

DENSITY AND FTIR STUDIES OF MULTIPLE TRANSITION METAL DOPED BORATE GLASS

Gurinder Pal Singh, Parvinder Kaur, Simranpreet Kaur, Deepawali Arora,
Prabhjot Singh, D.P. Singh*

Department of Physics, Guru Nanak Dev University, Amritsar 143005, India

*e-mail: dpsinghdr@yahoo.com

Abstract. Glass samples of compositions $x\text{CuO}-(30-x)\text{ZnO}-70\text{B}_2\text{O}_3$ and $x\text{MnO}_2-(30-x)\text{ZnO}-70\text{B}_2\text{O}_3$ (where $x = 5$ to 10 mol %) are prepared in the glass forming region. FTIR and density measurements are carried out for these glasses. IR transmission gives valuable information about the nature of bonds present in the glass matrix. It has been observed that, density of $\text{MnO}_2\text{-ZnO-B}_2\text{O}_3$ glasses has greater value. This is observed that the atomic structure changes more with the incorporation of MnO_2 .

1. Introduction

B_2O_3 is one of the best-known glass formers and it is present in varieties of commercial glasses. The structure of amorphous B_2O_3 is made up of planar BO_3 triangles linked through B–O–B linkages. The addition of a network modifier to pure B_2O_3 glass may result either in the conversion of the triangular BO_3 structural units to BO_4 tetrahedral or the formation of non-bridging oxygen atoms (NBOs).

Over the past few years, the study on the role of transition metal ions on the physical properties of various inorganic glass systems has been the subject of a great deal of interest [1-2]. These ions are being extensively used in the present days to probe the glass structure since their outer d-electron orbital functions have broad radial distribution and also possess a highly sensitive response to the changes in the surrounding actions. The transition metal ions such as iron, zinc, chromium, copper etc. When dissolved in B_2O_3 glass matrix even in very small quantities influence the physical properties very strongly. The occurrence of transition metal ions in different oxidation states with different coordination numbers is mainly responsible for conveying significant changes in the structural and physical properties of the glasses. In past many studies have been performed the effect of transition metals on different properties of borate glasses [3-4].

ZnO has attained a considerable attention due to its widespread applications in the field of glass–ceramics, thermal and mechanical sensors, reflecting windows, or may be used as layers for optical and opto-electronic devices, etc. These glasses have a long infrared (IR) cut-off, and high third-order non-linear optical susceptibility which makes them ideal candidates to be applicable in infrared transmission components, ultra fast optical switches, and photonic devices [5–11].

Among various transition metal ions, the copper ion when dissolved in glass matrices in very small quantities makes the glasses coloured and has a strong influence over the structural & optical properties of the glasses [12]. In different glasses, copper can exist as a monovalent (Cu^+) ion or as a divalent (Cu^{2+}) ion. Bright and prominent bluish green colour

32 *G. Pal Singh, Parvinder Kaur, Simranpreet Kaur, Deepawali Arora, Prabhjot Singh, D.P. Singh*
could be found due to the presence of Cu^{2+} ions from the point of view of ligand field theory [13].

The aim of the present work is to examine the effect of multiple transition metals on structural and physical parameters of the $\text{ZnO-B}_2\text{O}_3$ glasses. The structural property is analysed by using FTIR (Fourier transform infrared spectroscopy) and density measurement.

2. Experimental procedure

Sample preparation. Glass samples $x\text{M}-(30-x)\text{ZnO-70B}_2\text{O}_3$ (where M is CuO and MnO_2) with x varying from 5 to 20 mol % have been prepared by the conventional melt quench technique. The experimental details are same as present in previous study [14].

Table1. Nominal composition (mole %) and density of the glass samples respectively.

Glass code	MnO_2 (%)	CuO (%)	ZnO (%)	B_2O_3 (%)	Density (D) (g/cm^3) ± 0.008
cuo	0	5	25	70	2.19
cu1	0	10	20	70	2.29
cu2	0	15	15	70	2.34
cu3	0	20	10	70	2.32
mn0	5	0	25	70	2.31
mn1	10	0	20	70	2.38
mn2	15	0	15	70	2.45
mn3	20	0	10	70	2.49

The errors in the measurement of density and band gap are estimated to be 0.008 g cm^{-3} and 0.0084 respectively.

