

Investigations on Spectroscopic Properties of Manganese Ions in Sodium Lead Alumino Borate Glasses

Vijaya Babu karumuri (✉ kamalavijay007@gmail.com)

Department of Physics, The Bapatla College of Arts & Sciences, Bapatla-522101, A.P, India

Madhuri Vema

Department of Physics, The Bapatla College of Arts & Sciences, Bapatla-522101, A.P, India

Suresh Boddu

Department of Physics, Acharya Nagarjuna University, N. Nagar-522501, A.P, India

Research Article

Keywords: Glasses, melt quenching, Infrared spectroscopy, Optical absorption, Electron paramagnetic resonance

Posted Date: August 11th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-49497/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Investigations on Spectroscopic Properties of Manganese Ions in Sodium Lead Alumino Borate Glasses

K. Vijaya Babu^{1*}, V. Madhuri², B. Suresh³

¹*Department of Physics, The Bapatla College of Arts & Sciences, Bapatla-522101, A.P, India*

²*Department of Physics, The Bapatla College of Arts & Sciences, Bapatla-522101, A.P, India*

³*Department of Physics, Acharya Nagarjuna University, N. Nagar-522501, A.P, India*

Abstract:

Divalent manganese ions containing $20\text{Na}_2\text{O}-15\text{PbO}-(5-x)\text{Al}_2\text{O}_3-60\text{B}_2\text{O}_3:x\text{MnO}_2$ (x ranging from 0 to 1 mol%) NPAB glasses are prepared by using melt quenching technique and are characterized by several spectroscopic techniques. Various physical parameters are calculated from the measured density values. Structural properties of MnO_2 doped NPAB glasses are investigated by Powder XRD, EPR, UV-VIS absorption and FT-IR spectroscopic techniques. The amorphous nature of prepared glass samples are confirmed by X-ray diffraction spectra. EPR spectra of these glasses exhibited a well resolved six line hyperfine structure around $g = 2.00$ is the characteristic nature of Mn(II) ions in distorted octahedral site symmetry. Optical absorption spectra of these glasses revealed a single broad band at $\approx 21000 \text{ cm}^{-1}$ which has been assigned to the transition ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$ of Mn(II) ions. Optical band gap energies and Urbach energies are evaluated through the fundamental Ultra Violet absorption edges of the glasses. FT-IR spectra clearly exhibited different vibrational bands and assigned to borate groups and water molecules.

Key words: Glasses; melt quenching; Infrared spectroscopy; Optical absorption; Electron paramagnetic resonance

1. Introduction

Lead alumino borate glasses find several applications in battery ceiling and other microelectronic packaging because of their properties like toughness, good strength, transparency, excellent corrosion resistance, high mechanical strength and low thermal expansion coefficients [1]. B_2O_3 acts as one of the most important glass formers and flux materials. Melts with compositions rich in B_2O_3 exhibit rather high viscosity and tend to formation of glasses [2]. Thus, borate glasses are enormously studied by different groups across the world due to its rich structural variation [3]. By the addition of various alkali modifiers, drastic structural changes occur in the borate structural units with the evolution of four coordinated boron and non bridging oxygen (NBO) ions in the glass network. Alkali-borate glasses have high mechanical strength, high electrical conductivity and relatively moisture-resistant compared with pure borate glasses. Due to high electrical conductivity and ease in preparation of alkali-borate glasses, these are suggested as potential fast ion conducting solid electrolytes [4]. Al^{3+} ions are generally used as intermediate species [5]. When alkali-borate glasses consist of heaviest metal oxides such as Al_2O_3 , are more promising for photonics and optoelectronics. Because of its attractive properties of high melting point, excellent resistivity, high wears resistance, high chemical durability, and low cost availability of raw materials, these glasses have been widely studied [6-9]. Addition of PbO to these glasses makes the materials more magnetically and electrically inert and also decrease the viscosity, increase the electrical resistivity and the ability to absorb X-rays [10]. PbO in contrast with the conventional alkali metals, has ability to form stable glasses due to its dual role-one as modifier and the other as glass network former in both ionic [11] and covalent bonding [12, 13] with $PbO_{4/2}$ pyramidal units connected in puckered layers [14]. The study of the glasses doped with transition metal ions and its physical properties is of considerable interest in the application point of view. The physical properties of these glasses can be enhanced by the addition of PbO to alkali alumino borate glasses. In recent years the study of glasses doped with transition metal ions have a wide range of applications in electronic, tunable solid state lasers, luminescent solar energy concentrators (LSCs) and fibre optic communication systems due to their memory and photo conducting properties [15].

Among various transition metal ions, Mn(II) is a distinctive luminescent ion with good potential applications. Mn-doped semiconductors are commonly used in magneto-optical, magneto-transport, spintronics, lasers, and infrared devices. Manganese-based thin film oxides can be utilized as electrode materials [16, 17], electrochemical capacitors [18, 19], rechargeable batteries, catalysts, sensors [20], magneto electronic devices [21]. Manganese is next to iron element, one of the most common impurities in glasses and it is used as coloring and decoloring agent [22]. In glass matrices, manganese ions exist in different valence states viz. Mn^{2+} and Mn^{3+} , in borate and phosphate glasses with both tetrahedral and octahedral coordination [1]. The content of manganese oxide present in the glass matrix at a given temperature depends upon the quantitative properties of modifiers, glass formers, size of the ions in the glass structure, their field strength and mobility of the modifier cation, etc., [3].

Studies of the coordination, bonding characteristics and covalency state of transition metal ions in glasses are very useful to understand the structure of the glasses. Changes in the chemical composition of glass may change the local environment of the transition metal ion incorporated into the glass, leading to ligand field changes, which may be reflected in the optical absorption and EPR spectra. Structural properties of vitreous systems are frequently studied by means of EPR of Mn(II) ions used as paramagnetic probes [23]. To the best of our knowledge there is no previous literature reported on EPR and optical absorption studies of $Na_2O-PbO-Al_2O_3-B_2O_3$ glasses doped with manganese ions.

Hence the present spectral investigations of manganese-bearing $Na_2O-PbO-Al_2O_3-B_2O_3$ (NPAB) glasses is undertaken in view of understanding the site symmetry of the metal ion, its oxidation state from the optical absorption and EPR spectroscopic studies. Structurally different borate units exist in this glass system are investigated by FT-IR spectroscopy.

2. Experimental

For the present study, a particular composition $20Na_2O-15PbO-(5-x)Al_2O_3-60B_2O_3:xMnO_2$ with six values of 'x' ranging from 0 to 1 is taken. The detailed NPAB compositions of all the glass samples are listed in the Table 1.

2.1 Glass Preparation

The starting materials used in the present work are analar grade reagents sodium carbonate (Na_2CO_3), lead oxide (PbO), aluminum oxide (Al_2O_3), boric acid (H_3BO_3) and

manganese oxide (MnO_2) with 99.9% purity. All the chemicals are weighed accurately using an electrical balance which are grounded to fine powder and mixed thoroughly. The batches are taken in silica crucibles and melted in an automatic temperature controlled electrical furnace in air at 1100°C about 20 minutes. The resultant bubble free transparent liquid is then poured on a brass mould and subsequently annealed to relieve the structural stress, about 24 hours at 350°C . The glasses thus obtained are transparent and brown. After polishing, good quality glasses obtained have been used for optical measurements.

2.2 Measurement

By Archimedes principle, the density (d) of the glass samples is measured at room temperature using a sensitive micro balance with O-xylene (99.99% pure) as the immersion liquid. Average molecular weight (M), various physical parameters such as manganese ion concentration (N_i), mean manganese ion separation (r_i), the polaron radius (r_p) and optical basicity (Λ^{th}) are evaluated.

X-ray diffraction technique is employed to check for possible crystallinity of the samples after quenching and annealing. X-ray powder diffraction patterns of glass samples are recorded using copper target on Philips PW (1710) Diffractometer at room temperature. The optical absorption spectra of MnO_2 doped NPAB glasses are recorded at room temperature in the wavelength range 200-1200 nm up to a resolution of 0.1 nm using JASCO model V-670 UV-VIS-NIR spectrophotometer. Glass samples of thickness 1mm are used for optical measurements. The Electron paramagnetic resonance spectra of fine powders of the samples have been recorded at room temperature on JEOL JES-FA200 EPR Spectrometer operating in the X-band frequency ($\nu=9.732$ GHz) with a field modulation of 100 KHz. The magnetic field is scanned between 0 to 5000 Gauss with a scan speed of 250 Gauss per minute and the microwave power used is 5 mW. A powdered glass specimen of 100 mg has been taken in a quartz tube for EPR measurements. FT-IR spectra of various as prepared glass samples are obtained by Perkin Elmer 577 infrared Spectrometer to an accuracy of 0.1 cm^{-1} in the frequency range $4000\text{-}500\text{cm}^{-1}$ using KBr pellets (300mg) containing pulverized sample (1.5 mg). These pellets are pressed at a vacuum die at \square 680 Mpa.

