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Optical and luminescence properties of manganese doped sodium lead alumino borosilicate glass system

K. Vijaya Babu, V. Madhuri, Sandhya Cole*

Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur - 522 510, India

*Corresponding author. Address: Tel.: +91 863 2346383 (Lab.), mobile: +91 9441902295.
E-mail address: sandhya.cole@gmail.com*

Abstract *- Glass system of composition $20Na_2O$-$10PbO$-$(5-x)Al_2O_3$-$40B_2O_3$-$25SiO_2$: $xMnO$ with ranging from 0.3 to 0.9 mol% has been prepared by melt quenching technique. Further, the samples have been characterized by X-ray diffraction technique (XRD). A number of studies have been carried out, viz., Optical absorption and photoluminescence techniques. Glass formation is confirmed by X-ray diffraction spectra. The optical absorption spectra of these glasses has exhibited a predominant broad band peak at about 21,052 cm^{-1} (475 nm) is identified due to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ octahedral transition of Mn^{2+} ion. From the optical absorption spectral data, optical band gap (E_{opt}) and Urbach energy (ΔE) are evaluated. The emission spectra of Mn^{2+}: NPABS glasses have shown single and broad emission band at about 600 nm assigned to electronic transition $^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ displaying red emission upon excitation at 413 nm. Octahedral coordination of Mn^{2+} ions has been estimated from the positions of emission in luminescence spectra. Various physical properties and optical basicity are also evaluated with respect of the concentration of Mn (II) ions.*

Keywords*: Melt quenching method, amorphous glass, XRD, optical and luminescence properties.*

1. INTRODUCTION

Glasses are amorphous material and are transparent in the visible region[1]. The structure of oxide glasses reveals their ionic conductivity and potential usage as solid electrolytes in a variety of electrochemical devices like solid state batteries, fuel cells, chemical sensors and smart windows [2]. Among all the classical network formers, B_2O_3 and SiO_2 are one of the significant glass formers and flux material due to their high phonon energies [3]. The addition of Na_2O reduces the melting temperature and facilitates the homogenization of the glass system, reducing defects and bubbles. Al_2O_3 is an important component of the glass systems. In tetrahedral coordination, it replaces silicon in the glass network. But at larger concentrations, Al_2O_3 can act as both network former and modifier and enhance the glass forming ability, chemical durability and thermal stability. So, Al_2O_3 plays an important role in borosilicate glass system. Lead glasses are widely used for decorative purposes because of their bright brilliance due to high refractive index [4]. Borosilicate glass is widely used in the manufacture of laboratory glassware, pharmaceutical containers, High-power electric bulbs etc. Because of their good heat resistant properties and thermal shock resistance they are used in chemical industry, domestic kitchen cooking utensils (microwave or oven ware). The main ingredients of borosilicate glass are silica (SiO_2-70-80%) and boric acid (7-13%). Oxides of sodium, potassium and aluminium are added to borosilicate composition to get good chemical durability [5, 6]. An addition of small amount of MnO to borosilicate glasses facilitates the enhancement in mechanical, optical, electrical and non-linear optical properties. Mn^{2+} ions have strong bearing on the optical, magnetic and electrical properties of glasses. These ions can exist in different valence states with different co-ordinations in glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination whereas in silicate and germinate glasses as Mn^{2+} with both tetrahedral and octahedral environment [7]. Both Mn^{3+} and Mn^{2+} ions are well known paramagnetic ions. Mn^{2+} ion has half-filled d orbital with d^5 configuration and ^6S as the ground state. For these reasons, the total orbital angular momentum for Mn^{2+} ion is zero. Since the total spin is 5/2, this ion exhibits zero field splitting which is sensitive to the local environment [8]. Mn^{3+} ion has a large magnetic anisotropy due to its strong spin–orbit

interaction of the 3d orbital while Mn^{2+} ion has small anisotropy energy due to its zero orbital angular momentum. The manganese ions may be linked with antimony/borate groups, there by strengthening the glass structure and probably increasing the chemical resistance of the glasses [9]. The objectivity of the present investigation is to have a comprehensive understanding over the local environment of manganese ion in Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2 glass system, by a systematic study of various physical parameters, coupled with spectroscopic (Optical and luminescence properties) investigations.

