

Structural Study through Magnetic and Spectroscopic Properties on PbO-TiO₂-B₂O₃ Glass System Doped with Fe³⁺ Ion

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ABSTRACT

PbO-TiO₂-B₂O₃ glass system is prepared with different concentrations from 0.1 to 0.7 mol % of Fe₂O₃ doped in to the system by lowering the corresponding mol % in B₂O₃ by using melting and quenching technique. XRD, SEM and DTA analysis shows that the prepared samples are amorphous in nature. With the increase of the dopant concentration from 0.1 to 0.5 mol % the glass forming ability of the system is increased from 0.489 to 0.574 and on further increase of dopant up to 0.7 mol % the glass forming ability parameter is decreased to 0.517. The results of these studies have been analyzed in the light of different oxidation states of iron with the aid of the data on IR, ESR, optical absorption and magnetic susceptibility measurements. The analysis shows that iron ions exist mainly in Fe³⁺ state, occupy tetrahedral positions and increase the stability of the system with increasing concentrations of dopant up to 0.5 mol % and later on Fe²⁺ are increased at the expense of Fe³⁺. However, if Fe₂O₃ is present at 0.5 mol % in system, (i) BO₄ structural units are maximum and iron ion mainly exists in Fe³⁺ state and occupy tetrahedral sites in the glass matrix (ii) the intensity and the half width of the ESR signal has been observed to increase and (iii) the value of magnetic moment (evaluated from magnetic susceptibility) has been observed to increase to a value 5.8 μ_B at this concentration range. From these results it has been concluded that at higher concentration range (> 0.5 mol %) iron ions exist mainly in divalent state.

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INTRODUCTION

Boron trioxide is one of the oxides of boron. It is a white, glassy solid. It is almost always found as the vitreous form; however, it can be crystallized after extensive annealing. It is one of the most difficult compounds known to crystallize. B₂O₃ is a glass forming oxide, PbO is a conditional glass former and with these two chemicals in the glass matrix, a low rate of crystallization, moisture resistance, stable and transparent glasses could be achieved due to a dual role played by PbO as a glass former and also as a modifier[1].

Addition of TiO₂ in small quantities is observed to enhance the glass forming ability and chemical durability of the glasses[2]. From the literature survey it is evident that Ti ion enters the glass network in Ti⁴⁺ state and participate in the glass network forming with TiO₄, TiO₆ and some times with TiO₅ (comprising of trigonal bipyramids) structural units[3,4]. As per the reports available the titanium ion may enter the glass network in Ti³⁺ state[5,6]. Ti⁴⁺ ions are expected to improve the non-linear optical properties of lead borate glasses to a large extent, since the empty or unfilled d- shells of these ions contribute more strongly to the non-linear polarizabilities; usually, the d-orbital contribution to non-linear polarizability is found to be more for bond lengths less than 2 Å[7]. The bond length of Ti-O is estimated to be 1.96 Å.

PbO-TiO₂-B₂O₃ glasses are considered to be of special interest in view of their potential applications in IR fiber optics, laser windows and multifunctional optical components. These glasses are highly transparent in the mid-infrared range and are more stable against atmospheric moisture. They are also considered as promising candidates for electrochemical applications such as power sources especially in the field of solid state batteries[8]. Further, as any other heavy metal oxide based glasses, these glasses have also got the capacity to accept the transitional metal ions, like iron, both in network forming and modifying positions[9].

Literature survey on Iron ion dopant glasses showed that they have strong bearing on electrical, optical and magnetic properties of glasses. Number of inorganic glass systems with iron ion environment are available in the literature[10-15]. In those iron ion environment glass systems, the iron ions exist in different valence states with different coordinations in glass matrices, for example, Fe³⁺ occupy both tetrahedral and octahedral sites, whereas Fe²⁺ occupy only octahedral positions[16-25]. The existence of iron in different valence states in a glass mainly depends up on the content of iron in the glass, depends on 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., It is also evident that the physical properties of a glass are mainly dependent on the oxidation state of the iron ion. Thus, by knowing the

oxidation state and the position of the iron ion in the glass network by analytical methods and by studying the physical properties with certain physical measurements can analyze the systems clearly.