3. Results

3.1 Powder X-ray diffraction (PXRD) study

Fig. 1 shows the typical PXRD pattern of undoped and MnO₂ doped NPAB glasses did not reveal any crystalline phase which asserts the amorphous nature.

3.2 Physical parameters

Based on the measured glass density (d) and calculated molecular weight (M), various physical parameters such as manganese ion concentration (N_i), mean manganese ion separation (r_i), Polaron radius (r_p), and optical basicity (Λth) are evaluated using conventional formulae [24] and the values obtained are presented in Table 2.

3.3 Electron Paramagnetic Resonance (EPR)

Fig. 2 represents the typical EPR spectra of MnO₂ doped NPAB glass samples. EPR signal is not detected in the spectra of undoped glass which indicate that there are no paramagnetic impurities in the starting materials. The EPR spectra of all Mn(II) doped NPAB glass systems at room temperature exhibit the standard hyperfine sextet (hfs) structure around g = 2.001 which is a fundamental characteristic signal of Mn²⁺ ions. Each fine structure transition split into six hyperfine components due to the interaction of electron spin with the ⁵⁵Mn nucleus (I = 5/2). The significant data related to EPR spectra are listed in Table 3.

3.4 Optical absorption studies

The optical absorption spectra of MnO₂ doped NPAB glass samples recorded in the wavelength region of 200-1200 nm are shown in the Fig. 3. The absorption edge occurred at a wavelength of 310 nm for pure NPAB glass. The absorption edge shifts towards higher wavelength with the doping of manganese ions. The optical absorption spectra of MnO₂ doped NPAB glasses consist a broad absorption band in the visible region at λ 21000 cm⁻¹. This band is observed originated from ⁶A_{1g}(S) → ⁴T_{1g}(G) octahedral transition of Mn(II) ions belong to d⁵ configuration. The exact band positions for individual glasses studied are presented in Table 4. With an increase in the concentration of MnO₂, the intensity of octahedral band is observed to grow gradually with minor red shift. The position of the bands is shifted slightly towards the lower frequency side with increasing concentration of MnO₂.

The study of optical band gap in the amorphous materials is the subject of considerable research. This is related to the energy gap between valence and conduction bands [25]. In glasses, the study of optical absorption in the ultraviolet region is a useful method to understand

the band structure. The conduction band is influenced by the glass forming anions, the cations also play an indirect but important role [25]. In general, there are two kinds of optical transitions at the fundamental edge of crystalline and non-crystalline semiconductors; direct and indirect transitions. In the direct optical transition from the valence band to the conduction band, it is essential that the wave vector for the electron be unchanged [26]. In case of the indirect transitions, interactions with lattice vibrations (phonons) takes place, thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons. Plotting $(\alpha hv)^{1/2}$ as a function of hv suggested by Tauc [27] and discussed totally by Davis and Mott [28].

The absorption coefficient $\alpha(\nu)$ is given by [29]

$$\alpha(\nu) = (1/t) \ln(I/I_0) \quad (1)$$

where t is the thickness of the sample and $\ln(I/I_0)$ corresponds to absorbance factor.

The absorption coefficient $\alpha(\nu)$ can be related to optical band gaps of direct and indirect transitions following Davis and Mott [28].

$$\alpha(\nu) = B(h\nu - E_{opt})^n \quad (2)$$

where B is the energy-independent constant [30], E_{opt} is the energy of the optical band gap and $h\nu$ is the incident photon radiation. For indirect transitions $n = \frac{1}{2}$ and for direct transitions $n = 2$.

The main feature of the absorption edge of an amorphous semiconductor is an exponential increase of the absorption coefficient with photon energy in accordance with an empirical relation given by Hassan and Hogarth [31]

$$\alpha(\nu) = \alpha_0 \exp(h\nu/\Delta E) \quad (3)$$

where α_0 is a constant and ΔE is the Urbach energy which indicates the width of band tail of the localized states in the band gap.

The direct and indirect band gap energy values E_{opt} can be obtained by extrapolating the absorption coefficient to zero absorption in $(\alpha hv)^2$ vs. $h\nu$, $(\alpha hv)^{1/2}$ vs. $h\nu$ plot and is shown in Fig. 4 and 5. Plots have been also drawn between $\ln(\alpha)$ vs. $h\nu$ (Fig. 6) and the Urbach energy values (ΔE) are calculated by taking the reciprocal of the slopes of linear portion in the lower photon energy region of the curve [32]. The optical band gaps for direct, indirect transitions and Urbach energies obtained in the present work are listed in Table 5.

3.5 FT-IR study

Fig. 7 represents FT-IR transmittance spectra of NPAB glasses at room temperature. The undoped and manganese doped NPAB glasses exhibited three groups of prominent bands. (i) The first group of bands are appeared at $1200 - 1600 \text{ cm}^{-1}$, these are identified as symmetric stretching relaxations of B–O bonds of the trigonal BO_3 units. The second group of broad absorption bands are observed at $800 - 1200 \text{ cm}^{-1}$; these are identified as B–O asymmetric stretching vibrations of the tetrahedral BO_4 units and the third group of bands are observed in between the region $600 - 800 \text{ cm}^{-1}$ due to the bending of B–O–B linkages in the borate network [33]. The FT-IR band positions and their assignments are given in Table 6.

4. Discussion

4.1 Powder X-ray diffraction (PXRD) study

X-ray diffraction is a useful technique to detect the structural changes in any type of materials. The dimensions of glassy materials are greater than typically 100 nm [34]. The PXRD pattern exhibited a broad diffuse scattering at angle, which indicated a long-range structural disorder characteristic of vitreous solids. In glasses, the atoms are not regularly spaced and non-uniform as in the case of crystals. Due to the variations in inter atomic distances of glasses; the peaks get broader. Thus, the undoped and MnO_2 doped NPAB glass samples are found to be completely amorphous in nature.

4.2 Physical parameters

The modification of the geometrical configuration, co-ordination number, cross-link density and dimensions of interstitial space may have influenced the density of the glass matrix. Therefore, density is a powerful physical parameter which reveals the degree of change in structure with change in composition of glasses. From Table 2, it is observed that density values are increased gradually with the content of MnO_2 [35, 36]. Polaron radius (r_p) values are found consistently less than that of inter ionic distance (r_i) in all glasses. Further, the values of r_p and r_i gradually decreased with increasing concentration of MnO_2 .

4.3 Electron Paramagnetic Resonance (EPR)

The g values obtained for Mn(II) ions in the present glass system is comparable with that of other glass systems, such as lead alumino borate glasses [1], soda lime silicate glasses [37]

and alkali sulphate glasses [38]. For Mn(II) ion, if we neglect the nuclear Zeeman term, the spin Hamiltonian term can be written as

$$H = \mu_B g B S + A S I + D [S_Z^2 - \frac{1}{3} S(S+1)] + E(S_X^2 - S_Y^2) \quad (4)$$

where μ_B is the Bohr magneton, g is the electronic g factor, B is the Zeeman field, S is the Mn^{2+} electronic spin=5/2, A is the hyperfine interaction tensor, I is the Mn(II) nuclear spin=5/2 and D and E are the non-axial zero field splitting parameters.

The hyperfine splitting constant 'A' can be calculated from the position of the allowed hyperfine lines using the formula:

$$H_m = H_0 \pm A_m \pm (35 \pm 4 m^2) \frac{A^2}{8 H_0} \quad (5)$$

where H_m is the magnetic field corresponding to $m \leftrightarrow m$ hyperfine line, H_0 the resonance magnetic field. The g and A values have been calculated for all the glass samples under investigation. Within the experimental error, the g and A values are found to be independent of temperature, alkali size and manganese content.

