

Spectroscopic Properties of Borate Glasses Doped with a Transition Metal Ion

*K.Sreelatha, ¹C.S.AnandaKumar, ²P.Vijayalakshmi, ³DrS.V.G.V.A. Prasad

* Dept of Physics, Ch. S.D St Theresa's College for women (A), Eluru – 534003, A.P- India

¹ Dept of Physics, SVKP & Dr KS Raju Arts & Science College, Penugonda – 534320, A.P

² Assistant Professor in Physics, Sir CRR College of Engineering, Eluru – A.P – India

³ Dept of Physics, Pithapur Rajah's Government College(A)- Kakinada E.G.Dt, A.P - India

Abstract: Many inorganic glasses have been prepared during last few years to attain certain mechanical, electrical and optical properties. To improve certain physical properties like mechanical strength, electrical resistance, glass transparency, acceptance of transition metal ions in solid state devices, these characteristics are of great importance. Studies on spectroscopic properties like photoluminescence, ESR, optical absorption, infrared spectra have investigated structural aspects of some of these glasses. The valence states of Mn ions and their coordination in the glass network, quantitative analysis of the electrical properties results are very helpful. Electrochemical capacitors, analog devices, fuel cells electro chromic displays, smart windows etc are some of the potential applications of solid state ionic devices. Conductivity of silver iodide mixed glasses with super ionic properties in order to find latest solid state devices.

Keywords: Review on MnO work, Spectroscopic properties - Optical absorption, Electron Spin Resonance, Photoluminescence spectra

Introduction:

Influence of Mn ions on physical properties and electrical properties of various inorganic glass systems like silicate, borate, arsenate, phosphate, tellurite etc. [has been subject of wide investigation in recent years. In glass matrices like Mn that exists in different valence states, Mn³⁺ in borate glasses with octahedral coordination where as in silicate and germanate glasses as Mn²⁺ with both tetrahedral and octahedral environment. Mn²⁺ ions in both tetrahedral and octahedral environment exhibited luminescence emission in the green and red regions respectively in many glass systems. Paramagnetic ion Mn³⁺ ion due to its strong spin-orbit interaction of the 3d orbital has a large magnetic anisotropy and the paramagnetic Mn²⁺ ion because of its zero orbital angular momentum has small anisotropy energy. Depending upon the composition of the glass constituents LiI-AgI-B₂O₃ glasses when doped with multivalent transition metal ions like iron, vanadium and manganese mixed electronic and ionic, pure electronic or pure ionic conduction is anticipated. Quantitative properties of glass modifiers and formers, mobility of the modifier cation, size of the transition metal ions in the glass structure in different environments and in different valence states is characterised depending upon the content of manganese. Electrical properties of the host glass containing highly mobile ions like Ag⁺ and Li⁺ and the connection between the state and the position of the manganese ion is estimated to be more interesting.

Spectroscopic properties viz., optical absorption, ESR and photoluminescence spectra were studied to have some pre-assessment over the valence states of manganese ions and their coordination in the glass network; such information will facilitate the analysis of the results of electrical properties quantitatively.

Brief Review of the previous work on MnO glass systems:

As manganese was introduced, replacing lithium or sodium, it acts as a network modifier and the intensity of the second group of bands increases at the expense of the first group of bands. Liu *et al.*, [1] Novel SnO₂/ MnO co-doped phosphate glasses are prepared and their tunable luminescence properties are presented. Under excitation at 267 nm, all co-doped glasses exhibit an assembly of SnO₂ blue emission at 420 nm and MnO red emission around 600 nm.

Van Die *et al* [2] have also investigated luminescence properties, optical absorption and decay mechanisms of Mn²⁺ ions in germanate glasses; in their studies, the Mn²⁺ emission spectrum was observed to be red shifted to 700 nm.

Wang *et al* [3] have studied Mn²⁺ luminescence in phosphate glasses. Qiang Su *et al* [4] have also investigated the Photo-stimulated longlasting phosphorescence in Mn²⁺ doped zinc borosilicate glasses.

