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Structural Study of PbO-PbF_2-B_2O_3 glass system doped with MnO through Spectroscopic and Magnetic Properties

P. Bhavani[1], T.V. Nagalakshmi[2] A.W. Iqbal[3] and K.A. Emmanuel[4*]

1. Department of Chemistry, SRKR Engineering College, Bhimavaram-534 204, A.P., India.
2. Department of Chemistry, PPD College of Engineering, Nunna -520 008, A.P., India.
3. Department of Physics, S V P College of Engineering, Visakhapatnam-530 001, A.P., India.
4. Department of Chemistry, Sir C R Reddy Autonomous College, Eluru-534 007, A.P., India.

Email: kaekola@gmail.com

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ABSTRACT

Borate glasses (PbO-PbF_2-B_2O_3) doped with varying concentrations of MnO have been prepared by quenching and annealing techniques. These glasses are categorized by XRD, SEM and differential thermal analysis. The analysis of these studies has been done in the light of different oxidation states of Mn ion with air of the data on IR optical absorption and magnetic susceptibility measurements. It shows that Mn ion chiefly exists in Mn^{2+} state occupying tetrahedral positions. In the state of Mn^{3+} state at 0.1 and 0.2 mol% concentrations they occupy octahedral positions when MnO is present at 0.3 mol% concentration the stability of the glass is improved. The Mn ions enter into the glass matrix as Mn^{2+} state only and occupy tetrahedral positions. The presence of MnO at 0.3 mol% in the glass system (i) makes Hruby's parameter have a very good value of 0.53 and (ii) the value of magnetic moment (evaluated from magnetic susceptibility) has been raised to maximum value of 5.7 μβ. These results prove that, at 0.3mol% conc. Mn ions exist mainly in divalent state and occupy tetrahedral sites in the glass network.

Keywords: Glasses, Optical absorption, IR spectra and Magnetic Susceptibility.

INTRODUCTION

Borate glasses (PbO-PbF_2-B_2O_3) have widely been studied for their technological applications. B_2O_3 is a white glassy solid. It is almost always in the vitreous form. It is considered to have the highest glass formation tendency, since molten B_2O_3 does not crystallize by itself even at the lowest rate of cooling. It is one of the most difficult compounds known to crystallize. Even then it can be crystallized after extensive annealing. B_2O_3 is glass forming oxide and PbO is a conditional (insufficient) glass former. These two compounds (PbO, B_2O_3) in the glass matrix, help in achieving, moisture resistant, stable transparent glass with a low rate of crystallization. This is possible because of the double role played by PbO as a glass former and also a modifier[1]. PbF_2 in such glass networks, substantially changes their different properties. PbF_2 is highly ionic, so fluoride ions enter in to the glass network at various positions and form a stable glass. The properties of leadfluoroborate glasses with iron, and chromium as dopents were studied [2]. They showed that the system is very good for all applications of lead borate glasses and accept transitional metal ions at various concentrations. Borate glasses have good physical and chemical stability. These

glasses are extensively used in optoelectronic devices, since they are large transmission windows from 400 nm to 8 µm. These glasses have high refractive index of nearly 2.2. Lead oxy fluoro borate glasses can be manufactured over a wide range of compositions with PbO varying from 30-80%. Moreover these glasses, like any other heavy metal oxide based glasses, have the capacity to accept the transitional metal ions like Mn, both in network forming and modifying positions. A lot of literature available on the recent extensive studies. They include Glass transition temperature, ESR spectra, EXAFS and XANES on PbO-PbF_2 glasses containing different transition metal ions. These recent studies have shown that distorted octahedral structural units like PbO_2F_4 are formed in these glasses [3-7].
Transition metal ions are incorporated into these glasses in order to define their optical behaviors. Glasses containing transition metal ions have become the subject of interest owing to their potential applications[8-10]. Among the transition metal ions, Mn^{2+} is a typical luminescent ion with good potential applications[11-18]. Substantial number of investigations on the role of manganese ions on the physical properties of a variety of glass systems like phosphate, arsenate, borate, silicates etc. has also been reported by many researchers in recent years[19-23]. Manganese ions exist in different valence states with different coordinations in glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination where as $Mn^{2+}$with both tetrahedral and octahedral environment[24]. The content of manganese in different coordinations in different valence states exist in the glass depends upon the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Both Mn^{3+} and Mn^{2+} ions are well known paramagnetic ions. Further, it is also quite likely for manganese ions to have link with borate groups, thereby strengthen the glass structure and may raise the chemical resistance of the glass. The purpose of the present investigation is to understand the local environment of manganese ions in PbO-PbF_2–B_2O_3 glass network and their influence on the stability of glass.