2. MATERIALS AND METHODS

2.1 Sample preparation

A particular glass composition 20Na_2O-10PbO-(5-x)Al_2O_3-40B_2O_3-25SiO_2: x MnO with x ranging from 0.3 to 0.9 mol% is chosen for the present study. The details of the composition and their corresponding labelling are given below:

M_0: 20Na_2O-10PbO-5.0Al_2O_3-40B_2O_3-25SiO_2: 0MnO
M_1: 20Na_2O-10PbO-4.7Al_2O_3-40B_2O_3-25SiO_2: 0.3MnO
M_2: 20Na_2O-10PbO-4.4Al_2O_3-40B_2O_3-25SiO_2: 0.6MnO
M_3: 20Na_2O-10PbO-4.1Al_2O_3-40B_2O_3-25SiO_2: 0.9MnO

Raw materials of sodium carbonate (Na_2CO_3), lead oxide (PbO), aluminium oxide (Al_2O_3), Boric acid (H_3BO_3), Silicon dioxide (SiO_2) and Manganese oxide (MnO) were taken in appropriate ratios. All the materials of chemicals were of analytical-grade with purity of 99.9 %. All reagents were thoroughly mixed in an agate mortar and melted in a silica crucible in an electric furnace at temperature 1200^0C for 20 min until a bubble free liquid is formed. At the end of the melting process in order to obtain homogeneous and the melts are poured on brass plate and annealed at a temperature 400^0C for 3 h and cooled slowly to release the thermal stress associated with these glasses during the quenching process. The glass matrix is obtained transparent.

2.2 Characterization techniques

The optical absorption spectra were recorded on a JASCO UV-VIS-NIR spectrophotometer (Model V-670) at room temperature in the range 200-1400nm. The X-ray powder diffraction pattern of prepared glass samples were recorded using on XRD-6100 SHIMADZU X-Ray diffract meter in the scanning range of 10-80^0 (2θ) using Cu K_α radiation having a wavelength of 1.5406 Å at room temperature. The photoluminescence spectra (PL) were recorded at room temperature on the fluorescence spectrometer (SPEX Flouorolog-3) using with a 450 W Xe-lamp as the excitation source. By using Archimedes's principle, the density of the glasses was determined to an accuracy of ±0.001 by means of O-xylene (99.99% pure) as the buoyant liquid. The refractive index of the glasses was measured using Abbes Refractometer and mono- bromonaphthalene as the contact layer.

3. RESULTS AND DISCUSSION

3.1 XRD Spectra

From the **Fig. 1** the XRD pattern of all the glass samples shows no sharp Bragg's peak, but only a broad diffuse hump around lower angle region. This is indication of amorphous nature within the resolution limit of XRD instrument [10].

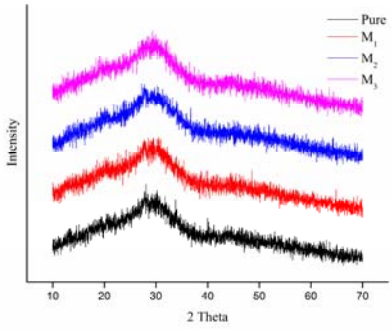

Fig. 1 XRD pattern of MnO doped NPABS glasses

3.2 Physical parameters

The physical properties of prepared glasses are very interesting and provide useful information regarding the structure and transmission mechanism due to transport of ions.