In spite of considerable literature available on manganese ion doped glasses, still there is a lot of scope to explore the influence of manganese ions especially in LiI-AgI-B₂O₃ glass network on dielectric and other physical properties.

Scholz *et al.*, [5] studied the silicate glasses doped with MnO. Small amounts of paramagnetic ions in the glass reduce the relaxation time but do not affect the electrode properties. The best spectra were obtained using 0.1 mol% MnO. Krishna Mohan *et al.*, [6] prepared the PbO-Nb₂O₅-P₂O₅ glasses containing different concentrations of MnO ranging from 0 to 2.5 mol%. A number of studies viz., differential thermal analysis, infrared, optical absorption, luminescence, Raman and ESR spectra, magnetic susceptibility and dielectric properties (constant ϵ' , loss $\tan \delta$, ac conductivity σ_{ac} over a range of frequency and temperature) of these glasses have been carried out. The results have been analysed in the light of different oxidation states of manganese ions.

Venkat Reddy *et al.*, [7] studied the alkali fluoroborate glass systems containing manganese cations and have been thoroughly investigated in order to obtain information about the structural role of manganese in such glass hosts. Liu *et al.*, [8] Novel SnO₂/MnO co-doped phosphate glasses are prepared and their tunable luminescence properties are presented. Under excitation at 267 nm, all co-doped glasses exhibit an assembly of SnO₂ blue emission at 420 nm and MnO red emission around 600 nm.

Ardelean *et al.*, [9] reported the EPR and FT-IR absorption measurements performed on $x \text{ MnO} \cdot (100-x) [\text{B}_2\text{O}_3 \cdot \text{Bi}_2\text{O}_3]$ glasses with $0 \leq x \leq 50$ mol%. The EPR spectra of all investigated samples exhibit resonance signals that are characteristic for the Mn²⁺ ions. Ardelean and Simon *et al.*, [10] studied the the valence states of manganese ions and the interactions involving them in $x \text{ MnO} \cdot (100-x) [\text{Bi}_2\text{O}_3 \cdot \text{PbO} \cdot \text{As}_2\text{O}_3]$ glasses with $0 < x \leq 30$ mol% by means of the temperature dependence of the magnetic susceptibility. Up to $x=5$ mol% of both Mn²⁺ and Mn³⁺ ions are evidenced.

Krishna et al [11] have studied the structural investigations of Mn^{2+} ions in alkali barium borophosphate glasses by EPR and optical absorption techniques. They have observed Mn^{2+} EPR hyperfine sextet centered at $g = 2$ and broad absorption bands in the absorption spectra of Mn^{2+} ions; from these results they have concluded that the symmetry around Mn^{2+} ions is octahedral in the glass network and the nature of the bonding character was dominantly ionic. Bogomolova et al [12] have analyzed EPR spectrum of Mn^{2+} ions in fluorogermanate and fluoride glasses using rhombic spin Hamiltonian (and observed an hyperfine sextet centered at $g = 2$). Jean Michael et al [13] have also performed EPR experiments of Mn^{2+} ions in fluoroaluminate glasses and concluded that the divalent manganese ions occupy octahedral distorted sites. Baiocchi et al [14] have reported optical and magnetic properties of manganese ions in lead silicate glasses; Jethwa et al [15] have studied the possibility of obtaining laser action from Mn^{2+} ions in phosphate glasses. Kashif et al [16] have reported magnetic susceptibility of lithium borosilicate glasses containing manganese ions. Wang et al [17] have studied Mn^{2+} luminescence in phosphate glasses. Lakshmana Rao et al [26] have reported the changes in the ESR and optical absorption spectra of Mn^{2+} ions in Na_2SO_4 - $ZnSO_4$ glasses with the change in concentration. Qiang Su et al [18] have also investigated the Photo-stimulated longlasting phosphorescence in Mn^{2+} doped zinc borosilicate glasses. Stefan and Simon [19] investigated EPR of Mn^{2+} ions doped bismuth borate glasses and structural data obtained from these measurements indicate various sites for Mn^{2+} ions in environments characterized by different crystalline field intensities.

