Spectroscopic features of Mn2+-doped Sodium Lead Alumino Borosilicate Glass System

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Abstract: Glass system of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2 (NPABS) doped MnO have been prepared by melt quenching technique. The prepared samples have been characterized by X-ray diffraction technique (XRD), UV-vis absorption, Electron Paramagnetic Resonance (EPR), Differential thermal analysis (DTA), Fourier transform infrared (FT-IR) spectroscopy techniques. The absorption spectra of these glasses exhibited a predominant broad band peak at 21,052 cm^{-1} (475 nm) is identified due to $^6A_{1g}$ (S) → $^4T_{1g}$ (G) octahedral transition of Mn^{2+} ion. From the absorption spectral data, the band gap (E_{opt}) and Urbach energy (ΔE) are evaluated. The emission spectra of Mn^{2+} doped NPABS glasses have shown single and broad emission band at about 600 nm assigned to electronic transition $^4T_{1g}$(G) → $^6A_{1g}$(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. The FT-IR structural studies have pointed out the existence of conventional structural units of these glasses. Various physical properties and optical basicity are also evaluated.

Keywords* — *Borosilicate glass, XRD, FT-IR, DTA, EPR and optical properties.

I. INTRODUCTION

Borosilicate glasses have wide range of technological applications due to its chemical and thermal resistances in various fields, such as solar energy technology, optoelectronics, sealing glasses, nuclear waste immobilization and also as construction materials. More over these materials have good optical clarity, for this reason they are used as lens in high quality flash lights and astronomical reflecting telescope in micro electrochemical systems [1-9]. Borosilicate glass results from the combination of network-forming oxides B_2O_3 and SiO_2 together with the network modifier oxide Na_2O, intermediate oxides, PbO and Al_2O_3. B_2O_3 increase the glass transparence, SiO_2 is transparent in optical window.

The addition of Na_2O reduces the melting temperature and facilitates the homogenization of the glass system [10-13]. PbO introduced into title glasses which results structural changes by strong influence of the local network due to its several properties such as low melting temperature, high density, high refractive index that improves the chemical durability and enhance the resistance against diversification [14-19]. Al_2O_3 acts as both network former and modifier and enhance the glass forming ability, chemical durability and thermal stability. Electron Paramagnetic Resonance (EPR) can be used to investigate the transition metal (TM) ions doped in different glass systems. This technique gives the characterization of local structure of a paramagnetic center and also the structural changes in the glasses. Studies of EPR and optical properties of transition metal ions in glasses give the information about the chemical and structural environments of the metal ion center. Glasses containing transition metal ions have great interest for their usages as photo-conducting devices, magnetic materials, etc [20]. Among transition metal oxides, Mn^{2+} ion is particularly an important one, because of its optical, magnetic and electrical properties and more number of applications of glasses. Manganese acts as probe of glass structure since it exhibits different valance states from +2 to +7 (Mn^{2+} ($3d^5$), Mn^{3+} ($3d^4$), Mn^{4+} ($3d^3$), Mn^{5+} ($3d^2$)) in different glass systems depending on quantitative properties of glass former and modifiers, ion size in glass matrix, field strength and mobility of the modifier cation. An addition of small amount of manganese (MnO) to borosilicate glasses facilitates the enrichment in mechanical, optical, electrical properties. These ions can exist in different valence states with different coordination in glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination, whereas in germinate and silicate glasses as Mn^{2+} with both tetrahedral and octahedral environment. Both Mn^{3+} and Mn^{2+} ions are well known paramagnetic ions, while Mn^{2+} and Mn^{4+} are luminescent activators [21]. Mn^{2+}ions have 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. The Mn^{3+} ion has a large amount of magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital whereas Mn^{2+} ion has little amount of anisotropy energy due to its zero orbital angular momentum [22, 23]. 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 absorption, EPR, FT-IR and DTA) investigations.

II. MATERIALS AND METHODS

GLASS PREPARATION

Title glasses doped with MnO were prepared, using melt-quenching technique. The content of manganese in the glass composition is varied from 0.3 to 0.9 mol%. The details of chemical compositions chosen for the present study are listed in **Table1**. The AR reagents of raw materials (Na_2CO_3, PbO, Al_2O_3, B_2O_3, SiO_2 and MnO of 99.99 % purity) were powdered and thoroughly mixed in an agate mortar. The mixture was taken in a silica crucible, placed in an automatic temperature controlled furnace at a temperature 1200^0C for 20min and subsequently annealed at 400^0C for 8hrs due to its thermal stress and increase the machanical strength of the material. The prepared samples were optically polished. Final dimensions of the samples used for the present study are 1 cm x 1 cm x 0.1 cm.