3. Results and discussion

Density. The density of glasses has been shown in Table 1. It has been observed that the density of glasses increases with increase in transition metal content in the glass network. But the value of density has a greater value for manganese glasses. For $\text{MnO}_2\text{-ZnO-B}_2\text{O}_3$ glass samples, density increases progressively with an increase in manganese content. This is due to availability of more oxygen's from MnO_2 which helps to convert $[\text{BO}_3]$ to $[\text{BO}_4]$. In $\text{CuO-ZnO-B}_2\text{O}_3$, from the sample cu0 to cu2, an increase in density is due to the formation of tetrahedral borate groups, which helps to compact the glass network. But the value of density decreases in sample cu3 which is due to formation of $[\text{BO}_3]$ groups with non bridging oxygen's.

The increase in the density reveals more compaction of the glass structure with increasing MnO_2 content as compared to CuO containing glasses. The variation of density with changing MnO_2 and CuO contents has been shown in Fig. 1.

FTIR. The Fourier transform infrared spectroscopy is used to analyze the influence of transition metal incorporation in the transition metal oxide borate glass network.

According to literature survey, the borate spectra are divided into following three regions [14-15]. The regions are:

- (I) $600\text{-}800\text{ cm}^{-1}$ for the B-O-B vibrations;
- (II) $800\text{-}1200\text{ cm}^{-1}$ for BO_4 groups;
- (III) $1200\text{-}1600\text{ cm}^{-1}$ for BO_3 groups.

There is another band from $2300\text{-}3000\text{ cm}^{-1}$, which is due to hydrogen bonding in OH group [16-17].

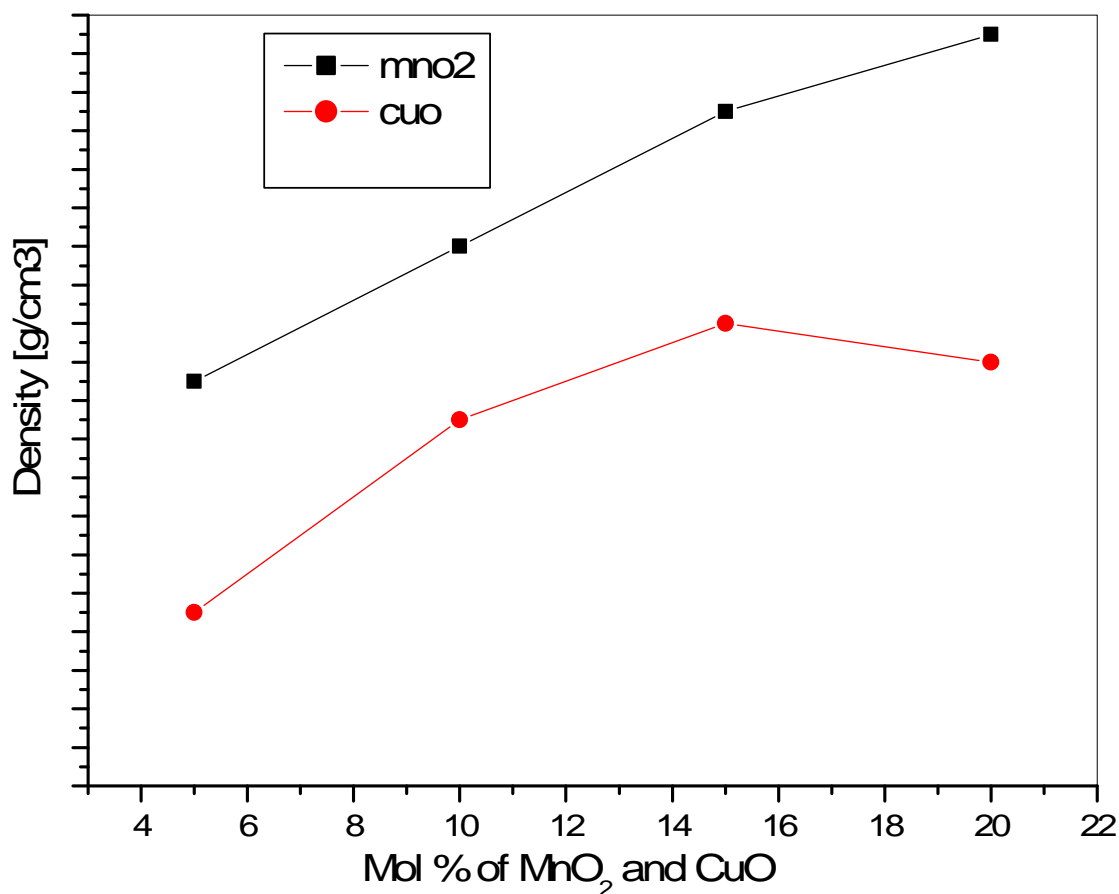


Fig. 1. Density of MnO₂-ZnO-B₂O₃ and CuO-ZnO-B₂O₃ glasses.

