RESEARCH REVIEW JOURNALS
Volume-03
Issue-06
June-2018

ISSN: 2455-3085 (Online)
RESEARCH REVIEW International Journal of Multidisciplinary
www.rrjournals.com [UGC Listed Journal]

# Influence of iron ions on characteristic and spectroscopic properties of zinc aluminum borate glass system

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**ARTICLE DETAILS**

**Article History**
*Published Online*: 19 June 2018

**Keywords**
XRD, SEM, spectroscopic

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## ABSTRACT

Small concentrations of iron oxide doped $ZnO–Al_2O_3–B_2O_3$ glasses were prepared by melt quenching technique. The characteristics of the samples were analyzed by X-Ray diffraction (XRD), scanning electron microscopy (SEM). The analysis of XRD spectra established the disorderly nature of the glass composition and no specialized crystalline species are observed. The surface morphology of the glass samples has also been systematically investigated by scanning electron microscopy. The overall inference of OA, ESR and IR studies is that the $Fe^{3+}$ ions might have changed from ionic environment to covalent environment progressively. With increase in the concentration of $Fe_2O_3$, a gradual increase in the intensity of the bands due to $Fe^{3+}$ ions at the expense of the band due to $Fe^{2+}$ ions could be observed.

## 1. Introduction

The ZnO, is a semiconducting material having wide band gap around 3.37 eV. It has excellent binding energy of excitons about 60 meV at room temperature. It exhibits piezoelectricity. It is nontoxic material which is cheaply available. Due to these properties, ZnO is a material of huge technological importance. It has applications in optoelectronic devices such as solar cell, optical wave guides, light emitting diodes and transparent thin film transistors [1].

Much attention has been attracted by boron and boron-based clusters because of their interesting physical and chemical properties. Boron is an element capable of forming strong covalent bonds and possesses an astounding variety of chemistry. Experimental and theoretical studies on the electronic structure [2].

$Fe_2O_3$ containing oxide glasses are known as semi conducting glasses since a long time [3]. Iron ions have strong bearing on optical, magnetic and electrical properties of glasses. A large number of interesting studies are available on the environment of iron ion in various inorganic glass systems viz., silicate, borate, phosphate, germinate, tellurite etc., glasses [4]. These ions exist in different valence states with different coordinations in glass matrices, for example as $Fe^{3+}$ with both tetrahedral and octahedral and as $Fe^{2+}$ with octahedral environment [5]. Both $Fe^{3+}$ and $Fe^{2+}$ ions are well known paramagnetic ions. $Fe^{2+}$ ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital where as such anisotropy energy of $Fe^{3+}$ ions is small because its orbital angular momentum is zero. The addition of iron oxide to zinc alumino borate glasses is anticipated to increase the chemical durability and the corrosion resistance in aqueous environments [6]. These ions exist in different valence states with different coordinations in glass matrices, for example as $Fe^{3+}$ in both tetrahedral and octahedral and as $Fe^{2+}$ in octahedral environment [7]. The content of iron in different environments and in different valence states exist 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. Hence, the connection between the state and the position of the iron ion and the physical properties of lead bismuth borate glass is expected to be is highly interesting.

The present investigation is aimed at an understanding the structural role of iron ions in $ZnO–Al_2O_3–B_2O_3$ glass system by means of investigation of spectroscopic studies (optical absorption, and IR studies). Within the glass forming region of $ZnO–Al_2O_3–B_2O_3$ glass system, the following compositions with successive increase in the concentration of $Fe_2O_3$ are chosen for the present study:

$F_0$: 20 ZnO–5 $Al_2O_3$–75 $B_2O_3$ (Pure)
$F_1$: 20 ZnO–5 $Al_2O_3$–74.9 $B_2O_3$: 0.1 $Fe_2O_3$
$F_2$: 20 ZnO–5 $Al_2O_3$–74.8 $B_2O_3$: 0.2 $Fe_2O_3$
$F_4$: 20 ZnO–5 $Al_2O_3$–74.6 $B_2O_3$: 0.4 $Fe_2O_3$
$F_8$: 20 ZnO–5 $Al_2O_3$–74.2 $B_2O_3$: 0.8 $Fe_2O_3$
$F_{10}$: 20 ZnO–5 $Al_2O_3$–74.0 $B_2O_3$: 1.0 $Fe_2O_3$

## 2. Experimental

ZnO, $Al_2O_3$, $B_2O_3$ and $Fe_2O_3$ analytical grade reagents of powders taken in suitable proportion (weighed to an accuracy of ± 0.001g) are well mixed; homogenized mixed was place into silica crucible and melted at 1200–1300 °C in PID controlled furnace. After 1hour bubble free liquid was formed then poured in a brass mold and subsequently annealed at another furnace operated at 400°C for 2 hours to avoid air cracks, finally required glass samples are formed. The X-ray diffraction patterns of the samples were recorded with Philips Xpert system using the step scan method with Cu–Kα radiation($\lambda$ = 1.5406 Å), a step size of 0.04 Å.

