

Effects of MoO₃ Addition on Spectroscopic Properties of Lithium Zinc Borate Glass

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Abstract The paper deals with the spectroscopic properties of Li₂O -ZnO-B₂O₃ glass containing different concentrations of MoO₃ (ranging from 1 to 5 mol %) were prepared by melt quenching. Spectroscopic (infrared, optical absorption spectra and ESR) properties of these glasses have been carried out. The Optical absorption Spectrum contains one broad absorption band at 681 nm, this attributed to the excitation of Mo⁵⁺ (4d¹) ion. ESR studies reveal Molybdenum ions are expected to exist mainly in the Mo⁶⁺ state in the glass network. As the concentration of MoO₃ is increased, especially beyond 5.0 mol %, the colour of the glasses increased, that indicating the reduction of molybdenum ions from the Mo⁶⁺ state to the Mo⁵⁺ state. ESR, IR and Optical absorption spectra of paramagnetic ion in the above glasses reveal that the site symmetry of the transition metal ion is elongated octahedral.

Keywords MoO₃, ESR Spectra, IR Spectra, Optical Properties

1. Introduction

The glasses containing transition metal ions (TMI) came into prominence because of their notable spectroscopic properties and their suitability for fiber optic communications, luminescent solar energy concentrators (LSC)¹. Among the conventional glasses, borate glasses have been known to be excellent host materials for transition metal oxides because of their glass forming nature compare to other conventional glass systems. Borate glasses are used as wave-guides, electro-optic switches, electro-optic modulators, magneto-optic materials, solid-state laser materials and non-linear optical parametric converters^{2,4}. In addition, they are often used as dielectric and insulating materials and it is known that borate glass constitute a good shield against IR radiation⁵. In general B₂O₃ glasses contain the greatest amount of boric oxide that shows a minimum expansion, a property which is of great importance in obtaining thermal durability. It also decreases the tendency for glass to devitrify or crystallize. B₂O₃ is a basic glass former because of its higher bond strength, lower cation size and smaller heat of fusion. Among the three modifier oxides, viz., ZnO, PbO, CaO; ZnO having covalent character⁶, is expected to shorten the time taken for solidification of glasses during the quenching process. ZnO, reduces the

coefficient of thermal expansion, thus making possible the production of glass products of high resistance to thermal shock. Molybdenum ions in the glasses have been the subject of many investigations due to their catalytic properties. The ions of molybdenum inculcate high activity and selectivity in a series of oxidation reactions of practical importance in the glass matrices^{7,8}. Mo-O bond in molybdenum hexavalent oxide is identified as covalent. The Mo ion exists at least in two stable valence states viz., Mo(V) and Mo(VI) in the glass network. Earlier ESR studies on the glasses containing molybdenum ions have identified the presence of octahedrally coordinated Mo(V) ions along with distorted octahedrons approaching tetragons^{9,10}. These ions act both as network formers as well as network modifiers depending upon their concentration and nature of the host network. The Mo⁶⁺ ions are expected to participate in the glass network with tetrahedral MoO₄²⁻ structural units and may alternate with BO₄ tetrahedral units. Most of the studies available on MoO₃ containing glasses are on the understanding of their structure by spectroscopic investigations^{11,12} and ionic conductivity studies¹³.

In the present contribution the influence of MoO₃ in varying concentrations, on resonance and absorption properties of lithium-zinc-borate glasses are described in some detail. Optical band gaps for both direct and indirect transitions and Urbach energies were calculated and those glasses were also characterized by EPR and IR studies.

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2. Experimental

The glasses of the system $10\text{Li}_2\text{O}-(10-x)\text{ZnO}-80\text{B}_2\text{O}_3:x\text{MoO}_3$ ($x=0, 1, 2, 3, 4$ and 5 mol %) have been prepared by adopting the melt quenching technique. The raw materials used were analytical pure ZnO , Li_2CO_3 , H_3BO_3 . Appropriate amounts of weighed chemicals were grounded thoroughly in a mortar to produce homogeneous mixture. This homogenized mixture was then placed in porcelain crucibles and melted in an electrical furnace in air at 870°C - 920°C for half an hour until a bubble free liquid was formed. The melt was then quenched to room temperature in air by pouring it on to a Brass slab. The glasses thus obtained were transparent and in color. Details of experimental procedure and calculations are similar to the earlier work¹⁴.

