

An Effectual Role of Molybdenum Ions on the Semiconducting Temperament of Na₂O-PbO-Bi₂O₃-SiO₂ Glasses

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Abstract

Melt quenching method is adopted to synthesize multi-component glasses $10\text{Na}_2\text{O} - 30\text{PbO} - 10\text{Bi}_2\text{O}_3 - (50-x)\text{SiO}_2 - x\text{MoO}_3$ (where $x = 0$ to 5 mol%). These samples are characterized by XRD as well as analysed by optical absorption, EPR, and FTIR spectroscopic techniques in order to discuss the structure of the glass network. The proportionate change of Mo^{6+} ions into Mo^{5+} local states, which depolymerize the glass network, is publicized by optical absorption studies. EPR spectral analysis of the samples revealed C_{4v} symmetry in a square pyramidal with a $\text{Mo}=\text{O}$ bond. FTIR spectra of doped glasses report the presence of MoO_4 and MoO_6 structural units. All spectroscopic studies propped up the semi-conducting nature of sodium lead bismuth silicate glasses doped with the higher content of MoO_3 .

1. Introduction

Amid all oxide glasses silica glasses are widely explored [1, 2] owing to their expansive domestic, mechanical and dental applications. Yet if the silicate glasses are added with heavy metal oxides like PbO and Bi_2O_3 their thermal, mechanical and electrical properties get enhanced due to the raised density, refractive index. Further these glasses display non-linear optical behaviour which promotes them as advanced materials applicable in ultrafast optical switching and photonic devices [3]. In association with heavy metal oxides the Modifier oxide Na_2O originate bonding distortions, which improves the ionic conductivity. Moreover, sodium silicate glasses are thermally as well as mechanically stable and chemically durable applicable in water treatment, paper industry and construction [4]. MoO_3 is catalytic in nature and an intermediate glass forming oxides. Also, it initiates the glass network on accompanying with the modifier oxide PbO with MoO_4^{2-} structural elements and exhibits modifying action through MoO_6 and $\text{Mo}^{5+}\text{O}^{3-}$ structural entities [5]. Further, the molybdenum oxide doped glasses grab potential applications in light modulation, smart windows and electro-chromic devices [6].

2. Experimental

Glass samples with composition $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-(50-x)\text{SiO}_2: x\text{MoO}_3$ ($0 \leq x \leq 5$) were prepared by the melt quenching technique. The compositional (all in mol %) details and their nomenclature of the samples are as follows:

M0: $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-50\text{-SiO}_2$

M1: $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-49\text{SiO}_2: 1\text{MoO}_3$

M2: $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-48\text{SiO}_2: 2\text{MoO}_3$

M3: $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-47\text{SiO}_2: 3\text{MoO}_3$

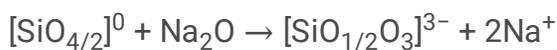
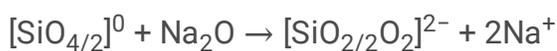
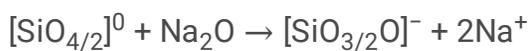
M4: $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-46\text{SiO}_2: 4\text{MoO}_3$

M5: $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-45\text{SiO}_2: 5\text{MoO}_3$

All chemicals Na_2CO_3 , PbO , Bi_2O_3 , SiO_2 , and MoO_3 utilized in this investigation are analytical grade reagents (99.9 % pure). Above discussed quantities of compounds were amalgamated in an agate mortar and thoroughly mixed until the homogeneous mixture was obtained. This mixture is transferred into a silica crucible. A programmable high temperature furnace was employed to heat up at 1200°C for 20 minutes. The bubble free liquid obtained was discharged onto a spotless and well-designed rectangular brass plate to quench it at ambient temperature. It was immediately transferred into annealing furnace maintained at 350°C . Later the samples were let to cool gradually to ambient temperature. The density of the synthesized samples was appraised by using VIBRA HT density measurement kit. The glasses were then cut, grounded and optically polished for optical absorption study. The leftover parts of the samples were pulverized into the fine powder for XRD, EPR and FTIR spectral investigations. The X-ray diffraction patterns of M0 and M5 samples were recorded with the SHIMADZU XRD 7000 Maxima system. A JASCO Model V-670 UV-vis-NIR spectroscope with a spectral resolution of 0.1 nm was employed to have optical absorption spectra in between 200–1000 nm at room temperature. The EPR spectra of $10\text{Na}_2\text{O}-30\text{PbO}-10\text{Bi}_2\text{O}_3-(50-x)\text{SiO}_2: x\text{MoO}_3$ ($1 \leq x \leq 5$) glasses were traced in the frequency range 8.8 to 9.6 GHz at ambient conditions by employing an X-band microwave spectrometer Model JEOL-FE-IX EPR with 100 kHz field modulation. The magnetic field was varied from 0 to 500 mT at the rate of 25 mT/min. SHIMADZU FTIR- 8400S spectrophotometer was employed to obtain FTIR spectra of glasses under investigation in the range $400-1200\text{ cm}^{-1}$.

