

## Glass formation domains and structural properties of nonconventional transition metal ion glasses

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**Abstract.** Glass formation domains and structural properties of some binary transition metal ion glasses based on nonconventional network formers  $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$  have been investigated. With the same network former, the glass formation domains depend on the transition metal ions. Homogeneous glasses with random network structure were obtained, as evidenced by the composition dependent density, molar volume and glass transition temperatures. Significant information about possible structural units in these glasses has been obtained from the IR spectra of these glasses.

**Keywords.** Glass formation domain; transition metal; nonconventional glass; glass transition temperature; molar volume; density; IR spectra.

### 1. Introduction

Oxide glasses based on nonconventional network formers like  $\text{PbO}$  and  $\text{Bi}_2\text{O}_3$  are of great interest because they form amorphous materials without traditional network formers like  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{SiO}_2$  etc and they can be used to produce glass-ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows etc (Dimitriev *et al* 1986; Mianxve and Peinan 1986; Aegerter *et al* 1990; Takahashi and Yamaguchi 1990). Fajans and Kreidl (1948) pointed out that  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$  cations are highly polarizable and the asymmetry of their polyhedra inhibits crystallization processes in the melts in which they participate. Multicomponent glasses based on  $\text{PbO}$  or  $\text{Bi}_2\text{O}_3$  have been successfully synthesized and their structures studied (Bishay and Maghrabi 1969; Dumbaugh 1978, 1986; Morikawa *et al* 1981; Rao *et al* 1984; Dimitriev *et al* 1986). The recently reported (Zheng and Mackenzie 1988; Tatsumisago *et al* 1990; Onisi *et al* 1991; Yuan *et al* 1991) multicomponent cuprate glasses in which  $\text{Bi}_2\text{O}_3$  is the main glass former are of particular interest because they can be used to produce high temperature superconductor glass-ceramics with controllable microstructure. In this paper, glass formation domains and structural properties of some  $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$  based nonconventional binary glasses containing transition metal ions such as V, Fe and Cu have been discussed. It is worth mentioning that these glasses exhibit semiconducting properties arising from the presence of multivalent states of the transition metal ions in the glassy materials and thus, have many applications, such as memory and threshold switching, ferrites, cathode materials, etc (Nakamura and Ichinose 1987; Ghosh 1988; Livage *et al* 1990; Sakuri and Yamaki 1990).

### 2. Experimental

Different binary glass compositions studied were prepared from reagent grade chemicals  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ . The binary mixtures of the

appropriate chemicals were melted in alumina crucibles for 2 h at temperatures depending on compositions. Glasses were obtained either by pouring the melts onto a twin-roller or by pressing the melts between two brass plates depending on glass systems and compositions. All the prepared glasses were tested for their amorphous structure using X-ray diffraction and scanning electron microscopy. Glass transition and crystallization temperatures were obtained from differential thermal analysis. Density was measured using Archimedes' principle. The IR spectra of these glasses in KBr matrices were recorded in the range  $200\text{--}4000\text{ cm}^{-1}$  in a Perkin-Elmer spectrophotometer. Final glass compositions were estimated either by atomic absorption or by chemical analysis. The concentrations of the reduced transition metal ions were determined by either chemical analysis or magnetic measurements.

### 3. Results and discussion

#### 3.1 Glass formation domain

Two systems of glasses of compositions  $(\text{PbO})_{1-x}(\text{TMO})_x$  and  $(\text{Bi}_2\text{O}_3)_{1-x}(\text{TMO})_x$ , where  $\text{TMO} = \text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  and  $x$  is the mol fraction of TMO, were studied. The glass formation domains for these two systems of glasses are shown in figure 1. It is clear that among the PbO based glasses, the glass formation domain  $0.25 \leq x \leq 0.90$  for the PbO- $\text{V}_2\text{O}_5$  system is the largest, while the domain  $0.05 \leq x \leq 0.30$  is the smallest for the PbO- $\text{Fe}_2\text{O}_3$  glasses. The PbO-CuO glasses have intermediate glass formation domain  $0.15 \leq x \leq 0.50$ . On the other hand, for the  $\text{Bi}_2\text{O}_3$  based glasses, the  $\text{Bi}_2\text{O}_3$ -CuO system has the largest glass formation domain  $0.25 \leq x \leq 0.70$ , while the glass formation domain  $0.70 \leq x \leq 0.95$  is the smallest for the  $\text{Bi}_2\text{O}_3$ - $\text{V}_2\text{O}_5$  glasses. The glass formation domain for the  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  system is the same as for PbO- $\text{Fe}_2\text{O}_3$  system. However, a larger glass formation domain for the  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  system has been reported using much faster quenching rate (Tanaka *et al* 1989). It is noted that glass formation occurs in the  $\text{Bi}_2\text{O}_3$ - $\text{V}_2\text{O}_5$  system for higher  $\text{V}_2\text{O}_5$  content.

