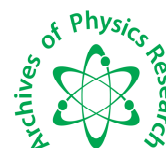




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Archives of Physics Research, 2014, 5 (1):42-50  
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CODEN (USA): APRRC7

# Effect of $Fe_2O_3$ on physical properties and structure of $Bi_2O_3$ - $B_2O_3$ - $Fe_2O_3$ glasses

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## ABSTRACT

Heavy metal based oxide glasses with composition  $(100-y) [30 B_2O_3 .70 Bi_2O_3] y Fe_2O_3$  ( $y=0,2,5,7,10$ ) were prepared by the standard melt quenching technique. The amorphous nature of the samples was ascertained using X-ray diffraction patterns. The microstructure of the glasses is identified by scanning electron microscopy (SEM) studies. The glass density ( $d$ ) and molar volume ( $V_m$ ) both decrease with increase in  $Fe_2O_3$  content. The change in both the density and molar volume were discussed in terms of the structural modifications that take place in the glass matrix upon increasing  $Fe_2O_3$  content. The theoretical optical basicity of the prepared glasses is also estimated. The structural changes in these glasses have been investigated by IR spectroscopy. The values of characteristic glass transition temperature ( $T_g$ ) crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) have been found from Differential Scanning Calorimetry (DSC) traces. The glass transition temperature ( $T_g$ ) increase as the content of  $Fe_2O_3$  increases.

**Keywords:** Oxide glasses, X-Ray diffraction, Density, Differential Scanning Calorimetry, IR Spectroscopy.

## INTRODUCTION

Heavy metal oxide (HMO) glasses have attracted considerable interest due to their high refractive index, high infrared transparency and high density [1, 2]. There has been an increasing interest in the synthesis, structure and physical properties of glasses containing bismuth-oxide due to their manifold possible applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows etc [3, 4]. Recently it was reported that heavy metal oxide glasses containing bismuth are investigated for possible use in scintillation detectors for high energy physics and that the large polarizability of bismuth makes them suitable for possible non-linear optical uses and environmental guide lines [5, 6].

$B_2O_3$  is one of the most common glasses former and the structure of vitreous  $B_2O_3$  consist of random network of boroxyl rings and  $BO_3$  triangles connected by B-O-B linkage [7]. It was reported that addition of a network modifier in a borate glass could produce the conversion of the triangular  $BO_3$  structural units to  $BO_4$  tetrahedra with a coordination number four [8, 9]. A survey of literature shows that there are many reports available on Bismuth Borate glasses [10-14]. However the studies with iron addition are very limited. Various studies have been carried out to establish the environments of  $Fe^{2+}$  and  $Fe^{3+}$  ions, mostly at a few percent levels in different glasses [15-17]. It was supposed that, at low concentrations, the ions act as modifiers similar to the alkali metals or alkaline earths [15]. It has been reported that  $Fe^{2+}$  ion can only be six fold coordinated in glasses [18], therefore, acting as a modifier,

while  $\text{Fe}^{3+}$  ion exists in both tetrahedral and octahedral environments. Further, the valence of the Fe ions determines the covalence of Fe-O bond and reflects the effects of ionic radius of the Fe atom on the Fe-O bond length. Thus both the Co-ordination geometry and valance of Fe ions determines the structural role. The goal of the present work is to investigate the glass formation, basic properties and local structure of  $\text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{Fe}_2\text{O}_3$  glasses and to identify both structural and valiant changes with  $\text{Fe}_2\text{O}_3$  content.

## MATERIALS AND METHODS

Glass samples of compositions  $(100-y) [30\text{B}_2\text{O}_3 .70 \text{Bi}_2\text{O}_3] y\text{Fe}_2\text{O}_3$  with  $y=0, 2, 5, 7, 10$  (mol %) were prepared using the normal melt-quench technique from reagent grade chemicals of  $\text{Bi}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$  and  $\text{Fe}_2\text{O}_3$ . The weighed quantities of the starting materials were thoroughly mixed in appropriate proportions and the batch materials were heated in porcelain crucibles placed in an electrically heated furnace for about 0.5h to prevent volatilization and then melted at  $1100^\circ\text{C}$  for about 0.5 h. The mixture was shaken frequently to ensure the homogeneity. The melts were then quickly poured onto a steel plate and pressed under another steel plate. The as prepared glass sample were cut and then finely polished to a thickness of 0.5-1.5mm and were stored in a desicater to prevent further oxidation or degradation. X-Ray diffraction measurements on the sample have been carried out using X' Pert Pro diffractometer which consist of  $\theta\theta$  goniometer having range of  $0^\circ$ - $160^\circ(2\theta)$ . The radiation used was Cu  $K\alpha$  whereas nickel metal was used as beta filter. The SEM (Model Jeol JSM-6510) has been used to study the microstructure of the glasses. The density (d) of glass sample was determined by the standard Archimedes principle. These measurements were done using density determination kit (Denver instrument YDK O1S) with S/SI balances with readability of 0.1 mg. All measurements were done in duplicate with maximum error of  $\pm 2\%$ .