In the case of d^5 metal ions, it is familiar that the axial distortion of Mn(II) octahedral symmetry gives rise to three Kramer's doublets $\pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$ [39]. The EPR spectra

exhibited only one prominent signal with six-line hyperfine structure (given by the isolated Mn^{2+} ions) with high intensity at $g = 2.0$ is observed. This multiplet is arises from the transition between the energy levels of the lower Kramer's doublet i.e. from $M_s = -\frac{1}{2} \pm \frac{1}{2}$, where M_s is the effective electronic spin component. The population of these doublets produce splitting in EPR signal. From the Fig. 2 it is observed that the sextet lines in $g = 2.00$ are not equally spaced and the separation between the hyperfine (hf) lines increases from low field side to high field side of the spectrum. The increase of the MnO_2 content leads to increase in the line width of the sextet, which is due to the dipole-dipole interaction of the paramagnetic ions. Moreover, the sextet gradually tends to become a broad single line spectrum. The resolved hyperfine spectra around $g = 2.00$ and the magnitude of hfs (A) constant is $93 \times 10^{-4} \text{ cm}^{-1}$ in the glass matrix are strongly indicate that the Mn(II) ions are present in octahedral symmetry [40]. According to Van Wieringen, there is a regular variation of hyperfine coupling constant (A) with covalence [41]. From the large hyperfine coupling constant values the ionic nature of bonding is high between

Mn(II) ions and its ligands. The nature of bonding is successfully explained based on the hyperfine splitting g-value. If g-value shows a negative shift ($g < g_e$) with respect to the free electron value ($g_e=2.0023$), then the bonding is ionic and conversely, if the shift is positive ($g > g_e$), then the bonding is more covalent in nature. In the present work, the observed 'g' value (2.0057) shows positive shift in Mn₁ glass sample, indicates the less covalent nature. The 'g' values (2.0010 □ 1.9969) show negative shift in all remaining glass samples, indicates the ionic nature. Hence, It is clear that the ionic character of Mn(II) ions in NPAB glasses gradually increases with increasing concentration of MnO₂ [41].

4.4 Optical absorption studies

The optical basicity of an optical glass serves in the first approximation as a measure [42] of the ability of oxygen to donate a negative charge to the probe ion. Duffy and Ingram [43] reported that the ideal values of optical basicity can be calculated from the composition of the glass and the basicity moderating parameters of the various cations present.

Theoretical optical basicity values of the glass can be estimated using the following formula.

$$\Lambda^{th} = \sum_{i=1}^n \frac{z_i r_i}{2\gamma_i} \quad (6)$$

where n be the total number of cations present, z_i is the oxidation number of the i^{th} cation, r_i is the ratio of number of i^{th} cations to the oxides present and γ_i is the basicity moderating parameter of the i^{th} cation. The basicity moderating parameter γ_i can be calculated from the following equation [42].

$$\gamma_i = 1.36(x_i - 0.26) \quad (7)$$

where x_i is the Pauling's electro negativity [44] of the cation. Pauling's electro negativity of boron, lead, aluminum, sodium and manganese ions is 2.04, 2.33, 1.61, 0.93 & 1.55 respectively. Theoretical values of optical basicity (Λ^{th}) have been calculated and presented in Table 4. In the present study from Table 4, it is observed that the optical basicity is increased indicates the covalence between manganese ions and oxygen ions decreased with increasing concentration of manganese ions.

Electronic configuration of Mn(II) ion is (Ar)3d⁵ corresponds to half-filled d orbital. This configuration gives ⁶S, ⁴P, ⁴F, ⁴D, ⁴G free ion terms and in addition to a number of doublet states of which ⁶S occupies the ground state. In octahedral symmetry, ⁶S and ⁴P transform as

spherically non-degenerate ${}^6A_{1g}$ and ${}^4T_{1g}$, 4F splits into ${}^4A_{2g} + {}^4T_{2g} + {}^4T_{1g}$, 4D splits into ${}^4E_g + {}^4T_{2g}$ and 4G splits into ${}^4A_{1g} + {}^4E_g + {}^4T_{1g} + T_{2g}$ respectively.

Generally, manganese ions can exist in different oxidation states such as divalent (Mn^{2+}) ions [1], trivalent (Mn^{3+}) ions [45] and also tetravalent (Mn^{4+}) ions [46] in lead oxide glasses. In the optical absorption spectra of MnO_2 doped NPAB glasses, a broad band appeared near 21000 cm^{-1} is assigned to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transition, indicates that the characteristic absorption of distorted octahedral site symmetry of Mn(II) ions [47]. The increasing value of absorption edge with increasing MnO_2 concentration also supports that manganese ions are predominantly in octahedral Mn(II) state which occupy network modifier positions. The gradual increase in the half width and intensity of octahedral band suggests that there is a growing concentration of Mn(II) ions in the glass network with increasing content of MnO_2 .

From Table 5, it is noticed that direct, indirect optical band gap energy values are decreased and Urbach energy values are increased with increasing concentration of MnO_2 . The decrease in the band gap may be explained as follows. The decrease in the band gap causes the increase in non-bridging oxygen (NBOs) in the glass matrix. This leads to increasing degree of localization of electrons thereby increase in the number of donor centers in the glass matrix. The presence of large concentration of these donor centers lowers the optical band gap and shifts the absorption edge towards lower energy side as observed. This suggests that growing concentration of Mn(II) ions are present in NPAB glasses. Increase in Urbach energy with MnO_2 concentration confirms that the number of defects increase with Mn content. In the present study, the optical band gap values for direct transitions of the samples are exist in between 3.628 and 3.829 eV and also in between 3.335 and 3.516 eV for indirect transitions. The Urbach energy values are varying in between 0.304 and 0.340 eV by increasing MnO_2 content in glass compositions. The lowest band gap is observed in glass Mn_5 and the highest band gap is observed in glass Mn_1 for direct, indirect transitions. It is obvious from Table 4 that the least Urbach energy suggests that the glass stability is more in Mn_1 sample compare to remaining glass samples. From the optical absorption data, it is noticed that the absorption band intensity increases with increase in the host glass basicity. This suggests that the ionic character increases with increasing MnO_2 content. Similar observations are reported in earlier literature for borate glasses [48].

A plot is drawn between optical band gap energy and Urbach energy as a function of MnO_2 content and is shown in Fig. 8. From this figure it is noticed that the band gap energy and Urbach energy for these NPAB glasses are existed in opposing manner.

4.5 FT-IR study

FT-IR spectroscopy is recognized to provide insights into the interaction between alkali metal ions and borate glass network. Boron has smallest mass as compared to other network forming elements, thus the major vibrational modes associated with the glass network resolve well above 500 cm^{-1} [49]. From the FT-IR spectra, one can clearly identify three broad and intense absorption bands centered around 1332 , 1050 and 769 cm^{-1} have been observed in Mn_0 sample. However, some shoulders and feeble bands located at 1246 and 697 cm^{-1} are found. The broad band at 1332 cm^{-1} and its shoulder at 1246 cm^{-1} are attributed to symmetric stretching relaxations of B–O bonds of the trigonal BO_3 units, whereas the band at 1050 cm^{-1} is identified due to asymmetric B–O stretching vibrations of BO_4 units [50]. The absorption band found at 769 cm^{-1} is due to B–O–B bending vibrations in the borate network, the feeble band at 697 cm^{-1} is due to B–O–B linkages. Boron is a network forming cation it may occupy the centers of oxygen triangles or tetragonal sites [51]. Besides the borate fundamental groups, this spectra also reveal a group of prominent absorption bands in the near infrared range from 2200 - 3200 cm^{-1} due to hydroxyl or water groups, these bands are persistent in all compositions [52]. However with increase in the content of MnO_2 it is observed that the position of the bands due to BO_3 , BO_4 and B-O-B units are shifted slightly towards the higher frequencies. The shifting of band positions in the IR spectra is observed as the concentration of manganese ions increased.

5. Conclusions

Density values are increased and r_p, r_i values are decreased gradually with the content of MnO_2 . From the powder X-ray diffraction patterns, the prepared glass samples are amorphous in nature. EPR and optical absorption spectral data revealed that the doped Mn(II) ions are occupied at octahedral site symmetry in the host lattice. Increasing values of optical basicity and negative g- shift strongly confirm that Mn(II) – ligand bonds are more ionic in nature. FT-IR spectral analysis confirms the presence of network structural BO_3 , BO_4 and B-O-B groups in all glass systems.

Acknowledgements

The authors are thankful to the **UGC – DST-FIST, New Delhi for sanctioning equipment** to the Department of Physics, Acharya Nagarjuna University to carry out the present research work.