The paramagnetic behaviour is exhibited by both ferrous and ferric ions. Fe^{2+} ion possesses a large magnetic moment due to spin-orbit interaction of the 3d orbital whereas the magnetic moment of Fe^{3+} ions is small as the orbital angular momentum of these ions is zero. Iron ions have strong affinity to make bonds with metal oxides such as PbO , TiO_2 & B_2O_3 groups that may reinforce the glass structure and raise the glass durability[26].

The main intention of the present study is to have a broad understanding over the influence of iron ions on the structure of $\text{PbO-TiO}_2\text{-B}_2\text{O}_3$ glasses, from a systematic study through IR, ESR, OA and Magnetic Susceptibility studies. It is also useful to reveal the role of iron ions and their structural modifying ability with the aid of data on magnetic and spectroscopic properties.

MATERIALS AND METHODS

Glasses are prepared with the following combination of chemicals in mol% are represented here under. All prepared samples are glasses (from the visual examination) and these are prepared with an increase in the concentration of Fe_2O_3 . We have prepared seven samples for the present study.

- F₀: 35 PbO-05 TiO₂-60 B₂O₃
- F₁: 35 PbO-05 TiO₂-59.9 B₂O₃: 0.1 Fe₂O₃
- F₂: 35 PbO-05 TiO₂-59.8 B₂O₃: 0.2 Fe₂O₃
- F₃: 35 PbO-05 TiO₂-59.7 B₂O₃: 0.3 Fe₂O₃
- F₄: 35 PbO-05 TiO₂-59.6 B₂O₃: 0.4 Fe₂O₃
- F₅: 35 PbO-05 TiO₂-59.5 B₂O₃: 0.5 Fe₂O₃
- F₆: 35 PbO-05 TiO₂-59.4 B₂O₃: 0.6 Fe₂O₃
- F₇: 35 PbO-05 TiO₂-59.3 B₂O₃: 0.7 Fe₂O₃

Calculated quantities of reagent of TiO_2 , PbO , H_3BO_3 and Fe_2O_3 powders were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range 950-1000 °C in a PID temperature controlled furnace for about 1 h until a bubble free transparent liquid was formed. The so formed liquid was then poured in a brass mould and subsequently annealed at 300 °C using an annealing chamber. X-ray diffraction and SEM analysis confirmed the amorphous state of the glasses.

The differential thermal analysis on these samples was carried out using STA 409C, Model DTA-TG with a programmed heating rate of 10 °C / min in the temperature range of 30-1000 °C.

The samples were then ground and optically polished. The density d of these glasses was determined to an accuracy of 0.001 by standard principle of Archimedes' using *o*-xylene (99.99% pure) as the buoyant liquid.

The IR spectra of the glasses were recorded by KBr pellet method. Glass powders (2 mg) were mixed with anhydrous potassium bromide powder (150 mg) and pressed into pellets at 2000 kg cm⁻². The spectra were recorded using a FT-IR Digital Excalibur 3000 Spectrophotometer with a resolution of 0.1 cm⁻¹ in the range 400-2000 cm⁻¹. The optical absorption spectra of these glasses were recorded at room temperature in the wavelength range 350-800 nm up to a resolution of 0.1 nm using Shimadzu UV-VIS-NIR Spectrophotometer Model 3101.

The ESR spectra of the fine powders of the samples were recorded at room temperature on JES-FA 200 ($\nu = 9.21$ GHz) ESR spectrometer with 100 KHz field modulation. The magnetic susceptibility measurements were made at room temperature by Guoy's method using fine powders of these glasses.

RESULTS AND DISCUSSION

The amorphous nature of prepared samples was conformed by the absence of peaks in the X-ray diffraction studies shown in Fig. (1). From the morphological study through SEM photographs (Fig.2), it is evident that the samples are amorphous and also the existence of glass transition temperature T_g and crystalline temperature T_c in the DTA traces (Fig.3), indicate that the samples prepared were of amorphous in nature.

From the measured values of density d and calculated average molecular weight \overline{M} , various physical parameters such as iron ion concentration N_i and mean iron ion separation R_i , polaron radius r_p and the field strength around the dopant ion F_i of these glasses are evaluated[27] and presented in Table 1.