3. Results and Discussion

3.1. Absorption Spectra

The Optical absorption spectra of the $\text{Li}_2\text{O}-\text{ZnO}-\text{B}_2\text{O}_3:\text{MoO}_3$ glasses recorded at room temperature in the wavelength range 400nm - 1400nm . The Optical absorption spectrum of molybdenum doped lithium zinc borate glass (with $x=3$ mol %) is shown in the Fig. 1. The absorption edge observed is observed to shift towards higher wavelength side. The spectrum of MoO_3 free glasses does not exhibit any

absorption band. But small amount of molybdenum is added to glasses matrix shows a broad optical absorption band at about 681 nm ¹⁵. The intensity of this band was observed to increase gradually as the concentration of MoO_3 increased. From an extrapolation of the linear portion of the curves of Fig. 2(a), 2(b), 2(c), gives direct, indirect band and Urbach energy gap so determined are presented in Table I. The values of direct and indirect band gap energies, decreases from M_1 to M_5 .

3.2. EPR Spectra

The ESR spectra of the glasses recorded at room temperature exhibit signals consisting of a central line surrounded by smaller satellites at about $g_{\parallel}=1.9286$ and $g_{\perp}=1.9486$ for M_3 glass system and is shown in Fig.3. The central line arises from even molybdenum isotopes ($I=0$) where as satellite lines correspond to the hyperfine structure from odd ^{95}Mo and ^{97}Mo ($I=5/2$) isotopes. The spectrums closely resembles that of the molybdenum ion in most oxide glasses, from the spectral analysis, the spin-Hamiltonian parameters were calculated using the following equation and are presented in the Table II. The EPR spectra are analyzed using spin-Hamiltonian:

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

Here Z is the symmetric axis, β is the Bohr magneton, S and I are the electron and nuclear spin operators, H_x , H_y and H_z are the static magnetic field components, g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the g tensor and, A_{\parallel} and A_{\perp} are the parallel and perpendicular components of the hyperfine tensor A . The values of A_{\parallel} are calculated using the following equations.

$$H_{\parallel}(-3/2) - H_{\parallel}(+3/2) = 3 A_{\parallel} \quad (2)$$

The analysis of ESR spectra of these samples suggest that Mo^{5+} ions are essentially coordinated in these glass ceramics by five oxygen ligands in a square pyramidal form C_{4v} symmetry with a $\text{Mo}=\text{O}$ double bond¹⁶.