Table1 Glass compositions of MnO doped NPABS glass system

Glass code	Na_2O	PbO	Al_2O_3	B_2O_3	SiO_2	MnO
Pure	20	10	5.0	40	25	-
M_1	20	10	4.7	40	25	0.3
M_2	20	10	4.4	40	25	0.6
M_3	20	10	4.1	40	25	0.9

Characterization techniques

The UV-vis 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 diffractometer in the scanning range of $10\text{-}80^0$ (2θ) using Cu K_α radiation having a wavelength of 1.5406 Å at room temperature. The Fourier transform infrared analysis was carried out by preparing glass matrix with KBr using SHIMADZU-IRAffinity-1SFT-IR sectrophotometer in the region of 4000-400 cm^{-1}. The EPR spectra of glass samples were recorded at room temperature on JEOL-JM FE_3 X-band (υ=9.205GHz) EPR spectrometer of 100 KHz field modulation. The magnetic field was scanned between 0 and 500G with a scan speed of 250 G per min and the microwave power used is 5mW. A powder glass specimen of 10 mg was taken in a quartz tube for EPR measurements. Differential thermal analysis was carried out by a Netzsch Simultaneous DTA/TG Thermal Analyzer STA409C with 32 bit controller to determine the glass transition temperature and temperature of devitrification. The samples of each composition weighing 10 mg were heated at a uniform rate of 20^oC/min using platinum crucibles in the temperature range of 30^oC -700^oC. The DTA instrument universal analysis programme was used to determine the average value of glass transition temperature (T_g) and crystallization temperature (T_c) evaluated from the DTA profiles. All the recordings were carried out in an argon (5N) atmosphere to prevent samples from oxidation. The photoluminescence spectra (PL) were recorded at room temperature on the fluorescence spectrometer (SPEX Flouorolog-3) using a 450W 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 Abbe's Refractometer and mono- bromonaphthalene as the contact layer.

Measurements

The density for the glasses was measured by using Archimedes principle with O-xylene as immersion liquid. The weights of the prepared glass samples were measured in air and O-xylene using a 4- digit sensitive microbalance. Then the density (ρ) was determined from the relation

$$\rho = \frac{W_1}{W_1 - W_2} \text{x d} \qquad (1)$$

where ‘w_1’is the weight in air, ‘w_2’ is the weight in O-xylene and ‘d’ is the density of O-xylene

The corresponding molar volume (V_M) was calculated using the relation

$$V_M = \frac{M_T}{\rho} \qquad (2)$$

where M_T is the total molecular weight of the multi-component glass system

The refractive index was measured at λ=589.3 nm on Abbe's Refractometer with monobromonaphthalene as the constant layer between the sample and prism of a refractometer by using sodium vapor lamp as the source and average molecular weight (M), Optical basicity have been evaluated [24-26]. The theoretical values for optical basicity of the glass were estimated using the formula

$$\Lambda_{th} = \sum_{i=1}^{n} \frac{Z_i r_i}{2\gamma_i} \qquad (3)$$

where n is total number of cations present, Z_i for oxidation number of the i^{th} cation, r_i ratio of number of i^{th} cation to the number of oxides present and γ_i basicity moderating parameter of the i^{th} cation. The basicity moderating parameter γ_i was calculated from the following equation

$$\gamma_{i} = 1.36(x_i - 0.26) \qquad (4)$$

where x_i is the Pauling electro negativity of the cation.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) Studies

Fig. 1 the XRD pattern of all title glass samples shows no sharp Bragg’s peak, but only a broad diffuse hump around lower angle (20-40°) region. This is the indication of amorphous nature of prepared glasses [27].

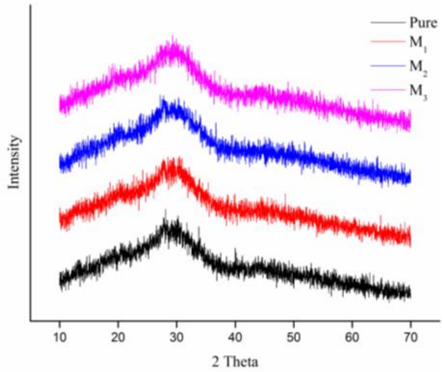

Fig. 1 XRD pattern of MnO doped NPABS glasses

Differential thermal analysis (DTA)

