according to the alkali oxide or modifiers content [2]. Recently, the interest in borate glasses has been renewed in views of the fast conductive properties exhibited by some of these glasses containing transition metal ions [3, 4]. This glass system is important in laser and infrared detection applications [5]. Borate glasses containing transition metal oxides are very useful materials for the radiation dosimetry applications in view of the fact that their effective atomic number is very close to that of human tissue [6]. The studies of transition metal ions in glasses by EPR and optical absorption techniques give information on the structure of the glass. Change in the composition of the glass may well change the local environment of the transition metal ion doped in the glass system causing to ligand field changes causing changes in the EPR and optical absorption spectra.

2. Experimental

2.1 Synthesis of xSrO-(20-x) Li₂O-(10-y)CaO-70B₂O₃ - y glasses

The starting materials, SrCO₃, Li₂CO₃, CaO, H₃BO₃ and MnO, used in the preparation of the glasses are of analar grade (AR). The batch compositions of the glasses, studied in the present work, are listed in Table 1.

Table.1

Composition of the glasses studied and their corresponding codes.

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

The weighed chemicals are mixed thoroughly and ground to fine powder. The batches are melted in air in an electrical furnace at 950°C for 20 min. The melts are then poured onto a polished brass plate and pressed quickly with another brass plate. The formed glasses are annealed at 400°C for about 1 h to make the glasses free from the structural stress. Highly transparent glasses are obtained.

2.2 Measurements

The optical absorption spectra of polished glass samples are recorded using double beam UV-VIS-NIR spectrophotometer (JASCO V-670) with an error of ±0.1nm in the region of 200-1200 nm with scan speed of 100 nm / min. The prepared glasses are taken in the form of powder and the EPR spectra were recorded on a JEOL JES-TE 100 spectrophotometer.

3. Results and discussion

3.1 EPR spectral Analysis

The EPR spectra of 0.1mol% Mn²⁺ ions doped SLCB glass system is shown in Fig.1.

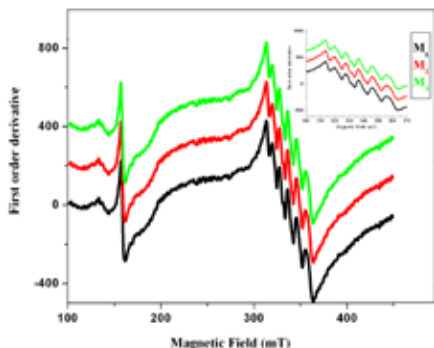


Fig.1. EPR spectra of Mn²⁺ ions doped SLCB glasses.

No EPR signal detected in the spectra of undoped glass, indicating that the chemicals taken in the starting for the preparation of base glass are free from spin probe ions. The EPR spectra of all Mn²⁺ ions doped investigated glasses have exhibited resonance signals around $g \approx 4.2$ at low magnetic field a shoulder around $g \approx 3.0$ at a medium value of magnetic field and a well resolved hyperfine sextet around $g \approx 2.0$ at high magnetic field, which is a characteristic of Mn²⁺ ions in a close environment to octahedral symmetry which have entered the glass matrix as paramagnetic species. The spectra of Mn²⁺ ions exhibit a six line hyperfine structure (hfs). The sextet is a result of hyperfine interaction of the electron spin with the ⁵⁵Mn nucleus ($I=5/2$). It can be concluded that the isotropic signal at $g \approx 2.0$ is due to the Mn²⁺ ion in an environment close to octahedral symmetry. The values for A also support that Mn²⁺ ions are in octahedral coordination [7]. It can be suggested from the values of 'A' obtained; the bonding between the Mn²⁺ in the dopent glasses is predominantly ionic in nature [8-11]. Since the g-value is showing a negative shift with respect to the free electron value (2.0023) the bonding is ionic in nature.

In general, EPR spectra of Mn²⁺ ions doped glasses are analyzed by using the spin-Hamiltonian of the form

$$H = g\beta BS + SA + SDS \quad (1)$$

where g is the isotropic factor, β is the Bohr magneton, B is the external magnetic field, S is the vector operator of the electron spin momentum and A is the hyperfine interaction parameter, I is the vector operator of nuclear spin momentum and D is the zero field splitting parameter. Investigations of the EPR spectra of Mn²⁺ in a variety of glasses have shown that the spectra have been characterized by an intense resonance signal at $g \approx 2.0$ with a hyperfine structure, an absorption around $g \approx 4.2$ and a distinct shoulder at $g \approx 3$ [12]. Each fine structure transition split into six hyperfine components due to the interaction of electron spin with the ⁵⁵Mn nucleus, having spin $I = 5/2$. Besides the resonance at $g \approx 2.0$, all the glass samples show resonance signals at $g \approx 3.0$ and $g \approx 4.2$ in their EPR spectra. The EPR spectra observed in the present work is similar to those reported for Mn²⁺ ions in various glass systems [13-18]. The resonance signal centered at $g \approx 3.0$ is broad, unresolved giving a shoulder like signal. The absorption centered at $g \approx 4.2$ is less intense and broadened due to the unresolved hfs. Overlapping this signal, a narrow and well-resolved line was observed. This line arises due to trace amounts (10-30 ppm) of transition metal (TM) impurities (mostly iron, Fe), which is observed as a weak signal of Fe³⁺ ions even in undoped glasses. Hence at $g \approx$