FTIR spectra of CuO-ZnO-B₂O₃ glasses. The FTIR spectra of CuO-ZnO-B₂O₃ glasses consists three major peaks at 679, 984, and 1344 cm⁻¹ in sample cu0 as shown in Fig. 2. The band centred at 679 cm⁻¹ has been assigned to B-O-B bending vibrations of BO₃ and BO₄ groups [18]. With an addition of copper oxide content, this band is shifting towards the higher wave number and an increase in intensity of this band has also been noticed. The band present at 984 cm⁻¹ is due to B-O bond stretching of BO₄ groups [19]. As the concentration of CuO is increasing, this band is also shifting towards the higher wave number side. The increased intensity of this peak indicates an increase of BO₄ groups. The band in the region 1200-1500 cm⁻¹ centered at 1344 cm⁻¹ is due to B-O stretching of BO₃ groups [20]. It has been revealed from the Fig. 2 the intensity of the band at 1344 cm⁻¹ has greater value than the intensity of band at 1007 cm⁻¹ which indicates presence of more [BO₃] groups than [BO₄].

FTIR spectra of MnO₂-ZnO-B₂O₃ glasses. The infrared transmittance spectra of MnO₂-ZnO-B₂O₃ glasses in the 400–4000 cm⁻¹ region as shown in Fig. 3 has prominent characteristic bands at 691 cm⁻¹, 996 cm⁻¹, and at 1370 cm⁻¹.

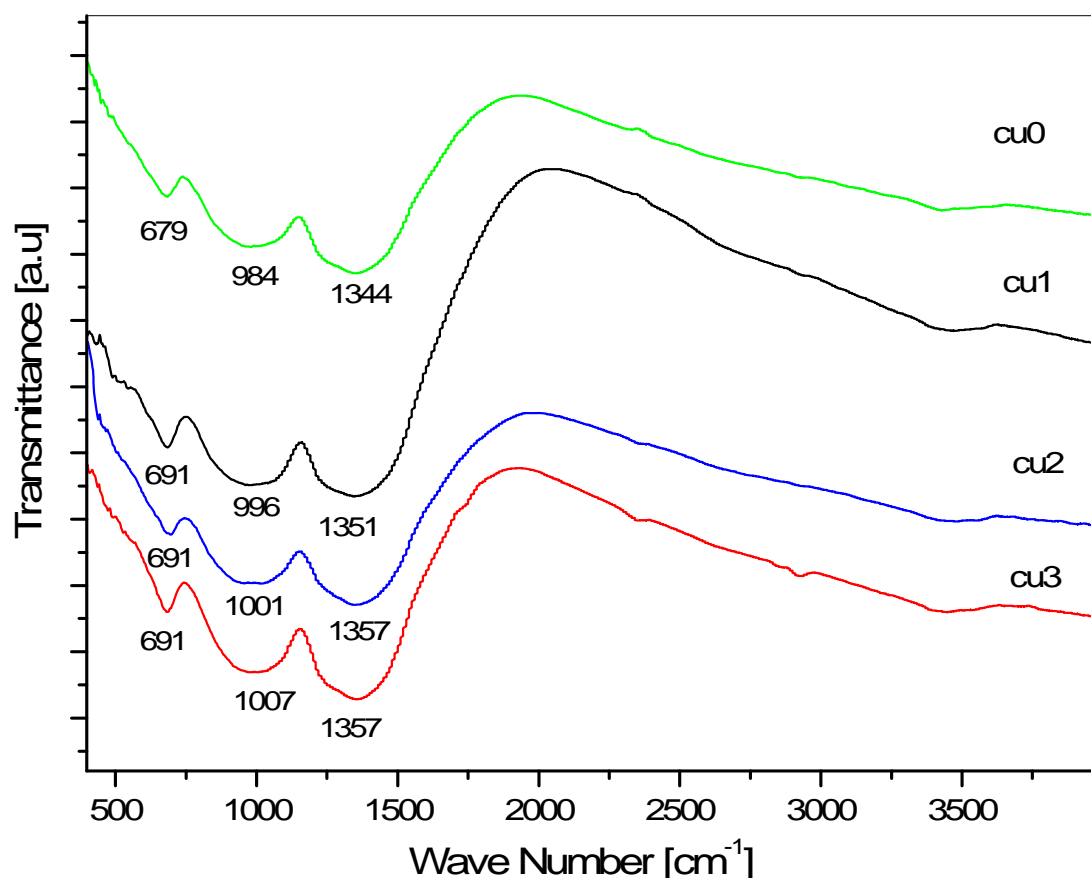


Fig. 2. FTIR spectra of CuO-ZnO-B₂O₃ glasses.