## 3. Characterization

### 3.1 X-Ray diffraction

As glassy or amorphous materials do not have long-range order, a diffraction pattern containing sharp peaks is not expected as in crystalline materials. The X-ray diffraction pattern for $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses recorded in the range $15^o \leq 2\theta \leq 75^o$ is shown in Fig. 1. The absence of sharp peaks in the pattern indicates the amorphous nature of the samples.

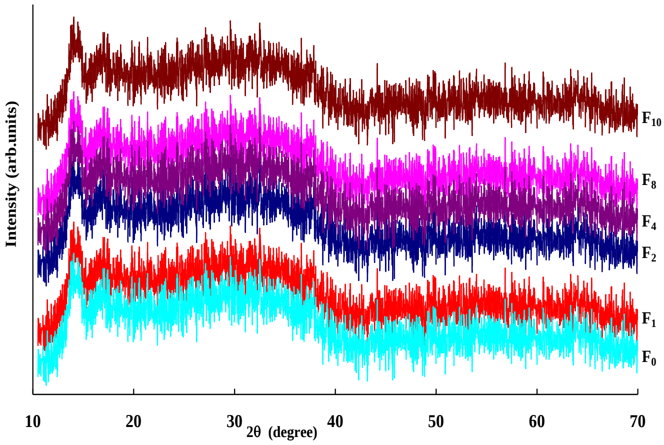

*Fig. 1 XRD patterns of $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses*

### 3.2 Scanning electron microscopy

The scanning electron microscopic pictures of $Fe_2O_3$ doped with $ZnO–Al_2O_3–B_2O_3$ glasses are shown in Fig. 2; close examination of these pictures indicate a slight devitrification of the glasses containing low concentration of $Fe_2O_3$ and virtually no crystallization is observed.

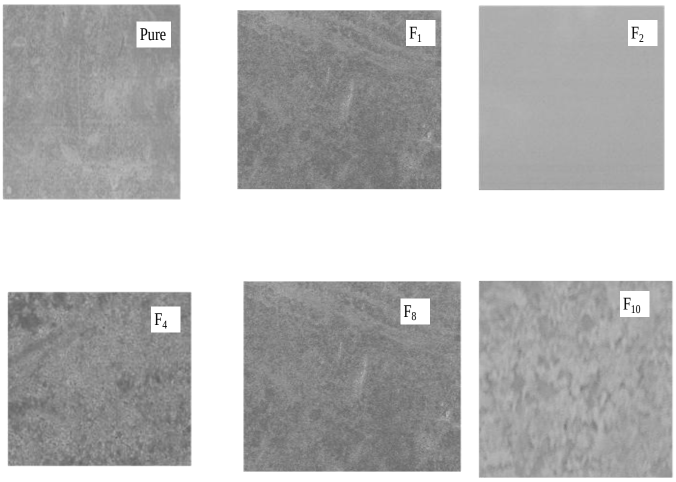

*Fig. 2 SEM pictures of $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses*

### 3.3 Physical parameters

From the measured values of density d and calculated average molecular weight $\overline{M}$, various physical parameters such as iron ion concentration $N_i$, mean iron ion separation $R_i$, which are useful for understanding the physical properties of these glasses are evaluated and presented in Table 1.