MATERIALS AND METHODS

Six samples of glasses are prepared for the present study, with the combination of chemicals in mol% as shown here under. All the samples of glasses are prepared with an increasing concentration of MnO.

M_0: 40 PbO-10 PbF_2-50 B_2O_3
M_1: 40 PbO-10 PbF_2-49.9 B_2O_3: 0.1 MnO
M_2: 40 PbO-10 PbF_2-49.8 B_2O_3: 0.2MnO
M_3: 40 PbO-10 PbF_2-49.7 B_2O_3: 0.3 MnO
M_4: 40 PbO-10 PbF_2-49.6 B_2O_3: 0.4 MnO
M_5: 40 PbO-10 PbF_2-49.5 B_2O_3: 0.5 MnO

Correct quantity (all in mol %) of reagent grade PbF_2, PbO, H_3BO_3 and MnO powders, thoroughly ground and mixed (in a agate mortar) and melted in a platinum crucible at 950-1000^{0}C temp. range, in a PID temp. controlled furnace for about 1hr. until a bubble free transparent liquid is formed .The resultant liquid was then poured into a brass mould and later annealed at 300^{0}C. The amorphous state of glasses was confirmed with the help of x-ray diffraction and scanning electron microscopy studies.
The differential thermal analysis on the samples under study was done using STA 409C, Model DTA-TG with a programmed heating rate of 10^{0}C min^{-1} in the temperature range of 30-1000^{0}C.
Then the samples were ground and optically polished. By using the standard principle of Archimedes, with the 99.99% pure O-xylene on the buoyant liquid, the density (d) of these glasses was estimated to 0.001 accuracy.
KBr pellet method was used to record the IR spectra of the glasses. 2mg of glass powders were mixed with anhydrous KBr powder of 150mg and were pressed into pellets at 2000 kg cm^{-2}. The spectra were recorded using an FT-IR digital Excalibur 3000 spectrometer with a resolution of 0.1cm^{-1} in the range of 400-2000 cm^{-1}.
Shimadzu UV-VIS-NIR spectrophotometer was used to record the optical absorption of these glasses at the room temperature in 350-650 nm range of wave length up to a resolution of 0.1 nm.

Fine powders of these glasses were used to measure their magnetic susceptibility at room temperature by Gouy's method.

RESULTS AND DISCUSSION

The samples thus prepared were amorphous in nature. This is indicated by visual examination, the absence of peaks in the x-ray diffraction pattern (fig.1), from the morphological study through SEM photographs (fig.2), and the existence of glass transition temperature T_g and crystalline temperature T_c, and melting temperature T_m in the DTA traces (fig.3). From the measured values of density d and calculated average molecular weight $\overline{M}$, various physical parameters such as manganese ion concentration Ni and mean manganese ion separation Ri of these glasses are evaluated[25] and presented in table-1. The thermal analysis of all the glasses under study was shown in fig.3. The curves show an endothermic effect due to the glass transition temperature T_g in all samples. Further at higher temperatures an exothermic peak T_c due to the crystal growth and an endothermic effect, due to the melting effect T_m were also detected. Table 2 shows the values of T_g, T_c and T_m obtained for all glasses. The good homogeneity of all the glass samples prepared is proved by the appearance of single peak due to the glass transition temperature in DTA pattern of all the glasses.

In glasses doped MnO, the quantity (T_c- T_g) which is proportional to glass forming ability, is found to increase. The quantity (T_m-T_c), which is inversely proportional to glass forming ability, is found to decrease (Table2). With the increase in the content of MnO up to 0.3 mol%. From the measured values of T_g, T_c, T_m, the parameters (T_c-T_g), (T_m-T_c) and Hruby's parameter (the glass forming parameter) K_{gl}=(T_c-T_g)/T_m-T_c)are calculated and shown in Table 2. The variation in the parameter (T_c-T_g)/(T_m-T_c) with the variation of concentration of MnO, shows the maximum value for glass M_3 (Table 2) shows its highest glass forming ability among all the glasses under study.