Thermal analysis was carried out on Differential Scanning Calorimeter (Q600 SDT) supplied by TA instruments. The samples, approximately 15 mg in weight were heated from  $40^\circ\text{C}$  to  $1000^\circ\text{C}$  in hermetically sealed alumina crucible under  $\text{N}_2$  atmosphere and scanned at a heating rate of  $10^\circ\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ), crystallization temperature and melting temp ( $T_m$ ) for all the glass samples were evaluated from the recorded thermo grams. FTIR transmission spectra of the glass samples were recorded at room temperature using KBr pellet technique with the Perkin-Elmer RX-1 FT-IR Spectrometer in the range  $250$ - $4000 \text{ cm}^{-1}$ . For this, powdered glass samples were thoroughly mixed with dry KBr in the ratio 1:20 by weight and the pellets were formed using a pellet press.

## RESULTS AND DISCUSSION

**3.1 X-ray diffraction and SEM studies:** From the XRD studies it is observed that homogeneous glasses were formed for  $\text{Fe}_2\text{O}_3$  concentration between 0 and 10 mol%. The XRD patterns of present glasses, which are shown in Fig.1, indicate a glassy behavior with a broad hump at about  $2\theta=30^\circ$ . No peak corresponding to  $\text{Fe}_2\text{O}_3$  is observed, which indicates that  $\text{Fe}_2\text{O}_3$  has completely entered the glass matrix. The microstructure of the glasses is identified by scanning electron microscopy (SEM) studies. Fig.2 shows the typical SEM micrograph of studied glasses, which is found to be glassy (amorphous) nature of the sample.

**3.2 Density, crystalline volume, molar volume and theoretical optical basicity:** The values of density (d) of the glass samples determined in the present study are given in Table1. The variation of density and molar volume is shown in Fig.3. It can be seen from Fig.3 and Table1 that the density of glasses decreases as  $\text{Fe}_2\text{O}_3$  content increases. This is due to the low relative molecular mass of  $\text{Fe}_2\text{O}_3$  compared to  $\text{Bi}_2\text{O}_3$ . It has already been reported that Bismuth-Borate glasses possess long chains of  $\text{BiO}_6$  distorted polyhedra and octahedral units linked together by Bi-O- Bi bonds [19-21]. Therefore it is assumed that there are already long chains of Bi-O- Bi linkages and with further addition and increase of  $\text{Fe}_2\text{O}_3$  content the Bismuth Borate network is modified and concentration of Bi-O non-bridging oxygen (NBOs) decreases which randomizes the structure and hence density decreases. This indicates that glass structure becomes less tightly packed with increasing  $\text{Fe}_2\text{O}_3$  concentration. Molar Volume ( $V_m$ ) of the samples were calculated using formula

$$V_m = \sum(x_i M_i) / d \quad (1)$$

Where  $x_i$  is the molar fraction and  $M_i$  is the molecular weight of  $i^{\text{th}}$  component, respectively. The crystalline volume ( $V_c$ ) of each glass sample is also calculated using formula:

$$V_c = \sum x_i V_i \quad (2)$$

Where  $V_i$  is the molar volume of the  $i^{\text{th}}$  component in crystalline phase and values thus calculated are given in Table 1. The data of molar volume and crystalline volume has been plotted in Fig. 4 for comparison. The molar volume and crystalline volume of the samples is found to increase with an increase in  $\text{Fe}_2\text{O}_3$  content. Perusal of the data plotted in Fig. 2 shows that  $V_m$  of the glasses is always greater than the corresponding values of  $V_c$ , indicating the presence of excess structural volume in these samples; this is characteristic of their glassy nature [22, 23]. The data supports the assertion of XRD studies.