Table 1 Physical parameters of MnO doped NPABS glass system

Parameters	Sample Code			
	Pure	M_1	M_2	M_3
Density (ρ) gcm^{-3}	2.960	2.981	2.989	2.999
Molar volume (V_m) cm^3mol^{-1}	29.854	29.629	29.526	29.411
ion conc. (N_i) $x10^{20}$ions cm^{-3}	-	0.611	1.228	1.858
Ionic radius (r_i) A°	-	25.8	20.4	17.8
Polaron radius (r_p) A°	-	10.236	8.116	7.081

Field strength (F_i) x10^{14} cm^2	-	2.862	4.554	5.983
Refractive index (n_d)	1.653	1.654	1.655	1.656
Optical basicity (Λ_{th})	0.429	0.431	0.432	0.439
Reflection loss (%)	3.195	3.203	3.211	3.219
Molar refractivity	10.928	10.859	10.837	10.809
Dielectric constant	2.732	2.735	2.739	2.742
Electronic polarizbility (x10^{-22})	-	14.355	7.163	4.762

The density of glass is one of the most important properties in manufacturing glass production and it is required for calculating other properties such as refractive index, elastic properties and thermal conductivity. The measured values of density and physical parameters such as dopant ion concentration (Ni), mean separation (r_i), refractive index and optical basicity of these prepared glasses have been evaluated in **Table 1**. The progressive introduction of MnO has caused enhance in the density of the samples, the degree of structural compactness, the modification of geometrical configuration of the glassy network [11].

3.3 Optical absorption spectra

UV-vis spectroscopy is one of the most widely used techniques for structural characterization of glass materials. The absorption spectra of transition metal ions are influenced by the nature of the host matrices into which those ions are accommodated owing to the excitation spectra of 3d electrons. The absorption spectra of transition metal ions are fairly broader and sensitive to the changes in coordination and symmetry. Due to the presence of various oxidation states, each of the states can give increase to different absorption spectra which can be explained by the application of ligand field theory.

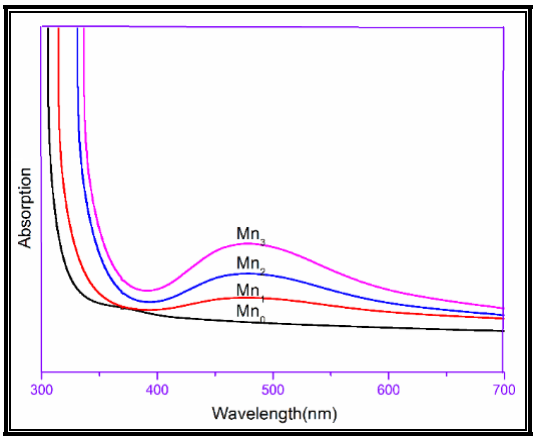

Fig. 2 Optical absorption spectra of NPABS glass doped with different concentration of MnO

Fig. 2 shows, the optical spectra of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2: MnO glasses in the wavelength region 300-700 nm. The absorption edge appeared at 305 nm for pure glass M_0 is shifted slightly towards to higher wavelengths with increasing concentration of MnO. The spectrum of these glasses has exhibited a single broad absorption band at 475 nm corresponding to the transition $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ of Mn^{2+} ions. This band is identified due to the octahedral transition of Mn^{2+} ions [12]. In general, the Mn^{2+} ($3d^5$) complexes with five unpaired electrons are expected to occupy octahedral positions in the glass network. The summary of data on the positions of bands in the optical absorption spectra of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2: MnO glasses are presented in **Table 2.**

Table. 2 Summary of data on optical absorption spectra of NPABS: MnO glass system

Glass samples	M_1	M_2	M_3
Mn^{2+}transitions (nm) $^6A_{1g}(S)\rightarrow{}^4T_{1g}(G)$	475	476.2	478.8
Cut-off wavelength (nm)	314	331	336
Optical band gap E_o (±0.01) (eV)	3.956	3.697	3.753