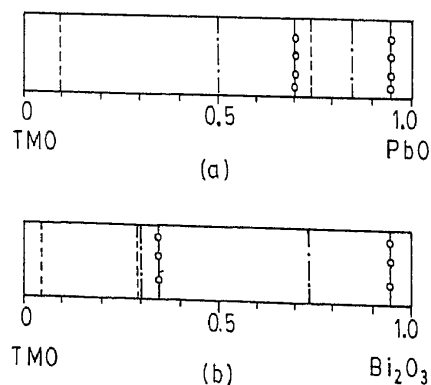


Figure 1. Glass formation domains for (a) PbO-TMO systems and (b)  $\text{Bi}_2\text{O}_3$ -TMO systems. Domain boundaries are shown by  $\circ$  for  $\text{V}_2\text{O}_5$ ;  $\triangle$  for  $\text{Fe}_2\text{O}_3$  and  $\square$  for CuO glasses.

### 3.2 Analyzed glass compositions

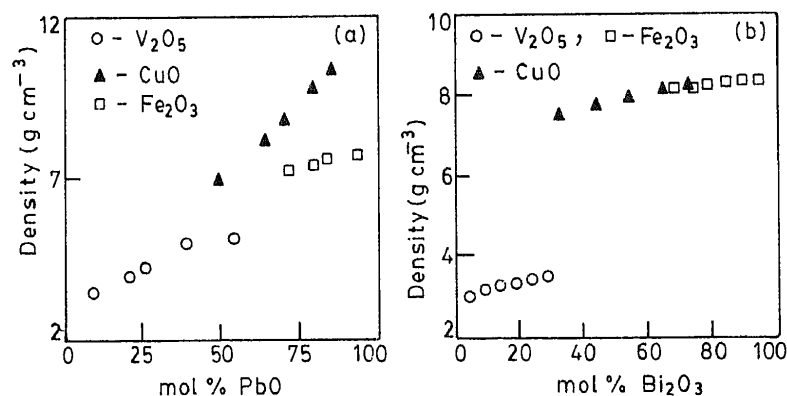
Wet chemical and atomic absorption spectroscopic analysis showed that all glass compositions changed slightly from the batch compositions due to evaporation loss. These measurements coupled with the magnetic measurements indicated that in all glass compositions, transition metal ions exist in two oxidation states, e.g.  $V^{4+}$  and  $V^{5+}$ ,  $Cu^+$  and  $Cu^{2+}$  and  $Fe^{2+}$  and  $Fe^{3+}$  for the vanadate, cuprate and ferric glasses, respectively. However, the concentrations of the reduced ions depend on the glass compositions. The fraction of the reduced ion concentration was observed to be the highest for cuprate glasses, while it was the lowest for ferric glasses.

### 3.3 Density and molar volume

The variation of density and molar volume of the two systems of glasses are shown in figures 2 and 3 respectively. It is clear from figure 2a that for the PbO based glasses, the density increases with the increase of PbO content. The density for the PbO–CuO glasses is higher than that for the PbO– $V_2O_5$  glasses. For the  $Bi_2O_3$  based glasses, the variation of density with composition is small for all glass compositions (figure 2b). The density of  $Bi_2O_3$ –CuO glasses is comparable with that of the  $Bi_2O_3$ – $Fe_2O_3$  glasses, while the density for the  $Bi_2O_3$ – $V_2O_5$  glasses is the lowest. On the other hand, the variation of the molar volume of the PbO–CuO glass system (figure 3a) with composition shows opposite trends to the variation of density, while for the other glass systems (figures 3a and b), molar volume changes with composition in a fashion similar to the density. Thus for the glass systems studied, except for PbO– $V_2O_5$  with PbO content > 50 mol%, the density and the molar volume change monotonically with composition. This indicates that all the glass systems are probably in a single phase with random network structure and that the geometry and topology of the random network do not change significantly with compositions.