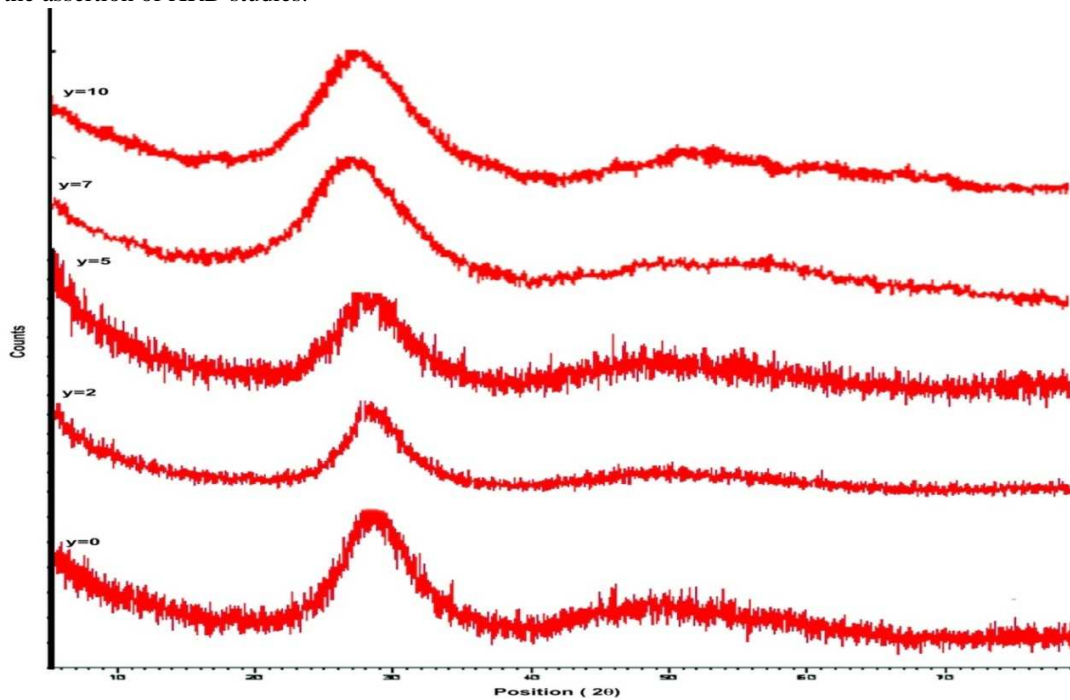


Fig.1. XRD patterns of  $(100-y)[30 \text{ B}_2\text{O}_3, 70 \text{ Bi}_2\text{O}_3] y \text{ Fe}_2\text{O}_3$  glasses

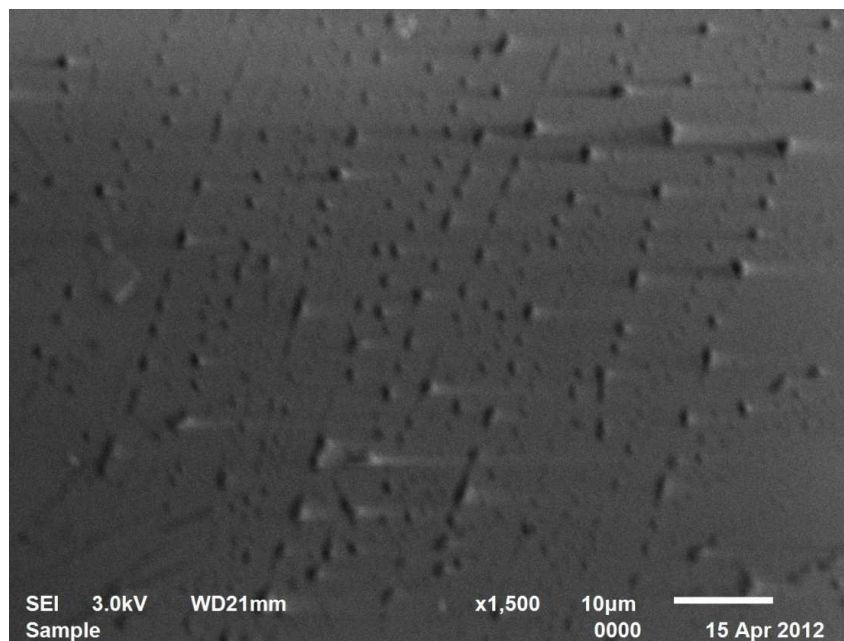
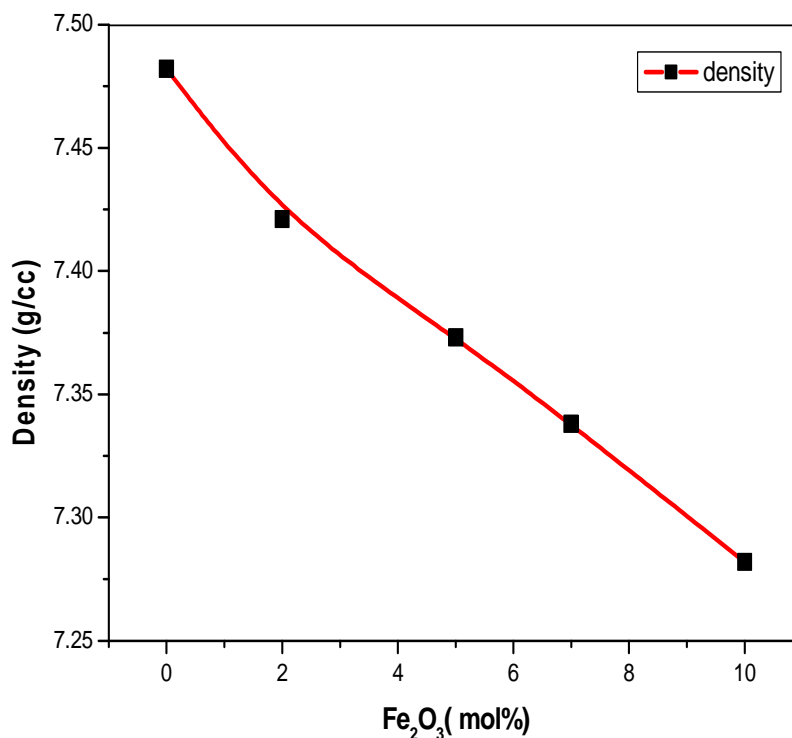