In spite of considerable literature available on manganese ion doped glasses, still there is a lot of scope to explore the influence of manganese ions especially in LiI - AgI - B_2O_3 glass network on dielectric and other physical properties.

The chemical compositions of the samples used for the present study are:

- Mn_0 : 39 LiI -1.0 AgI -60 B_2O_3
- Mn_1 : 38.9 LiI -1.0 AgI -60 B_2O_3 : 0.1 MnO
- Mn_2 : 38.8 LiI -1.0 AgI -60 B_2O_3 : 0.2 MnO
- Mn_4 : 38.6 LiI -1.0 AgI -60 B_2O_3 : 0.4 MnO
- Mn_6 : 38.4 LiI -1.0 AgI -60 B_2O_3 : 0.6 MnO
- Mn_8 : 38.2 LiI -1.0 AgI -60 B_2O_3 : 0.8 MnO

The details of the studies are

- (i) Optical absorption studies in the wavelength range 280-600
- (ii) Electron spin resonance measurements at room temperature
- (iii) Photoluminescence spectra at room temperature

Optical absorption: Study of the absorption spectra of transition metal ions embedded in solids had been extensively used to obtain information about the local symmetry in which the ion sits, its valence state, its site preference and determination of the degree of covalency of the metal-ligand bond. When a transition metal ion is embedded in a glass it need not have a centre of symmetry. This leads to mixing of d- and p- orbitals of the ion and, therefore, an electronic transition involves some charge transfer from a d- to a p- orbital leading to weak absorption bands.

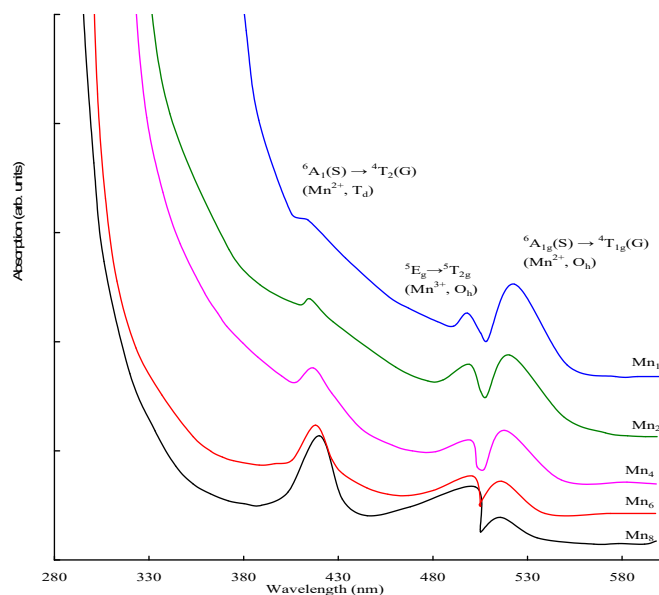


Fig.1 Optical absorption spectra of LiI-AgI-B₂O₃: MnO glasses recorded at room temperature. If an ion is at the center of symmetry, such a mixing does not occur but during the inevitable molecular vibrations make an ion spend part of the time away from the equilibrium position which enables mixing of d- and p-

orbitals and allow such transitions.

Fig. 1 shows the optical absorption spectra of glasses in the wavelength region of 280-600 nm. The absorption edge observed at 381 nm for the glass M₁ is shifted gradually to a lower wavelength with increase in the concentration of MnO. The spectrum of this glass exhibited an intense absorption band at 523 nm corresponding to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ octahedral transition of Mn²⁺ ions; the spectrum also exhibited a weak kink at about 418 nm due to ${}^6A_1(S) \rightarrow {}^4T_2(G)$ tetrahedral transition of Mn²⁺ ions [20].