DTA profiles for each composition in the temperature range 400^oC-700^oC are shown in the **Fig. 2**, for the doped glass samples two peaks were ontained, caused by the exothermic events above the glass transition temperature. The presence of two peaks could be due to distinct phase transformations or due to different crystallization mechanisms. DTA traces indicate an inflection due to the glass transition temperature (T_g), in the region 436-455^oC followed by exothermic effect due the crystallization temperature (T_c) between 540-565^oC. The first peak above T_g, is a sign of crystallization T_c. It is observed that there has been some shift in the T_g and T_c values for the transition metal ions (Mn^{2+}) doped glasses. The glass transition temperature (T_g) and the parameter, (T_c-T_g) as a measure of thermal stability of glass against devitrification increase with an increase in the concentration of MnO. Such trend indicates the increase of augmented cross-link density of various structural groups in the glass network. The glass transition temperatures (T_g), exotherms corresponding to crystallization temperature (T_c) of all compositions are shown in the **Fig. 2** and their values are presented in the **Table 2** [28-31].

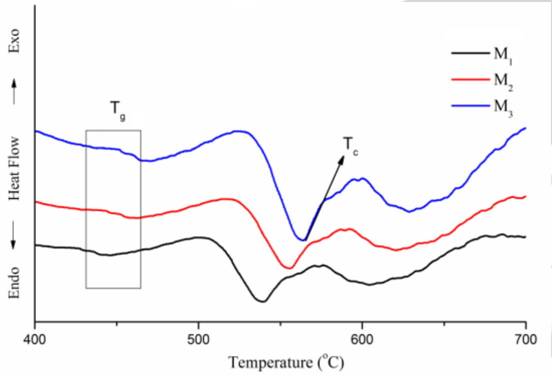

Fig. 2 DTA traces different concentrations of MnO doped NPABS glasses

Table 2 Summary of data on differential thermal analysis (DTA) studies of MnO doped NPABS glass system

Glass code	Glass transition temperature T_g (° C)	Crystallization . Temperature T_c (° C)
M_1	436	540
M_2	447	556
M_3	455	565

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. 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 (N_i), mean separation (r_i), refractive index and optical basicity of these prepared glasses are given in **Table 3**. The progressive introduction of MnO has caused the enhance in density of the samples, the degree of structural compactness, the modification of geometrical configuration of the glassy network [32].

Table 3 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
Molarvolume (V_m) cm^3mol^{-1}	29.854	29.629	29.526	29.411
ionconc. (N_i) x10^{20}ions cm^{-3}	-	0.611	1.228	1.858
Ionic radius (r_i) A^o	-	25.8	20.4	17.8
Polaron radius (r_p) A^o	-	10.236	8.116	7.081

Optical absorption Studies

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. The optical absorption coefficient, α, of a material can be evaluated from the optical transmittance and reflectance using the relation

$$\alpha = \frac{1}{d}\frac{\ln(1-R)}{T} \qquad (5)$$

where d is the thickness of the prepared sample, while the absorption coefficient α(υ) as a function of photon energy (hυ) for direct and indirect optical transitions, according to Pankove [33] is given by

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \qquad (6)$$

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. 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 as shown in **Fig. 3** (a), (b) and (c) [34].

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. **Fig. 4** 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 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 broad absorption band at 480 nm corresponding to the transition $^6A_{1g}$ (S) → $^4T_{1g}$ (G) of Mn^{2+} ions. This band is due to the octahedral transition of Mn^{2+} ions [24, 35]. 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 4.**

Table 4 Summary of data on optical absorption of MnO doped NPABS glass system

Glass sample code	Band position (nm) $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$	Band gap energy (eV)		
		Direct	Indirect	Urbach (ΔE)
Pure	----	4.053	4.040	0.249
M_1	474.5	3.959	3.911	0.257
M_2	476	3.722	3.709	0.271
M_3	477	3.656	3.664	0.275