The Infrared transmission spectra of pure Pbo-PbF_2-B_2O_3 glasses have revealed two main groups of bands in the regions of (i) 1300-1400cm^{-1} (ii) 1100-1200cm^{-1} (iii) at about 712cm^{-1}. These bands are identified due to (i) the stretching relaxation of B-O bond of the trigonal BO_3 units (ii) the vibrations of BO_4 structural units and due to the bending vibration of B-O-B linkages respectively[2,8,26,27]. A band is also seen in the spectra of all glasses at about 485 cm^{-1}[28,29] due to PbO_4 structural units.

With the introduction of MnO up to 0.3 mol % into the glass network, the intensity of second group of bands (bands due to BO_4 units) is observed to increase with a shifting of meta-center towards slightly lower wave number , whereas, the intensity of the first group of bands (bands due to the BO_3 structural units) is observed to decrease. For further increase of MnO, the intensity of the first group of bands is observed to increase at the expense of second group of bands. The wave numbers corresponding to these groups are presented in table 3.

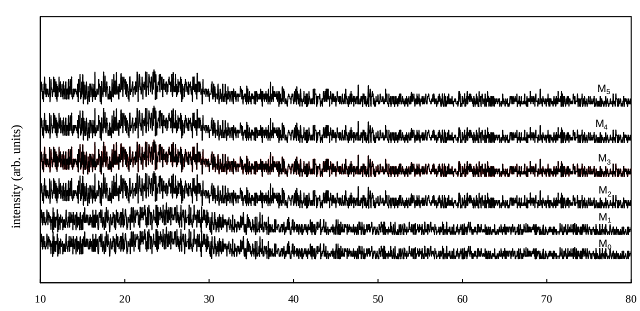

Fig.1. X-Ray diffraction pattern of PbO-PbF_2 -B_2O_3 glasses doped with MnO

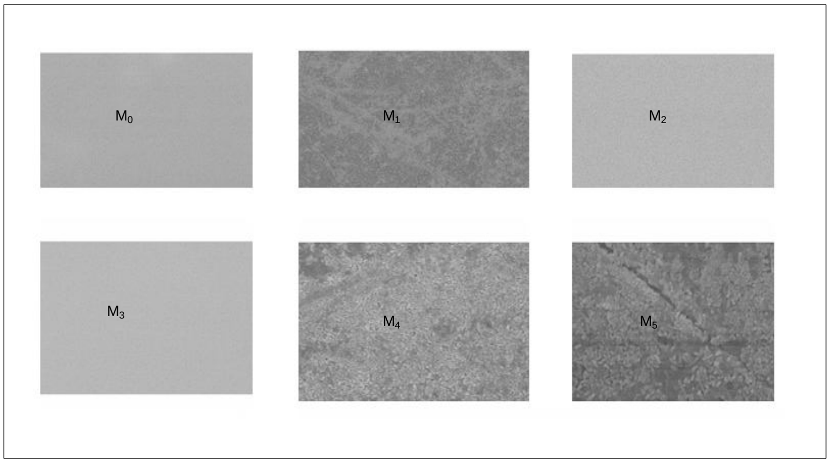

Fig.2: Scanning Electron Microgram of PbO-PbF_2-B_2O_3: MnO

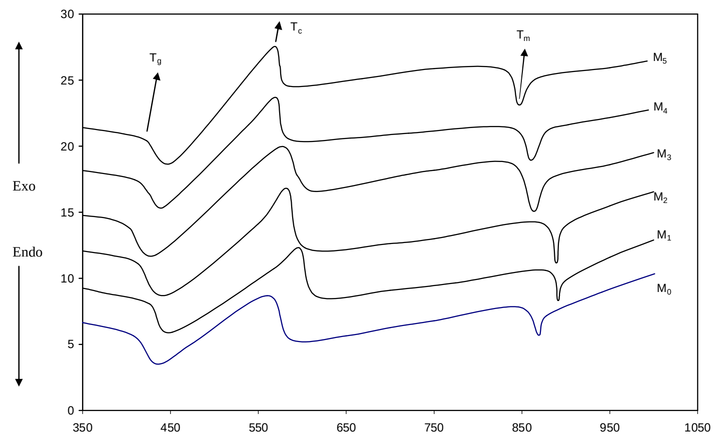

Fig.3. Differential Thermal Analysis patterns of PbO-PbF_2-B_2O_3: MnO glasses

Table 1. Summary of data on various physical parameters of PbO- PbF_2 -B_2O_3: MnO glasses