Fig. 2. Typical SEM micrograph of  $(100-y)[30 \text{ B}_2\text{O}_3, 70 \text{ Bi}_2\text{O}_3] y \text{ Fe}_2\text{O}_3$  glasses

**Table 1:** The density ( $d$ ), crystalline volume ( $V_c$ ), molar volume ( $V_m$ ), theoretical optical basicity ( $\wedge_{th}$ ), glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) of  $(100-y)[30 B_2O_3 \cdot 70 Bi_2O_3] y Fe_2O_3$  glasses

Sample	$d$ (g/cc) ( $\pm 0.001$ )	$V_c$ (cc/mol) ( $\pm 0.001$ )	$V_m$ (cc/mol) ( $\pm 0.001$ )	$\wedge_{th}$	$T_g$ ( $^{\circ}C$ ) ( $\pm 1$ )	$T_c$ ( $^{\circ}C$ ) ( $\pm 1$ )	$T_m$ ( $^{\circ}C$ ) ( $\pm 1$ )
y = 0	7.482	45.003	46.385	0.960	361	590	644
y = 2	7.421	44.712	46.262	0.962	385	693	722
y = 5	7.373	44.276	45.794	0.963	399	702	730
y = 7	7.338	43.985	45.508	0.965	417	704	742
y = 10	7.282	43.549	45.086	0.966	421	718	744

**Fig.3.** Composition dependence of density ( $d$ ) of  $(100-y) [30 B_2O_3 \cdot 70 Bi_2O_3] y Fe_2O_3$  glasses

The decrease in molar volume ( $V_m$ ) with increase in  $Fe_2O_3$  content can be explained on the basis of structural changes. With increasing the  $Fe_2O_3$  content  $FeO_n$  polyhedra units increase and participation of  $FeO_6$  groups play the role of modifying units. The decrease in molar volume of glass samples may also be due to the fact that  $Bi_2O_3$  provides excess structural free volume. The theoretical optical basicity ( $\wedge_{th}$ ) for the glass system under study has been calculated using the relation [24].

$$\wedge_{th} = X(B_2O_3) \wedge(B_2O_3) + X(Bi_2O_3) \wedge(Bi_2O_3) + X(Fe_2O_3) \wedge(Fe_2O_3) \quad (3)$$

Where  $X(B_2O_3)$ ,  $X(Bi_2O_3)$ ,  $X(Fe_2O_3)$  are the equivalent fractions of the different oxides i.e. the proportion of the oxide atom that contributes to the glass system and  $\wedge(B_2O_3)$ ,  $\wedge(Bi_2O_3)$ ,  $\wedge(Fe_2O_3)$  are the optical basicity values of the constituent oxides. Here the values of  $\wedge(B_2O_3) = 0.425$ ,  $\wedge(Bi_2O_3) = 1.19$  and  $\wedge(Fe_2O_3) = 1.02$  have been used as from literature [25].