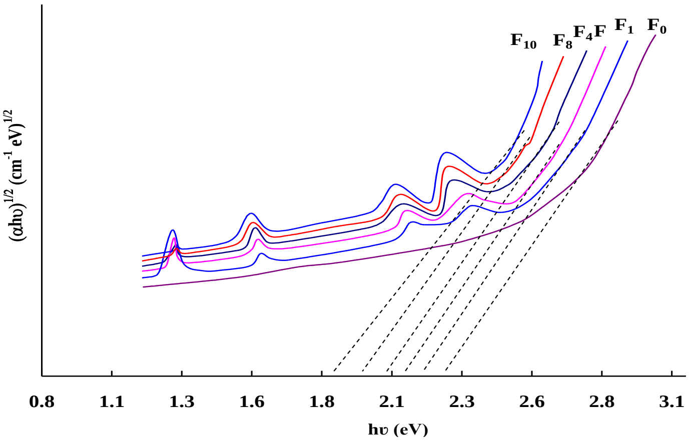

Fig. 3 Optical absorption spectra of $ZnO–Al_2O_3–B_2O_3: Fe_2O_3$ glasses

**Table-1**
**Various physical parameters of $Fe_2O_3$ doped $ZnO–Al_2O_3–B_2O_3$ glasses**

| Glass | Density ($g/cm^3$) | Average molecular weight | Total iron ion concentration | Inter ionic distance of $Fe^{2+}$ ions | Polaron radius |
|---|---|---|---|---|---|
| $F_0$ | 3.165 | 73.58 | --- | --- | --- |
| $F_1$ | 3.168 | 73.67 | 0.2592 | 7.28 | 2.93 |
| $F_2$ | 3.171 | 73.76 | 0.5178 | 5.77 | 2.32 |
| $F_4$ | 3.176 | 73.94 | 1.0350 | 4.58 | 1.84 |
| $F_8$ | 3.188 | 74.30 | 2.0677 | 3.64 | 1.46 |
| $F_{10}$ | 3.193 | 74.48 | 2.5822 | 3.38 | 1.36 |

### 3.4 Results

#### *3.4.1 Optical absorption spectra*

The optical absorption spectra of $ZnO–Al_2O_3–B_2O_3: Fe_2O_3$ glasses recorded in the wavelength region 350-1100 nm are shown in Fig. 3. The absorption edge observed at 431nm for iron free glass is found to be shifted to higher wavelength with increase in the concentration of $Fe_2O_3$. The spectra of all these glasses exhibited three absorption bands in the region 530–550, 580–600 and 780–800 nm due to $Fe^{3+}$ ion transitions. Additionally a band at about 960 nm, identified due to transition of $Fe^{2+}$ ($d^6$) ions [8] is also located in the spectra of all the glasses. With increase in the concentration of $Fe_2O_3$, a gradual increase in the intensity of the bands due to $Fe^{3+}$ ions at the expense of the band due to $Fe^{2+}$ ions could be observed. From the observed absorption edges, we have evaluated the optical band gaps ($E_0$) of these glasses by drawing Tauc plot between $(\alpha \hbar \omega)^{1/2}$ and $\hbar \omega$ as per the equation:

$$\alpha(\omega)\hbar \omega = C (\hbar \omega - E_o)^2 \qquad (1)$$

**Table 2**
**Infrared spectral band positions of $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses**

| Glass | Borate groups | | | | | | Band due to $ZnO_4$ /$AlO_6$ |
|---|---|---|---|---|---|---|---|
| | $BO_3$ | $BO_4$ | B–O–B | $AlO_4$ units ($cm^{-1}$) | $FeO_4$ units ($cm^{-1}$) | $FeO_6$ units ($cm^{-1}$) | |
| $F_0$ | 1358 | 1105 | 710 | 737 | --- | --- | 481 |
| $F_1$ | 1345 | 1120 | 710 | 742 | 641 | 573 | 481 |
| $F_2$ | 1339 | 1127 | 710 | 747 | 634 | 554 | 479 |
| $F_4$ | 1333 | 1133 | 710 | 729 | 629 | 563 | 476 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $F_8$ | 1326 | 1138 | 713 | 759 | 625 | 558 | 473 |
| $F_{10}$ | 1321 | 1145 | 715 | 762 | 621 | 555 | 470 |