The fundamental optical band gap of these glasses has been computed based on their optical absorption spectra, for understanding their optically induced transitions. There are two types of transitions, which can occur at the fundamental absorption edge of glass materials. They are direct and indirect transitions. In both cases, electromagnetic waves interact with the electrons in the valence band,

which rise across the fundamental band gap to the conduction band. These photon energies hυ just above the fundamental edge, the absorption α follows the standard relation,

$$\alpha = \frac{A(h\vartheta - E_g)^n}{h\vartheta} \qquad (1)$$

where A is a constant and E_g is the optical band gap energy and the exponent 'n' take the values ½ or 2 for allowed direct or indirect transitions, respectively. To estimate the optical energy band gap values for direct or indirect transitions we have to plot $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^2$ as a function of hυ. The respective values of the band gap energies can be obtained by extrapolating the linear portion of the plot for $(\alpha h\upsilon)^{1/2}=0$ for indirect transition, the optical band for indirect transition values varies from 4.040 - 3.664 eV and $(\alpha h\upsilon)^2=0$ for direct transitions, whose values vary from 4.053 - 3.656 eV. The optical band gap energies decrease with the increase of Manganese ion concentration. Also Urbach energy values increases from 0.249- 0.275 eV with the increase of Manganese ion concentration are shown in Fig's. 4(a), and 4(b). 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 NPABS glasses are given in **Table. 3**.

Table. 3 Optical band gap energies (E_g) and Urbach energies (E_g) of Mn^{2+} ions doped NPABS glasses

Glass Code	Direct band gap E_g(eV)(±0.001)	Indirect band gap E_g(eV)(±0.001)	UrbachEnergy ΔE(eV)(±0.001)
Pure	4.053	4.040	0.249
M_1	3.959	3.911	0.257
M_2	3.722	3.709	0.271
M_3	3.656	3.664	0.275

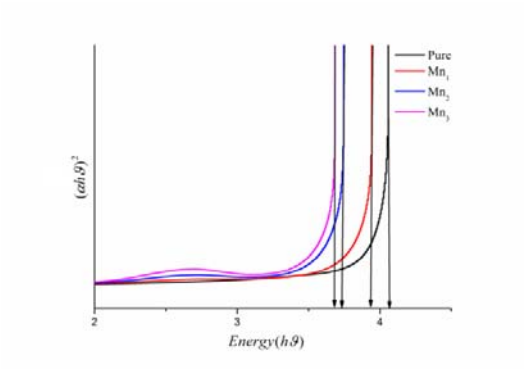

Fig. 4(a)

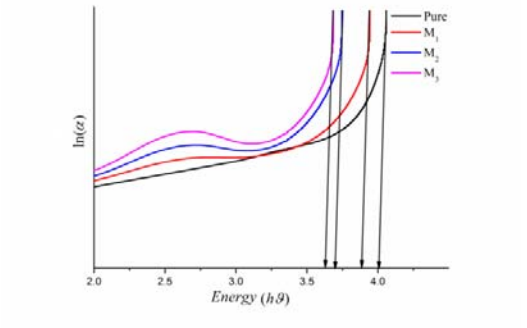

Fig. 4(b)

Fig. 4 (a) Direct plots for evaluation the optical band gap of NPABS: MnO glass, (b) Urbach plots for evaluating band gap of NPABS: MnO glasses.

3.4 Photoluminescence spectra

Luminescence characteristics are very sensitive and complex property mainly depends on the spin and parity forbidden transitions of electronic configuration and also on the local structure of luminescent species which is affected by the surrounding matrix. **Fig. 5** shows emission spectra of sodium lead alumino borosilicate (NPABS) glasses. The excitation spectrum exhibiting a couple of bands at 367 nm and 413 nm assigned to d-d transitions of $^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$ and $^6A_{1g}(S) \rightarrow {}^4T_{1g}(D)$, $^4E_{1g}(G)$. From the excitation spectrum, the band at 413 nm has been chosen to measure emission spectra of MnO: NPABS glasses. Upon exciting at 413 nm, manganese ions in ground are excited to upper excited ligand field status there upon they relax non radiatively from these localized states to $^4T_{1g}(G)$ state through $^4E_{1g}(D)$, $^4T_{2g}(D)$, $(^4E_{1g}, {}^4A_{1g})(G)$ and $^4T_{2g}(G)$ intermediate energy levels and decay radiately to $^6A_{1g}(S)$ state via

phonon emission generating a broad red emission band around 600 nm assigned to a spin forbidden transition of $^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ with a invertion symmetry. The emission spectra of Mn^{2+} doped glasses are broad indicating broad distribution of Mn^{2+} sites and sensitive to change in coordination and symmetry. Generally, the emission color of Mn^{2+} varies depending on its coordination number, ligand field strength and also on the host composition. Mn^{2+} ion in tetrahedral environment exhibits emission in green region while Mn^{2+} ion in octahedral environment shows in the red region. The color intensity coordinates of CIE are mentioned in