References

- [1] M. Sathish, B. Eraiah Inter. “Synthesis, Characterization and Optical Properties of Niobium Doped Silver-Lead-Borate Glasses”, *J. Engg. Res. and Appl.* **2**, 1264-1270 (2012).
- [2] Y.D. Siva Prasad, A. Veerabhadra Rao, K. Srikanth and K.A. Emmanuel, “Spectroscopic and magnetic properties as probe in the structural study of pbo-zno-b2o3 glass system doped with mnO”, *Rasayan J. chem.* **4**, 358-370 (2011).
- [3] N.C.A. deSousa, M.T. deAraujo , C. Jacinto , M.V.D. Vermelho , N.O. Dantas , C.C. Santos, I. Guedes , “The role of TiO₂ in the B₂O₃–Na₂O–PbO–Al₂O₃ glass system”, *J. Solid State Chem.* **184**, 3062-3065 (2011).
- [4] P. Venkat Reddy, C. Laxmi Kanth, V. Prashanth Kumar, N. Veeraiah, P. Kistaiah, “EPR and optical properties of alkali halo cadmium borate glasses containing vanadium ions”, *J. Non-Cryst. Solids* **351**, 3752-3759 (2005).
- [5] J. Mauro, Glass Laboratory, College of Ceramics, Alfred University. (Private communication through the Internet) (2000).
- [6] M. Yasuoka, K. Hirao, M.E. Brito, S. Kanzaki, “High- Strength and High- Fracture-Toughness Ceramics in the Al₂O₃/LaAl₁₁O₁₈ Systems”, *J. Am. Ceram. Soc.* **78**, 1853-1856 (1995).
- [7] B.K. Jang, T. Kishi, “Fabrication and Microstructure of Al₂O₃ Matrix Composites by In-situ Reaction in the Al₂O₃-La₂O₃ System”, *J. Ceram. Soc. Jpn.* **106**, 739-743 (1998).
- [8] C. Barrera Solano, L. Esquivias, G.L. Messing, “Effect of Preparation Conditions on Phase Formation, Densification, and Microstructure Evolution in La- β- Al₂O₃/Al₂O₃ Composites”, *J. Am. Ceram. Soc.* **82**, 1318-1324 (1999).
- [9] C.K. Narula, J.E. Allison, D.R. Bauer, H.S. Gandhi, “Materials Chemistry Issues Related to Advanced Materials Applications in the Automotive Industry”, *Chem. Mater.* **8**, 984-1003 (1996).

- [10] James F Shackelford, Robert H Doremus, , Ceramic and Glass Materials: Structure, Properties and Processing, Springer, 2008.
- [11] G. Cormier, J.A. Capobianco, A. Monteil, “Molecular dynamics simulation of lead metaphosphate $\text{Pb}(\text{PO}_3)_2$ glass”, *J. Non-Cryst. Solids* 168, 115-124 (1994).
- [12] M.D. Ingram, “Ionic Conductivity in Glasses”, *Phys. Chem. Glasses* 28, 215-234 (1987).
- [13] S. Music, M. Gotic, S. Popovic, K. Furic and V. Mohacek, “Structural-Properties of Lead Vanadate Glasses Containing La^{3+} Or Fe^{3+} Ions”, *J. Mater. Sci.* 29, 1227-1232 (1994).
- [14] B. Vaidhyathan, S. Asokan, K.J. Rao, *J. Mater. Res.* 15, 518-529 (2000).
- [15] M. Ramireddy, G. Nagaraju, N. Veeraiah *Indian J Engg. Mater. Sci.* 13, 426-434 (2006).
- [16] N.J. Kreidl, Recent applications of glass science, *J. Non-Cryst. Solids* 123, 377-384 (1990).
- [17] J.C.Z.Nardi, Characterization of the Li / MnO_2 Multistep Discharge, *J. Electrochem. Soc.* 132, 1787-1791 (1985).
- [18] L. Sanchez, J. Faray, J.P. Pereira – Ramos, L. Hernan, J. Morales, L. Tirado, “Low-temperature mixed spinel oxides as lithium insertion compounds”, *J. Mater. Chem.* 6, 37-39 (1996).
- [19] R. N. Reddy, R.G. Reddy, “Synthesis and electrochemical characterization of amorphous MnO_2 electrochemical capacitor electrode material”, *J. Power Sourc.* 132, 315-320 (2004).
- [20] C-N Xu, K. Miyazaki, T. Watanable, “Humidity sensors using manganese oxides”, *Sens. Actu. B* 46, 87-96 (1998).
- [21] K. J. Kim, Y. R. Park. “Sol–gel growth and structural and optical investigation of manganese-oxide thin films: structural transformation by Zn doping”, *J. Cryst. Growth* 270, 162-167 (2004).
- [22] G. Krishna Kumari, Ch. Rama Krishna, Sk. Muntaz Begum, V. Pushpa Manjari, P.N. Murthy, R.V.S.S.N. Ravikumar, “Mixed alkali effect in Mn^{2+} doped $20\text{ZnO} + x\text{Li}_2\text{O} + (30 - x)\text{K}_2\text{O} + 50\text{B}_2\text{O}_3$ ($5 \leq x \leq 25$) glasses”, *Spectrochim. Acta Part A: Mol. Bio. Spect.* 101, 140-147 (2013).
- [23] S. Sreehari Sastry, S. Vedavyas, B. Rupa Venkateswara Rao, “Influence of Various Glass Compositions on Physical and Spectroscopic Properties of $\text{CaO-Pb}_3\text{O}_4\text{-ZnO-P}_2\text{O}_5$ Glass System”, *Inter. J. Innov. Res. in Sci., Engg. and Tech.* 3(4) (2014).

- [24] Akiyoshi Osaka, Yu-hu Wang, Masanori Kobayashi, Yoshinari Miura, Katsuaki Takahashi, "Packing of atoms in lead halo silicate glasses of low silica content", *J. Non-Cryst. Solids* 105 (1988) 63-68.
- [25] G. Fuxi, *Optical and Spectroscopic Properties of Glasses*, (Springer, Berlin, 1992), p. 62.
- [26] M. Altaf, M.A. Chaudry, M. Zahid, "Study of Optical Band Gap of Zinc-Borate Glasses", *J. Res. Sci.* 14 (2), 253-259 (2003).
- [27] J. Tauc, "Amorphous and Liquid Semiconductor", (plenum, New York, 1974).
- [28] N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd edn., (Oxford University Press, Oxford, 1979), p. 273.
- [29] R.H. Sands, Paramagnetic Resonance Absorption in Glass, *Phys. Rev.* 99, 1222-1226 (1995).
- [30] S. Sindhu, A. Sanghi, A. Agarwal, V.P. Seth, N. Kishor, "Structural, optical, physical and electrical properties of V_2O_5 -SrO- B_2O_3 glasses", *Spectrochim. Acta, Part A.* 64, 196-204 (2006).
- [31] M.A. Hassan, C.A. Hogarth, "A study of the structural, electrical and optical properties of copper tellurium oxide glasses", *J. Mater. Sci.* 23, 2500-2504 (1988).
- [32] Zhiwei Luo, Anxian Lu, "Thermal properties and optical band gap of a novel high UV-transmitting glass", *Opto elec. Adv. Mater. Rap. Com.*, 6, 993-996 (2012), P.
- [33] K. El-Egili, "Infrared studies of Na_2O - B_2O_3 - SiO_2 and Al_2O_3 - Na_2O - B_2O_3 - SiO_2 glasses", *Physica B* 325, 340-348 (2003).
- [34] G.W. Anderson, W.D. Luehrs, "Structural Characterization of and Phase Separation in Vanadate Glasses", *J. Appl. Phys.* 39, 1634-1638 (1968).
- [35] Ch. Srinivasa Rao, V. Ravikumar, T. Srikumar, Y. Gandhi, N. Veeraiah, "The role of coordination and valance states of tungsten ions on some physical properties of Li_2O - Al_2O_3 - ZrO_2 - SiO_2 glass system", *J. Non-Cryst. Solids* 357, 3094-3102 (2011).
- [36] G. Little Flower, G. Sahaya Baskaran, N. Krishna Mohan, N. Veeraiah, "The structural role of tungsten ions in PbO - Sb_2O_3 - As_2O_3 glass-system by means of spectroscopic investigations", *Mater. Chem. Phys.* 100, 211-216 (2006).