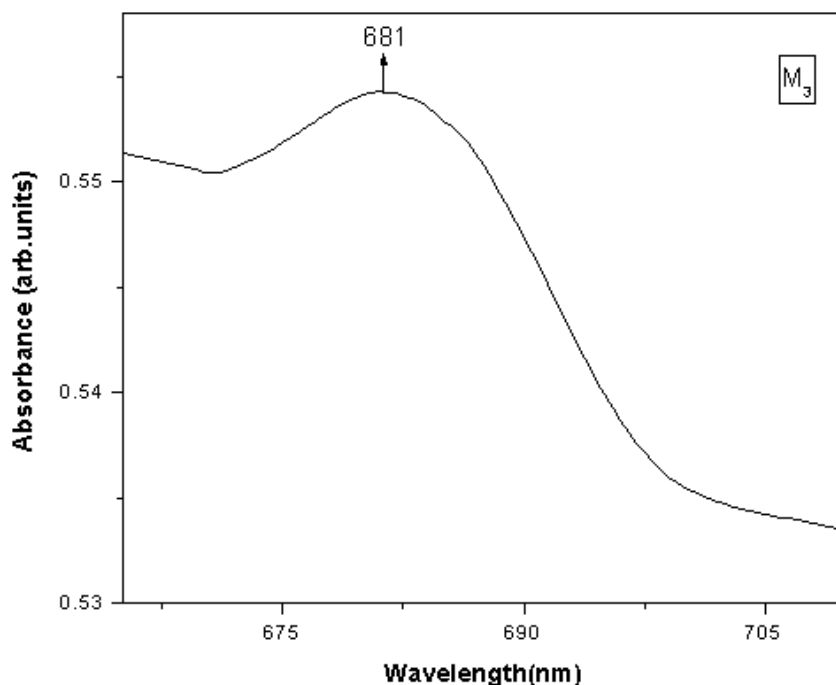


Figure 1. Optical absorption spectrum of Lithium-Zinc-Borate glass system containing 3 mol % of Mo^{5+} ions at room temperature

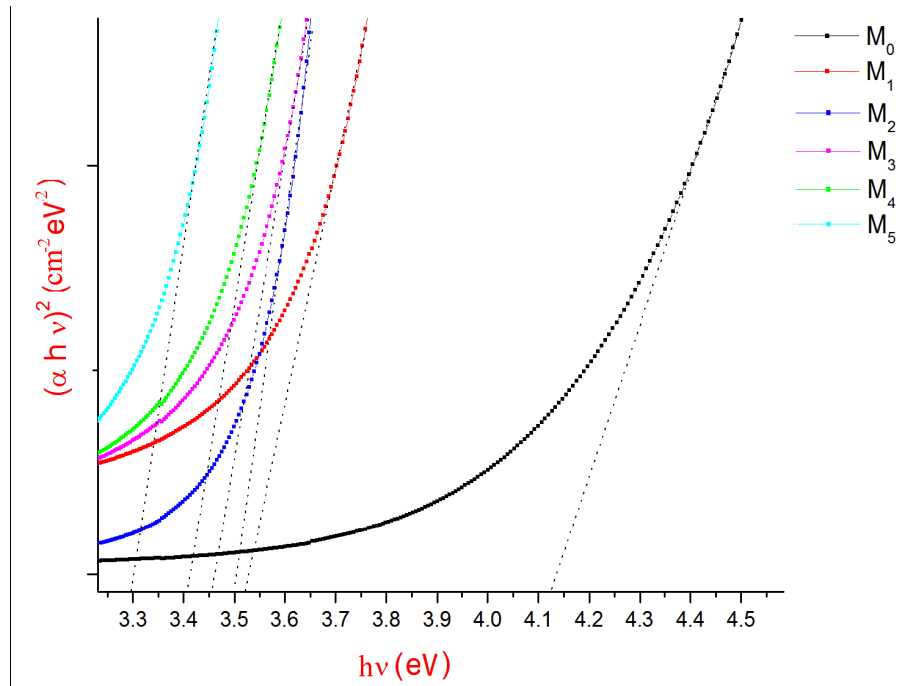


Figure 2(a). A plot between $(\alpha hv)^2$ and $h\nu$ for M_0, M_1, M_2, M_3, M_4 and M_5 glass samples

