

# Structural study of TM doped alkali bismuth borate glasses

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## ABSTRACT

The study of ternary alkali bismuth borate glasses doped with various 3d transition metals (TM) has been carried out to give more information on the oxidation states of 3d transition metal ions doped in a host of ternary alkali bismuth borate glasses. The compositional variation in density and molar volume has been investigated in terms of the structural modification that takes place in the glass matrix on introducing various 3d TM in these glasses. Analysis of FTIR spectra shows the peak positions ( $\text{cm}^{-1}$ ) at around  $700 \text{ cm}^{-1}$  corresponds to B-O-B bending while the broad peak at  $900\text{-}1150 \text{ cm}^{-1}$  result due to combined contributions of stretching vibrations of B-O bonds in  $\text{BO}_3$  units from pyro-orthoborate groups and stretching vibrations of B-O bonds in tetrahedral  $\text{BO}_4$  units in tri-borate, tetraborate and penta-borate groups. Another broad peak around  $1300\text{-}1500 \text{ cm}^{-1}$  attributes to vibrations attached to large segments of borate network. Copyright © 2013 VBRI Press

**Keywords:** Glasses; oxides; FTIR spectroscopy.



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## Introduction

Glasses containing  $\text{Bi}_2\text{O}_3$  with a high refractive index are promising material for advanced optical telecommunication and processing devices [1]. The large polarisability of bismuth makes it suitable for possible nonlinear optical uses and recent environmental guidelines [2]. Glasses having high- $\text{Bi}_2\text{O}_3$  content have found uses as an efficient  $\gamma$ -ray absorber [3, 4] and also in scintillation detectors [5, 6] for high energy physics. Moreover, bismuthate glasses are excellent precursors for the fabrication of ceramic superconductors [7, 8]. Glasses doped with transition metal ions exhibit interesting optical, magnetic, and electrical properties due to the possible presence of such TM ions in two or more valence or coordination states [9–12]. Recent contributions on optical studies of 3d TM ions in various glasses have reached the conclusion that transition metal ions predominantly exhibit the high valence or tetrahedral coordination states in alkali borate, alkali silicate, cabal, bioglass [13–15], while in alkali phosphate and lead phosphate glasses [16, 17] they exist mostly in the low valence or octahedral forms. Therefore, the FTIR absorption spectroscopic study of ternary alkali bismuth borate glasses doped with various 3d transition metals (TM) has been carried out to give more information on the oxidation states of 3d transition metal ions doped in a host of ternary alkali bismuth borate glasses.

## Experimental

The glass systems  $20\text{Na}_2\text{O} \cdot 30\text{Bi}_2\text{O}_3 \cdot (50-x)\text{B}_2\text{O}_3 \cdot x\text{TMO}$  (where, TMO may be  $\text{V}_2\text{O}_5$  or  $\text{Fe}_2\text{O}_3$  with  $x = 0, 0.2, 0.3, 0.5, 2.0$  mol%), have been prepared using the normal melt-quench technique. Analytical grade chemicals of  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$  were taken in appropriate amounts and thoroughly mixed to form a batch of 20 g. The well-mixed chemicals were then melted at 1373K in porcelain crucibles using an electrical muffle furnace for 0.5 h. The mixture was stirred frequently to ensure homogeneity. The melt was rapidly quenched in between two stainless steel plates at room temperature (RT). Density has been calculated using Archimedes Principal taking Xylene as an immersion liquid. The molar volume 'VM' of each glass sample was calculated using the formula [18]  $\text{VM} = \Sigma(x_i M_i)/D$ , where  $x_i$  is the molar fraction and  $M_i$  is the total molecular weight of the  $i$ th component. The composition of the prepared glass was used for the calculation of VM. The infrared transmission spectra of the glass samples were recorded at RT using KBr pellet technique on a Perkin-Elmer PC spectrophotometer in the range  $450\text{--}4000\text{ cm}^{-1}$ .

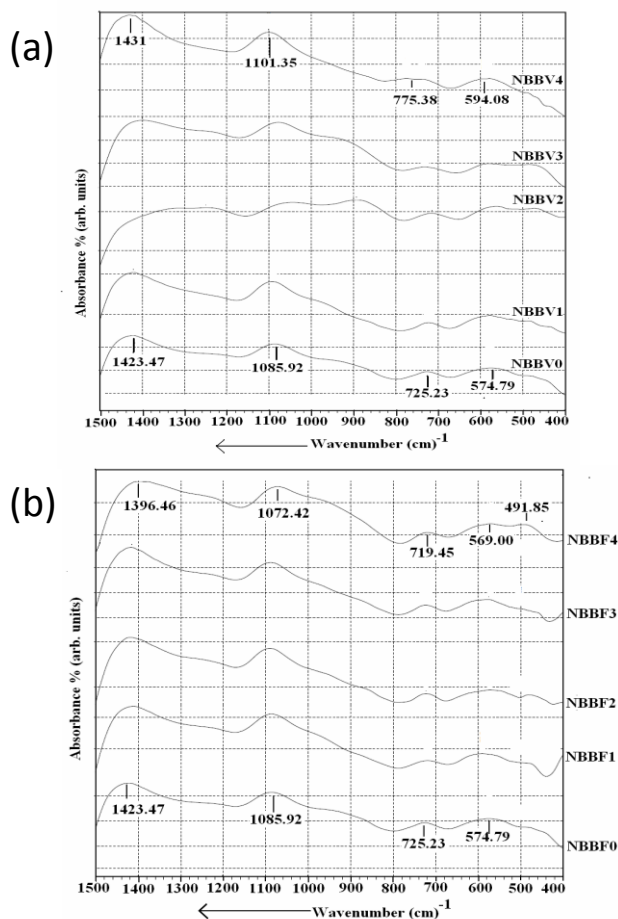


Fig. 1. IR Spectra of (a) NBBV and (b) NBBF glass series.