The observed optical absorption bands are from the Mn²⁺ ion ground state ${}^6A_{1g}$ to some quartet states and these are both spin and parity forbidden. The transitions ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ involves a change of configuration from $(t_{2g})^3(e_g)^2$ to $(t_{2g})^4(e_g)^1$ and is therefore observed to be comparatively broad [21]. Since all the excited states are spin quartet states, no spin allowed transitions would occur for Mn²⁺ ions. Hence, Mn²⁺ ions are characterized by weak bands as observed which arise due to the spin forbidden transitions.

The appearance of a clear broad band in the spectra of the glasses at about 490 nm (due to spin allowed ${}^5E_g \rightarrow {}^5T_{2g}$ transition) indicates that a part of manganese ions exist in Mn³⁺ (d⁴) and occupy octahedral positions [22, 22a].

Electron spin resonance:

Electron spin resonance (ESR) has been developed as an extremely sensitive and important spectroscopy technique, which is widely used to study systems having unpaired electrons. In condensed matter physics, ESR is used as a powerful technique to study the lowest energy levels, hence, the electronic state of the unpaired electrons of paramagnetic species in solids. This technique provides information on understanding of the symmetry of the surroundings of the paramagnetic ion and the nature of its bonding to the nearest diamagnetic neighbours. The ESR technique, basically is the observation of the transitions induced by an electromagnetic radiation of appropriate polarization and energy (frequency) between these Zeeman levels. The energy separation of these levels is typically of the order of 1 cm⁻¹ (microwave frequency range) in atomic and

molecular systems. Thus, a microwave spectrometer is normally required to observe ESR. For ESR signals, the line widths are measured from the maximum and minimum line positions at the first derivative curve. The ESR lines always have a finite width due to electrons interacting magnetically with the environment of the sample. Hence, from the line width and the rate of build up or decay of the line intensity, one can obtain information about spin environment.

The intensity of ESR signals depends on various factors (1) Concentration of the paramagnetic ion (2) the micro wave frequency (3) the power of micro waves (4) the transition probability and (5) the temperature.

The spectra are characterized by six-line hyperfine structure centered at $g \sim 2.005$ and another signal at $g \sim 4.3$. The values of g obtained for Mn^{2+} ions in the present glass system is comparable with that of other systems; for example, $Bi_2O_3 - GeO_2$, lead phosphate, alkali sulphate glasses. The value of g for hyperfine splitting may also give some information about the nature of the bonding with which the manganese ions participate in the glass network. The high is the shift in the g value towards positive side from 2.0023, the bonding is more covalent in nature [23].

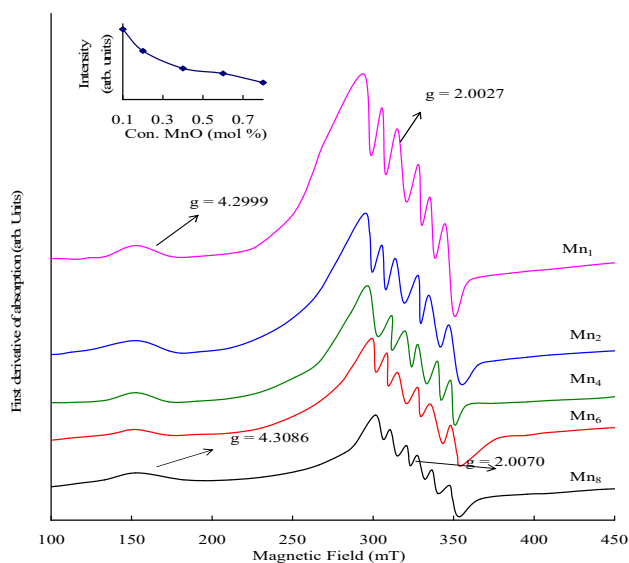
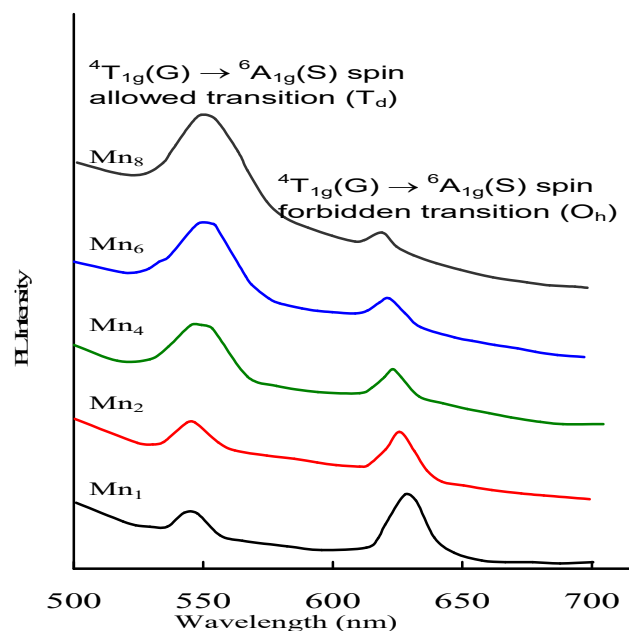