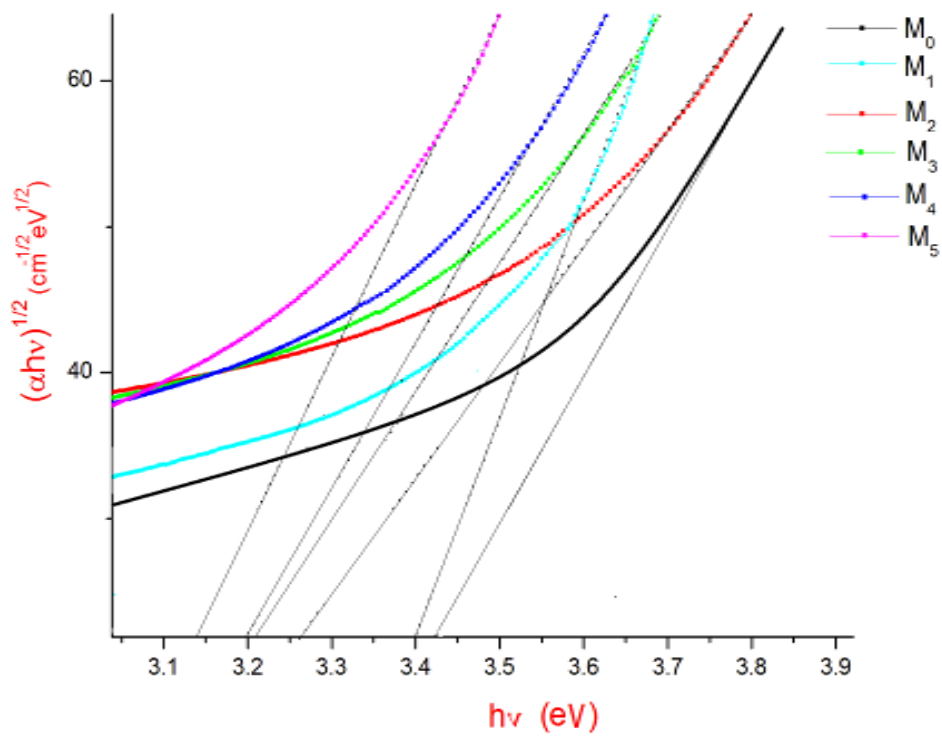


Figure 2(b). A plot between $(\alpha hv)^{1/2}$ and $h\nu$ for M_0, M_1, M_2, M_3, M_4 and M_5 glass samples

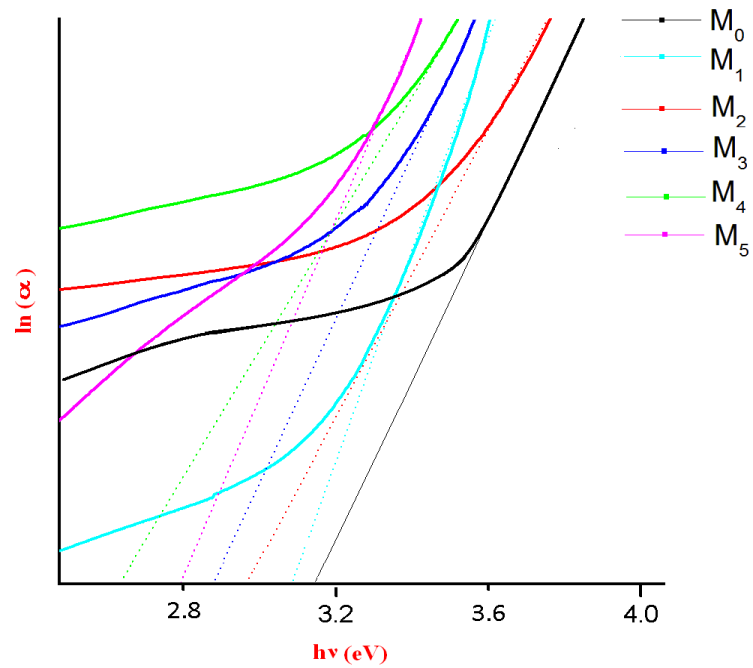


Figure 2 (c). A plot between $\ln(\alpha)$ and $h\nu$ for M_0 , M_1 , M_2 , M_3 , M_4 and M_5 glass samples