4.2, the signal is often observed for Fe³⁺ ions rather than Mn²⁺ ions [19]. It is assigned the above signal as accidental impurities of Fe³⁺ ($3d^5, ^6S$) ions. This is confirmed by comparing the line width of the signal at $g = 4.2$ of Fe³⁺ ions in different glass systems. A well resolved intense signal around $g \approx 2.0$, characterized by weakly deformed cubic sites are observed which does not vary with mol% variation of SrO and Li₂O. According to Van wieringen, there is a regular variation of hyperfine coupling constant with covalence [20]. The g -value for the hyperfine splitting is indicative of the nature of the bonding. If g -value shows a negative shift with respect to the free electron value (2.0023), then the bonding is ionic and if the shift is positive, then the bonding is more covalent in nature. The negative value of Δg confirms the ionic bonding in SLCB glasses. The spin-Hamiltonian parameters evaluated from EPR spectra of 0.1 mol% of Mn²⁺ ions doped SLCB glasses are given in Table 2.

Table 2
The spin-Hamiltonian parameters of Mn²⁺ ions doped SLCB glasses

Glass Code	g value at the sites		Δg	A (10 ⁻⁴ /cm)
	At low magnetic field	At High magnetic field		
M ₁	4.250	1.9952	- 0.0067	93.54
M ₂	4.247	1.9938	-0.0085	95.09
M ₃	4.246	1.997	-0.0052	93.82

3.2 Optical absorption spectra of Mn²⁺ ions doped (SLCB) glasses

The optical absorption spectra of Mn²⁺ ions doped glasses are shown in Fig.2. 2(a), 2(b) and 2(c).

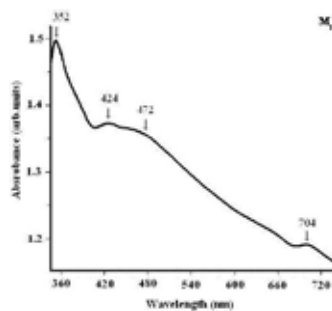


Fig.2.The optical absorption spectrum of Mn²⁺ ions doped M₁ glass 2(a)

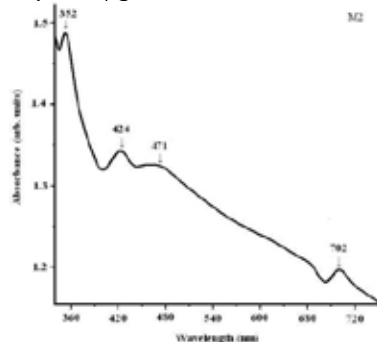


Fig.2.The optical absorption spectrum of Mn²⁺ ions doped M₂ glass 2(b)

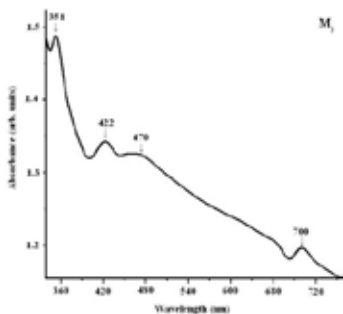


Fig.2. The optical absorption spectrum of Mn²⁺ ions doped M₃ glass.2(c)

The spectrum of Mn²⁺ free ion SLCB glasses does not reveal any absorption bands. The spectra of SLCB glasses doped with 0.1 mol% of MnO exhibited four absorption bands for each glass. The bands have assigned to ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → (⁴E_g + ⁴A_{1g}) [G], ⁶A_{1g} → ⁴T_{2g}, ⁶A_{1g} → ⁴T_{1g} (D) transitions of Mn²⁺ ions in an octahedral symmetry. The spectra show various spin-forbidden d-d bands which are characteristics of octahedral site symmetry for Mn (II) ions in the framework material. The crystal field parameter D_q, Racah parameters B and C have been calculated by fitting the experimental frequencies to an energy level diagram for an octahedral d⁵ high spin system [21] with Tree's correction factor (for Mn (II), (α = 76 cm⁻¹). The values obtained for D_q, B, and C are in the range which are usually found for octahedral Mn (II) compounds [22]. The band data along with the calculated values are tabulated in Table 3.

Table 3
Optical absorption band positions and their assignments.