- [37] Nattapon Srisittipokakun, Chittra KedKaew, Jakrapong Kaewkhao, Treedej Kittiauchawal, Kheamrutai Thamaphat and Pichet Limsuwan Kasetsart, "Electron Spin Resonance (ESR) and Optical Absorption Spectra of a Manganese Doped Soda-Lime-Silicate Glass System", *J. Nat. Sci.* 43, 360-364 (2009).
- [38] A. S. Rao, B. Sreedher, and J. L. Rao, "Electron paramagnetic resonance and optical absorption spectra of Mn^{2+} ions in alkali zinc borosulphate glasses", *J. Non-Cryst. Solids* 144, 169-174 (1992).
- [39] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, (Clarendon Press, Oxford, (1970).
- [40] H.B. Premkumar, D.V. Sunita, H. Nagabhushana, S.C. Sharma, B.M. Nagabhushana, C. Shivakumara, J.L. Rao, R.P.S. Chakradhar, "Synthesis, characterization, EPR, photo and thermoluminescence properties of $YAlO_3:Ni^{2+}$ nanophosphors", *J. Lumin.* 135, 105-112 (2013).
- [41] J.S. Van Wieringen, "Paramagnetic resonance of divalent manganese incorporated in various lattices", *Discuss. Faraday Soc.* 19, 118-126 (1955).
- [42] V.P. Seth, S. Gupta, A. Jindal, S.K. Gupta, "ESR of vanadyl ions in $Li_2O-BaO-B_2O_3$ glasses," *J. Non-Cryst. Solids* 162, 263-267 (1993).
- [43] J.A. Duffy, M.D. Ingram, *Optical basicity-IV: "Influence of electronegativity on the Lewis basicity and solvent properties of molten oxyanion salts and glasses"*, *Inorg. Nucl. Chem.* 37, 1203-1206 (1975).
- [44] L. Pauling, *The Nature of Chemical Bond*, 3rd edn., (Cornell University press, NewYork, 1960), p. 93.
- [45] G. Lakshminarayana, S. Buddhudu, "Spectral analysis of Mn^{2+} , Co^{2+} and Ni^{2+} : $B_2O_3-ZnO-PbO$ glasses", *Spectrochim. Acta A* 63, 295-304 (2006).
- [46] N.W. Barnett, B.J. Hindson, P. Jones, A.S. Trevor, "Chemically induced phosphorescence from manganese (II) during the oxidation of various compounds by manganese (III), (IV) and (VII) in acidic aqueous solutions", *Anal. Chim. Acta* 451, 181-188 (2002).
- [47] R.P. Sreekanth Chakradhar, B. Yasoda, J.L. Rao, N.O. Gopal, EPR and "Optical Studies of Mn^{2+} ions in $Li_2O-Na_2O-B_2O_3$ Glasses-An Evidence of Mixed Alkali Effect", *J. Non-Cryst. Solids* 353, 2355-2362 (2007).

- [48] A. Murali, J.L. Rao, "Spectroscopic investigations on Cu(II) ions doped in alkali lead borotellurite glasses", *J. Phys. Condens. Matter* 11, 7921-7935 (1999).
- [49] A.J. Karki, S. Feller, H.P. Lim, J. Stark, C. Sanchez, M.J. Shibata, "The Density of Sodium-Borate Glasses Related to Atomic Arrangements", *J. Non-Cryst. Solids* 92, 11-19 (1987).
- [50] C.P.E. Varsamis, E.I. Kamitsos, T. Minami, "Structural investigation of superionic AgI-containing orthoborate glasses", *J. Non-Cryst. Solids* 345&346, 93-98 (2004).
- [51] Y. Cheng, H. Xiao, G. Wenming, G. Weiming, "Structure and crystallization kinetics of $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses", *Thermochim. Acta* 444, 173-178 (2006).
- [52] G. El-Damrawi, K. El-Egili, "Characterization of novel $\text{CeO}_2\text{-B}_2\text{O}_3$ glasses, structure and properties", *Physica B* 299, 180-186 (2001).
- [53] Khalifa F A, Batal H a El & Azooz A "Infrared absorption spectra of gamma irradiated glasses of the system $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ ", *Indian J Pure Appl. Phys.* 36, 314-318 (1998).