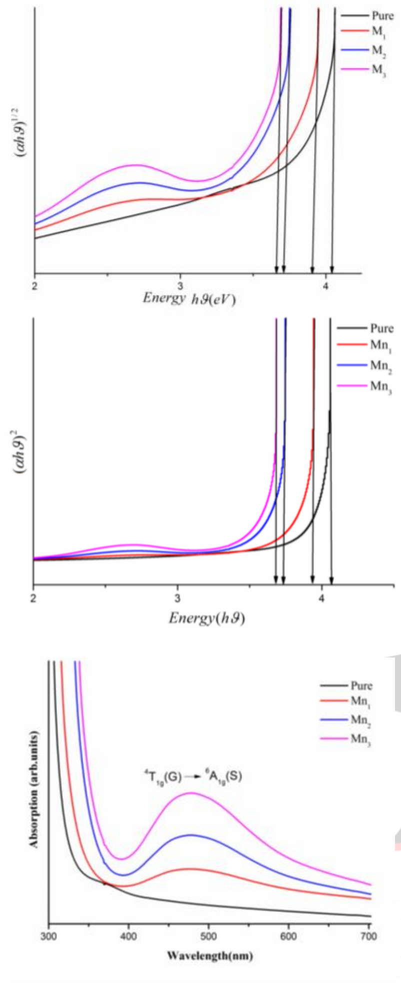

Fig. 3(a) Indirect plots to evaluate optical band gap of MnO doped NPABS glasses, **Fig. 3(b)** Direct plots to evaluate optical band gap of MnO doped NPABS glasses and Fig. 3(c) Optical absorption spectra of MnO doped NPABS glasses.

Electron Paramagnetic Resonance (EPR) Spectra

Fig. 5 represents the typical EPR spectra of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2: MnO glasses. No EPR signal is detected in the spectra of undoped glass, indicating that the chemicals taken in the starting for the preparation of base glass are free from spin probe ions. The EPR spectra of all Mn^{2+} ions doped investigated glasses have exhibited resonance signals around $g \approx 4.3$ at low magnetic field, a shoulder around $g \approx 3.3$ at a medium value of magnetic field and a well resolved hyperfine sextet around $g \approx 2.0$ at high magnetic field, which is a characteristic of Mn^{2+} ions in a close environment to octahedral symmetry, which have entered the glass matrix as paramagnetic species. The spectra of Mn^{2+} ions exhibit a six line hyperfine structure (hfs). The sextet is a result of hyperfine interaction of the electron spin with the ^{55}Mn nucleus (I=5/2). The isotropic signal at $g \approx 2.0$ is assumed to the Mn^{2+} ion in an environment close to octahedral symmetry [36, 37]. The d^5 electronic configuration has a $^6S_{5/2}$ ground state in the free atom and possesses zero orbital angular momentum and hence an EPR signal is expected with 'g' value very close to the free electron value 2.0023. As the Mn^{2+} ion has a half-filled 3d shell, its ground state is consequently ^6S state. Since the total orbital momentum is zero, in the first order there can be no interaction with the crystal fields any higher order interactions must arise from fine structure terms [23, 38, 49].

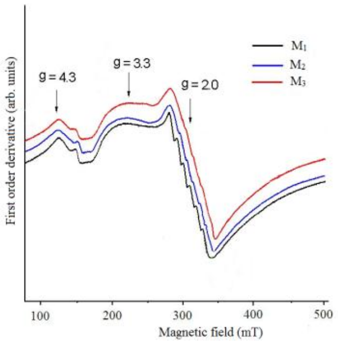

Fig. 5 EPR spectra of MnO doped Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2 glasses

Fourier transformed infrared spectroscopy (FT-IR)

Fourier transmission infrared spectra of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2 glasses recorded at room temperature exhibited different bands due to the vibrations of borate, silicate and aluminium oxide structural units. The FT-IR transmission spectra of undoped and Mn^{2+} doped glasses are presented in **Fig. 6** and the observed bands are assigned to the following structural units. The spectra exhibited prominent bands at around 1375, 1112-960, 720, 480 and 450 cm^{-1}. The band around 1375 cm^{-1} is due to B-O stretching vibration related to $[BO_3]$ groups [40]. One more band at 720 cm^{-1} is observed due to symmetric vibrations of Si-O-Si units and due to the vibrations of AlO_4 structural units. The band at about 711 cm^{-1} is associated with the bending of B-O-B linkage in the borate network [41] .The band around 450 cm^{-1} is due to Si-O-Si bending vibrations, and rocking vibrations of Si-O-Si units. The band having higher intensity is in the range of 1112-960 cm^{-1}, and they are due to anti-symmetry, and those of the lower range are due to symmetric stretching vibrations of Si-O-Si bond of $[SiO_4]$ units. All the samples have a complex group of bands in the range corresponding to the asymmetric and symmetric stretching vibrations of Si-O bonds [42-43]. These phenomena are reflected in to the splitting of the IR band having higher intensity. Another band at 1115 cm^{-1} is assigned due to the combined vibrational modes of asymmetric vibrations of Si-O-Si and BO_4 structural units. The pertinent data related to spectral positions of various bands are furnished in **Table 5.**