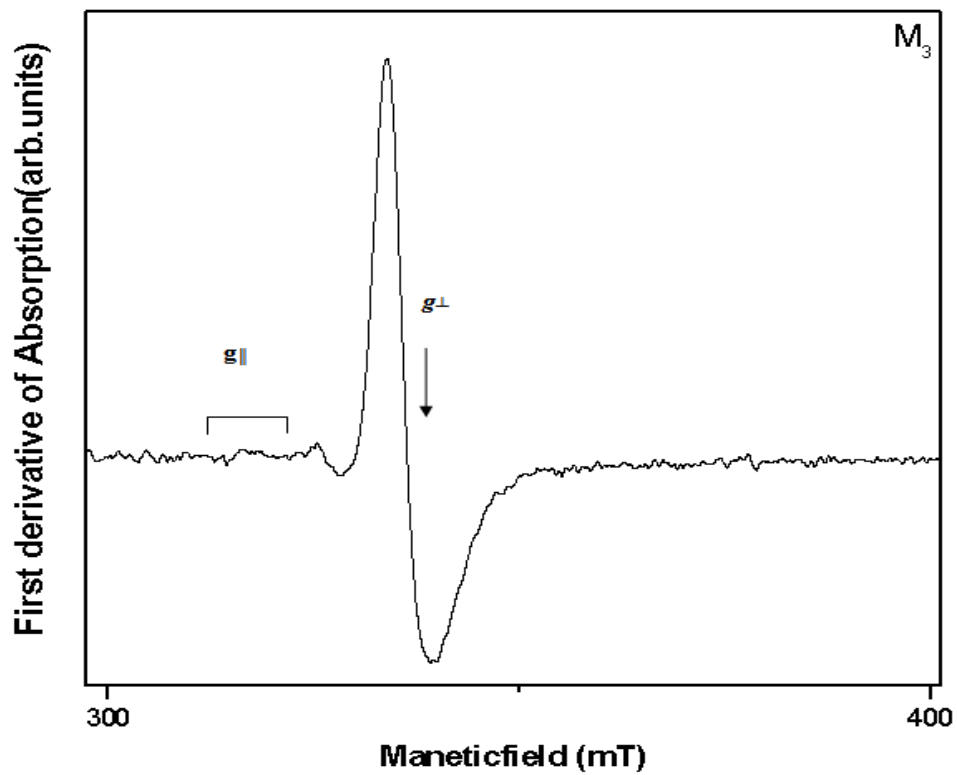


Figure 3. EPR spectra of M_3 glass sample ($\nu = 9.205\text{GHz}$)

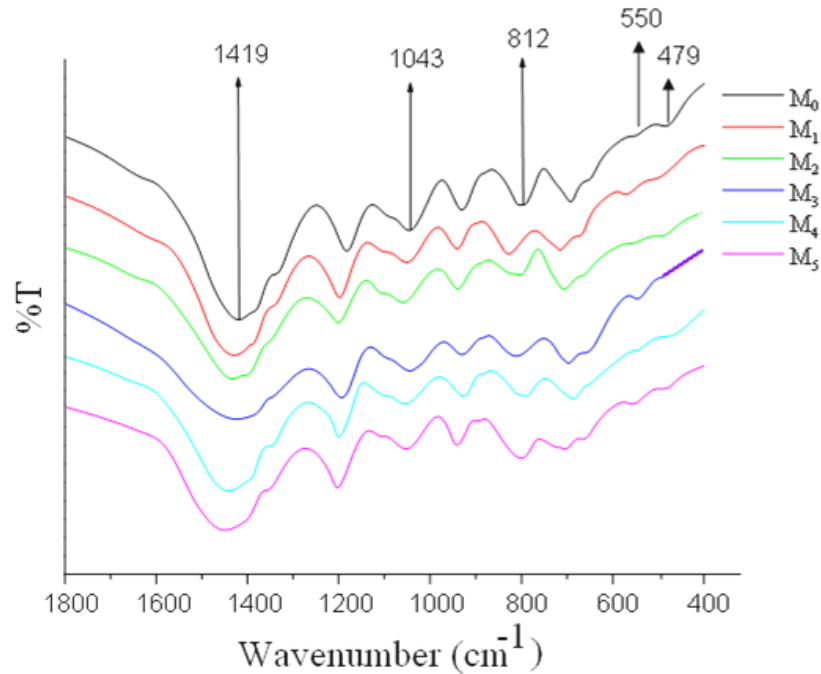


Figure 4. IR spectra of the M₀, M₁, M₂, M₃, M₄ and M₅ glass samples

Table I. Summary of the data on optical absorption spectra Li₂O-ZnO-B₂O₃: MoO₃ glasses