Figures

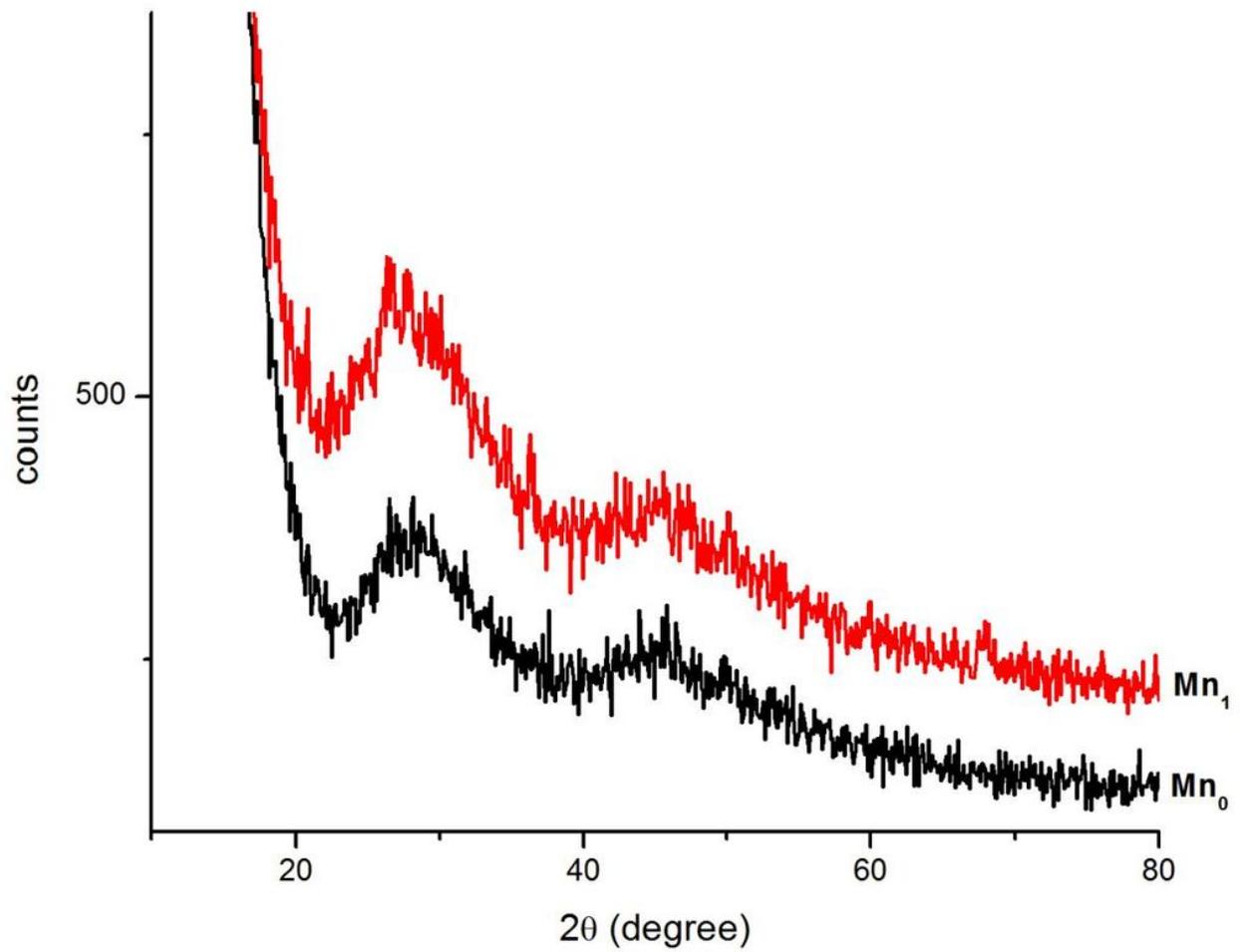


Figure 1

X-ray diffraction patterns of MnO₂ doped NPAB glasses

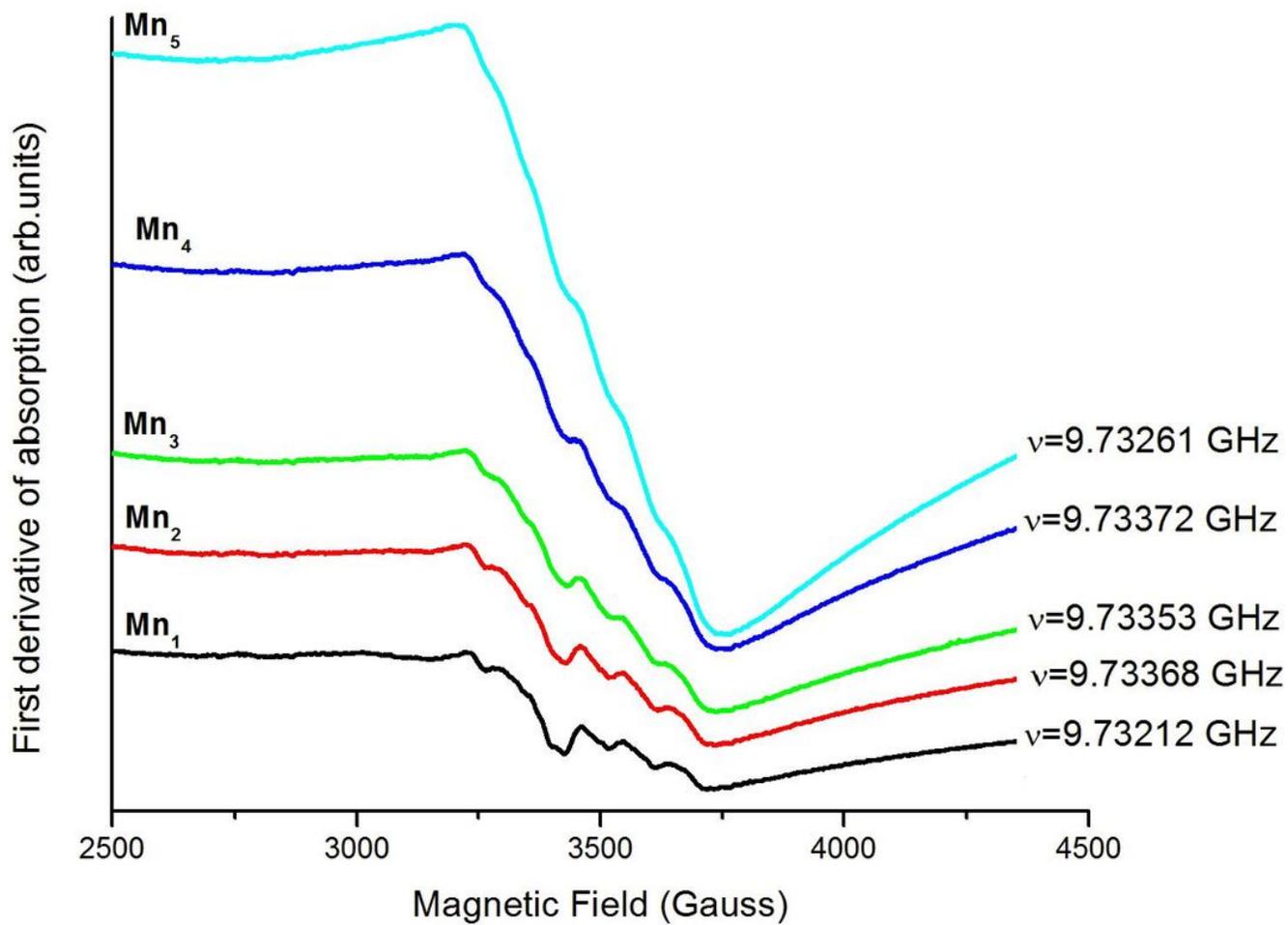


Figure 2

EPR spectra of MnO₂ doped NPAB glasses

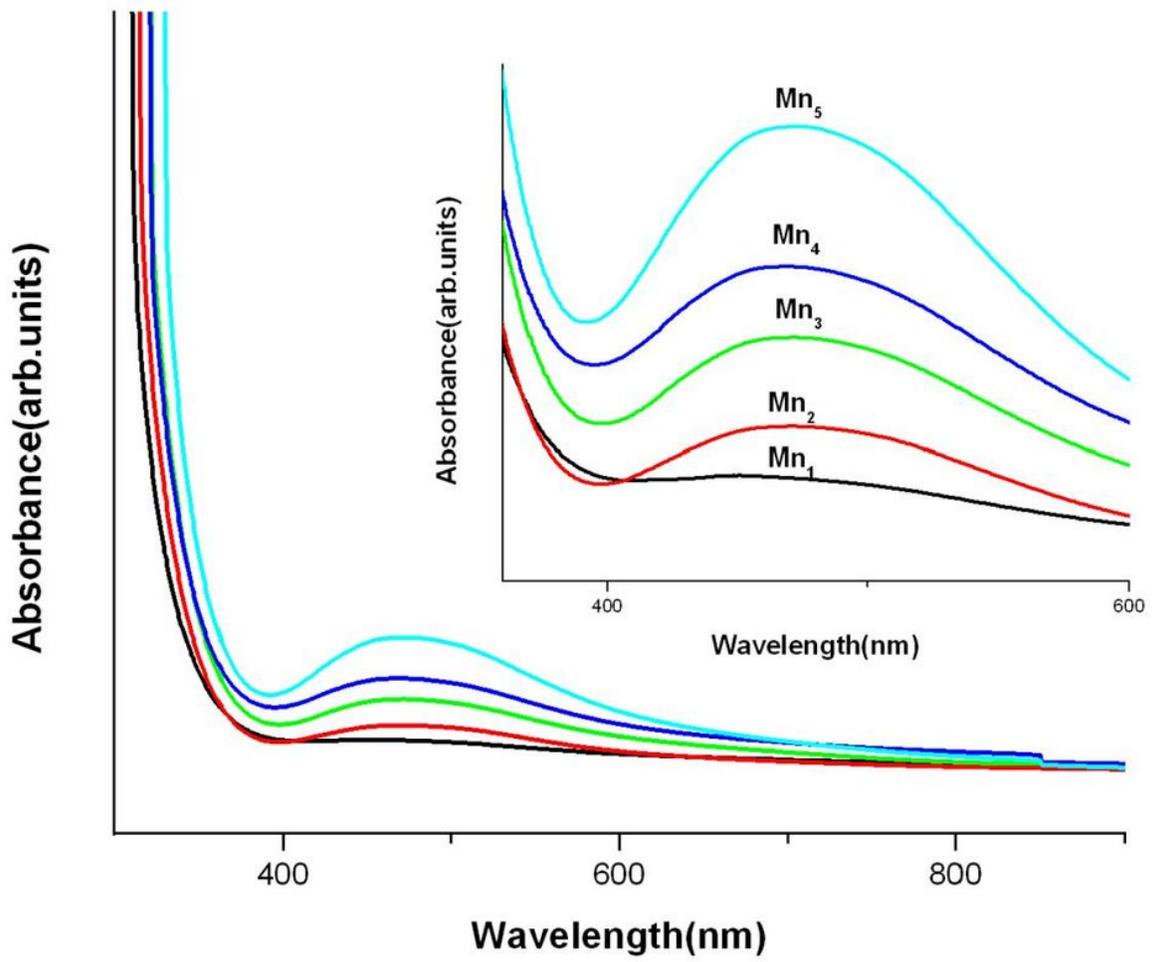


Figure 3

Optical absorption spectra of MnO₂ doped NPAB glasses