3. Results And Discussion

SiO_2 is a familiar glass former amongst all components of the glasses under study, with tetrahedral $[\text{SiO}_{4/2}]^0$ units. The following chemical equilibrium, de-polymerization, arises upon the addition of modifiers like Na_2O , PbO [7]:



Further Bi_2O_3 exhibits the weak glass forming nature with BiO_3 structural units when associated with SiO_2 in addition to modifying action with BiO_6 octahedral units [8]. Molybdenum ions may occur in two valance states viz., Mo^{6+} and Mo^{5+} in the glass network. There is a possibility for the reduction of Mo^{6+} ions to Mo^{5+} state, which take the position at octahedral sites with distortions due to John-Teller effect [9].

3.1 Physical parameters

Evaluation of density ρ , molar volume V_m and average molecular weight M of the prepared samples guided to calculate various physical parameters such as Mo ion concentration N_i , Mo mean ion separation R_i and polaron radius R_p . All the computed parameters are furnished in Table 1. The gradual increment in the values of density from M0 (4.338 g/cm³) to M5 (4.633 g/cm³) is owing to the structural modification and the continuous substitution of relatively insubstantial silicon ions by the weighty molybdenum ions.

3.2. XRD

The XRD patterns of M0 and M5 glasses are shown in Fig. 1. The noisy broad Bragg peaks reported endorse the glassy arrangement of the investigated specimens.

3.3 Optical absorption spectra

Optical absorption spectra, of the specimens prepared in this study, recorded in the wavelength region 200 to 1000 nm are represented in Fig. 2. The cut off wavelength of Mo free sample is observed at 367 nm. Where the optical absorption edge of M1 sample with 1 mol% of MoO₃ is significantly increased to 425 nm and it has red shifted with the amalgamation of MoO₃ up to 5.0 mol%. This abrupt escalation of the cut-off wavelength is a sign of the depolymerization of the network. The spectra also exhibited a wide absorption band between 550 to 800 nm which is ascribed to the excited Mo⁵⁺ (4d¹) ion [10]. With the increase of MoO₃ content from 1 to 5 mol % the intensity as well as half width of the spectra are noticed to increase with a red shift of peak position. This increase of intensity proposes the gradual conversion of Mo⁶⁺ ions into Mo⁵⁺ ions during melting and it suggests the existence of the highest concentration of Mo⁵⁺ ions in the glass network of the sample with 5 mol % MoO₃. Such Mo⁵⁺ ions cause added bonding imperfections and NBOs by forming Mo⁵⁺O³⁻ molecular orbitals leading to depolymerization of the glass network.

An optical band gap (E_g) of glasses under study are estimated from the extrapolated curves between $(\alpha h\nu)^{1/2}$ and $h\nu$ as presented in Fig. 3 and values are furnish in Table 2. As an outcome the optical band gap is found to decrease from 3.38 eV to 3.03 eV with the rise of MoO₃ Concentration. Further, Urbach energy (ΔE) explores the information about the breadth of the extensions of localized states in the band gap, values are assessed by plotting the Urbach's relation [11].

$$\ln(\alpha) = (h\nu/\Delta E) + \text{const} \quad (4)$$

Fig. 4 represents these Urbach curves between $\ln(\alpha)$ and $h\nu$ of the glasses taken for study. The Urbach energy values are also presented in Table 2. It is identified that the Urbach energy ΔE of M0 (0.14 eV) is minimum and maximum for M5 (0.35 eV) sample. This type of spectroscopic analysis indicates that growth in the density of Mo⁵⁺ (O_h) ions in the samples from lower to higher concentrations of MoO₃. The development of donor centres and the ensuing overlap of excited states of localized electrons entrapped on Mo⁵⁺ sites with the vacant 4d Mo states on the nearest Mo⁶⁺ sites lead to more invade of polaron

band into the main band gap. The red shift of absorption edge, significant fall in the band gap and enhancement in Urbach energy can be attributed to this polaronic development [9].

3.4. EPR spectra

Fig. 5 depicts the EPR signals of MoO₃ contained Na₂O–PbO–Bi₂O₃–SiO₂ glasses traced at ambient temperature. A main central line, aroused due to molybdenum isotopes (I = 0), bounded by satellite lines, corresponding to the hyperfine structure of odd ⁹⁵Mo and ⁹⁷Mo (I = 5/2) isotopes [12], with wee intensity is discernible in the EPR spectra. From these spectra the peak height and half width of the central line is observed to amplify with the rise of MoO₃ content in the glass. It noticeably indicates the enhancement of Mo⁵⁺ ions with the increasing content of MoO₃ in the glass composition. The maximum intensity observed in the spectrum of M5 sample shows the existence of higher proportions of Mo⁵⁺O³⁻ ions compared to other ones. It is well known that molybdenum take part in the glass network as MoO³⁺ complex. The high charge lingering on the central molybdenum in the interim the drop of the net charge on the neighbouring oxygen ions and accordingly reduced the ability to donate an electron (σ-bonds) stimulates the strong π-bond with two axial oxygens of the compressed octahedron. As a result, MoO₆ transforms into complex Mo⁵⁺O³⁻ molybdenum ion. In other words, in the axially distorted environment Mo(V) is strongly displaced in its octahedron so that it adopts a pyramidal MoO₅ configuration with a very short Mo–O bond length matching to the molybdenyl ion. This endorses the coordination of Mo⁵⁺ ions with five oxygen ions by C_{4v} symmetry through Mo=O in studied glasses.