Property	M_0	M_1	M_2	M_3	M_4	M_5
Density d (g/cm^3)	4.514	4.728	4.795	4.913	4.936	5.068
Avg. mol. wt. $\overline{M}$	148.59	148.601	148.602	148.603	148.604	148.606
Manganese ion conc. N_i (10^{21} ions/ cm^3)	----	1.92	3.89	5.9	8.0	10.3
Inter ionic distance of manganese ions R_i (Å)	----	8.05	6.36	5.53	5.0	4.6
Field Strength F_i (10^{15} cm^{-2})	----	1.9	3.05	4.02	4.93	5.82
Polaron Radius r_p (Å)	----	3.24	2.56	2.23	2.01	1.85

Fig.5 shows the optical absorption spectra of $PbO-PbF_2-B_2O_3$: MnO glasses recorded in the wave length region of 350-650 nm. The absorption edge of glass Mn observed at 396.7 nm was seen to shift to 380 nm. when MnO (0.3 mol%) was introduced. Further increase in the concentration of MnO, makes the absorption edge gradually shift towards higher wavelength. The spectra of glasses M_1, M_2, M_3 and M_4 have shown the absorption bands at 403, 420 and 510 nm due to Mn^{2+} transitions and a broad band at 493 nm due to Mn^{3+} ions is observed in the spectra of M_4 and M_5. With increase in the concentration of MnO beyond 0.3 mol %, the bands due to Mn^{2+} ions have been observed to fade away slowly where as the intensity of the band due to Mn^{3+} ions is observed to increase gradually.

Table 2.Summary of data on differential thermal analysis of PbO- PbF_2 -B_2O_3: MnO glasses

Sample	T_g	T_c	T_m	T_c-T_g	T_m-T_c	$K_{gl} = \frac{Tc - Tg}{Tm - Tc}$
M_0	415	561	883	146	322	0.453
M_1	423	569	888	146	319	0.458
M_2	431	585	891	154	306	0.503
M_3	**433**	**592**	**892**	**159**	**300**	**0.530**
M_4	428	582	886	154	304	0.507
M_5	422	572	881	150	309	0.485

Table 3.Summary of the data on band positions (cm^{-1}) of various absorption bands in the IR spectra of PbO- PbF_2 -B_2O_3: MnO glasses

Glass	Borate groups			Band due to PbO_2F_4 (cm^{-1})	Band due to PbO_4 units (cm^{-1})
	BO_3 (cm^{-1})	BO_4 (cm^{-1})	B-O-B (cm^{-1})		
M_0	1361	1109	712	1047	521
M_1	1367	1099	712	1050	521
M_2	1372	1086	712	1052	521
M_3	1381	1077	712	1054	521
M_4	1361	1098	712	1051	521
M_5	1352	1109	712	1047	521

The optical band gaps [Eo] of these glasses was calculated from the observed absorption edges, by drawing Urbach plot between $(\alpha\ h\ \omega)^{1/2}$ and hν as per the equation:

$$\alpha(\omega)\hbar\omega = X(\hbar\omega - E_o)^2.$$

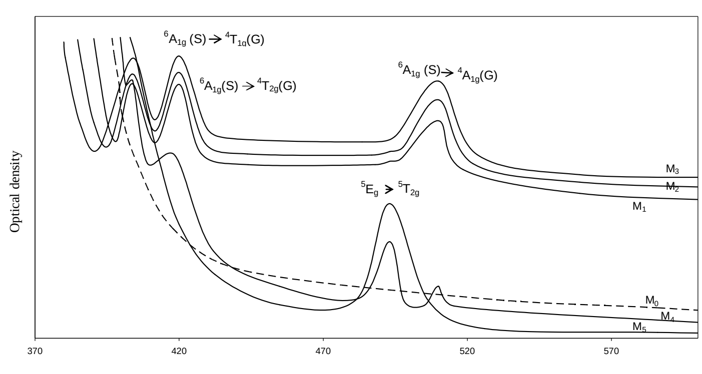

Fig. 5. Optical absorption spectra of $PbO-PbF_2-B_2O_3$: MnO glasses.