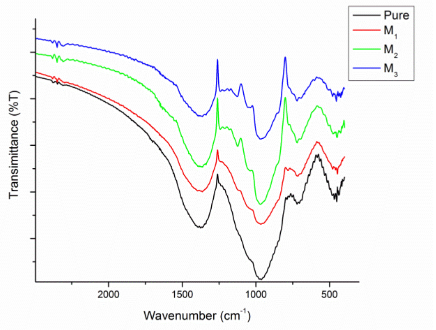

Fig. 6 FT-IR spectra of Na_2O-PbO-Al_2O_3-B_2O_3-SiO_2 glasses

Photoluminescence studies (PL)

Fig. 7 shows emission spectra of (NPABS) glasses. The excitation spectrum exhibiting a couple of bands at 367 nm and 413 nm is 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 this 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 ligand field status there upon they relax non radiatively from these localised 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 inversion 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+} 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 is in the red region. 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 the octahedral site symmetry of Mn^{2+} [23, 31, 44-46].

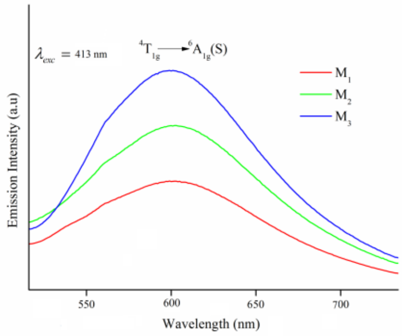

Fig. 7 Emission spectra of MnO doped NPABS glasses

Table 3 FT-IR spectral data of MnO doped Na_2O-PbO-l_2O_3-B_2O_3-SiO_2 glasses

Pure	M_1	M_2	M_3	Assignment
1371	1375	1377	1377	B-O bonds stretching vibration in BO_3 triagles (cm^{-1})
1112	1115	1118	1122	B-O bonds stretching vibration in BO_4 units (cm^{-1})
970	958	960	964	Combined vibrational modes of asymmetric stretching vibrations of Si-O-Si groups and BO_4 structural unnits (cm^{-1})
783	721	723	719	symmetric vibrations of Si-O-Si and AlO_4 structural units (cm^{-1})
476	480	480	466	Octahedral structural units of Mn-O (cm^{-1})
440	448	448	450	Bending and rocking motions of Si-O-Si units

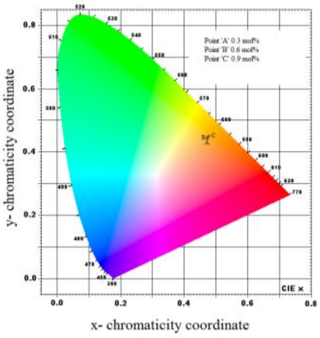

Fig. 8 1931 CIE color chromaticity diagram of the Mn^{2+} doped NPABS glasses

Fig. 8 shows CIE diagram of MnO doped in sodium lead alumino borosilicate glasses. In order to inspect the quality of light, colour correlated temperature (CCT) values have been calculated from colour coordinates using McCamy empirical formula [47]:

$$CCT = - 437n^3 + 3601n^2 - 6861n + 5514.31$$

where $n = (x - x_e)/(y - y_e)$ and the chromaticity epicentre is at $x_e = 0.3320$ and $y_e = 0.1858$, (x, y) are the calculated coordinates of prepared samples. The evaluated CIE coordinates are denoted as (x = 0.4759, y = 0.4477), (x = 0.4749, y = 0.4488) and (x = 0.4879, y = 0.4508) respectively. CCTs of MnO doped NPABS glasses range between 2770-2707 K respectively. Generally, CCT value greater than 5000 K indicates the cold white light used for commercial lighting purpose and less than 5000 K indicates the warm white light used for home appliances [48-50]. The color intensity coordinates of CIE are mentioned in **Table 6** along with CCT values, CIE coordinates also acclaim that these glasses are suitable for red emission. Hence, MnO doped NPABS glasses emits a near warm white light emission.

Table 6 Glass label, chromaticity coordinates (x, y) and correlated color temperature (CCT) for various Mn^{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

IV. CONCLUSION

The conclusion 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. The EPR spectra of these glass samples exhibit a resonance signal with effective g value at g = 2.0 with six line hyperfine structures (hfs) and resolved hfs that indicates distorted octahedral site symmetry of the paramagnetic Mn^{2+} ions. The FT-IR spectra of the present glasses reveal the presence of Mn^{2+} ions in the form of network modifier. Optical absorption spectra of these glasses exhibits 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 Mn^{2+} doped NPABS 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 it is concluded that the Mn^{2+} ions predominately occupy octahedral positions in this glass network.

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