

# OPTICAL CHARACTERIZATION OF SODIUM BORATE GLASSES WITH DIFFERENT GLASS MODIFIERS

J. Singh<sup>1</sup>, D. Singh<sup>2\*</sup>, S.P. Singh<sup>3</sup>, G.S. Mudahar<sup>3</sup>, K.S. Thind<sup>4</sup>

<sup>1</sup>District Education Office, Patiala, India-147001

<sup>2</sup>Deptt. of Physics, Sri Guru Granth Sahib World University, Fatehgarh Sahib, India-140406

<sup>3</sup>Department of Physics, Punjabi University, Patiala, India-147002

<sup>4</sup>Surrey, B.C., Canada

\*e-mail: devinderphy@yahoo.co.in, drdevinderphysics@gmail.com

**Abstract.** The sodium borate glasses with fixed alkali content of 10 mole % and different modifiers have been prepared. The concentration of the modifiers (PbO, Al<sub>2</sub>O<sub>3</sub> and fly-ash) has been kept at 5 mole % and results are compared with binary sodium borate glasses. From the optical data, the optical band gap and cutoff wavelength were calculated and structural changes induced by addition of these modifiers have been investigated by UV-VIS, FTIR spectroscopy, XRD and density measurements. This work can lead to future utilization of fly-ash in glass forming materials.

## 1. Introduction

The sodium borate system has potential applications in metallurgical processes and it is interesting to investigate the change in their structure with addition of different modifiers using XRD, UV-VIS and FTIR. Spectroscopic measurements have proven to be an important tool for investigation of the structure and dynamics of ionic solids. The infrared spectra of these materials are a sensitive function of glass composition and might help in explaining the nature of modes of vibration in vitreous system. Therefore, sodium borate glasses with different modifiers are both of scientific and technological interest due to their structural peculiarities.

Structural characterization of borate glasses has always been an interesting subject due to their numerous applications in technology. Borate glasses are characterized by complex dependences of the properties on the composition. The structural interpretation of these dependences in different investigations is very contradictory and does not always agree with experimental data [1-7]. The most widely accepted model for structure of vitreous B<sub>2</sub>O<sub>3</sub> is random network of corner linked BO<sub>3</sub> triangles as suggested by Zachariasen [8]. The triangular BO<sub>3</sub> structural units are deduced from the boron-oxygen configuration in crystalline borates. Although boron occurs in both triangular and tetrahedral coordination in crystalline compounds, it is believed to occur only in triangular state in vitreous boric oxide. The structure of vitreous boric oxide is also believed to contain a large concentration of unit consisting of three boron-oxygen triangles joined to form boroxol ring structure [9].

The introduction of oxygen as a modifier to boric oxide glass can create structural changes and modify the properties of glass matrix. It is therefore interesting to visualize the effect of different modifiers on structure of borate glasses. Glasses with fly-ash have been under investigation due to environmental concerns [10-16]. Park et al. [17] explained that the glass network connectivity of alkali borosilicate glasses is improved by boron anomaly, which



flex Table Top spectrometer with Cu-K $\alpha$  line of wavelength  $\lambda = 1.5418 \text{ \AA}$  at the scanning rate of  $2^\circ/\text{min}$  and  $2\theta$  was varied from  $0^\circ$  to  $60^\circ$ .

**Density measurements.** The density was obtained from Archimedes' principle using benzene as buoyant. The density was determined by employing the following relation

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b, \quad (1)$$

where  $W_a$  is the glass sample weight in air,  $W_b$  is the glass sample weight in buoyant, and  $\rho_b$  is the density of buoyant.

**Optical measurements.** The optical measurements were made using a UV-VIS spectrometer (Shimadzu, Japan) together with a dual light source capable of giving ultraviolet and visible light as output. Working in the wavelength range of 200–1000 nm, percentage transmission spectra was calculated using air as the reference. Further optical cut off was obtained by finding the intercept of the steepest slope of the rapid transmission drop-off with the baseline preceding it. Optical band gap has been calculated by model proposed by Mott and Davis [19]. According to this model, the absorption coefficient  $\alpha$  varies with the angular frequency  $\omega$  in the following manner:

$$\hbar\omega\alpha(\omega) = B[\hbar\omega - E_0]^2, \quad (2)$$

where  $B$  is a constant. In order to calculate the mobility gap ( $E_0$ ), a graph was plotted between  $[\hbar\omega\alpha(\omega)]^{1/2}$  and  $\hbar\omega$  for each sample and from the linear extrapolation to zero ordinate, the value of  $E_0$  was calculated and listed in Table 3.