Glass Code	Cut-off wavelength(nm)	Band position(nm)	Direct band gap(eV)	Indirect band gap(eV)	Urbach Energy(eV)
M ₀	259	670	4.13	3.42	0.316
M ₁	310	672	3.53	3.49	0.320
M ₂	327	675	3.50	3.22	0.335
M ₃	332	681	3.46	3.20	0.346
M ₄	333	683	3.41	3.19	0.358
M ₅	348	691	3.29	3.14	0.380

Table II. EPR data of Li₂O-ZnO-B₂O₃: MoO₃ glasses

Glass Code	g	g _⊥	A (x 10 ⁻⁴ cm ⁻¹)	A _⊥ (x 10 ⁻⁴ cm ⁻¹)
M ₁	1.9448	1.9681	129.04	31.52
M ₂	1.9391	1.9535	129.42	30.23
M ₃	1.9286	1.9486	129.12	30.32
M ₄	1.9114	1.9325	128.17	29.03
M ₅	1.9093	1.9296	127.68	29.52

Table III. The summary of various band positions of IR spectra of Li₂O-ZnO-B₂O₃: MoO₃ glasses

Glass Code	Trigonal[BO ₃] units (cm ⁻¹)	Stretching vibrations of [BO ₄]Units (cm ⁻¹)	ν ₁ vibrational modes of [MoO ₄] ²⁻ tetrahedral units (cm ⁻¹)	ν ₃ vibrational modes of [MoO ₄] ⁶⁺ / Zn-O tetrahedral units (cm ⁻¹)	Vibrations of ZnO ₄ structural units(cm ⁻¹)
M ₀	1336	1047	-	-	479
M ₁	1340	1047	811	550	479
M ₂	1340	1049	812	550	478
M ₃	1342	1051	809	550	475
M ₄	1340	1049	808	550	474
M ₅	1336	1047	807	548	479

3.3. Infrared Spectra

The prominent IR bands shown in Fig. 4 are observed for $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3:\text{MoO}_3$ glasses and these bands are effectively influenced by the molybdenum content in the glasses network. The molybdenum free glasses exhibited in the regions $1300\text{-}1450\text{ cm}^{-1}$, $1100\text{-}1200\text{ cm}^{-1}$. These bands are identified as stretching relaxations of B-O bonds of the trigonal BO_3 units. Broad absorption bands are observed at $1050\text{-}900\text{ cm}^{-1}$ and $800\text{-}650\text{ cm}^{-1}$; these bands are identified due to stretching vibrations of the $[\text{BO}_4]$ units. A band at 525 cm^{-1} is due to Zn-O tetrahedral units and a band due to vibrations of ZnO_4 structural units is located at about 470 cm^{-1} in the spectra of all the glasses¹⁷. When molybdenum is added, two new bands attributed, to ν_1 and ν_3 vibrational modes of $[\text{MoO}_4]^{2-}$ tetrahedral units and $[\text{MoO}_6]^{6-}$ have also been located at about 810 and 550 cm^{-1} is observed. The summary of various band position of $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3:\text{MoO}_3$ is furnished in the Table III.

4. Conclusions

The conclusions drawn from analysis of the results of the various properties of $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3:\text{MoO}_3$ glasses reported in this study are as follows:

- The Optical absorption Spectra of $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3:\text{MoO}_3$ glasses exhibits bands associated with transitions at Mo^{5+} ions, indicating that the molybdenum ions is in pentavalent state, in addition to tetravalent and hexavalent states respectively in these glass samples.

- The EPR Spectra of these glasses exhibit a signal consisting of a triplet separated by smaller satellites. The signal has been identified as arising from tetragonally distorted octahedral positions of Mo^{5+} ions.

- The IR Spectral studies indicate that the molybdenum ions occupy tetrahedral positions in larger concentrations in sample M_5 .

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