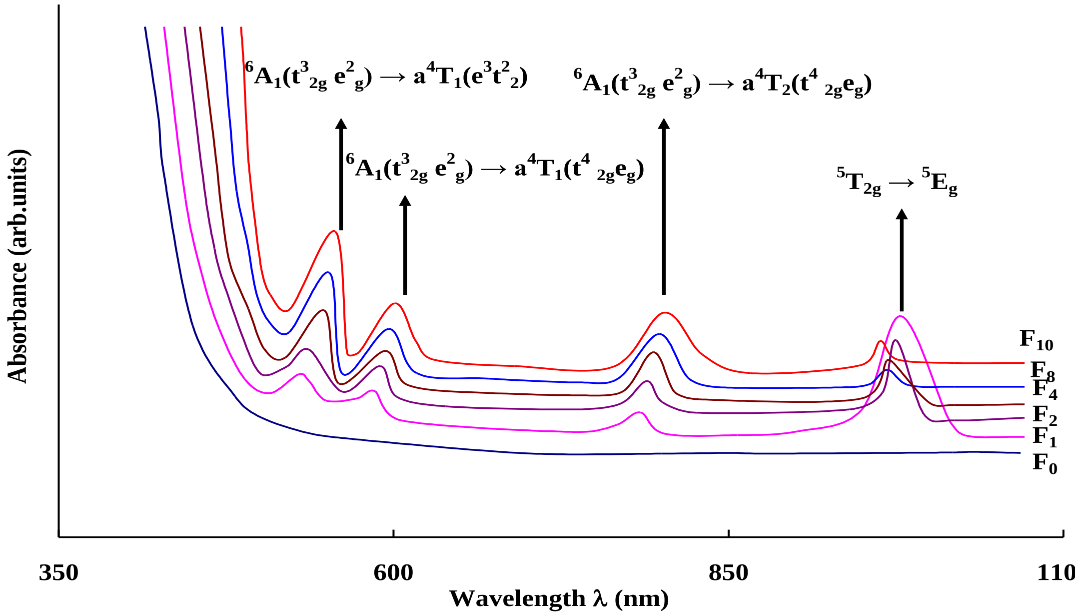

Fig. 4 Tauc plots of $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses.

Fig. 4 represents the Tauc plots of all these glasses in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap (E0) obtained for $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses. e2.

### *3.4.2 Infrared spectra*

The infrared transmission spectra of pure $ZnO–Al_2O_3–B_2O_3$ glasses have exhibited two main groups of bands: (i) in the region 1300-1400 $cm^{-1}$, (ii) in the region 1100–1200 $cm^{-1}$ and another band at about 710 $cm^{-1}$ (Fig. 5); these bands are identified due to the conventional stretching relaxation of B–O bond of the trigonal $BO_3$ units, vibrations of $BO_4$ structural units and due to the bending vibrations of B–O–B linkages respectively [9]. A vibrational band associated with vibrations of $AlO_6$ /$ZnO_4$ structural units is also located at about 470 $cm^{-1}$ in the spectra of all the glasses $Zn^{2+}$ cations play dual role in the formation of glass structure. In the low concentrations it acts as a network modifier in the glass matrix and when present in higher concentrations these ions do participate in the glass network with $ZnO_4$ structural units [10]. Incidentally, the vibrational frequency of Al–O stretching in $AlO_4$ structural units is found to exhibit band at about 760 $cm^{-1}$ and band due to $AlO_6$ structural units lie at about 470 $cm^{-1}$ [11]. Additionally, the $Fe_2O_3$ doped glasses have exhibited a band at about 575 $cm^{-1}$ due to $V_1$ vibrations of $FeO_6$ groups [12]. The spectra of these glasses have also exhibited a band centered at about 630 $cm^{-1}$ identified due to the vibrations of $FeO_4$ tetrahedra. As the concentration of $Fe_2O_3$ is increased, the intensity of the bands due to $FeO_4$ and $BO_3$ units is observed to increase at the expense of bands due to $BO_4$ units and $FeO_6$ octahedral units. The IR summary of data is presented Table 2.

