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OPTICAL CHARACTERIZATION OF SODIUM BORATE GLASSES WITH DIFFERENT GLASS MODIFIERS

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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_2O_3 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_2O_3 is random network of corner linked BO_3 triangles as suggested by Zachariasen [8]. The triangular BO_3 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 was identified by a nuclear magnetic resonance analysis.

Therefore the main objective of the present work is to study structural changes induced by different modifiers on optical and physical properties of sodium borate glasses and to compare the structural changes induced by fly-ash in borate network.

2. Experimental procedure

Preparation of glasses. For the preparation of sodium borate glasses all chemicals used were of analytical reagent grade with the purity level of 99.9 %. Fly ash used in present work was obtained from National Fertilizers Limited, Bathinda, India and analyzed by EDXRF and its chemical composition is listed in Table 1.

Table 1. Chemical composition of fly ash.

Compound	wt %	Compound	wt %
SiO_2	56.78	TiO_2	3.92
Al_2O_3	26.09	K_2O	2.61
FeO	8.79	MgO	–
CaO	1.80	SO_3	–
Na_2O	–	Unburnt C	–

Glass samples were prepared by using the melt–quenching technique [18]. Appropriate amounts of oxides were weighed by using an electronic balance having an accuracy of 0.001 g. The chemical compositions of all these glasses are shown in Table 2. The chemicals were mixed with the help of pestle and mortar for a minimum period of 20 minute so as to ensure complete mixing and then the mixture was added to silica crucible.

Table 2. Composition mole fraction of glass samples.

Sample No.	Na_2O	B_2O_3	Al_2O_3	PbO	Ti_2O	Fe_2O_3	Fly ash
N_1	0.10	0.90	–	–	–	–	–
N_2	0.10	0.85	0.05	–	–	–	–
N_3	0.10	0.85	–	0.05	–	–	–
N_4	0.10	0.85	–	–	0.02 T	–	–
N_5	0.10	0.85	–	–	–	0.02 T	–
N_F	0.10	0.85	–	–	–	–	0.05

The crucible containing the batch was placed in an electric furnace capable of reaching a temperature of 1400 ºC and heated to a temperature well above melting point of the mixture and was maintained at the same temperature for half an hour under normal atmospheric conditions. Dry oxygen was bubbled through it using a quartz tube to ensure homogeneity of the glass melt and was poured into rectangular moulds made of graphite, which was preheated to 300 ºC. The sample was transferred to annealing furnace set at temperature of 300 ºC and retained at the same temperature for the period of half an hour. The furnace was switched off and sample was cooled to room temperature in 20 hrs.

To give the proper rectangular shape, the sample was grinded with the help of an electric machine using abrasive no. 302 and no. 304. Then it was polished with ceramic oxide in order to obtain the proper flatness. All the samples were prepared by same procedure and their thickness measurement was carried out by micrometer.

X-ray diffraction study. In order to confirm the amorphous nature of the glass samples, X-ray diffraction (XRD) study was made on each glass sample using Rigaku Mini–

flex Table Top spectrometer with Cu–Kα line of wavelength λ = 1.5418 Å at the scanning rate of 2 °/min and 2θ was varied from 0° to 60°.

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

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b\,, \tag{1}$$

where W_a is the glass sample weight in air, W_b is the glass sample weight in buoyant, and ρ_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 α varies with the angular frequency ω in the following manner:

$$\hbar\omega\alpha(\omega) = B\left[\hbar\omega - E_0\right]^2, \tag{2}$$

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 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_2) have been observed in comparison to pure sodium borate glasses (N_1). 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_2O_3 as a modifier have a weak and less dense network structure. In contrast, for N_3 glass, i.e. lead containing glass, highest density is observed because PbO as modifier strengthens glass network. The addition of TiO_2 to sodium borate glass (N_4) shows a decrease in density and increase in molar volume. This indicates that TiO_2 decreases the strength of sodium borate glasses. With addition of Fe_2O_3 there is increase in density and molar volume of sodium borate glasses due to shift of BO_3 units to BO_4 which increases the density.

The increase in molar volume with the addition of Fe_2O_3 to alkali borate glass can be understood in terms of role played by iron oxide in glass network. Fe_2O_3 can charge balance three of tetrahedral units whereas the addition of lead ion can act as a dual charge balance providing the positive charge necessary for formation of two tetrahedral units. Further iron, as a modifier, form structural units which occupy a significantly larger volume. The density of N_F decreases very sharply. The plausible explanation for this could be the difference in size/activity of alkali leads to the different density behavior with addition of fly ash.