The band centered at 691 cm⁻¹ has been assigned to B-O-B bending vibration of BO₃ and BO₄ groups. Its intensity increases with an increase in MnO₂ concentration. In the sample WA1 the band observed at 996 cm⁻¹ is due to B-O bond stretching of BO₄ groups. This band is shifting towards the lower wave number (from 996 to 984 cm⁻¹) side in other samples with an increase in the percentage of MnO₂. Its intensity also increases which is due to an increase in tetrahedral BO₄ groups in the borate network [21-22]. This is due to availability of more oxygen's from manganese contents in glasses.

The band in the region 1200-1500 cm⁻¹ centered at 1370 cm⁻¹ is due to B-O stretching of BO₃ groups in ortho and meta-borate units [22]. It has been observed that the intensity of peak at 1378 cm⁻¹ also decreases with increasing MnO₂ content.

Above results show that the incorporation of CuO and MnO₂ has shifted the position and changed the intensity of the bands. This is due to change in coordination of borate network either due to formation of [BO₃] or [BO₄] units. It has been observed that for MnO₂-ZnO-B₂O₃ glass system the intensity of band in 800-1200 cm⁻¹ region increases corresponding to a decrease in intensity of the band from 1200-1600 cm⁻¹ with an increase in the manganese concentration. This shows that the manganese provides the oxygen's to form more [BO₄] groups in the glass network. In case of CuO-ZnO-B₂O₃ intensity of the bands between region 800-1200 cm⁻¹ has lesser value than MnO₂-ZnO-B₂O₃ glasses. Also at higher

concentrations, copper helps to form more $[\text{BO}_3]$ groups which have been revealed from the sample cu3 in Fig. 2. Hence manganese incorporation helps to form more stable glass as compared to copper addition.