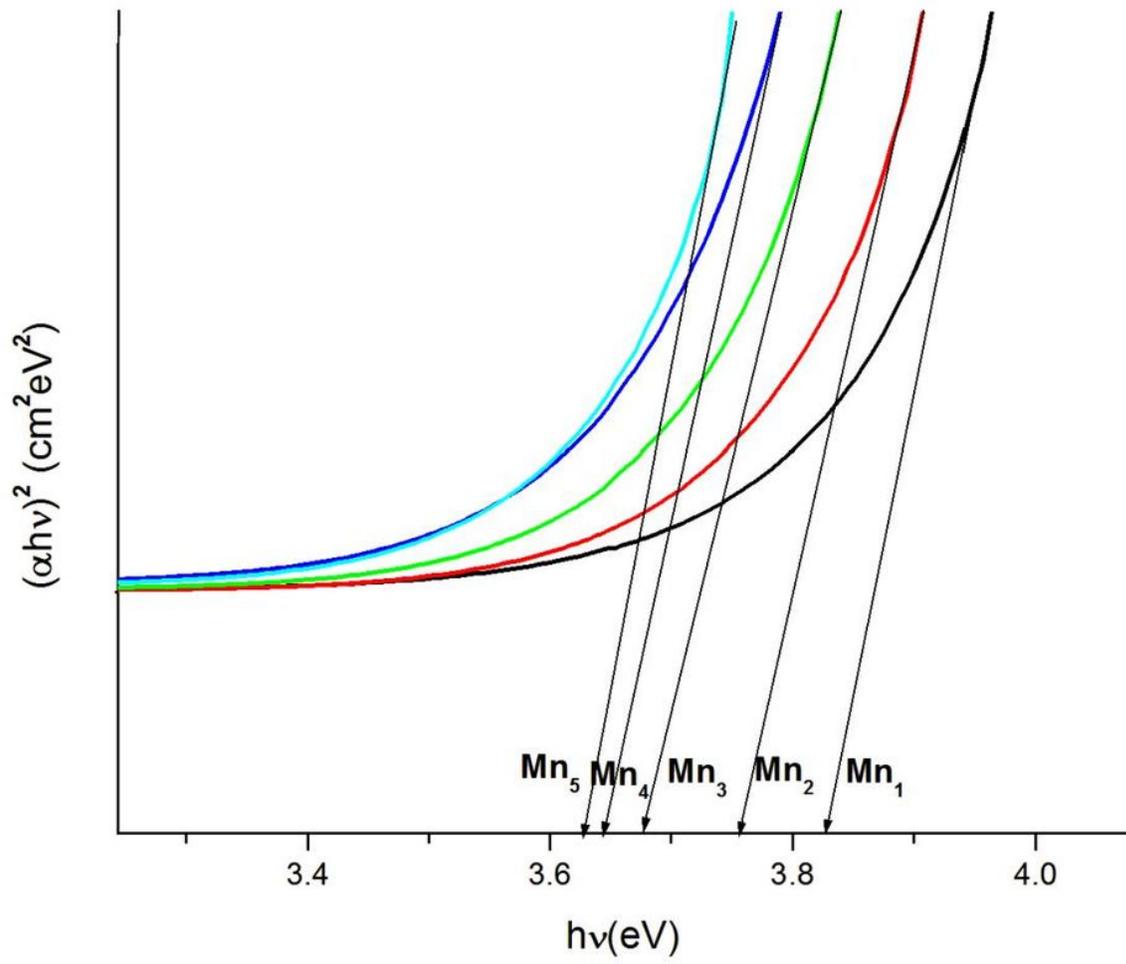


Figure 4

Direct bands of MnO₂doped NPAB glasses

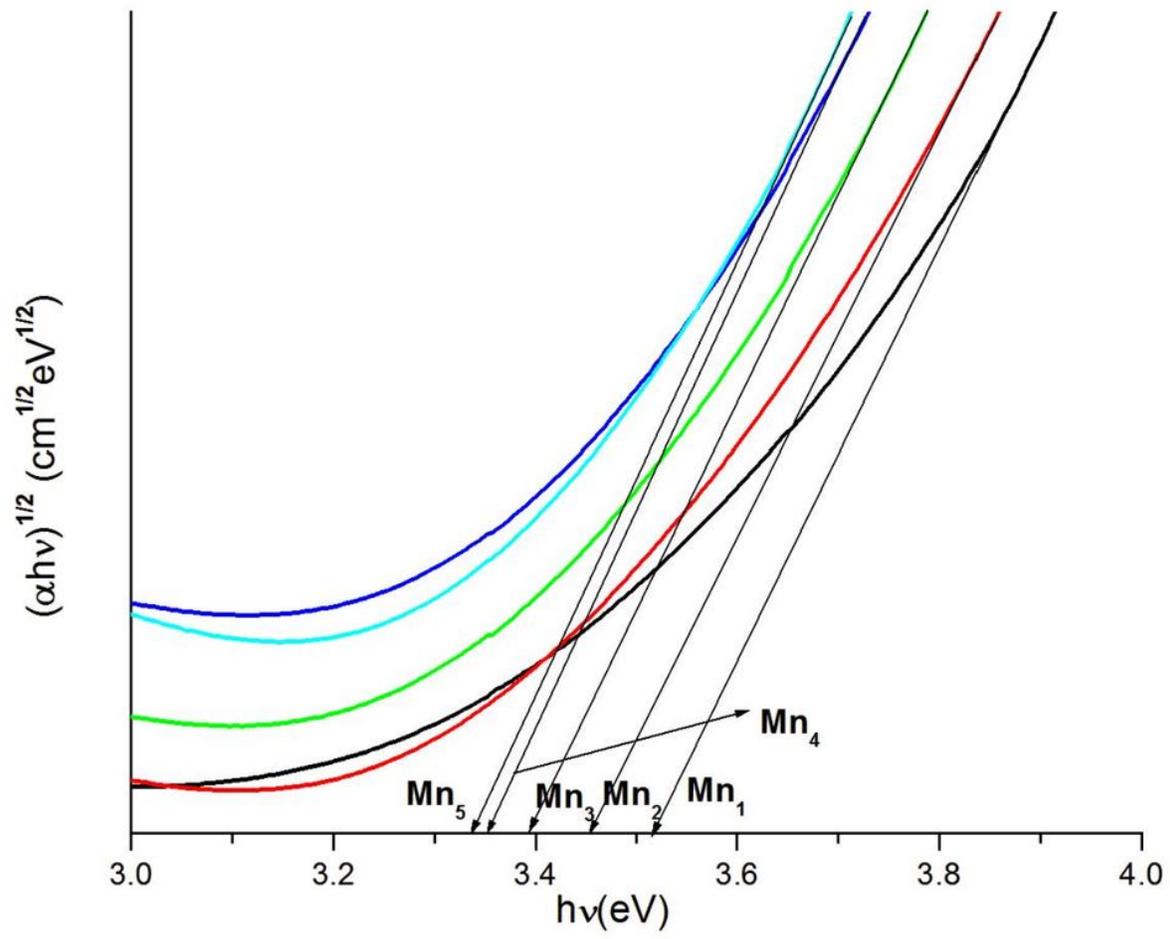


Figure 5

Indirect bands of MnO₂ doped NPAB glasses

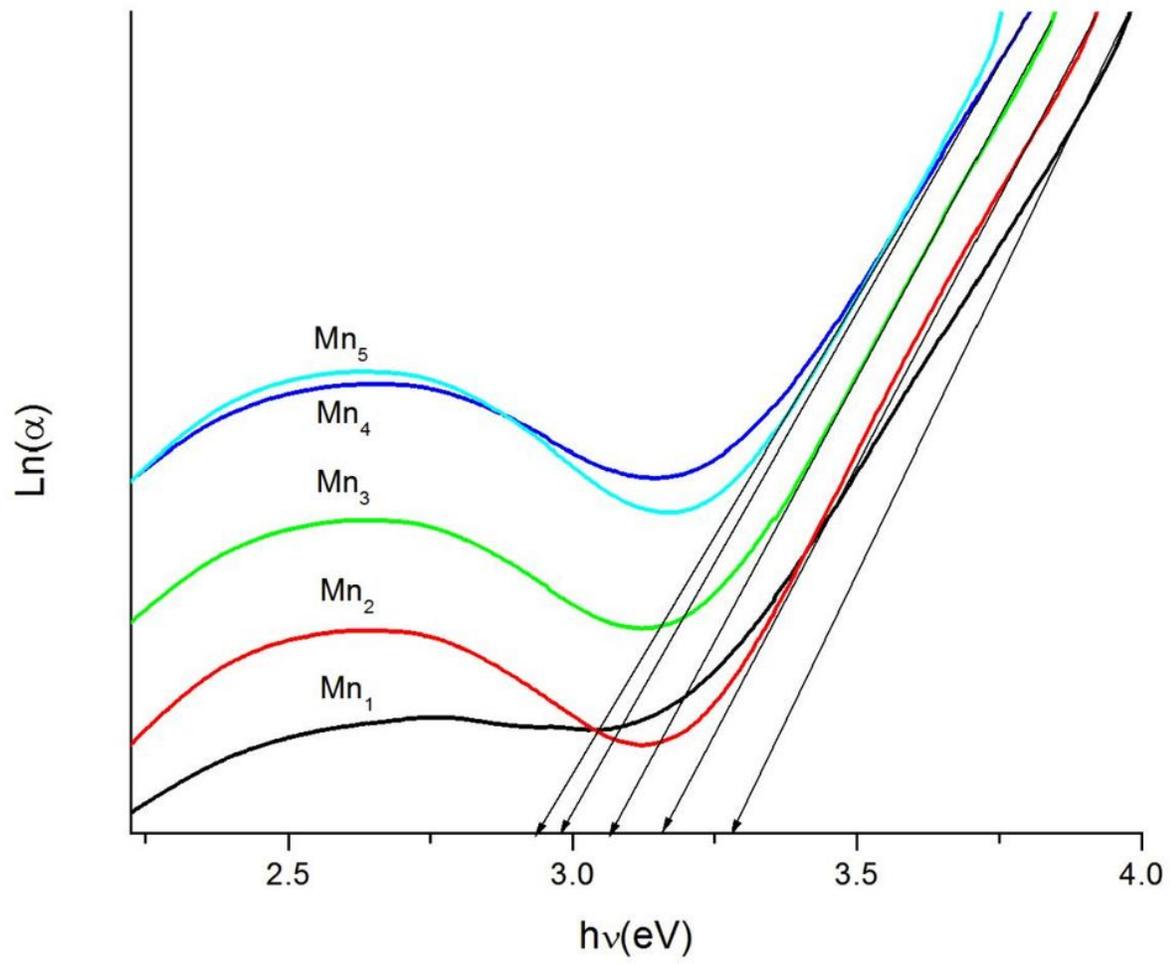


Figure 6

Urbach plots of MnO₂ doped NPAB glasses