### 3.4 Glass transition temperatures

The glass transition temperatures ( $T_g$ ) determined from the differential thermal analysis curves are shown in figure 4, as a function of compositions. Figure 4a indicates



**Figure 2.** Variation of density with glass composition: (a) PbO–TMO glasses and (b)  $Bi_2O_3$ –TMO glasses.

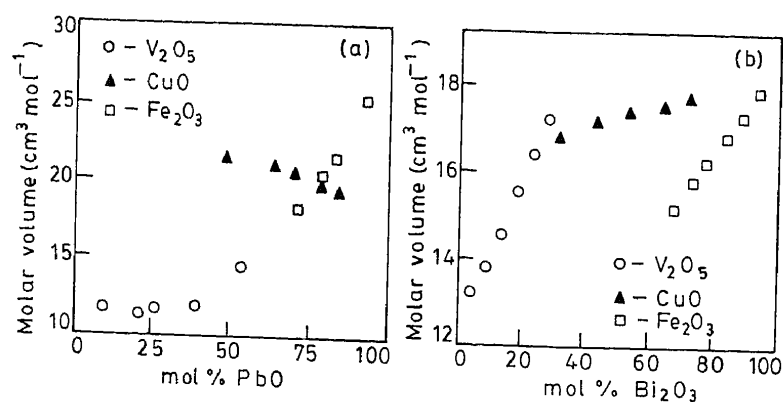


Figure 3. Variation of molar volume with glass compositions: (a) PbO-TMO glasses and (b)  $\text{Bi}_2\text{O}_3$ -TMO glasses.

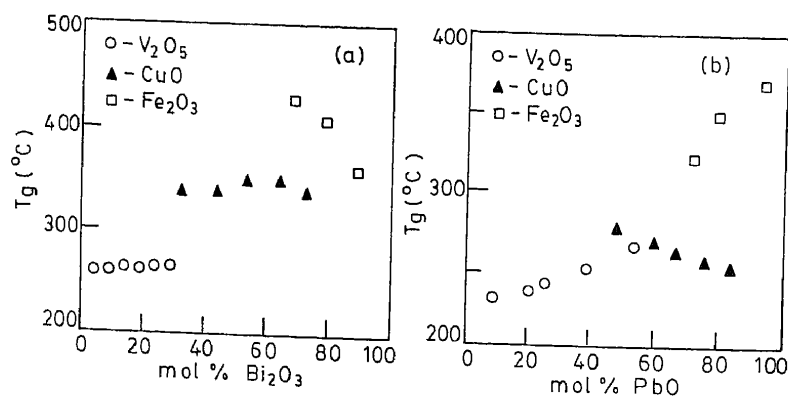
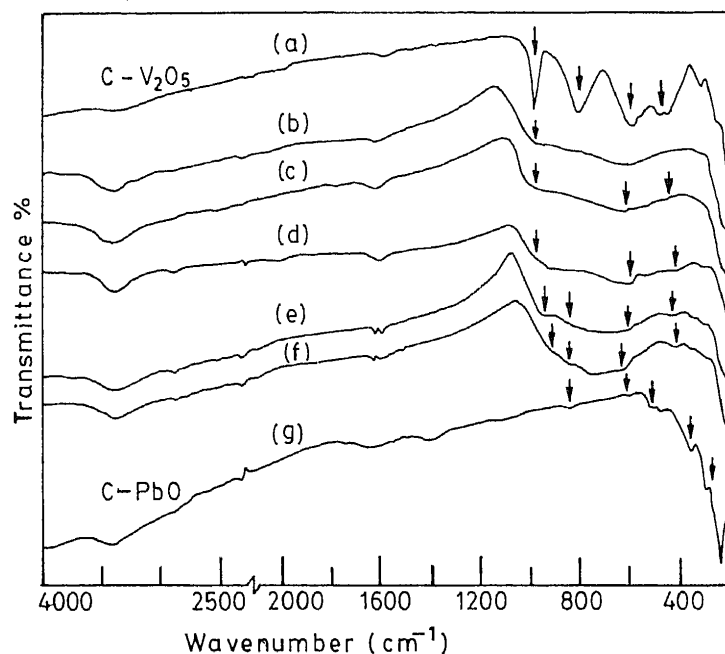


Figure 4. Composition dependence of the glass transition temperature ( $T_g$ ): (a)  $\text{Bi}_2\text{O}_3$ -TMO glasses and (b) PbO-TMO glasses.