The curves exhibited in Fig.3 shows differential thermal analysis of all the glasses under study. From the curves it is clear that an endothermic effect due to glass transition temperature T_g is noted in all samples. At still higher temperatures, an exothermic peak T_c due to the crystal growth followed by an endothermic effect due to the melting effect denoted by T_m , are also observed. The values of T_g , T_c and T_m are tabulated which are obtained for all

the glass samples and they are furnished in Table 2. The single peak due to the glass transition temperature obtained in DTA pattern of all the glasses shows a good homogeneity of the prepared glass samples.

The glasses which were doped with Fe₂O₃, the quantity (T_c-T_g), which is proportional to glass forming ability, is found to increase where as the quantity (T_m-T_c) which is inversely proportional to glass forming ability is found to decrease (Table 2) with increase in the content of Fe₂O₃ from 0.1 mol % to 0.5 mol % and beyond this concentration these parameters are reversed in nature.

Table 1 Summary of data on various physical parameters of PbO- TiO₂ -B₂O₃: Fe₂O₃ glasses

Property	Glass Samples							
	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇
Density d (g/cm ³)	4.48	4.52	4.67	5.06	5.12	5.19	5.22	5.29
Avg. dissociation rate(mg/h/cm ²)	---	1.0	0.9	0.8	0.6	0.4	0.9	1.2
Avg. mol. wt. \bar{M}	123.87	124.05	124.23	124.41	124.59	124.77	124.95	125.22
Titanium ion conc. N _i (10 ²¹ ions/cm ³)	----	4.39	9.06	14.70	19.80	25.05	30.19	38.17
Inter ionic distance of titanium ions R _i (Å)	----	6.11	4.80	4.08	3.70	3.42	3.21	2.97
Field Strength F _i (10 ¹⁵ cm ⁻²)	----	3.30	5.35	7.39	9.02	10.50	11.90	14.00
Polaron Radius r _p (Å)	----	2.46	1.93	1.64	1.49	1.38	1.29	1.20

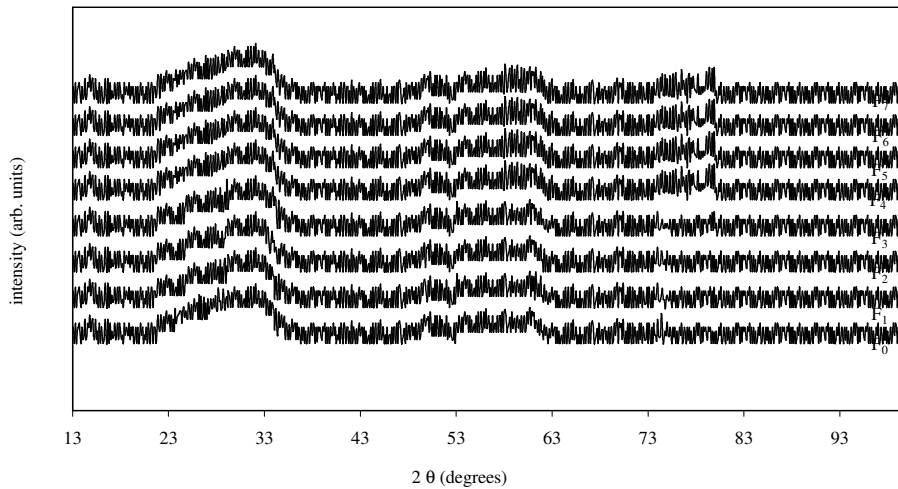


Fig.1. X-Ray diffraction pattern of PbO-TiO₂-B₂O₃ glasses doped with Fe₂O₃

Table-2: Summary of data on differential thermal analysis of PbO-TiO₂-B₂O₃: Fe₂O₃ glasses

Sample	T _g	T _c	T _m	(T _c -T _g)	(T _m -T _c)	K _{gl} =(T _c -T _g)/ (T _m -T _c)
F ₀	411	563	874	152	311	0.489
F ₁	417	575	880	158	305	0.518
F ₂	419	575	873	156	298	0.523
F ₃	422	580	874	158	294	0.537