Fig. 2 represents the typical ESR spectra of LiI-AgI- B_2O_3 : MnO glasses.

The close examination of the g values obtained for the present glasses indicates the increasing covalent environment of Mn^{2+} ions with the increase in the concentration of MnO in the glass matrix.

Photoluminescence spectra:

At room temperature for all the samples a Photon Technology International Spectro fluorometer is used for recording the photoluminescence spectra. Several LiI- AgI- B_2O_3 glasses doped with different transition metal oxides are found. In general it is to be pointed out the data have been taken with the several LiI- AgI- B_2O_3 glasses doped with different transition metal oxides are found to be reproducible with in the accuracies mentioned.



Luminescence spectra: At the wavelength corresponding to the absorption edge the fluorescence spectra of LiI–AgI– B₂O₃: MnO glasses is shown in fig.1. At 628 nm and 546nm two emission bands assigned to ⁴G→⁶S transitions [24] are exhibited for the spectrum of glass Mn₁.⁴T_{1g}(G) → ⁶A_{1g}(S) spin forbidden transition is attributed at 628 nm band for octahedrally positioned Mn²⁺ ions.⁴T₁(G) → ⁶A₁(S) spin

Fig.3 Photoluminescence spectra of LiI–AgI–B₂O₃Glasses doped with different concentrations of MnO recorded at room temperature allowed transition is identified for green emission band in tetrahedrally positioned Mn²⁺ ions [26]. With the gradual increase in the concentration of MnO it is observed that the tetrahedral band is observed to increase upto 0.8 mol %, at the expense of octahedral band. From the studies of luminescence in the glass network it is observed that as the concentration of MnO is gradually increased there is a gradual change of Mn²⁺ ions from octahedral to tetrahedral positions. It is observed that the rise of Mn²⁺ ions in tetrahedral occupancy is more than octahedral as the concentration of MnO is increased in the glass network.

The results of spectroscopic properties summarise that in LiI–AgI– B₂O₃ glass network, the manganese ions do exist in both the states Mn²⁺ and Mn³⁺. Silver iodide mixed glass network provide suitable environment to exhibit high luminescence properties for Mn³⁺ ions when compared with Mn²⁺ ions.

Conclusion:

Different concentrations of MnO ranging from 0 to 0.8 mol% for LiI–AgI– B₂O₃ glasses are synthesized. Spectroscopic properties viz., optical absorption, ESR and photoluminescence spectra were studied to have some pre-assessment over the valence states of manganese ions and their coordination in the glass network. Spectroscopic studies indicate that manganese ions do exist in both Mn²⁺ and Mn³⁺ states in LiI–AgI– B₂O₃ glass network. Luminescence spectral studies of LiI–AgI– B₂O₃ glass network indicate that with the increase in the concentration of MnO, there is a gradual transformation of Mn²⁺ ions from octahedral to tetrahedral position. Because of the increase in the content of MnO in the glass network, it is observed that the increasing insulating strength of LiI–AgI– B₂O₃ glass samples increases,