The spin Hamiltonian function [12] for the illustration of Mo⁵⁺ spectrum is

$$H = \beta SgB + SAI \quad (5)$$

Here the symbols have the standard meaning, i.e., the Bohr magneton β, electron spin S = ½, g-tensor g, the nuclear spin of molybdenum 'I', hyperfine structure tensor 'A' and the applied field B. The degree of axial distortion α of the coordination polyhedron is estimated by (g_e–g_{||})/4(g_e–g_⊥). The values of g_{||}, g_⊥, A_{||}, A_⊥ and α evaluated from the spectra are presented in Table 3 and also observed g_{||} < g_⊥ < g_e (2.0023) together with A_{||} > A_⊥, demonstrating the octahedral site with tetragonal compression. The observed trends of these parameters with the rise of MoO₃ content support the above viewpoints.

3.5. FTIR spectra

FTIR spectra of glasses considered for the present study are portrayed in Fig. 6. The bands noticed at about 941, 781 and 486 cm⁻¹ are assigned to the asymmetric, symmetric and bending vibrations of Si–O–Si linkages of silicate structural units, respectively. The weak band reported at about 415 cm⁻¹ is attributed to the vibrations of Bi–O bonds in BiO₆ units. Another band observed at about 1112 cm⁻¹ is assigned to O–Si–O asymmetric stretching mode of vibrations of SiO₄ structural entities linked with NBOs [13]. Another two bands at about 843 and 877 cm⁻¹ are detected which are due to the vibrations of

MoO_4^{2-} and MoO_6 structural units [14]. The intensity of the vibrational band due to MoO_4^{2-} tetrahedral units is found to reduce and shifted towards greater wave number side whereas the peak height of the band due to MoO_6 structural units is found to increase with a red shift, with the increase of MoO_3 content [14-16]. Thus it is confirmed that the conversion of molybdenum ions from MoO_4 to MoO_6 state with the rise of concentration of MoO_3 . As well the intensity of the bands pertinent to asymmetric stretching vibrational modes (Si-O-Si, O-Si-O) is noticed to rise at the cost of intensity of symmetric stretching vibrations of Si-O-Si with the rise of MoO_3 content. The above spectral analysis strongly evidences the modifier role of molybdenum ions at higher concentrations of MoO_3 and consequent depolymerisation of the present glass network.

4. Conclusions

$\text{Na}_2\text{O} - \text{PbO} - \text{Bi}_2\text{O}_3 - \text{SiO}_2$ glasses blended with diverse concentrations (0 to 5 mol % in steps of 1 mol %) of MoO_3 were made by using melt quenching technique. Glassy nature is confirmed by XRD and Physical parameters were also measured. The conventional spectroscopic techniques viz., optical absorption, EPR and FTIR were conducted. Optical absorption spectra elucidated the existence of molybdenum ions in Mo^{5+} and Mo^{6+} localized states and also revealed the gradual enhancement in the redox ratio ($\text{Mo}^{5+}/\text{Mo}^{6+}$) with the hike in the concentration of MoO_3 . The EPR spectroscopic investigation of the glasses supported the enrichment of Mo^{5+} ions and their coordination with five oxygen ligands in a square pyramidal, C_{4v} symmetry, with a Mo = O bond. These Mo^{5+} ions produce non bridging oxygens by breaking the Si-O-Si linkages in SiO_4 structural units which enhances the discreteness and consequent depolymerisation in the glass network. The increase in the intensity of asymmetrical vibrations at the expense of symmetrical vibrations of various structural units with a rise in the concentration of MoO_3 in the FTIR spectra also supports the increasing degree of disorder in the glass network which causes depolymerisation. As a whole, the investigations carried out strongly suggest the semiconducting nature of samples with the high concentration of MoO_3 and also strengthen the proposal of usefulness of MoO_3 doped sodium lead bismuth silicate glasses as electronic devices, such as non-crystalline semiconducting materials, IR transmission modules, thermal and mechanical sensors, and scintillators in nuclear instruments.

Declarations

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Tables

Table 1 Physical parameters of MoO₃ doped Na₂O–PbO–Bi₂O₃–SiO₂:MoO₃ glasses.

Sample	Density r (g/cm ³) (±0.001)	Molar Volume V_m (cm ³) (±0.01)	Conc. of Mo ions N_i ($\times 10^{21}$ ions/cm ³) (±0.01)	Inter ionic distance of Mo ions R_i (Å) (±0.01)	Polaron radius R_p (Å) (±0.01)
M0	4.338	24.95	—	—	—
M1	4.414	24.54	24.88	3.42	2.19
M2	4.468	24.46	49.57	2.72	1.74
M3	4.508	24.42	73.86	2.38	1.52
M4	4.578	24.29	98.47	2.16	1.38
M5	4.633	24.20	122.68	2.01	1.28

Table 2 Data on optical absorption spectra of MoO₃ doped Na₂O–PbO–Bi₂O₃–SiO₂ glasses.