The Theoretical optical basicity expresses the electron density carried by oxygen and is strongly dependent on electronic polarizability. This may be explained according to the relation suggested by Duffy [26].

$$\wedge_{th} = 1.67 \left[ 1 - \frac{1}{\alpha_o^2} \right] \quad (4)$$

Where  $\alpha_o$  is the oxide ion polarizability.

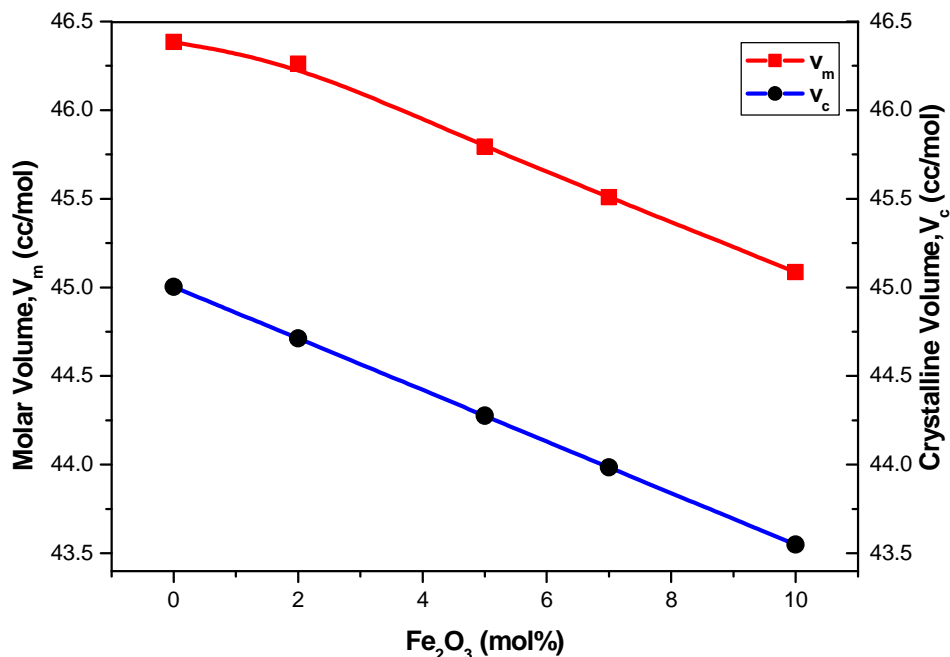


Fig.4. composition dependence of crystalline volume ( $V_c$ ) and molar volume ( $V_m$ ) of  $(100-y) [30 B_2O_3.70 Bi_2O_3] y Fe_2O_3$  glasses

This equation shows that basicity increases with increase in polarizability. The calculated values of Theoretical optical basicity are reported in Table 1 and variation of basicity with the  $Fe_2O_3$  content is shown in Fig.5 which shows that optical basicity is increased with increase of  $Fe_2O_3$  content which indicates the decrease in covalent character resulting into the increase of tendency of oxygen to donate electron and increase in polarizability of the glass samples.

**3.3 Differential scanning calorimetry (DSC):** Fig.6 shows DSC thermograms for the glass samples. The glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) determined from DSC thermograms for all the samples are presented in Table.1 along with probable error of  $\pm 1^\circ C$ . These characteristic temperatures are important for qualitative estimation of thermal stability and forming ability of glasses. The melting temperature ( $T_m$ ) of glasses increase gradually as content of  $Fe_2O_3$  is increased. The crystallization temperature ( $T_c$ ) also changes appreciably from  $590^\circ C$  to  $718^\circ C$  on increasing content of  $Fe_2O_3$ .