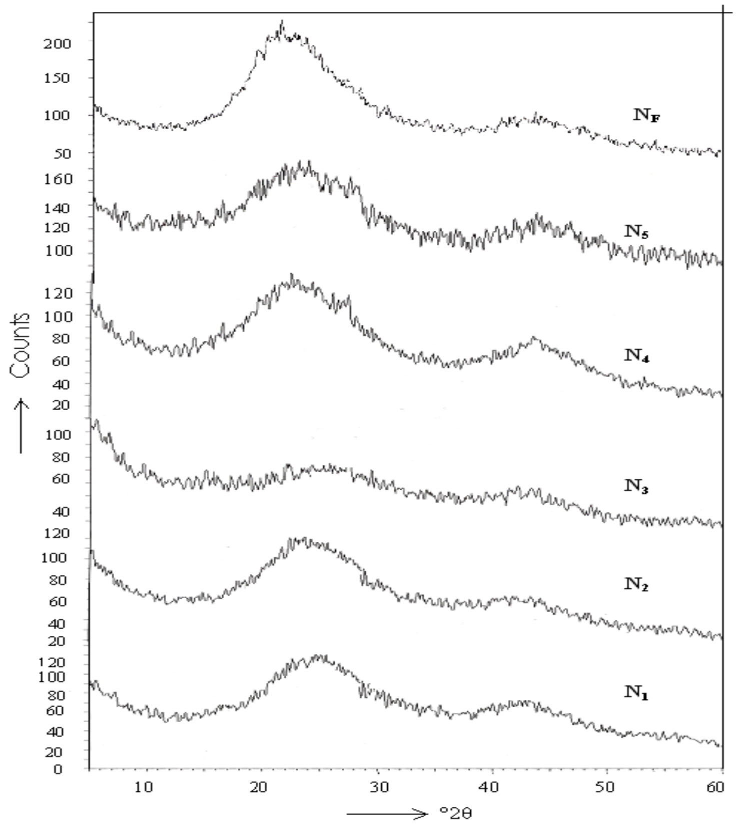

Fig. 1. XRD pattern of N_1, N_2 N_3, N_4, N_5 and N_F.

Optical band gap. The mobility gap for sodium borate glasses with different modifiers have been calculated is listed in Table-3. An increase in band gap of N_2, N_3, and N_4 is observed in comparison to N_1 (base glass). This indicates that addition of Al_2O_3, PbO, and TiO_2 modify the network structure in a way that gap between valence and conduction band increases. A possible explanation for this can be attributed to formation of various structural units in borate glasses. Addition of a modifier to pure borate leads to formation of pyroborates, orthoborate, metaborates i.e. three coordinated boron units or diborate, pentaborate, tetraborate, i.e. four coordinated units. Hence it is possible that addition of modifier decreases the density as in case of N_2 or increases the density as in case of N_3 and N_4 (Table 3) but band gap increases with addition of Al_2O_3, PbO, and TiO_2 as a modifier. So it can be concluded that modification of network induced by a modifier strongly depends on the nature of alkali. For glass sample with 5 mole % fly ash content (N_F) this decrease in band gap can be attributed to increase in non-bringing oxygen with addition of silica.

Infrared studies. Figure 2 shows the FTIR spectrum of sodium borate glasses with different modifiers. The base glass (N_1) shows a small but noticeable peak at 520 cm^{-1} and a broad peak at 700 cm^{-1}. A very clear shoulder is seen at 1032 cm^{-1} and a sharp peak at 1426 cm^{-1} with a small edge at 1330 cm^{-1}.

The peak around 700 cm^{-1} is assigned to bending vibration of various borate arrangements like pentaborate and the peak at 1032 cm^{-1} is due to B-O stretching tetrahedral units. The region about 1426 and 1330 cm^{-1} is due to B-O stretching of trigonal BO_3

units [20]. With the addition of Al_2O_3 (N_2) significant changes are observed in IR spectrum. A very clear peak at 700 cm^{-1}in N_1 sample disappears and an indefinite shoulder appears at 715 cm^{-1} in N_2. Two clear sharp peaks are observed for N_2 at 1057 and 1420 cm^{-1} with a mid-band at 1250 cm^{-1}. This indicates that with addition of Al_2O_3, there is decrease in formation of four coordinated units and increase in three coordinated borate units. Addition of Al_2O_3 to the borate glasses lowers the conversion rate of BO_4 units that depends on the molar ratio Al_2O_3/Na_2O. 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, g/cm^3	Molar volume, cm^3/mol	Optical Band Gap, eV
N_1	0.733	2.12	34.55	2.82
N_2	0.733	2.08	36.00	3.16
N_3	0.862	2.19	36.95	2.99
N_4	0.734	2.08	35.99	3.20
N_5	0.773	2.14	35.72	1.33
N_F	0.880	1.98	37.12	2.64