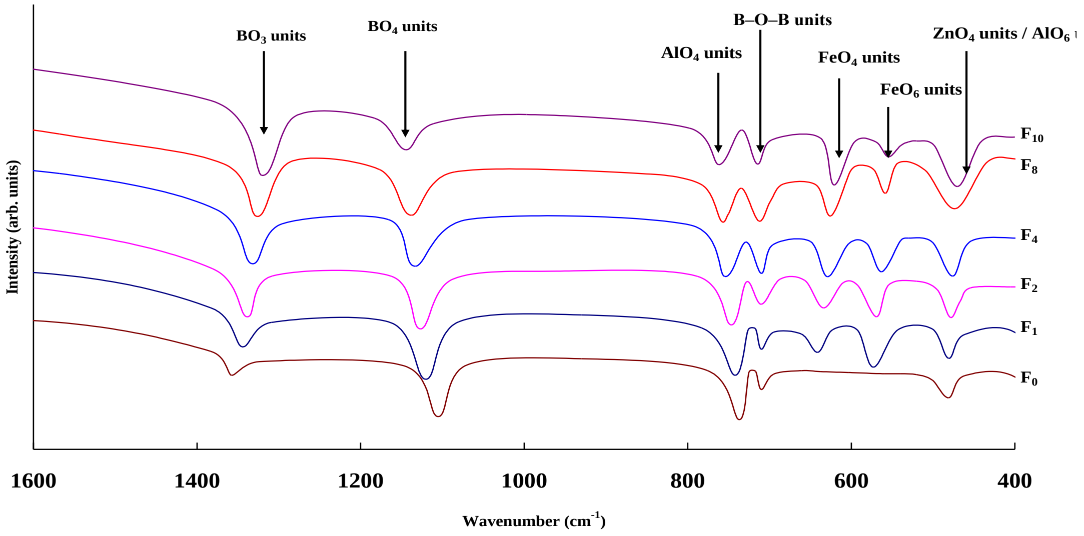

Fig. 5 Infrared spectra of $ZnO–Al_2O_3–B_2O_3:Fe_2O_3$ glasses

### 3.5. Discussion

$B_2O_3$ is a network former with $BO_3$ and $BO_4$ structural units. ZnO when incorporated into $B_2O_3$ glass network, it normally converts $sp^2$ planar $BO_3$ units into more stable $sp^3$ tetrahedral $BO_4$ units and may also create non-bridging oxygens (depending upon whether ZnO goes into modifying positions or network forming positions. The presence of such $BO_3$ and $BO_4$, $ZnO_4$ units in the ZnO–$Al_2O_3$–$B_2O_3$ glass network is evident from infrared spectra. Each $BO_4$ unit is linked to two other such units and one oxygen from each unit with a metal ion and thus the structure leads to the formation of long tetrahedron chains.

Iron ions are expected to exist mainly in $Fe^{3+}$ state in ZnO–$Al_2O_3$–$B_2O_3$ glass network. However, regardless of the original oxidation state of the iron in the starting glass batch, the final glass contains both $Fe^{3+}$ and $Fe^{2+}$ ions [13].

$Fe^{3+}$ ions are expected to occupy both tetrahedral and octahedral positions in the glass network. Nevertheless, the four-fold coordination of $Fe^{3+}$ is observed to be more common than the six fold coordination in many of the glasses [14]. Both of these $Fe^{3+}$ sites can be considered as substitutional and subjected to strong interaction between its external orbitals and the p-orbitals of the neighboring oxygens [15].Basing on the above discussion, the anticipated structure of ZnO–Al2O3–B2O3: Fe2O3 glass network.

The optical absorption spectra of these glasses have exhibited three absorption bands in the regions region 530–550, 580–600 and 780–800 nm. Using Tanabe-Sugano-diagrams for d5 ion, the spectra have been analyzed and the bands are assigned to 6A1 $(t_{2g}^3 e_g^2)$ → a4T2 $(t_{2g}^4 e_g)$, 6A1 $(t_{2g}^3 e_g^2)$ → a4T1 $(t_{2g}^4 e_g)$, and 6A1($e^2 t_2^3$) → a4T1($e^3 t_2^2$) (spin forbidden) transitions of Fe3+ ions respectively with LF parameters, Dq (crystal field splitting energy) =1270 cm-1 and Racah inter electronic repulsion parameters B = 845 cm-1. More precisely basing 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. The band observed at 960 nm is identified due to 5T2g → 5Eg transition of Fe2+ (d6) ions [16].

The observed increase in the intensity of the bands due to Fe3+ ions at the expense of the 5T2g → 5Eg band, further, these Fe2+ ions are expected to occupy only interstitial positions since the ratio of cation-oxygen radii is 0.63 for Fe2+ ion, which is far from the value of 0.19 to be possessed by an ion to occupy tetrahedral or substitutional sites [17].

In IR spectra of ZnO–$Al_2O_3$–B2$O_3$: $Fe_2O_3$ glasses, the intensity of the tetrahedral bands $FeO_4$ and $BO_3$ is observed to increase at the expense of the bands due to $BO_4$, $FeO_6$ tetrahedral units with the increase in the concentration of $Fe_2O_3$. This result clearly suggests a gradual increase in the tetrahedral occupancy of iron ions in these glasses that alternate with $BO_4$ units.

### 3.6. Conclusions

The conclusions drawn from the study of various properties of ZnO–$Al_2O_3$–$B_2O_3$ glasses doped with different concentrations of $Fe_2O_3$ are as follows: The spectroscopic (optical absorption, IR and ESR) investigations pointed out that when the concentration of $Fe_2O_3$ is increased, the iron ions mostly exist in trivalent state and occupy tetrahedral and octahedral substitutional positions and strengthen the glass network.

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