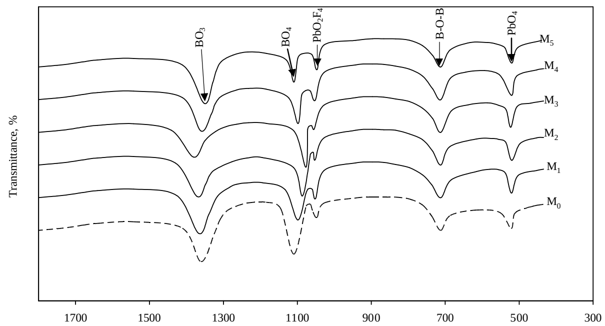

Fig.4: Infrared Spectra of $PbO-PbF_2-B_2O_3$: MnO glasses

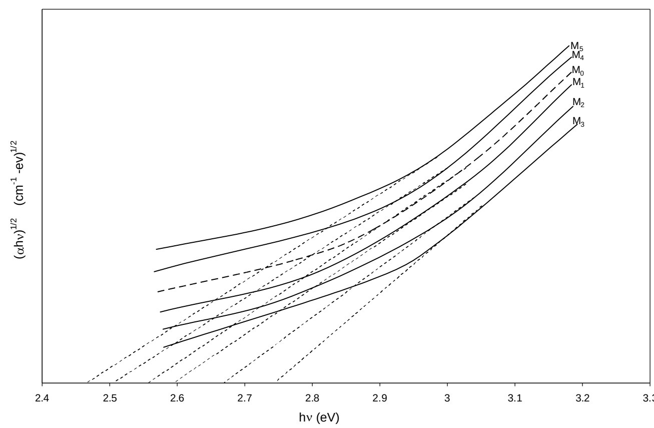

Fig. 6: Urbatch plots of $PbO-PbF_2-B_2O_3$ glasses containing different concentrations of MnO

Fig. 6 shows the Urbach plots of all these glasses, in which a considerable part of each curve is observed to be linear. The values of optical band gap (E_o) obtained from the extrapolation of the linear portions of these plots are presented in table 4. The value of E_o is found to decrease with the increase in concentration of MnO from 0.4 mol %.

Table 4. Summary of data on optical absorption spectra of $PbO-PbF_2-B_2O_3$: MnO glasses

Transition	Glass Sample					
	M_0	M_1	M_2	M_3	M_4	M_5
Mn^{2+} transitions (nm)						
$^6A_{1g}(S)\rightarrow{}^4T_{1g}(G)$	--	403	403	403	403	-
$^6A_{1g}(S)\rightarrow{}^4T_{2g}(G)$	--	420	420	420	420	-
$^6A_{1g}(S)\rightarrow{}^4A_{1g}(G)$	--	510	510	510	510	-
Mn^{3+} transition (nm)						
$^5E_g\rightarrow{}^5T_{2g}$	--	493.1	493	-	493	493
Cut-off wavelength (nm)	396.7	390.4	384.8	380	399.6	403
Optical band gap (eV)	--	3.149	3.152	3.158	3.136	3.133

Magnetic susceptibility of $PbO\text{-}PbF_2\text{-}B_2O_3$: MnO glasses measured at room temperature is observed to increase with increase in MnO content in the glass composition (Table 5) up to 0.3 mol %, beyond that the magnetic moment is found to decrease. From the values of magnetic susceptibilities, the effective magnetic moments(μ_{eff}) are evaluated and presented in Table 5. The value of μ_{eff} is found to increase gradually from a value of 5.3 (for glass M_1) to a value of 5.7 μ_B (for glass M_3) with increase of MnO up to 0.3 mol %. Later on with the increase of MnO in the glass matrix the magnetic moment is decreased.