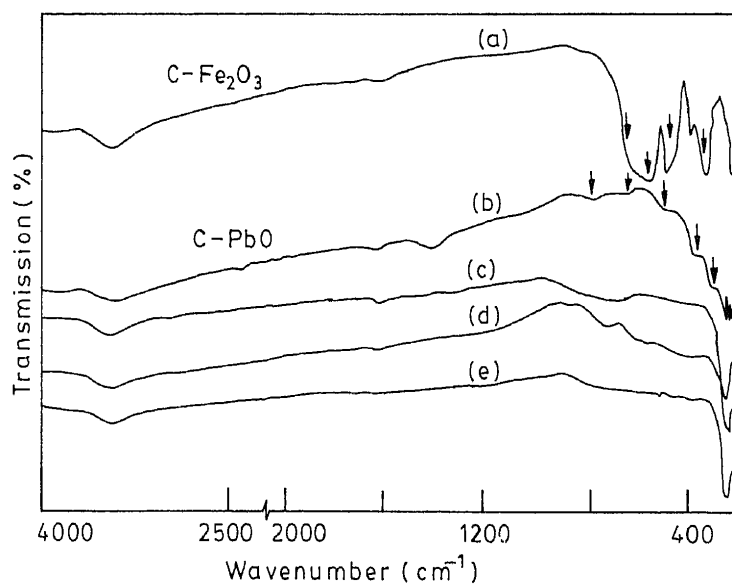
that the  $T_g$  increases with  $\text{Bi}_2\text{O}_3$  content in the  $\text{Bi}_2\text{O}_3$ - $\text{V}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3$ - $\text{CuO}$  glasses, while  $T_g$  decreases for the  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  glasses. The  $T_g$  also increases with PbO content in PbO- $\text{V}_2\text{O}_5$  and PbO- $\text{Fe}_2\text{O}_3$  systems while  $T_g$  decreases slightly for the PbO- $\text{CuO}$  system (figure 4b). Since glass transition temperature depends on the strength and connectivity of the network, it is clear from figure 4 that the strength and connectivity of the network increase with the increase of PbO or  $\text{Bi}_2\text{O}_3$  content in all glass systems except for the  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  systems. In the  $\text{Bi}_2\text{O}_3$ - $\text{CuO}$  and PbO- $\text{CuO}$  systems, however, the variation of  $T_g$  with composition is small. The effect of the coulombic field of substitution can account for such a small variation in  $T_g$ . The increase of  $T_g$  with  $\text{Bi}_2\text{O}_3$  or PbO content in the vanadate glass system also suggest a continuous change of the glass matrix having a 2D vanadate layer structure into a more complicated 3D structure (Mandal and Ghosh 1993). These conclusions are also supported by the IR results.

### 3.5 Infrared spectra

Infrared (IR) spectra of the glass compositions yield important information about structural units. The spectra of several glass compositions have been reported elsewhere



**Figure 5.** Room temperature IR spectra of PbO- $V_2O_5$  glasses: (a) Crystalline  $V_2O_5$ , (b) 90 mol%  $V_2O_5$ , (c) 80 mol%  $V_2O_5$ , (d) 70 mol%  $V_2O_5$ , (e) 60 mol%  $V_2O_5$ , (f) 50 mol%  $V_2O_5$  and (g) crystalline PbO.



**Figure 6.** Room temperature IR spectra of PbO- $Fe_2O_3$  glasses: (a) crystalline  $Fe_2O_3$ , (b) crystalline PbO, (c) 10 mol%  $Fe_2O_3$ , (d) 15 mol%  $Fe_2O_3$  and (e) 20 mol%  $Fe_2O_3$ .