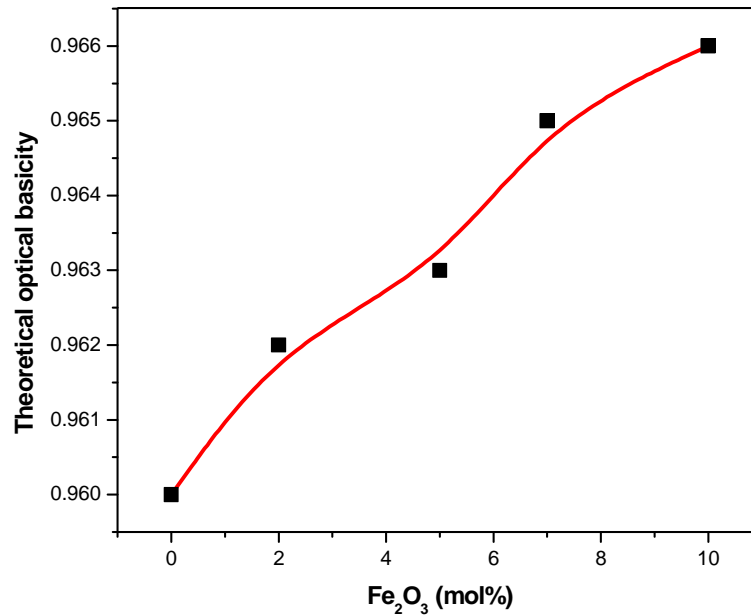


Fig.5 Composition dependence of theoretical optical basicity of  $(100-y)[30\text{B}_2\text{O}_3 \cdot 70\text{Bi}_2\text{O}_3]_y\text{Fe}_2\text{O}_3$  glasses

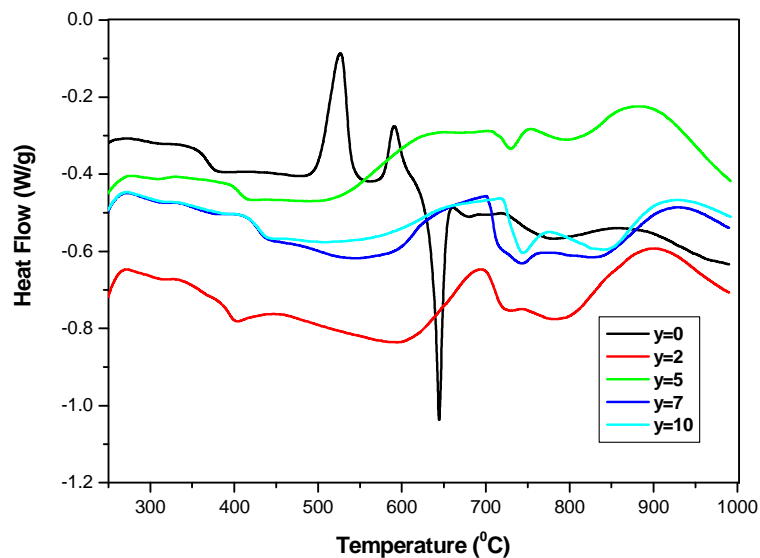


Fig.6. DSC thermograms of  $(100-y)[30\text{B}_2\text{O}_3 \cdot 70\text{Bi}_2\text{O}_3]_y\text{Fe}_2\text{O}_3$  glasses

The composition dependence of glass transition temperature ( $T_g$ ) is shown in Fig 7. The increase in  $T_g$  with increase of  $\text{Fe}_2\text{O}_3$  concentration is consistent with network strengthening. It is known that addition of  $\text{Fe}_2\text{O}_3$  can also improve durability very significantly [27,28] because  $\text{Fe}_2\text{O}_3$  can act both as an intermediate and a glass modifying oxide and can be present in both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states in glass network. With increasing  $\text{Fe}_2\text{O}_3$  content, number of Fe-O bonds replace Bi-O bonds and provide the thermal stability which is indicated by shifting both glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ). Thermal stability is an important factor in glasses for both fundamental and technological reasons. Thermal stability refers to the temperature range ( $T_c - T_g$ ) which facilitate the glass formation and hampers the process of crystallization. The higher is the thermal stability; the better is the

glass quality. The addition of  $\text{Fe}_2\text{O}_3$  is seen to result in glasses which are thermally more stable and less prone to crystallization.