References:

- [1] Y. Liu, J. Ren, C. Shen, Z. Xing, G. Chen, J. Alloys Compd. 509 (2011) 161.
- [2] A. Van Die, A.C.H. ILeenaers, G. Blasse W.F. Van Der Weg, *J.Non-Cryst.Solids* 99(1988) 32.
- [3] I.M. Wang and X. Fan, *J. Chin. Ceram. Soc.* 23 (1995) 61.
- [4] Chengyu LiYingning Yu, Shubing Wang, Qiang Su, *J.Non-Cryst.Solids* 32 (2003)191.
- [5] K. Scholz, B. Thomas, *Solid State Nucl. Magn. Reson.* 4 (1995) 309
- [6] N. KrishnaMohan, M.RamiReddy C.K.Jayasankar N.Veeraiah, *JAlloyCompd.* 458(2008)66
- [7] P. Venkat Reddy, C. Laxmi Kanth, V. Prashanth Kumar, N. Veeraiah, P. Kistaiah, *J. Non- Cryst. Solids* 35(2005) 3752.
- [8] Y. Liu, J. Ren, C. Shen, Z. Xing, G. Chen, J. Alloys Compd. 509 (2011) 161.
- [9] I.Ardelean, Simona Cora, Raluca Ciceo Lucacel, Octavia, *Solid State Sciences* 7(2005)1438.
- [10] I. Ardelean, S. Simon, M. Peteanu, V. Simon, F.Ciorcas, C.Bob, *Mater. Lett.* 9(1999) 42.

- [11] R.M. Krishna, J.J. Andre, J.L. Rao, W.E. Antholine, *Mater. Res. Bull.* 34 (1999) 1521.
- [12] L.D. Bogomolova, N.A. Krasil'nikova, V.V. Mitrofanov, *J. Non-Cryst. Solids* 188(1995) 130.
- [13] D. Jean Michel, J. Videau and J. Portier, *J. Non-Cryst. Solids* 86 (1986) 88.
- [14] E. Baiocchi, A. Montenero, M. Bettinelli, *J. Non-Cryst. Solids* 46 (1981) 203.
- [15] J. Jethwa, F.P. Schafer and R. Reisfeld, *Appl. Phys. B.* 50 (1990) 231.
- [16] I. Kashif, *J. Mater. Sci. Mater. Electron.* 1 (1990) 49.
- [17] I.M. Wang and X. Fan, *J. Chin. Ceram. Soc.* 23 (1995) 61.
- [18] J. L. Rao, B. Sreedhar, S.V.J. Lakshman, *J. Non-Cryst. Solids* 92 (1987) 175.
- [19] Chengyu Li, Yingning Yu, Shubing Wang, Qiang Su *J. Non-Cryst. Solids* 321(2003) 191.
- [20] R. Dummy, *J. Non-Cryst. Solids* 41 (1980) 273. [21
- [21] AV Chandrasekhar, RVSSN Ravikumar, B.J. Reddy, *Phys. Chem Glasses* 43 (2002) 173.
- [22] I. Ardelean, M. Peteanu, I. Todor, *Phys. Chem. Glasses* 43 (2002) 276.
- [22a] A. Mogus-Milankovic, L. Pavic, K. Srilatha, Ch. Srinivasa Rao, T. Srikumar et al *AIP Journal of Applied Physics* 111.013714(2012)(doi: 10.1063/1.3676254)
- [23] T. Sanada, K. Yamamoto, N. Wada, K. Kojima, *Thin Solid Films* 496 (2006) 169.
- [24] K. Srilatha et al / *Journal of Non Crystalline Solids* 357 (2011) 3538 -3547
- [25] C. Li, Y. Yu, S. Wang, Q. Su, *J. Non-Cryst. Solids* 321 (2003) 191.