Sample	Cut-off wavelength λ_c (nm) (± 1nm)	Band position	Optical band gap E_g (eV) (± 0.01eV)	Urbach energy ΔE (eV) (± 0.01 eV)	Table 3 Spin – Hamiltonian parameters of MO ⁵⁺ ions in Na ₂ O–PbO–Bi ₂ O ₃ – SiO ₂ : MoO ₃ glasses.
M0	367	—	3.38	0.14	Table 4 Data on FTIR spectra (cm ⁻¹) of Na ₂ O–PbO–Bi ₂ O ₃ – SiO ₂ :MoO ₃ glasses
M1	425	683	3.30	0.20	
M2	430	686	3.20	0.24	
M3	445	688	3.12	0.27	
M4	451	691	3.06	0.29	
M5	462	694	3.03	0.35	

Sample	$g_{ }$		$A_{ }$	A_{\perp}	a
			($\times 10^{-4} \text{ cm}^{-1}$)	($\times 10^{-4} \text{ cm}^{-1}$)	
M1	1.912	1.941	81.34	46.53	0.368
M2	1.915	1.943	89.46	52.37	0.374
M3	1.917	1.946	94.34	56.82	0.379
M4	1.920	1.949	99.25	62.75	0.386
M5	1.924	1.952	106.3	70.52	0.389

M0	M1	M2	M3	M4	M5	Assignment
422	421	419	417	416	415	Bi-O bonds in BiO_6 units.
474	476	479	482	484	486	Rocking vibrations of Si-O-Si linkages
772	774	776	778	780	781	Si-O-Si symmetric stretching vibrations
-	828	830	835	839	843	Vibrations of MoO_4 units
-	889	886	883	880	877	Vibrations of MoO_6 units
951	949	947	944	943	941	Si-O-Si asymmetric stretch vibrations
1122	1120	1117	1115	1113	1112	O-Si - O asymmetric stretching vibrations in SiO_4 units associated with NBOs

Figures

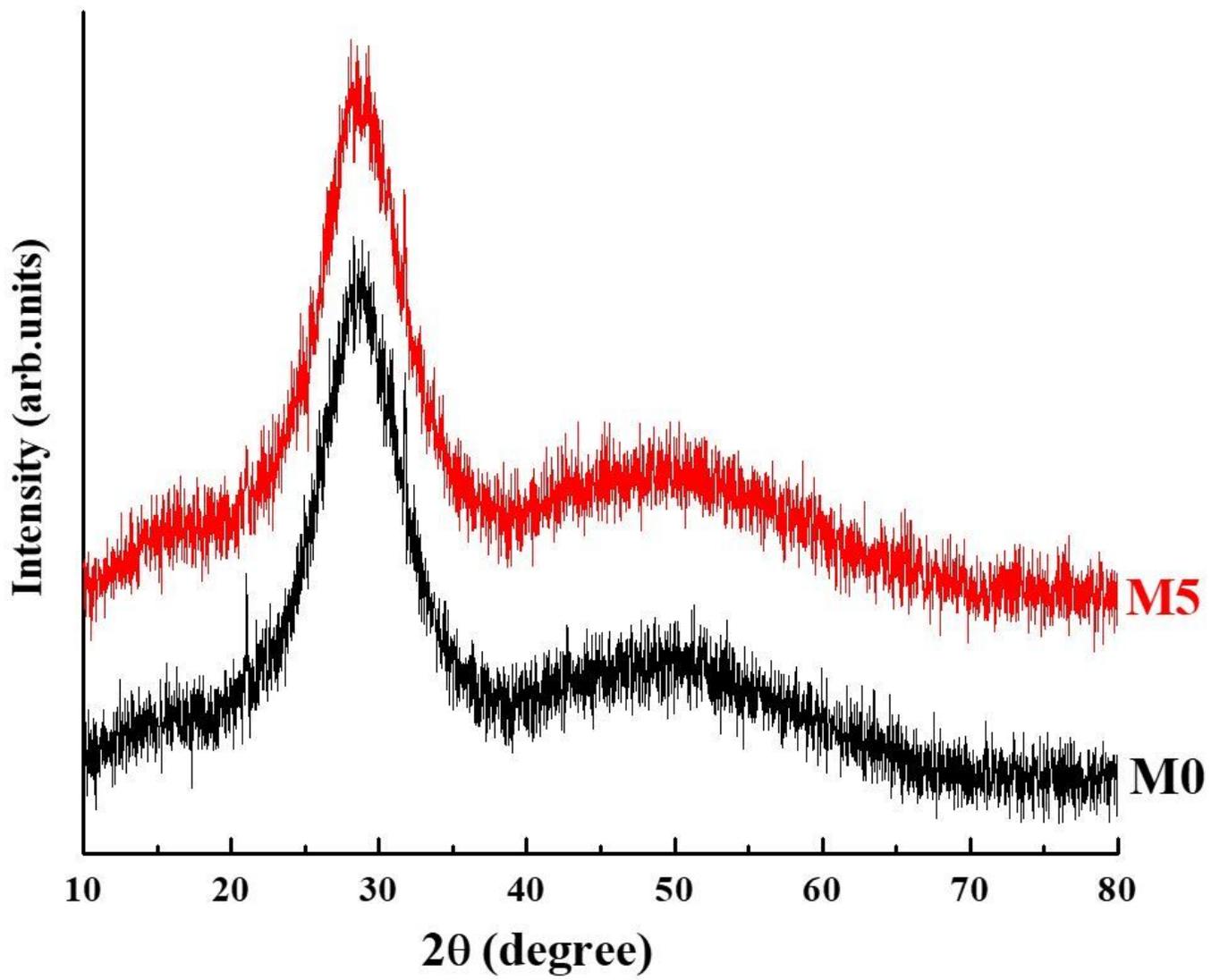


Figure 1

XRD patterns of some of MoO₃ doped Na₂O–PbO–Bi₂O₃–SiO₂ glasses.