F ₄	423	583	880	160	297	0.539
F ₅	426	597	895	171	298	0.574
F ₆	422	583	891	161	308	0.523
F ₇	418	581	896	163	315	0.517

Table-3: Summary of the data on band positions (cm⁻¹) of various absorption bands in the IR spectra of PbO-TiO₂-B₂O₃: Fe₂O₃ glasses

Glass	Borate groups			Band due to TiO ₄ (cm ⁻¹)	Band due to Ti-O-Ti (cm ⁻¹)	Band due to PbO ₄ units (cm ⁻¹)
	BO ₃ (cm ⁻¹)	BO ₄ (cm ⁻¹)	B-O-B (cm ⁻¹)			
F ₀	1362	1038	723	723	650	480
F ₁	1367	1035	723	723	650	480
F ₂	1373	1031	723	723	650	480
F ₃	1383	1030	723	723	650	480
F ₄	1393	1023	723	723	650	480
F ₅	1398	1021	723	723	650	480
F ₆	1386	1033	723	723	650	480
F ₇	1360	1058	723	723	650	480

Table-4: Summary of data on optical absorption spectra of PbO-TiO₂-B₂O₃: Fe₂O₃ glasses

Transition	Glass Sample							
	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇
Fe ³⁺ transitions (nm)								
⁶ A ₁ (t ³ _{2g} e ² g) → a ⁴ T ₁ (t ⁴ _{2g} e _g)	--	540	540	540	540	540	540	540
⁶ A ₁ (t ³ _{2g} e ² g) → a ⁴ T ₂ (t ⁴ _{2g} e _g)	--	580	580	580	580	580	580	580
⁶ A ₁ (t ³ _{2g} e ² g) → a ⁴ T ₁ (e ₃ t ² ₂)	--	787	787	787	787	787	787	787
Fe ²⁺ transition (nm)								
⁵ T _{2g} → ⁵ E _g	--	955	955	955	955	955	955	955
Cut-off wavelength (nm)	401	391	389	386	383.1	378	393	396
Optical band gap (eV)	--	2.32	2.4	2.47	2.5	2.65	2.25	2.20

Table-5: Data on magnetic properties of PbO-TiO₂-B₂O₃: Fe₂O₃ glasses

Glass	Conc. of Fe ₂ O ₃ (mol %)	Susceptibility, χ (10 ⁻⁵ , emu)	μ (μ_B)
F ₁	0.1	12.32	5.2
F ₂	0.2	13.56	5.3
F ₃	0.3	14.25	5.4
F ₄	0.4	19.24	5.5
F ₅	0.5	21.56	5.8
F ₆	0.6	7.25	4.7
F ₇	0.7	3.61	4.6

The observed values of T_g, T_c and T_m, the parameters (T_c-T_g), (T_m-T_c) and glass forming ability parameter known as Hrubby's parameter, K_{gl} = (T_c-T_g)/(T_m-T_c) are evaluated and presented in Table 2. The disparity of the

parameter $(T_c - T_g)/(T_m - T_c)$ with the concentration of Fe^{3+} ion indicates the maximum value for glass F_5 (Table 2) showing its highest glass forming ability among all the glasses prepared.

The variation of glass forming ability parameter called Hurby's Parameter K_{gl} with the concentration of Fe_2O_3 in the present glass system is increased with the increase in the concentration of Fe_2O_3 up to 0.5 mole % and later on with the increase in the concentration of Fe_2O_3 the Hurby's parameter is decreased.