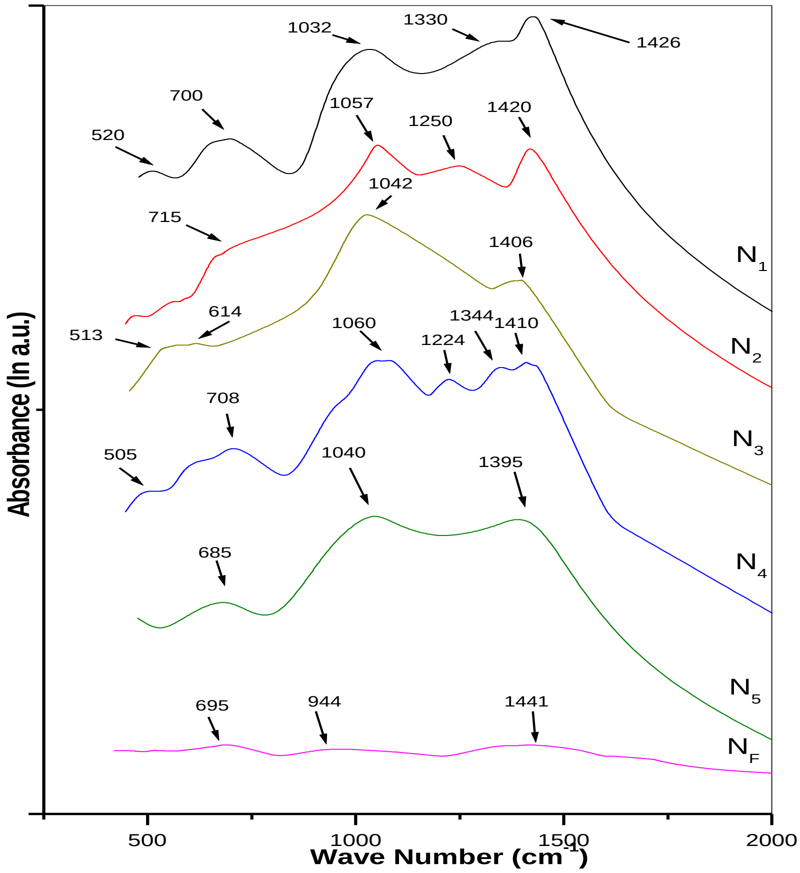

Fig. 2. FTIR Spectra of N_1, N_2, N_3, N_4, N_5, and N_F.

For N_3 glass with PbO as a modifier, a broad band appears centered around 610 cm^{-1}. A very sharp and highly intense peak appears at 1042 cm^{-1}, whereas the band intensity at higher frequency centered at 1406 cm^{-1} is reduced. These indicate increase in formation of four coordinated boron units with addition of heavy metal oxide. The addition of TiO_2 in sample N_4, results in appearance of marked peaks at 1224 cm^{-1}, 1344 cm^{-1} and at 1410 cm^{-1} in the 1600-1200 cm^{-1} band. A shoulder can be seen around 930 cm^{-1} in addition to peak at 1060 cm^{-1} in 1200-800 cm^{-1} band. A new peak appears around 600 cm^{-1} which is assigned to vibrations of sodium in their oxygen linkage. The addition of iron to sodium borate glass N_5 causes a shift accompanied by a decrease in the frequency of band around 1040 cm^{-1} where as a strong band appears at 1400-1200 cm^{-1} (with new peak at 1395 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 cm^{-1} gets shifted to 685 cm^{-1}.

In case of N_F, the addition of fly ash to sodium borate glasses results in decrease in the intensity of IR spectrum. In the band region 1200-800 cm^{-1}, maxima shift to 944 cm^{-1}, which may be a result of decreased conversion of BO_3 to 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 1600-1200 cm^{-1} remains centered around 1441 cm^{-1} with marked decrease in its intensity. The peak position remains unchanged at 700 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.

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