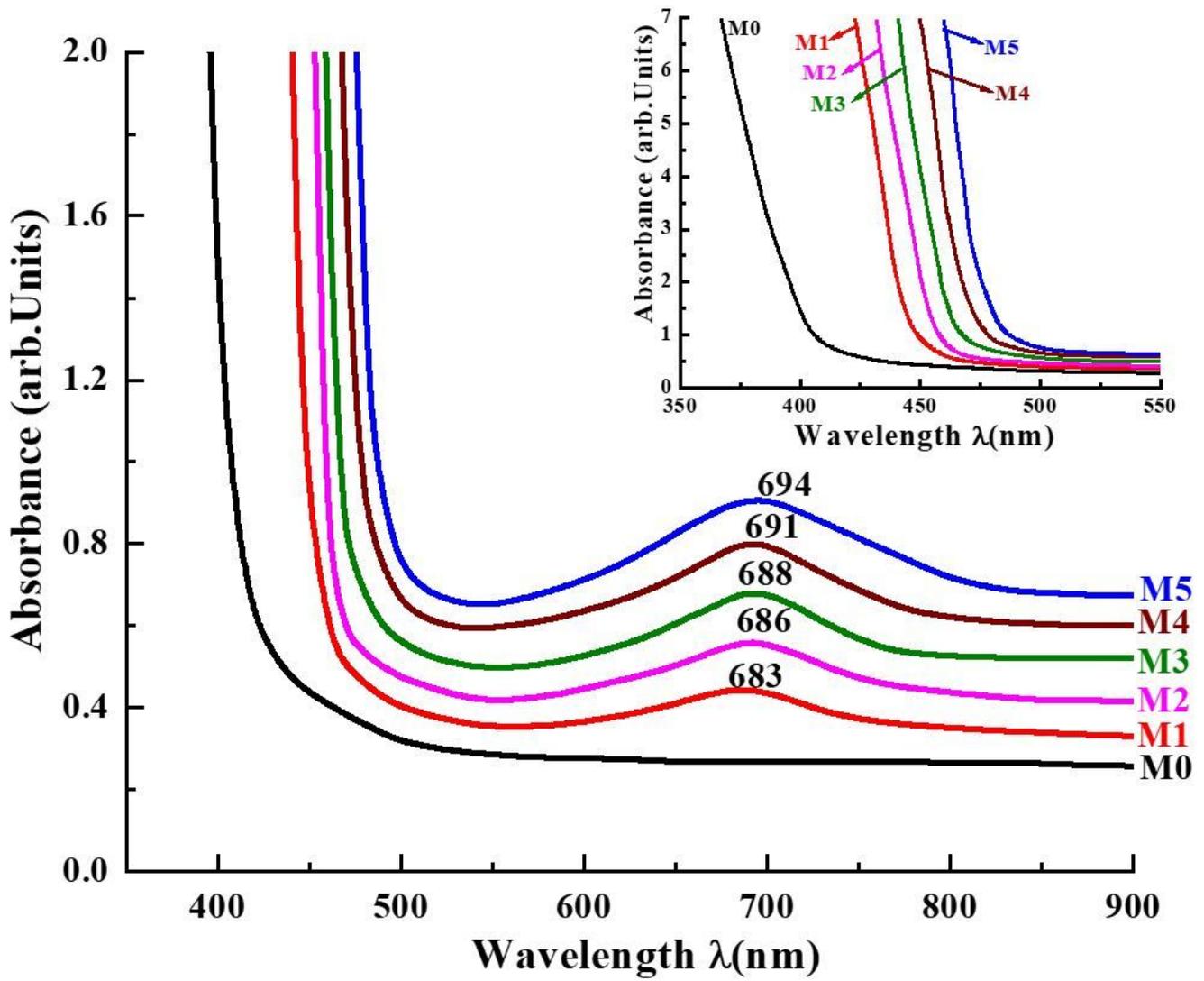


Figure 2

Optical absorption spectra of MoO₃ doped Na₂O-PbO-Bi₂O₃-SiO₂ glasses.