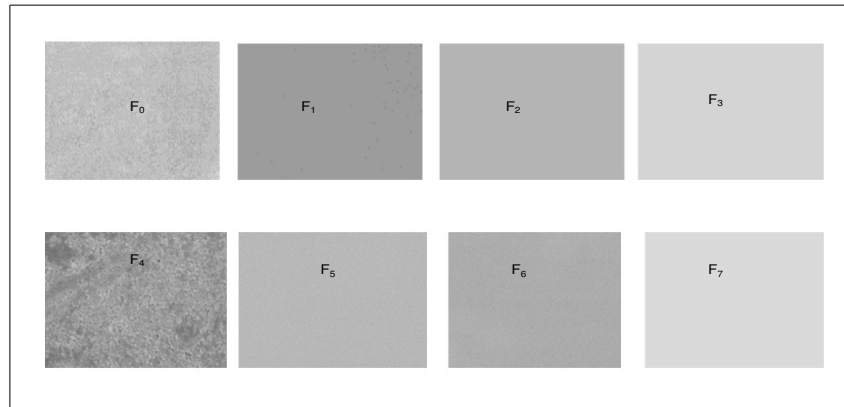


Fig.2: Scanning Electron Microgram of $PbO-TiO_2-B_2O_3: Fe_2O_3$ glasses.

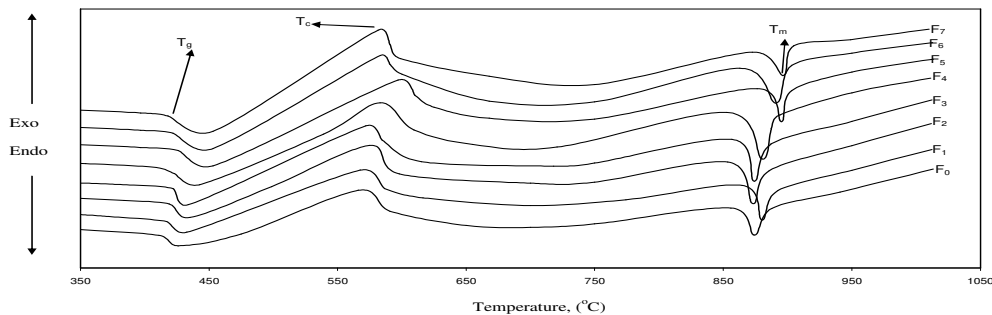


Fig.3. Differential Thermal Analysis patterns of $PbO-TiO_2-B_2O_3: Fe_2O_3$ glasses

The IR spectra of the samples prepared consists of following bands; (i) B-O bond of the trigonal BO_3 units in the region $1300-1400\text{ cm}^{-1}$ and these bands are identified due to stretching relaxation of BO bonds (ii) the bands due to vibration of BO_4 structural units in the region $1100-1200\text{ cm}^{-1}$ and (iii) the band due to bending vibrations of B-O-B linkages are present in the region 722 cm^{-1} [26,28,29]. In all the glasses prepared PbO_4 structural units exhibited a band at about 480 cm^{-1} [30,31]. With the introduction of TiO_2 (0.1 mol %) into the glass network, two new bands due to TiO_4 (730 cm^{-1}) and Ti-O-Ti symmetric stretching vibrations of TiO_6 (650 cm^{-1}) structural units have appeared[32,33].

When we move from Sample F_0 to Sample F_5 , 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 wavenumber, where as, the intensity of the first group of bands (bands due to the BO_3 structural units) is observed to decrease. For further increase of Fe_2O_3 , i.e., for the samples F_6 & F_7 , the intensity of the first group of bands is observed to increase at the expense of second group of bands.

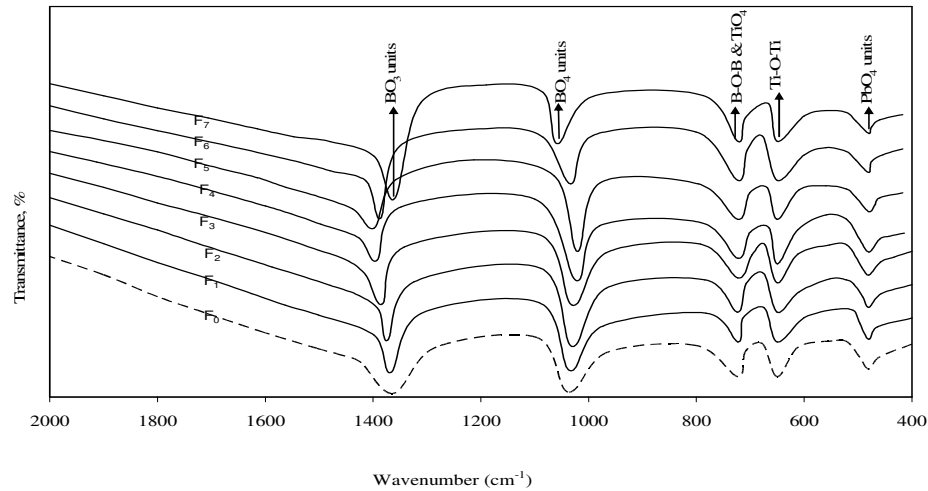


Fig. 4: IR spectra of PbO-TiO₂-B₂O₃:Fe₂O₃ glasses.