Infrared absorption spectra of powdered glass samples were measured in the range 400–4000  $\text{cm}^{-1}$  using KBr technique at room temperature. A recording spectrometer of type Perkin Elmer-1600 was used. Infrared spectra were corrected for the dark current noise and background using a two point baseline correction. The spectra were normalized by making absorption of any spectrum varying from zero to one arbitrary unit.

### 3. Results and discussion

**X-ray diffraction.** Figure 1 shows the X-ray diffraction spectrum of prepared glass samples. Absence of sharp peaks and presence of broad humps confirms amorphous nature of glasses. In glasses the probability of finding atoms is neither regularly spaced nor uniform as in crystals. Due to variations in the inter-atomic distances, the peaks get broader in the spectrum.

**Density.** It can be seen from Table 3 that the decrease in density and increase in mole volume of sodium borate glass with aluminium oxide as a modifier (sample no. N<sub>2</sub>) have been observed in comparison to pure sodium borate glasses (N<sub>1</sub>). Hence for sodium borate glasses it can be concluded that with addition of aluminium oxide, increase in molar volume and decrease in compactness is observed. Alkali borate glasses with Al<sub>2</sub>O<sub>3</sub> as a modifier have a weak and less dense network structure. In contrast, for N<sub>3</sub> glass, i.e. lead containing glass, highest density is observed because PbO as modifier strengthens glass network. The addition of TiO<sub>2</sub> to sodium borate glass (N<sub>4</sub>) shows a decrease in density and increase in molar volume. This indicates that TiO<sub>2</sub> decreases the strength of sodium borate glasses. With addition of Fe<sub>2</sub>O<sub>3</sub> there is increase in density and molar volume of sodium borate glasses due to shift of BO<sub>3</sub> units to BO<sub>4</sub> which increases the density.

The increase in molar volume with the addition of Fe<sub>2</sub>O<sub>3</sub> to alkali borate glass can be understood in terms of role played by iron oxide in glass network. Fe<sub>2</sub>O<sub>3</sub> can charge balance three of tetrahedral units whereas the addition of lead ion can act as a dual charge balance



units [20]. With the addition of  $\text{Al}_2\text{O}_3$  ( $\text{N}_2$ ) significant changes are observed in IR spectrum. A very clear peak at  $700\text{ cm}^{-1}$  in  $\text{N}_1$  sample disappears and an indefinite shoulder appears at  $715\text{ cm}^{-1}$  in  $\text{N}_2$ . Two clear sharp peaks are observed for  $\text{N}_2$  at  $1057$  and  $1420\text{ cm}^{-1}$  with a mid-band at  $1250\text{ cm}^{-1}$ . This indicates that with addition of  $\text{Al}_2\text{O}_3$ , there is decrease in formation of four coordinated units and increase in three coordinated borate units. Addition of  $\text{Al}_2\text{O}_3$  to the borate glasses lowers the conversion rate of  $\text{BO}_4$  units that depends on the molar ratio  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ . It is assumed that the oxygen ions introduced by modifier oxide are consumed first for the four coordinations of aluminum before the conversion of boron from three to four coordinations.

Table 3. Optical and physical data of sodium borate glasses.

Sample No.	Thickness, cm	Density, $\text{g/cm}^3$	Molar volume, $\text{cm}^3/\text{mol}$	Optical Band Gap, eV
$\text{N}_1$	0.733	2.12	34.55	2.82
$\text{N}_2$	0.733	2.08	36.00	3.16
$\text{N}_3$	0.862	2.19	36.95	2.99
$\text{N}_4$	0.734	2.08	35.99	3.20
$\text{N}_5$	0.773	2.14	35.72	1.33
$\text{N}_F$	0.880	1.98	37.12	2.64