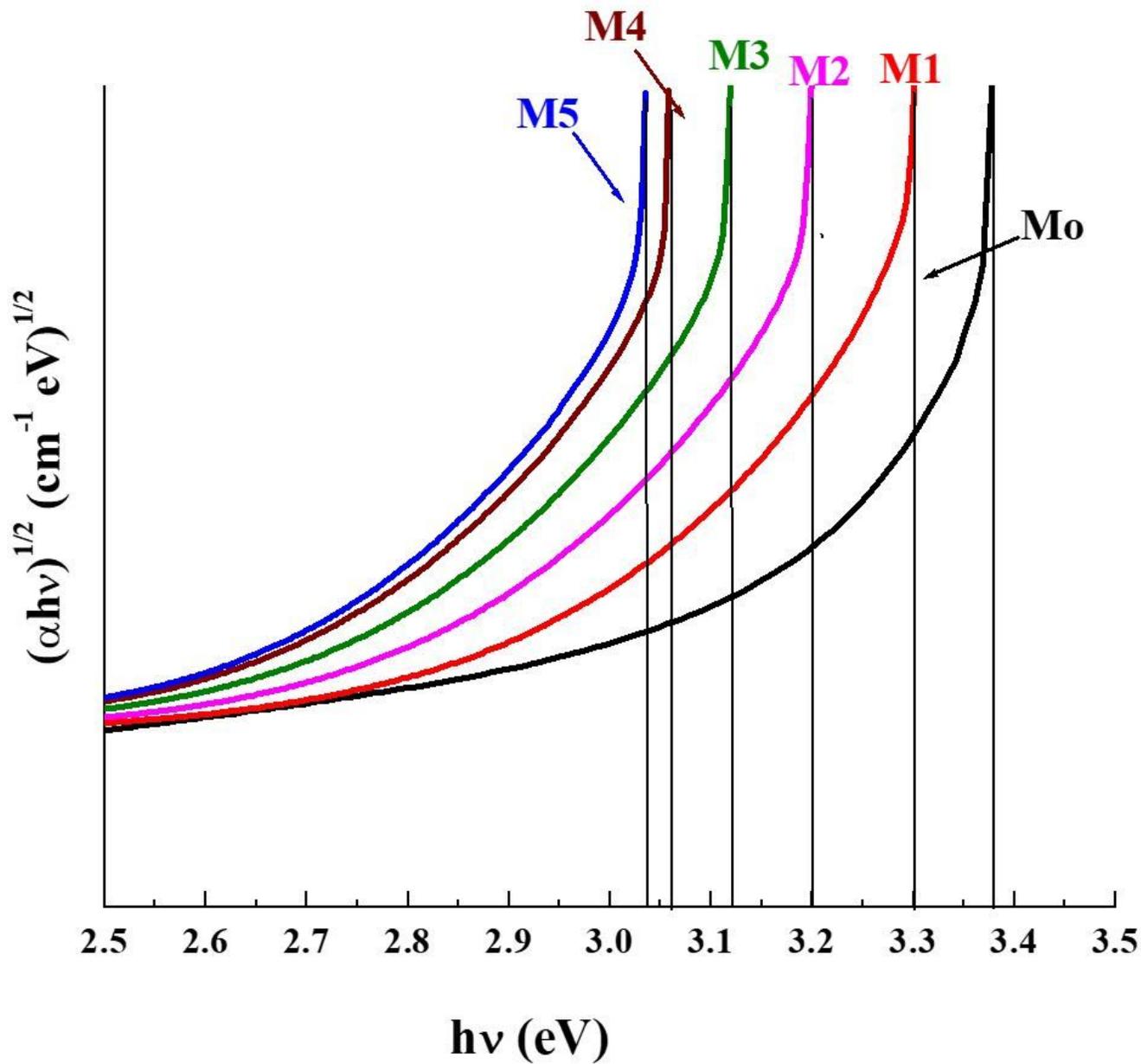


Figure 3

Tauc plots of MoO₃ doped Na₂O–PbO–Bi₂O₃–SiO₂ glasses.