The OA spectra of prepared glasses recorded in the wavelength region 350-1100 nm are shown in Fig. 5. The absorption edge observed at 401 nm for the glass F₀ is observed to shift to 378 nm when we move from F₀ to F₅. With further increase in the concentration of Fe₂O₃, the edge is observed to shift gradually towards higher wavelength. The spectra of the glasses F₁, F₂, F₃, F₄ and F₅ have exhibited absorption bands at 540, 580 and 787 nm due to Fe³⁺ ion transitions and a band at 955 nm due to Fe²⁺ ions is observed in the spectra of F₆ and F₇. With increase in the concentration of Fe₂O₃ beyond 0.5 mol %, the bands due to Fe³⁺ ions have been observed to fade away slowly where as the intensity of the band due to Fe²⁺ ions is observed to increase gradually. Urbach plot is drawn between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ and this plot is represented in Fig (6). In Fig. 6, it is clear that some part of each curve of every sample is linear. The values of optical band gap (E_0) obtained from the extrapolation of the linear portions of these plots are presented in Table 4. The value of E_0 is found to increase with the increase in concentration of Fe₂O₃ from 0.1 to 0.5 mol % from a value 2.32 eV to 2.65 eV later on this value is decreased to 2.2 eV on further increasing the dopant to 0.7 mol %.

The ESR spectra of prepared glasses recorded at room temperature are shown in Fig. 7. The intensity of the ESR signal is observed to increase gradually with increase in the concentration of Fe₂O₃ in the glass matrix up to 0.5 mol %. This intense line centered at about $g = 2$. However, the intensity of this signal is decreased with the increase of the concentration of Fe₂O₃ beyond 0.5 mol %. In the spectra of all the prepared samples a weak signal at $g=4.3$ also be detected.

Magnetic susceptibility of the prepared glasses measured at room temperature is observed to increase with increase in Fe₂O₃ content in the glass composition (Table 5) up to 0.5 mol %, beyond that the susceptibility 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 5.2 (for glass F₁) to a value of 5.8 μ_B (for glass F₅) with increase of Fe₂O₃ up to 0.5 mol %. Later on with the increase of Fe₂O₃ in the glass matrix the magnetic moment is decreased.

B₂O₃ is a well known glass former. Both lead oxide and titanium dioxide are modifiers. The introduction of PbO and TiO₂ into B₂O₃ glass network is to convert the sp² planar BO₃ into more stable sp³ tetrahedral BO₄ units in addition to non-bridging oxygens (NBO's). The existence of such BO₄ units in the present glass system is evident from IR spectral studies.

When PbO is added into B₂O₃ glass network it enters into the glass network by breaking up the B-O-B bonds and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. PbO may also participate in the glass network with PbO₄ structural units when lead ion is linked to four oxygens in a covalency bond configuration. Addition of TiO₂ in small quantities will enhance the glass forming ability and chemical durability of the glasses. Ti ion enters the glass network in Ti⁴⁺ state and participate in the glass network forming with TiO₄, TiO₆ and some times with TiO₅ structural units. Ti⁴⁺ ions are expected to improve the non-linear optical properties of lead borate glasses. The structure of the PbO-TiO₂-B₂O₃: Fe₂O₃ glass is represented in Fig. 8.