Table 5. Data on magnetic properties of PbO- PbF_2 -B_2O_3: MnO glasses

Glass	Conc. of MnO (mol %)	Susceptibility, χ (10^{-5}, emu)	μ (μ_B)
M_1	0.1	3.73	5.3
M_2	0.2	8.17	5.5
M_3	0.3	13.2	5.7
M_4	0.4	15.7	5.3
M_5	0.5	18.9	5.2

Introduction of modifiers like PbO & PbF_2 into B_2O_3 network, converts the SP^2 planar BO_3 into more stable SP^3 tetrahedral BO_4 units in addition to the creation of non-bridging oxygen's [NBO's]. This is a well known fact. Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion gives rise to a structure which leads to the formation of long chain tetrahedrons. The presence of such BO_4 units in the present glass system is very clear from the infrared spectral studies. Generally PbO is a glass modifier. It enters the glass net –work breaking up the B-O-B bonds (The oxygen of PbO break the local symmetry and Pb^{2+} ions occupy interstitial positions). PbO introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. The change in geometrical configuration, co-ordination number, cross-link density and the dimensions of the interstitial space in the glass decide the density. Hence the density is a tool in revealing the degree of change in the structure of the glass composition. In borate glasses, the trend in density is controlled by the fraction of four-coordinated borons[30]. It is an established fact that boron can have a coordination number of three and/or four[31-34].

As a result boron can have its structure in a triangular and/or tetrahedral form. Tetrahedral groups are more firm compared to triangular groups. In pure B_2O_3 glasses most of the boron is involved in [B_3O_6] boroxol rings. In our present system of $PbO\text{-}PbF_2\text{-}B_2O_3$ glasses, an increase in density with fixed modifier content of PbF_2 and PbO and an increased content of MnO is observed. As PbO and PbF_2 are added, more boron atoms go into four coordination. The separation between BO_4 tetrahedral and a neighboring BO_3 should be less than the separation between two adjacent BO_3 triangles, i.e. the conversion of three coordinated boron to four-coordinated boron is the cause of network contraction. With the addition of PbF_2 and PbO, breaking of these rings and an increase in the formation of [BO_4] units was observed. Moreover, the maximum amount of [BO_4] units at about 0.3 mol% of MnO is noticed in the table 1 with an increase of density for M_3 due to more number of BO_4 structural units. On further increase of MnO in the glass matrix the density is not abruptly changed and it is an indication that the BO_4 structural units are decreased by further increase of MnO content in the system[35].

Pb should be sp^3d^2 hybridized (6s, 6p and 6d orbitals)[2] to form octahedral units. Nevertheless, PbO may also participate in the glass net-work with PbO_4 structural units when Pb ion is linked to four oxygens in covalent bond configuration. In that case the net work structure is believed to be built up from PbO_4 and BO_4 pyramidal units, which are linked together by B-O-Pb bonds. In $PbO\text{-}PbF_2\text{-}B_2O_3$ glass network Mn ions seem to exist in Mn^{2+} and Mn^{3+} states. The electronic configuration of Mn^{2+} ion is $3d^5$, which corresponds to a half-filled d shell. Most of the Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons[36].

On IR spectra in general, the optical absorption bands of Mn^{2+} complexes are observed in the visible and ultraviolet regions. In octahedral symmetry the ground state of Mn^{2+} is spherically non-degenerate $^6A_{1g}$ state. In a cubic crystalline field of low and moderate strengths, the five d electrons of Mn^{2+} are distributed in the t_{2g} and e_g orbitals, with three in the former and two in the latter. Therefore, the ground state configuration is normally written as $(t_{2g})^3(e_g)^2$. This configuration gives rise to electronic states $^6A_{1g}$, $^4A_{1g}$, ^4E_g, $^4T_{1g}$, $^4T_{2g}$, and $^4A_{2g}$ besides number of doublet states of which $^6A_{1g}$ lies lowest according to Hunds'rule. The observed optical absorption bands are from the ground state $^6A_{1g}$ to some quartet states and these are both spin and parity forbidden. In general, $^6A_{1g}(S) \rightarrow {}^4E_g(G)$, $^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4E_g(D)$ bands are sharp as they arise from intra configurationally transitions. The transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ involve a change of configuration from $(t_{2g})^3(e_g)^2$ to $(t_{2g})^4(e_g)^1$ and are therefore observed to be broad[37,38]. Since all the excited states are spin quartet states, no spin allowed transitions would occur for Mn^{2+} ions. Hence, Mn^{2+}ions are characterized by weak bands, which arise due to the spin forbidden transitions. By diagonalising the energy matrices for d^5 configuration, the clearly resolved bands observed at 510, 419 and 403 nm in the optical absorption spectrum of PbO-PbF_2-B_2O_3 glasses (containing MnO up to 0.3 mol%) are assigned to $^6A_{1g}(S)\rightarrow{}^4T_{1g}(G)$, $^6A_{1g}(S)\rightarrow{}^4T_{2g}(G)$ and $^6A_{1g}(S)\rightarrow{}^4A_{1g}(G)$) transitions. The existence of these bands indicates the presence of manganese ion in Mn^{2+} (d^5) state in the glasses M_1 to M_3. With the increase of MnO concentration from 0.1 to 0.3 mol % the intensity of Mn^{2+} transition bands are increasing and at 0.3 mol % Mn^{2+} bands posses maximum intensity. Again after increasing the concentration to 0.4 mol % the intensity of Mn^{2+} bands are decreased and the intensity of the band formed due to Mn^{3+} state which is a broad band from 481 – 506 nm is increasing. At the concentration of 0.5 mol % of MnO the bands due to Mn^{2+} state are disappeared and band due to Mn^{3+} are increased. This proves that at 0.3 mol % of MnO most of the Mn ions exists in 2+ state and occupy tetrahedral sites in the glass matrix.