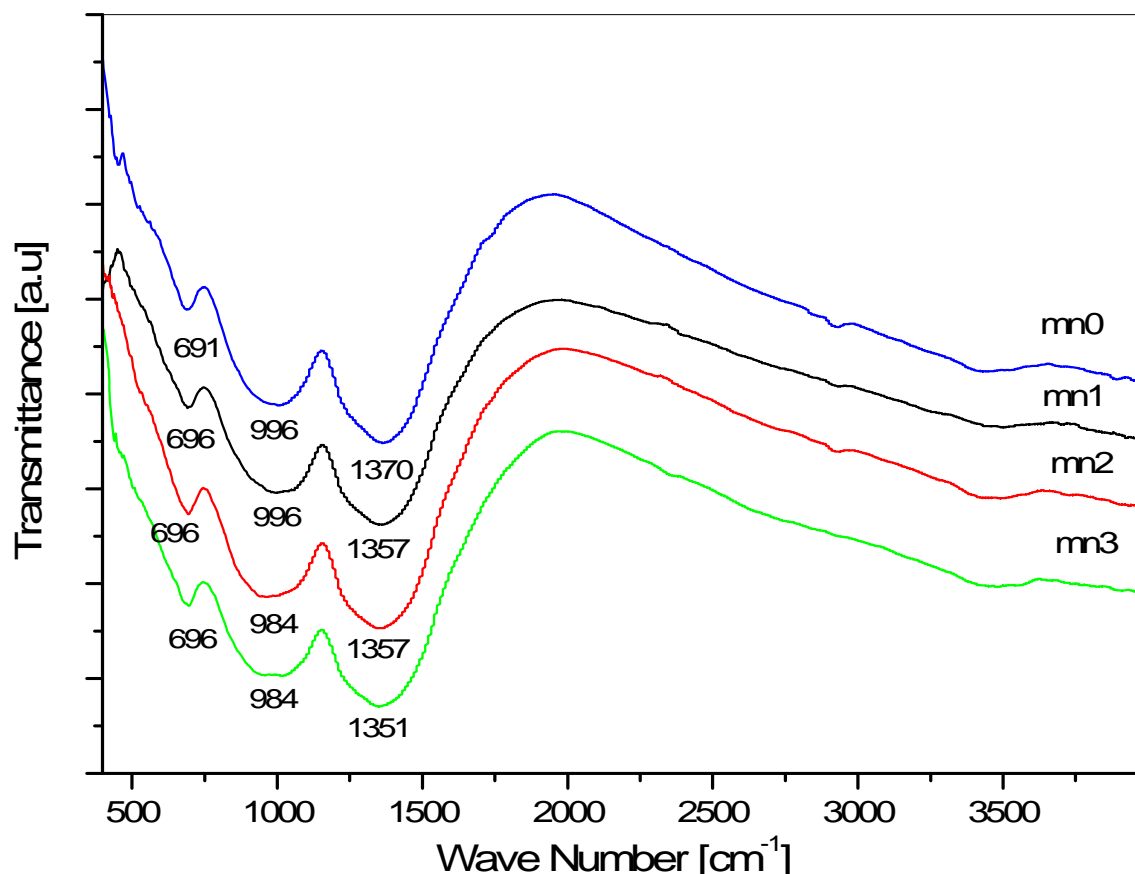


Fig. 3. FTIR spectra of MnO₂-ZnO-B₂O₃ glasses.

4. Conclusion

The FTIR study shows the incorporation of MnO₂ and CuO in ZnO-B₂O₃ helps to modify the borate network. It has been observed that MnO₂ content helps in converting more $[\text{BO}_3]$ group to $[\text{BO}_4]$ units. This reveals that manganese ions have a dominate role in zinc borate glass system.

References

- [1] G. Pal Singh, Simranpreet Kaur, Parvinder Kaur, Sunil Kumar, D.P. Singh // *Physica B* **406** (2011) 1890.
- [2] G. Pal Singh, D.P. Singh // *Physica B* **406** (2011) 3402.
- [3] H. Doweider, G.M. El-Damrawi, Y.M. Moustafa // *J. Phys.: Condens. Matter.* **6** (1994) 8829.
- [4] Y.M. Moustafa, A.K. Hassan, G.M. El-Damrawi, N.G. Yevtushenko// *J. Non-Cryst. Solids* **194** (1996) 34.
- [5] B.H. Venkataraman, K.B.R. Varma // *Opt. Mater.* **28** (2006) 1423.
- [6] Y. Dimitriev, V. Mihailova, E. Gattef // *Phys. Chem. Glasses* **34** (1986) 114.
- [7] Y. Cheng, H. Xiao, Wenming Guo, Weiming Gu // *Thermochimica Acta* **444** (2006) 173.

- 36 G. Pal Singh, Parvinder Kaur, Simranpreet Kaur, Deepawali Arora, Prabhjot Singh, D.P. Singh
- [8] H. Zheng, R. Xu, J.D. Mackenzie // *J. Mater. Res.* **4** (1989) 911.
- [9] M. Onishi, M. Kyoto, M. Watanabe // *Jpn. J. Appl. Phys.* **30** (1991) L988.
- [10] W.H. Dumbaugh // *Phys. Chem. Glasses* **19** (1978) 121.
- [11] Huaxin Li, Huixing Chen, Wei Lin, Lan Luo // *J. Non-Cryst. Solids* **352** (2006) 3069.
- [12] EzzEldin Metwalli // *J. Non-Cryst. Solids* **317** (2003) 221.
- [13] C.R. Bamford // *Phys. Chem. Glasses* **3** (1962) 189.
- [14] G. Pal Singh, Parvinder Kaur, Simranpreet Kaur, D.P. Singh // *Mater. Phys. and Mech.* **12** (2011) 58.
- [15] G. Pal Singh, D.P. Singh// *Physica B* **406** (2011) 640.
- [16] R.D. Husung, R H Doremus // *J. Mater. Res.* **5** (1990) 2209.
- [17] H. Dunken, R.H. Doremus // *J. Non-Cryst. Solids* **92** (1987) 61.
- [18] G. Pal Singh, D.P. Singh // *Journal of Molecular Structure* **1012** (2012) 137.
- [19] G. Pal Singh, Simranpreet Kaur, Parvinder Kaur, D.P. Singh // *Physica B* **407** (2012) 1250.
- [20] H. Doweider, Y.B. Saddeek // *J. Non-Cryst. Solids* **355** (2009) 348.
- [21] P. Poscuta, G. Borodi, E. Culea // *J. Non-Cryst. Solids* **354** (2008) 5475.
- [22] G. Pal Singh, Parvinder Kaur, Simranpreet Kaur, D.P. Singh // *Physica B* **406** (2011) 4652.