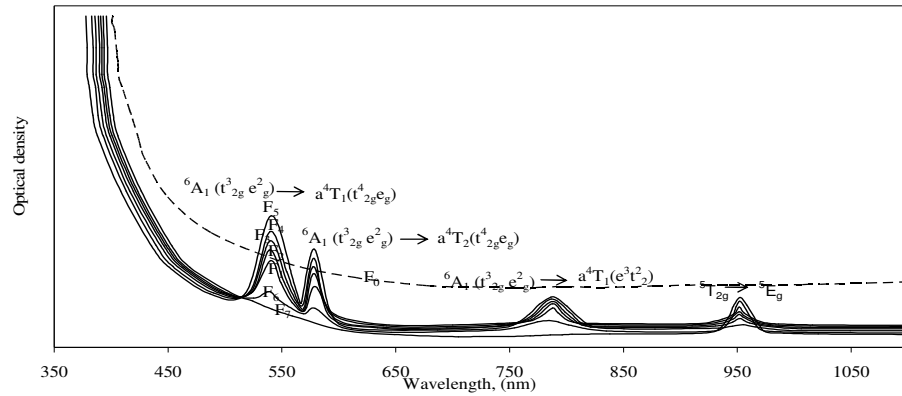


Fig. 5. Optical absorption spectra of PbO-TiO₂-B₂O₃: Fe₂O₃ glasses.

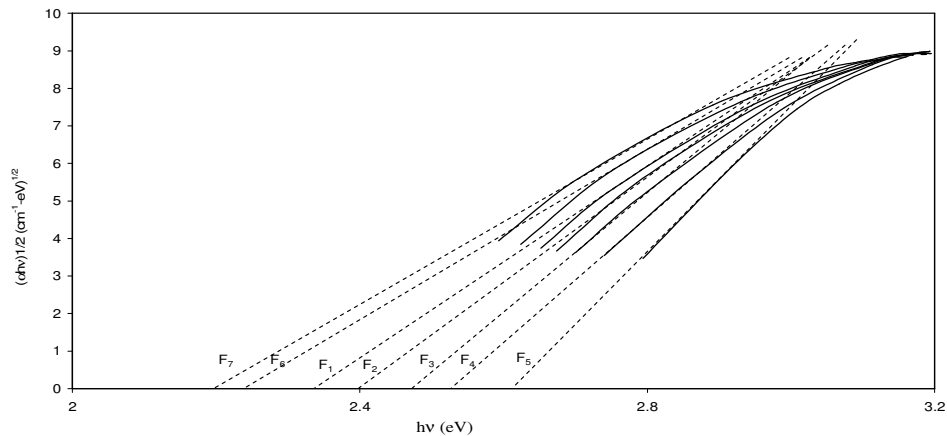
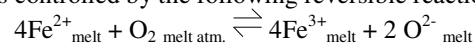


Fig. 6 A plot for evaluating the optical band gap of PbO-TiO₂-B₂O₃: Fe₂O₃ glasses

Iron ions are expected to exist mainly in Fe³⁺ and Fe²⁺ state in the present PbO-TiO₂-B₂O₃ glass network. The speciation of iron in these glasses is controlled by the following reversible reaction:



The OA spectra of the prepared glasses have exhibited three absorption bands at 787, 580 and 540 nm. Based on selection rules and ligand field calculations, the first two bands are identified due to FeO₆ group and the third band is due to FeO₄ group^{34, 35}. With increase in the concentration of Fe₂O₃ up to 0.5 mol %, the intensity of these bands slowly increased at the expense of the absorption band at 955 nm which is a characteristic band for Fe²⁺ ions. This band is identified due to ⁵T_{2g} → ⁵E_g transition of Fe²⁺ (d⁶) ions³⁶.

The diminishing intensity of the ESR signal with the increase in the concentration of Fe₂O₃ beyond 0.5 mol % indicates a gradual decrease in the concentration of Fe³⁺ ions in the glass network.

The value of the effective magnetic moment (5.8 μ_B) obtained for glass F₅ confirms the highest concentration of Fe³⁺ ions in this glass. The decrease in the value of μ_{eff} from 5.8 μ_B to a value of 4.6 μ_B (for glass F₇) indicates a gradual growing concentration of Fe²⁺ ions that take modifying positions in the glass network. Such Fe²⁺ ions may increase the degree of disorder in the glass network.

From the data of IR spectra, with the raise in the concentration of Fe_2O_3 , 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 0.5 mol%. This observation suggests a gradual increase in the concentration of trivalent iron ions in the glass network that acts as former; as former, these ions create more orderly arrangement in the glass network.