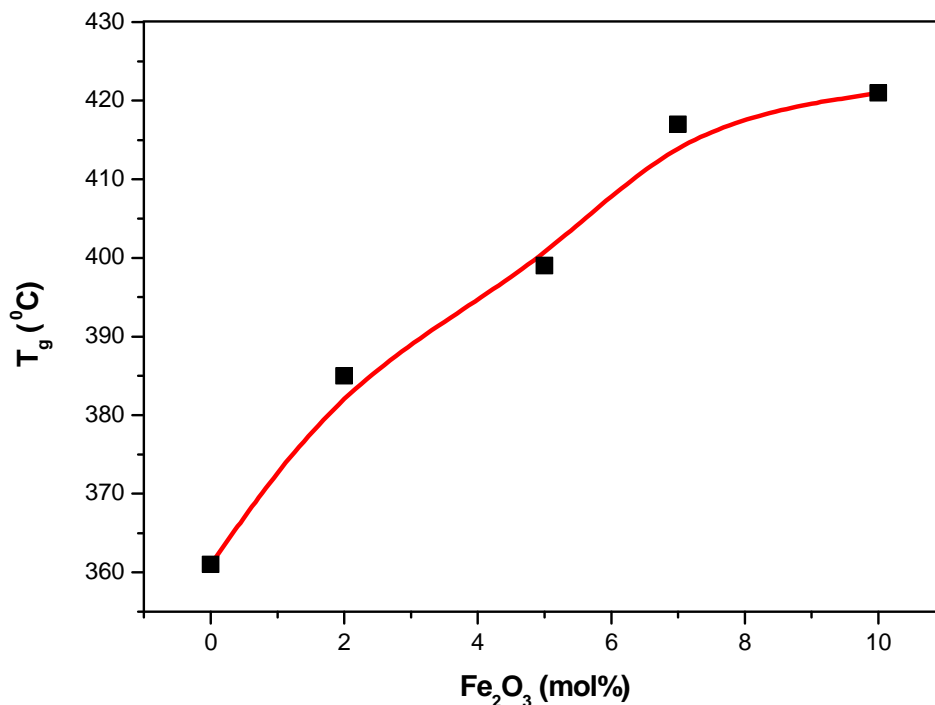


Fig.7. Composition dependence of glass transition temperature ( $T_g$ ) of  $(100-y)[30\text{B}_2\text{O}_3.70\text{Bi}_2\text{O}_3]_y\text{Fe}_2\text{O}_3$  glasses

**3.4 Infrared transmission spectra:** IR transmission spectra of the glasses were recorded over the range  $400\text{--}4000\text{ cm}^{-1}$  and are shown in Fig.8. The infrared band around  $1200\text{ cm}^{-1}$  is attributed to B-O and B-O stretching vibrations in borate triangular units. The bands between  $900\text{--}1100\text{ cm}^{-1}$  spectral range arise from pentaborate units. The influence of distorted ( $\text{BiO}_6$ ) polyhedra on the  $\text{B}_2\text{O}_3$  structure is evidenced from bands around  $700\text{ cm}^{-1}$ . It was shown that  $\text{Bi}_2\text{O}_3$  appears in the bismuth-borate glass networks as deformed ( $\text{BiO}_6$ ) groups, as ( $\text{BiO}_3$ ) pyramidal units or both ( $\text{BiO}_6$ ) and ( $\text{BiO}_3$ ) polyhedra [29]. The most important condition for the existence of ( $\text{BiO}_3$ ) polyhedra is the presence of band around  $830\text{ cm}^{-1}$  in the IR Spectra. The absence of this band after adding  $\text{Fe}_2\text{O}_3$  in the IR Spectra of the glasses proves that only the ( $\text{BiO}_6$ ) octahedra build up the bismuthate structure of these samples. The bands in the  $500\text{--}550\text{ cm}^{-1}$  range are ascribed to the vibrations of Fe-O bonds of the  $\text{FeO}_n$  polyhedra. Analysis of the IR spectrum shows that  $\text{BiO}_6$  &  $\text{FeO}_6$  groups play the role of modifying units and hinder the aperiodic network of  $\text{BO}_3$  &  $\text{BO}_4$  units and indicate that strong bonds between polyhedra are necessary to form stable glasses.