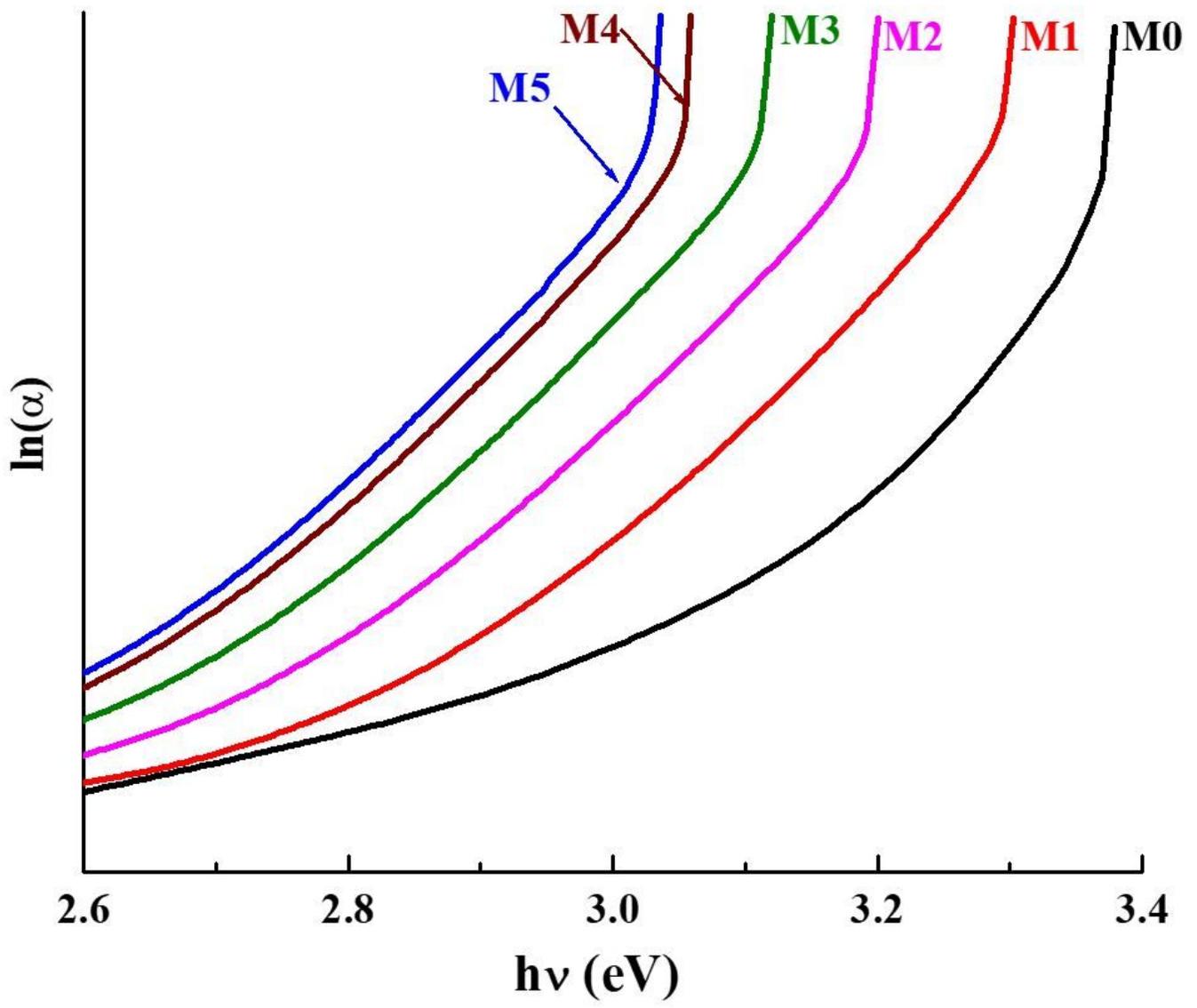


Figure 4

Urbach energy of MoO₃ doped Na₂O-PbO-Bi₂O₃-SiO₂ glasses.