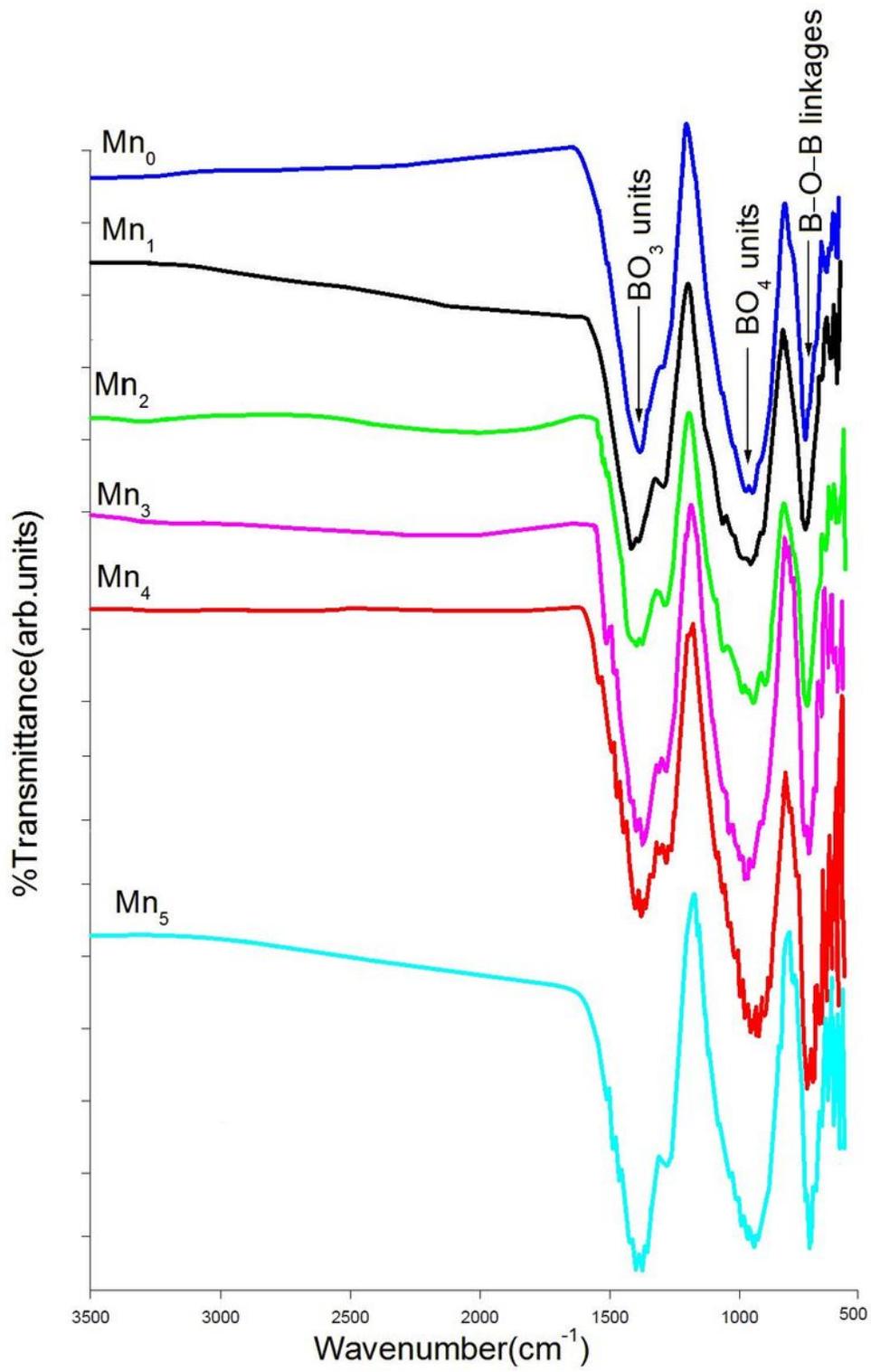


Figure 7

FT-IR spectra of MnO₂ doped NPAB glasses

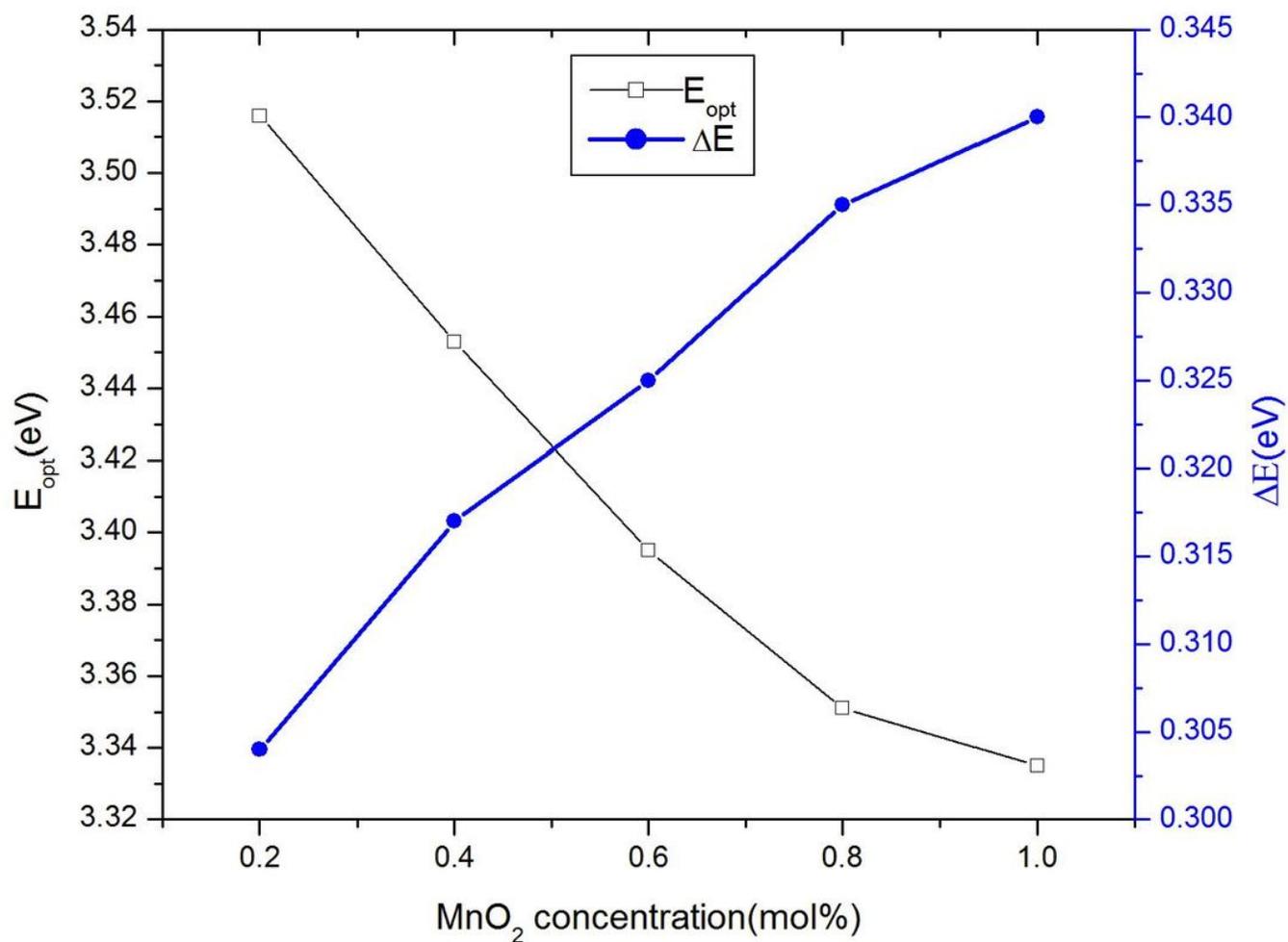


Figure 8

A plot of optical band gap (E_{opt}) and Urbach (ΔE) energies vs concentration of MnO_2 in NPAB glasses

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GRAPHICALABSTRACT.docx](#)