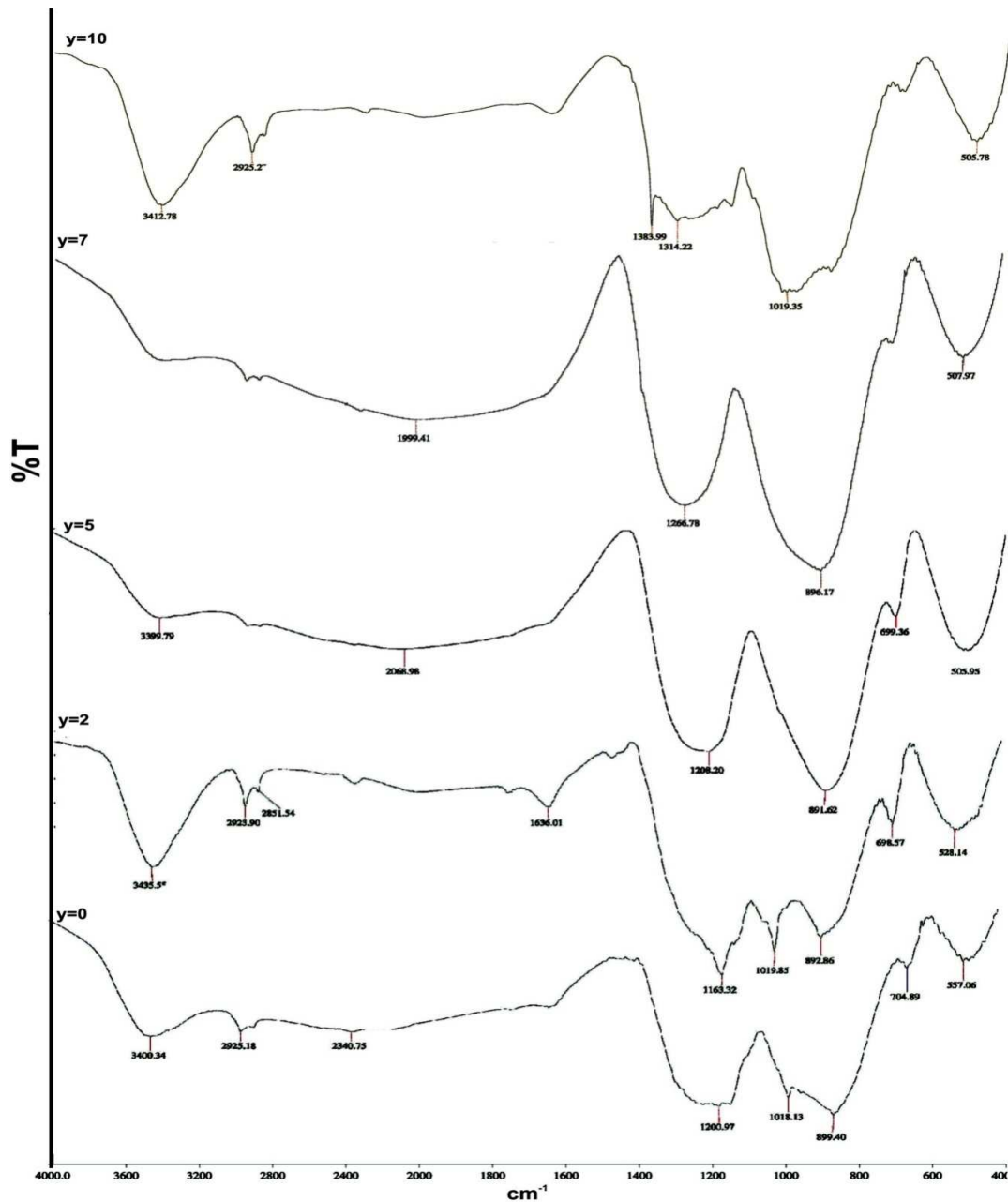


Fig.8. Infrared Spectra of  $(100-y)[30\text{ B}_2\text{O}_3.70\text{ Bi}_2\text{O}_3] y\text{ Fe}_2\text{O}_3$  glasses

### CONCLUSION

Physical and thermal properties are investigated for  $(100-y)[30\text{ B}_2\text{O}_3.70\text{ Fe}_2\text{O}_3] y\text{ Fe}_2\text{O}_3$  glasses ( $y=0, 2, 5, 7, 10$ ). Both density and molar volume decrease with increasing  $\text{Fe}_2\text{O}_3$  content while the thermal stability of glasses increases. IR Spectra shows that with increasing the  $\text{Fe}_2\text{O}_3$  content the influence of  $\text{Fe}_2\text{O}_3$  on the structure of bismuth borate matrices becomes stronger, a more ordered bismuthate structure occurring when higher  $\text{Fe}_2\text{O}_3$  content is added to the  $\text{B}_2\text{O}_3 - \text{Bi}_2\text{O}_3$  glass structure. Their result is further supported by the presence of bands attributed to Bi-O and Fe-O vibrations.

The results obtained in the present study show that the higher iron content strongly influences the structure of the bismuth-borate matrices determining more ordered bismuth vicinity and stabilizing the glass network.



**Acknowledgement**

Authors would like to thank University Grants Commission, New Delhi for providing financial support.

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