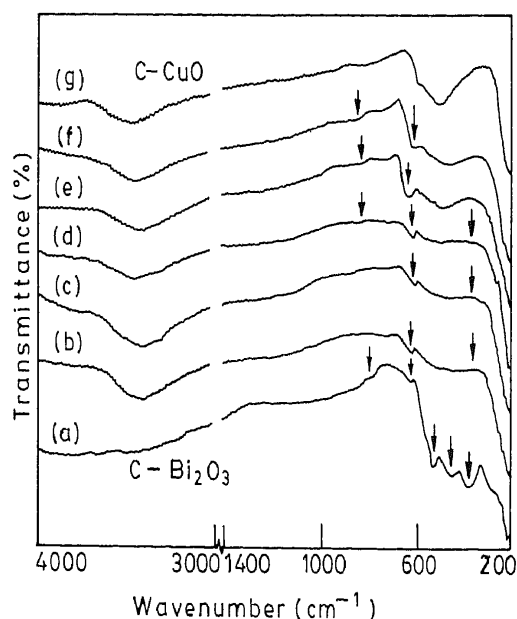


Figure 7. Room temperature IR spectra of  $\text{Bi}_2\text{O}_3$ -CuO glasses: (a) crystalline  $\text{Bi}_2\text{O}_3$ , (b) 27 mol% CuO, (c) 35.4 mol% CuO, (d) 46 mol% CuO, (e) 56 mol% CuO, (f) 68 mol% CuO and (g) crystalline CuO.

(Mandal and Ghosh 1993; Hazra and Ghosh 1995). For brevity, IR spectra of three glass systems for different compositions are shown in figures 5–7.

**3.5a  $\text{PbO-V}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$  glass systems:** It is clear from the IR spectra of  $\text{PbO-V}_2\text{O}_5$  glasses presented in figure 6 that the band at  $1020\text{ cm}^{-1}$  for the  $\text{V=O}$  bond vibration of the crystalline  $\text{V}_2\text{O}_5$  becomes very weak for the glass compositions and shifts to lower frequencies with increasing PbO content. Also new bands appear in the range  $950\text{--}970\text{ cm}^{-1}$ . For PbO content  $>40\text{ mol}\%$ , the band at  $1020\text{ cm}^{-1}$  vanishes and new bands appear at  $950\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$ . According to the mechanism suggested earlier (Dimitriev *et al* 1983), the  $\text{Pb}^{2+}$  ions occupy position between the  $\text{V-O-V}$  layers and have a direct influence on the isolated  $\text{V=O}$  bond of the  $\text{VO}_5$  groups of the crystalline  $\text{V}_2\text{O}_5$ . This leads to a drop in the wave numbers down to  $970\text{--}950\text{ cm}^{-1}$  for the compositions with PbO content below  $40\text{ mol}\%$  and thus for these glass compositions, unaffected  $\text{VO}_5$  polyhedra are preserved along with the affected  $\text{VO}_5$  polyhedra. However, for glass compositions with PbO content above  $30\text{ mol}\%$ , only affected  $\text{VO}_5$  polyhedra are present. The IR spectra of the  $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$  glasses, reported earlier (Ghosh 1987) indicate that the band at  $1020\text{ cm}^{-1}$  for the  $\text{V=O}$  bond vibration in the  $\text{VO}_5$  polyhedra is observed for glass composition with  $95\text{ mol}\%$   $\text{V}_2\text{O}_5$ . However, with decreasing  $\text{V}_2\text{O}_5$  content, this band becomes very weak shoulder at  $1000\text{--}980\text{ cm}^{-1}$ . Thus for these compositions,  $\text{Bi}^{3+}$  ions occupy positions between vanadate layers and chains and thus affect directly  $\text{V=O}$  bond similar to  $\text{Pb}^{2+}$  ions in  $\text{PbO-V}_2\text{O}_5$  glass compositions.