The magnetic properties of these glasses arise from the paramagnetic Mn^{2+} and Mn^{3+} ions with $3d^5$ and $3d^4$ electrons, respectively. The value of the effective magnetic moment, 5.7 μB, obtained for glass M_3 confirms the presence of the highest concentration of Mn^{2+} ions in this glass. The decrease in the value of μ_{eff} from 5.7 to 5.2 μB (M_5) indicates that the glass M_5 consists of manganese ions mostly in Mn^{3+} state[36] that take part modifying positions in PbO-PbF_2-B_2O_3 glass network.
Recollecting the data, with the raise in the concentration of MnO, the intensity of the bands due to BO_3 structural units has been observed to decrease at the expense of the bands due to BO_4 units up to 0.3 mol %. This observation suggests a gradual increase in the concentration of divalent manganese ions in the glass network that acts as modifiers; improved the tetrahedral sites in the glass matrix at this concentration. These conclusions are supported by (i) increase in the glass transition temperature T_g and related parameters with MnO concentration, (ii) increase in the intensity of band in the IR spectra, due to BO_4 structural units, (iii) the shifting of absorption edge towards lower wavelength (or increase in the value of optical band gap E_o) and (iv) a increase in the value of effective magnetic moment from $5.3\mu_B$ to $5.7\mu_B$ (a value corresponds to the magnitude expected for Mn^{2+} ions).

APPLICATIONS

The present investigation is to understand the local environment of manganese ions in PbO-PbF_2–B_2O_3 glass network and their influence on the stability of glass.

CONCLUSIONS

The synopsis of the conclusions elicited from the study of $PbO-PbF_2-B_2O_3$: MnO is as follows:
(i) The optical absorption spectral study show the presence of Mn ions in Mn^{2+} state, occupying tetrahedral positions in the glass net work – when MnO is present up to 0.3 mol% concentrations. When the concentration of MnO is higher (>0.3mol %) Mn ions exist in Mn^{3+} state.
(ii) The magnetic moment, calculated from magnetic susceptibility measurements of the glasses, increases from 5.3μB to 5.7μB with increasing concentration of MnO in the glass matrix up to 0.3 mol % and beyond this concentration the magnetic moment decreased from 5.7 to 5.2 μB . The result has been ascribed to the fact that Mn ion exists mainly in Mn^{2+} state at 0.3 mol % and on further increase of MnO, gradual conversion of Mn ions from Mn^{2+} state to Mn^{3+} state.
(iii) The IR spectral studies show that –when the concentration of MnO increases up to 0.3mol% in the glass matrix- the concentration of Mn^{3+} ions increase and occupy octahedral positions and they enhance the disorderliness in the glass net work.
Finally the studies of $PbO-PbF_2-B_2O_3$: MnO glasses show that - when the concentration of MnO in the glass net work is low up to 0.3mol%, Mn ions seem to exist mainly in Mn^{2+} state and occupy net work forming positions and strengthen the glass structure. If the concentration is increased beyond 0.3mol% Mn ion seen to exist mainly in Mn^{3+} state and occupy modifying positions and increase disorder in the glass net work.

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