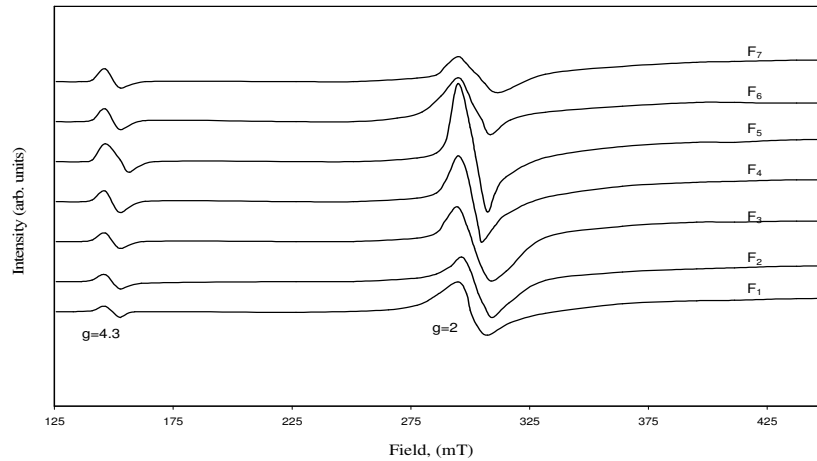


Fig. 7: ESR spectra of $PbO-TiO_2-B_2O_3:Fe_2O_3$ glasses

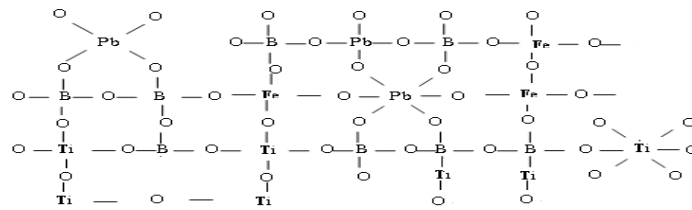


Fig. 8 - A Schematic illustration of $PbO-TiO_2-B_2O_3:Fe_2O_3$ glasses

CONCLUSIONS

The following are the conclusions drawn on $PbO-TiO_2-B_2O_3:Fe_2O_3$ glass system:

1. The magnetic moment evaluated from magnetic susceptibility measurements of the glasses, increases from 5.2 to 5.8 μ_B with increasing concentration of Fe_2O_3 up to 0.5 mol % in the glass matrix and decreased to 4.6 μ_B on further increase of Fe_2O_3 up to 0.7 mol %. From this result it is clear that Fe^{3+} ion concentration is increasing with the increase of Fe_2O_3 concentration and posses max at 0.5 mol % and beyond this as the concentration of Fe_2O_3 increases then Fe^{3+} ions are converted into Fe^{2+} state. Thus from the magnetic susceptibility measurements we can conclude that the Sample-F₅ is a stable one when compared to the other samples.
2. The IR spectral investigations shows that with the increase in the concentration of Fe_2O_3 in the glass matrix from 0.1 to 0.5 mol % a gradual increase in the concentration of Fe^{3+} ions that occupy tetrahedral positions which improves the orderliness of the glass matrix and pick up the stability of the sample. On further increase of Fe_2O_3 concentration beyond 0.5 mol % Fe^{2+} ions are increased with the expense of Fe^{3+} ions. Fe^{2+} ions occupy the octahedral positions which decrease the stability of the glass system. Thus sample F₅ represents a good glass.
3. The optical absorption and ESR spectral studies indicate the presence of part of iron ions in Fe^{3+} state and occupy tetrahedral positions when Fe_2O_3 is added from 0.1 – 0.5 mol % ; when the concentration of Fe_2O_3 is in higher quantities (> 0.5 %), these ions seems to exist in Fe^{2+} state .

Finally the analysis of the results of the studies on the various physical properties (viz., optical, magnetic) and DTA indicates that the structure of $\text{PbO-TiO}_2\text{-B}_2\text{O}_3$ glass is more stable when the concentration of Fe_2O_3 is about 0.5 mol%.

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