**3.5b  $\text{PbO-Fe}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3$  glass systems:** As shown in figure 6, the intensity of the absorption bands for the  $\text{PbO-Fe}_2\text{O}_3$  glass compositions is very

weak compared to the crystalline PbO and Fe<sub>2</sub>O<sub>3</sub>. However, weak bands at 820 cm<sup>-1</sup> and 630 cm<sup>-1</sup> are observed in all glass compositions. These bands also correspond to the bands of crystalline PbO for Pb–O bond vibration in PbO<sub>4</sub> tetrahedra. The band at 350 cm<sup>-1</sup> corresponding to the orthorhombic PbO is not observed in the glass compositions. It may be noted from figure 6 that the bands corresponding to the Fe–O bond are not significant in the glasses. However, Mössbauer studies (Mandal *et al* 1994, 1995) indicate the presence of FeO<sub>4</sub> tetrahedra in all glass compositions and the Fe–O bond covalency is large compared to the conventional ferric glasses.

The IR spectra of the Bi<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> glasses have been reported earlier (Ghosh 1987). The bands at 840 cm<sup>-1</sup>, 540–620 cm<sup>-1</sup>, 470 cm<sup>-1</sup> and 350 cm<sup>-1</sup> are observed in all glass compositions, suggesting that these glasses are built up of BiO<sub>3</sub> pyramidal unit similar to Bi<sub>2</sub>O<sub>3</sub>–CuO glasses. Mössbauer studies (Tanaka *et al* 1989) showed that Fe exists as Fe<sup>3+</sup> ions in FeO<sub>4</sub> tetrahedra (isomer shift < 0.4 mms<sup>-1</sup>) and the covalency of Fe–O bond decreases with the increase of Fe<sub>2</sub>O<sub>3</sub> content in the glass compositions.

### 3.6 Bi<sub>2</sub>O<sub>3</sub>–CuO and PbO–CuO glass systems

For all glass compositions, four fundamental absorption bands at 830 cm<sup>-1</sup>, 620 cm<sup>-1</sup>, 450 cm<sup>-1</sup> and 350 cm<sup>-1</sup> are observed in the IR spectra (figure 7). These absorption bands are characteristic of BiO<sub>3</sub> pyramidal units of the crystalline Bi<sub>2</sub>O<sub>3</sub>. The intensity of these bands, however, decreases and broadens significantly for the glass compositions due to their disordered structure. Thus the IR spectra suggest that the glass compositions consist of BiO<sub>3</sub> pyramidal units. The symmetric vibration bands at 830 cm<sup>-1</sup> and 450 cm<sup>-1</sup> for the glasses have higher wave numbers compared to the vibrational bands of fused Bi<sub>2</sub>O<sub>3</sub>, suggesting that the stronger Bi–O bonds are present in the glass compositions caused by the polarization effects. These observations for the binary bismuth cuprate glasses are in sharp contrast to the multicomponent bismuth cuprate glass compositions (Zheng *et al* 1989), in which both BiO<sub>6</sub> octahedral and BiO<sub>3</sub> pyramidal units are present depending on compositions. In these glasses with increasing SrO and CaO contents, a conversion of BiO<sub>6</sub> units to BiO<sub>3</sub> units was observed producing nonbridging oxygen atoms. For the PbO–CuO glasses, IR bands have been observed at 830 cm<sup>-1</sup>, 620 cm<sup>-1</sup> and 460 cm<sup>-1</sup> corresponding to the bands of crystalline PbO and this might be due to Pb–O bond vibration in the PbO<sub>4</sub> tetrahedra. However, the presence of the band at 720 cm<sup>-1</sup>, which is absent in either PbO or CuO, is not clear at the moment.

### 3.7 Magnetic properties

Magnetic susceptibility of all glass compositions showed paramagnetic character of these materials and increased with the increasing transition metal ion. The magnetic properties of these materials arise from the paramagnetic transition metal ions with 3d electrons. The concentrations of the reduced transition metal ions estimated from magnetic susceptibility data were found to be close to their estimates from the chemical analysis.

#### 4. Conclusions

Glass formation domains and structural properties of some binary transition metal ion glasses based on nonconventional glass network formers PbO and Bi<sub>2</sub>O<sub>3</sub> have been studied. Glass formation domains depend on the glass systems as evidenced by X-ray diffraction studies. The composition dependence of density and molar volume shows that the prepared glasses are homogeneous with random network structure. The variation of the glass transition temperature indicates that the strength of the network structure depend on the nature of transition metal ions and glass formers. The structural units building up of these glasses have been obtained from the IR spectra.

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