Glass code	Transitions 6A _{1g} →	Wavelength (nm)	Wavenumber (cm ⁻¹)		D _q cm ⁻¹	B cm ⁻¹	C cm ⁻¹
			Obs	Cal			
M ₁	⁴ T _{1g}	470	14200	14194	820	725	2490
	⁴ E _g + ⁴ A _{1g} [G]	472	21180	21206			
	⁴ T _{2g} (D)	424	23578	23562			
	⁴ T _{1g} (D)	352	28401	28368			
M ₂	⁴ T _{1g}	702	14241	14237	820	720	2505
	⁴ E _g + ⁴ A _{1g} [G]	471	21225	21231			
	⁴ T _{2g} (D)	424	23578	23562			
	⁴ T _{1g} (D)	352	28401	28413			
M ₃	⁴ T _{1g}	700	14281	14268	820	730	2495
	⁴ E _g + ⁴ A _{1g} [G]	470	21270	21281			
	⁴ T _{2g} (D)	422	23690	23665			
	⁴ T _{1g} (D)	531	28482	28449			

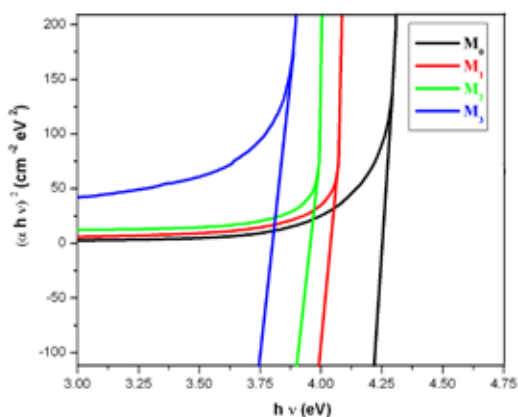


Fig.3. Direct bands of Mn²⁺ ions doped SLCB glasses.

The position of the bands, the evaluated crystal field (D_q), and Racah parameters B and C are similar to those obtained for various related Mn (II) containing open-framework materials [23–25].

3.3 Optical band gap energy (E_g) and Urbach energy (E_u)

The optical band gap and Urbach energies of MnO doped xSrO-(20-x)Li₂O-(10-y)CaO-70B₂O₃-y (SLCB) glasses with (5 ≤ x ≤ 15mol%) and y= 0.1mol% are obtained from the

absorption edge in UV region. From the observed absorption edges, the optical band gaps (E_g) of these glasses are evaluated by drawing Urbach plot between (α h ω)^{1/2} and h ω as per the equation,

$$\alpha(\omega)h\omega = C(h\omega - E_g)^2 \quad (2)$$

The direct and indirect plots of all these glasses exhibited are shown in Fig.3 and Fig.4.

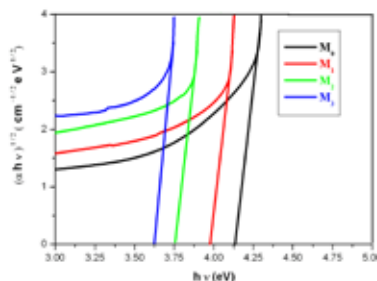


Fig.4. Indirect bands of Mn²⁺ ions doped SLCB glasses.

A considerable part of each curve is linear. The extrapolation of the linear portion of these curves gives an optical band gap (E_g) for glasses under study. Optical band gap (E_g) values are presented in Table 4. Plots are also drawn with logarithmic function hν against hν as shown in Fig.5.

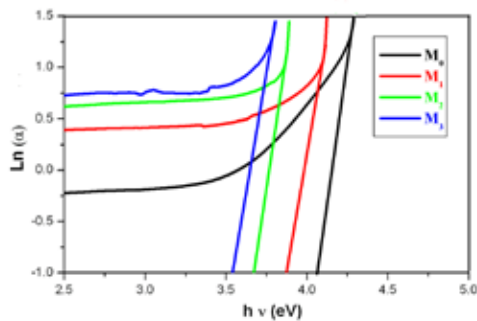


Fig.5. Urbach energy plots of Mn^{2+} ions doped SLCB glasses.

The values of Urbach energies (E_g) are calculated by determining the slopes of the linear regions of the curves and taking their reciprocals. The Urbach energies obtained for the SLCB glasses are given in Table 4.

Table 4
Optical band gap energies (E_g), Urbach energies (E_g) of Mn^{2+} ions doped SLCB glasses

Glass Code	Direct band gap E_g (eV)(± 0.001)	Indirect band gap E_g (eV)(± 0.001)	Urbach Energy (E_g) eV (± 0.001)
M_0	4.222	4.137	0.2458
M_1	3.993	3.975	0.2581
M_2	3.904	3.755	0.2727
M_3	3.742	3.620	0.2824

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