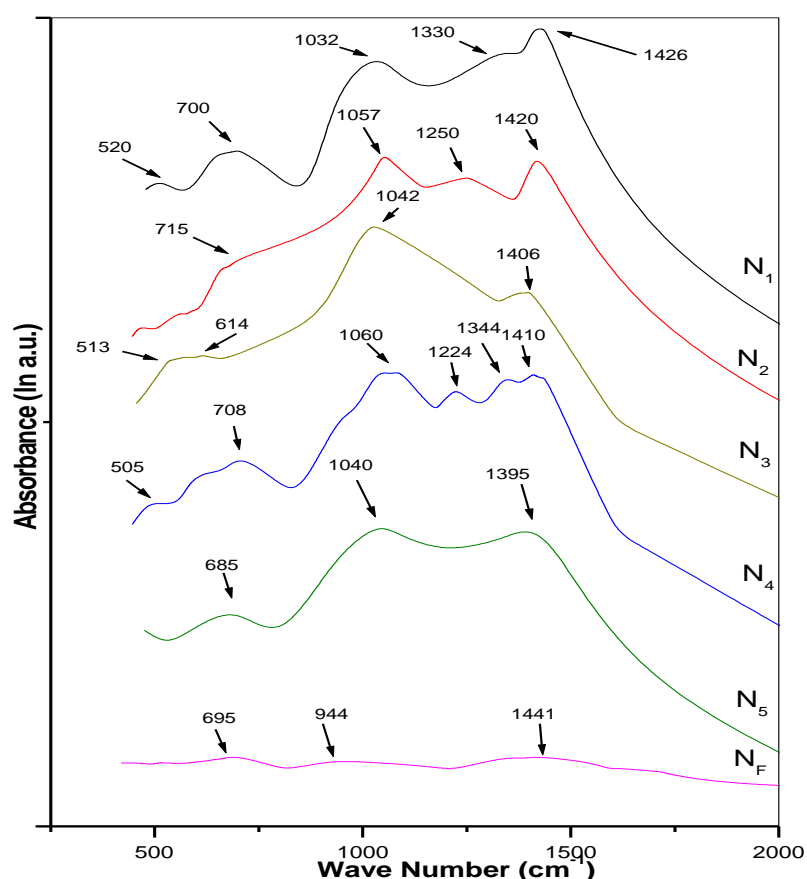


Fig. 2. FTIR Spectra of  $\text{N}_1$ ,  $\text{N}_2$ ,  $\text{N}_3$ ,  $\text{N}_4$ ,  $\text{N}_5$ , and  $\text{N}_F$ .

For  $\text{N}_3$  glass with  $\text{PbO}$  as a modifier, a broad band appears centered around  $610\text{ cm}^{-1}$ . A very sharp and highly intense peak appears at  $1042\text{ cm}^{-1}$ , whereas the band intensity at higher

frequency centered at  $1406\text{ cm}^{-1}$  is reduced. These indicate increase in formation of four coordinated boron units with addition of heavy metal oxide. The addition of  $\text{TiO}_2$  in sample  $\text{N}_4$ , results in appearance of marked peaks at  $1224\text{ cm}^{-1}$ ,  $1344\text{ cm}^{-1}$  and at  $1410\text{ cm}^{-1}$  in the  $1600\text{-}1200\text{ cm}^{-1}$  band. A shoulder can be seen around  $930\text{ cm}^{-1}$  in addition to peak at  $1060\text{ cm}^{-1}$  in  $1200\text{-}800\text{ cm}^{-1}$  band. A new peak appears around  $600\text{ cm}^{-1}$  which is assigned to vibrations of sodium in their oxygen linkage. The addition of iron to sodium borate glass  $\text{N}_5$  causes a shift accompanied by a decrease in the frequency of band around  $1040\text{ cm}^{-1}$  where as a strong band appears at  $1400\text{-}1200\text{ cm}^{-1}$  (with new peak at  $1395\text{ cm}^{-1}$ ). These new bands may correlate to B-O- and B-O-Fe- vibrations in which boron and iron atoms are coordinated [21]. The band at about  $700\text{ cm}^{-1}$  gets shifted to  $685\text{ cm}^{-1}$ .

In case of  $\text{N}_F$ , the addition of fly ash to sodium borate glasses results in decrease in the intensity of IR spectrum. In the band region  $1200\text{-}800\text{ cm}^{-1}$ , maxima shift to  $944\text{ cm}^{-1}$ , which may be a result of decreased conversion of  $\text{BO}_3$  to  $\text{BO}_4$ . This is also evident from density data where a decrease in density has been observed with the addition of fly ash to sodium borate glass. The band at  $1600\text{-}1200\text{ cm}^{-1}$  remains centered around  $1441\text{ cm}^{-1}$  with marked decrease in its intensity. The peak position remains unchanged at  $700\text{ cm}^{-1}$  with addition of fly ash whereas its intensity is decreased. All these values obtained are in agreement with literature [22-26]

#### 4. Conclusion

Alkali-borate glasses have been prepared with the addition of different modifiers. Because each modifier has its own unique role in glass structure, optical and physical properties of glasses are strongly dependent on glass structure. A new attempt has been made to explain the role of fly-ash as a modifier. As fly-ash consist of number of well-known glass modifier and former such as silica, therefore the property of fly-ash as a glass modifier will help in its utilization in glass making. Addition of fly-ash to alkali borate leads to change in borate network structure and plays a role in the formation of borate and silicate structural units by contributing silica. Further attempt can also be made to increase the content of fly-ash to study its network modifier behavior. This work can lead to further applications of fly-ash in glasses for its potential utilization.

#### 5. References

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