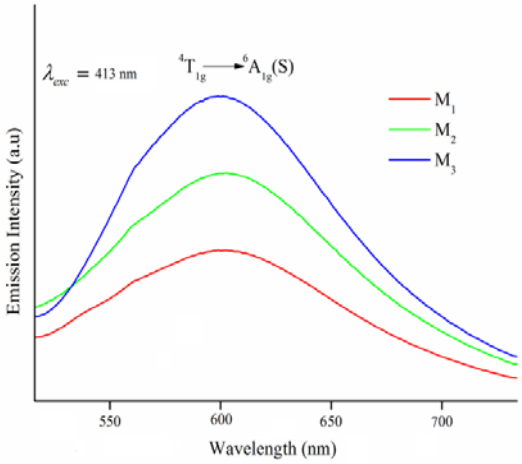

Fig. 5 Emission spectra of MnO doped NPABS glasses

Table. 4 along with CCT values, CIE coordinated also acclaimed that these glasses are suitable for red emission as shown in **Fig 6**. In the present case, spectral position of emission band peaking at 600 nm exhibiting red emission having six coordination number with strong ligand field strengths confirms octahedral site symmetry of Mn^{2+} [13-15].

Table. 4 Glass label, chromaticity coordinates (x, y) and correlated color temperature (CCT) for variousMn^{2+}: glass systems

Glass label	Chromaticity		CCT (K)
	x	y	
$NPABSM_1$	0.4759	0.4477	2770
$NPABSM_2$	0.4749	0.4488	2743
$NPABSM_3$	0.4879	0.4508	2707

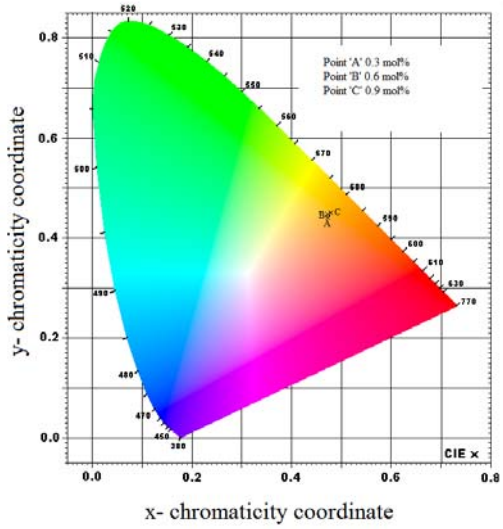

Fig. 6 1931 CIE color chromaticity diagram of the MnO doped NPABS glasses

CONCLUSIONS

The conclusions are drawn from studying various properties of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2 glasses doped with manganese ions are as follows:

Amorphous nature of the samples is confirmed by the broad diffused haloes in XRD pattern. The density and refractive index of the samples are found to increase with increasing concentration. Optical absorption spectra of these glasses exhibit a predominant broad band peak at about 475 nm is identified due to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ octahedral transition of Mn^{2+} ion. MnO doped NPABS glasses have displayed a broad red emission band at 600 nm assigned to a spin forbidden transition of $^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$. The CIE chromaticity color coordinates calculated from emission spectra of NPABSMn glasses show that the glasses emit warm white light. The band position of manganese emission confirms Mn^{2+} state in octahedral position having six coordination numbers with strong crystal field strength. From this observation we have to conclude that the Mn^{2+} ions predominately occupy octahedral positions in this glass network.

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