## Results and discussion

The calculated values of density (D) and molar volume (VM) for all the glass samples under investigation have

been given in **Table 1**. It is seen from **Table 1** that density increases while molar volume decreases with increase in  $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$  content for both the series suggests the compactness of glass structure doped with transition metal oxides. The interpretation of IR bands observed in the present 3d-doped bismuth borate glasses has been carried out in accordance with the concept introduced by Tarte [19] and Condrate [20, 21] about the independent vibrations due to different structural groups in glass. It is assumed that the IR vibrations of characteristic network groups or atoms are independent from vibrations of other constitutional groups. The IR transmission spectra of the present glasses (**Figs. 1 (a) and 1(b)**) exhibit three groups of bands: (i) The broad peak around  $1300\text{--}1500\text{ cm}^{-1}$  attributes to vibrations attached to large segments of borate network, while one additional band near  $1200\text{--}1300\text{ cm}^{-1}$  may attributed to presence of isolated  $\text{BO}_3$  units [22] (ii) The broad peak at  $900\text{--}1150\text{ cm}^{-1}$  results due to combined contributions of stretching vibrations of B-O bonds in  $\text{BO}_3$  units from Pyro-orthoborate groups and stretching vibrations of B-O bonds in tetrahedral  $\text{BO}_4$  units in tri-borate, tetraborate and penta-borate groups [23] (iii) Peak position at around  $700\text{ cm}^{-1}$  corresponds to bending vibrations of B-O-B linkages in the borate network [24, 25]. The absence of absorption peak at  $806\text{ cm}^{-1}$  indicates the absence of boroxol ring formation [26]. The absence of boroxol ring suggests that the present glass system consist of randomly connected  $\text{BO}_3$  &  $\text{BO}_4$  groups. Due to very small concentration of the transition metal oxide, a very weak band at  $840\text{ cm}^{-1}$  may obscured by strong bands from B-O vibrations in these glasses. Therefore, a probability of tetrahedral coordination may expect in these glasses. The observed broad bands in the IR spectra arise because of the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples.

**Table 1.** Chemical composition and physical properties of TM doped  $\text{Na}_2\text{O} - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$  glasses.

Sample code	Glass composition in (mol%)					Density (gm/cm <sup>3</sup> )	Molar volume (cm <sup>3</sup> /mol)
	$20\text{Na}_2\text{O}$	$30\text{Bi}_2\text{O}_3$	$(50-x)\text{B}_2\text{O}_3$	$x\text{TMO}$			
NBBV0	20	30	50.0	0.0	-	4.89	38.25
NBBV1	20	30	49.8	0.2	-	4.95	37.66
NBBV2	20	30	49.7	0.3	-	4.94	37.58
NBBV3	20	30	49.5	0.5	-	5.06	37.08
NBBV4	20	30	48.0	2.0	-	5.12	36.90
NBBF1	20	30	49.8	-	0.2	5.06	37.39
NBBF2	20	30	49.7	-	0.3	5.04	37.19
NBBF3	20	30	49.5	-	0.5	5.03	37.14
NBBF4	20	30	48.0	-	2.0	5.15	36.87

It has been reported that  $\text{Bi}_2\text{O}_3$  appears in bismuth borate network as deformed  $[\text{BiO}_6]$  groups [27, 28], both  $[\text{BiO}_6]$  and  $[\text{BiO}_3]$  polyhedral [29, 30] or only as  $[\text{BiO}_3]$  pyramidal units [31]. The band around  $480\text{ cm}^{-1}$  corresponds to Bi-O bonds in  $\text{BiO}_6$  octahedra [32], while existence of  $[\text{BiO}_3]$  polyhedra must show its characteristic band at  $830\text{ cm}^{-1}$  in IR spectra [28]. The absence of band at  $830\text{ cm}^{-1}$  in **Fig.1 (a & b)**, indicates that the formation of  $[\text{BiO}_3]$  polyhedra does not occur, which suggest that only  $[\text{BiO}_6]$  octahedra form the bismuthate structure in present

glasses. **Fig. 1(a)** shows all the peaks becomes broader and shifts to lower wavenumber upto NBBV3 glass composition, while for NBBV4 glass the peaks are more defined and are observed at higher wavenumber suggest some structural changes at this composition. In **Fig. 1(b)** all the peaks observed at the lower wave number and become more intensified upto NBBF3 glass composition, while for NBBF4 glass the peaks are broader. The shifting of peaks towards lower wavenumber suggests the compactness in glass structure at this composition. It was earlier reported that  $V_2O_5$  can act as a network former in the unit of the  $VO_4$  tetrahedron when added as a minor component in a borate glass [33]. This result is also supported by the observed increase in density with decreasing molar volume on successive addition of TM ( $V_2O_5/Fe_2O_3$ ) which suggests that the glass network becomes more closely bound and shows enhanced compactness of glass structure.

## Conclusion

The glass structure remains nearly unchanged at lower concentration of various doped 3d transition metals in the glass composition while their doping affects the structural units at high concentrations.  $BO_3$  units from pyro-orthoborate groups and tetrahedral  $BO_4$  units in tri-borate, tetraborate and penta-borate groups are the main structural units in these studied glasses.

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