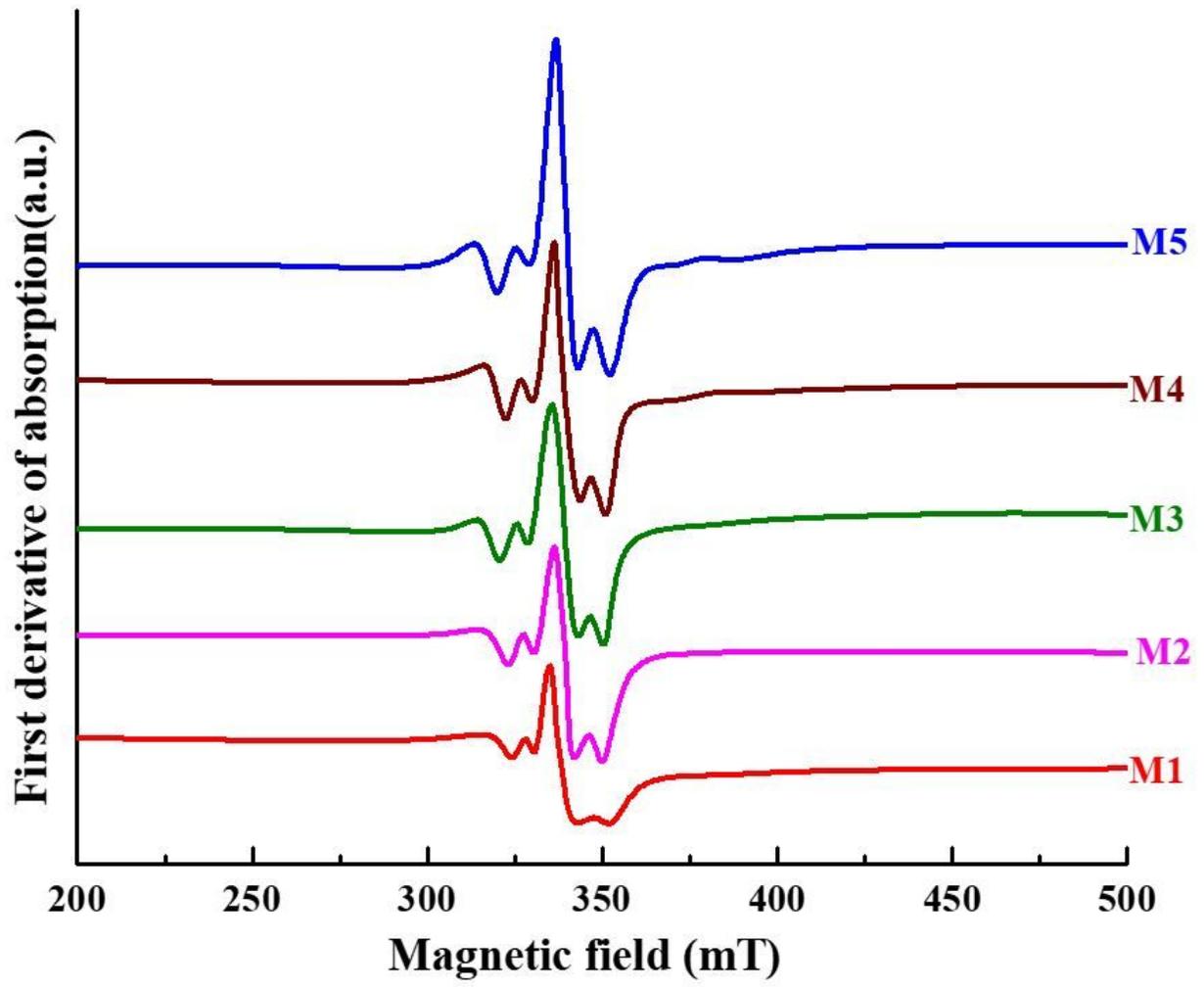


Figure 5

EPR spectra of MoO₃ doped Na₂O–PbO–Bi₂O₃–SiO₂ glasses.

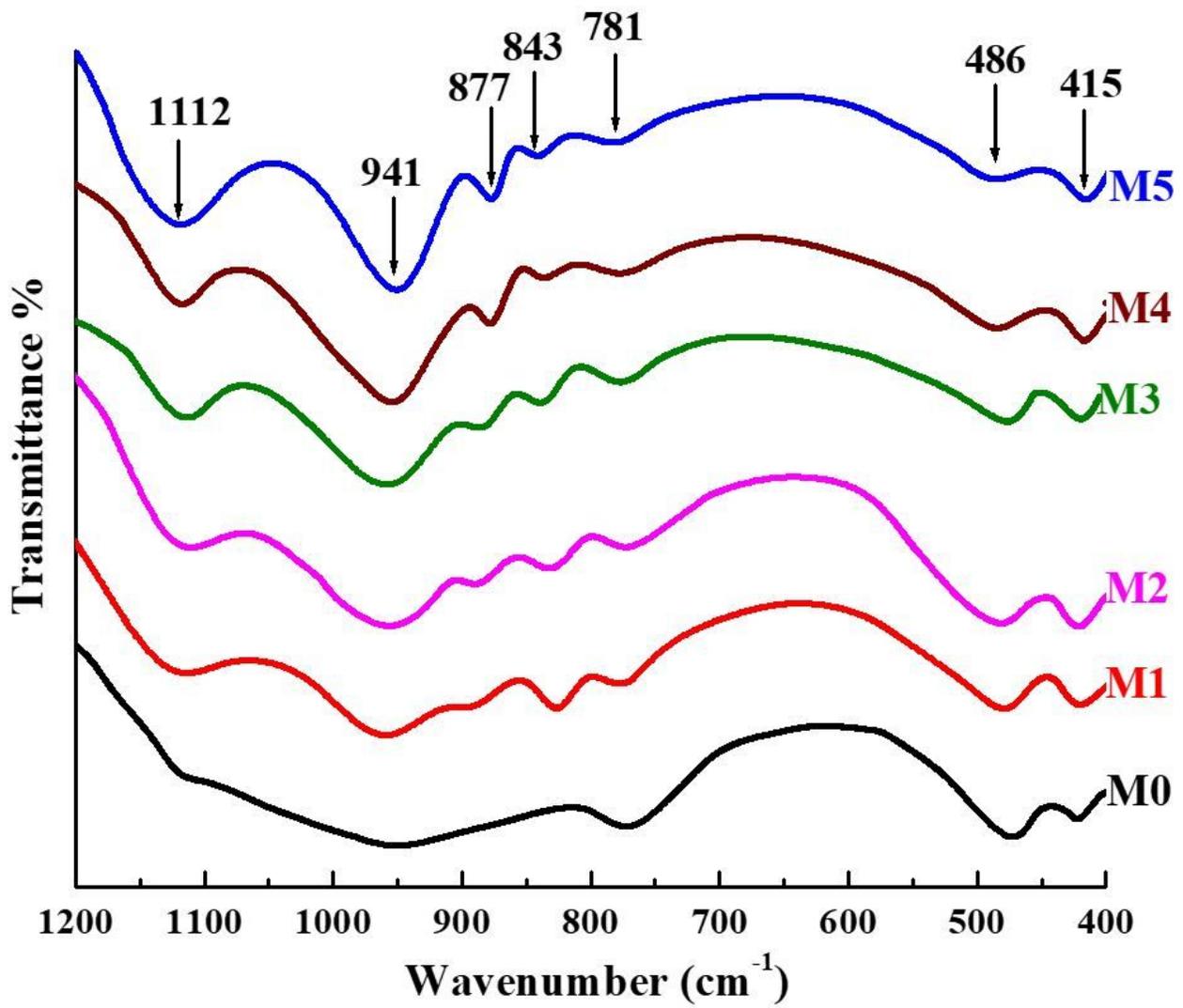


Figure 6

FTIR spectra of Na₂O-PbO-Bi₂O₃-SiO₂:MoO₃ glasses.