

# OPTICAL CHARACTERIZATION OF FLY ASH AS A GLASS MODIFIER IN POTASSIUM BORATE GLASSES

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**Abstract.** We have prepared alkali borate glass with fly ash as a network modifier (upto 5 mole %). Results have been compared with binary potassium borate glass and potassium borate glass with lead oxide as a modifier having same content as that of fly ash. Structural changes induced by addition of fly ash have been investigated by UV-VIS and FTIR spectroscopy, XRD and density measurements. This work can lead to future application of utilization and characterization of fly ash in glass forming materials.

## 1. Introduction

Utilization of fly ash produced during combustion of coal is a global problem. Fly ash as a resource in cellular concrete blocks, road construction, land fill application, paint and plastic industry have been well reported [1–10] but still its utilization is at small scale. In the past decade, the development of glass and glass ceramic from fly ash has acquired particular importance [11–19]. In these studies chemical durability, mechanical properties, and thermal behavior of fly ash based glasses have been reported. To utilize fly ash as a substitute for the silica source in the manufacturing process of an alkali glasses, its role as a glass network modifier should be well defined. Recently, Park et al. [20] explained that the glass network connectivity of alkali borosilicate glasses is improved by boron anomaly, which was identified by a nuclear magnetic resonance analysis. But so far, to best of our knowledge, no work has been done on optical characterization of fly ash based glasses by UV-VIS and FTIR spectroscopy. Absorption of light in UV, Visible and IR region can be used to study the short range structure of glasses that is the immediate surroundings of the absorbing atoms. The optical properties of solids are not directly dependent on the form or even existence of long range order but on the nature and local arrangement of the constituent atoms or ions.

In the present investigation, optical data of fly ash doped potassium borate glasses have been compared with potassium borate glasses (with and without doping of lead oxide). So, this study is an attempt directed towards understanding of change in optical properties and structure of borate glass matrix with addition of fly ash.

## 2. Experimental details

**Glass making.** Glass samples of the type 0.10 K<sub>2</sub>O–0.90 B<sub>2</sub>O<sub>3</sub> (sample no. K<sub>1</sub>), 0.10 K<sub>2</sub>O–0.85 B<sub>2</sub>O<sub>3</sub>–0.05PbO (sample no. K<sub>2</sub>), 0.10 K<sub>2</sub>O–0.85 B<sub>2</sub>O<sub>3</sub>–0.05 Fly ash (sample no. K<sub>3</sub>) were prepared using the melt–quenching technique. Commercial grade chemicals of K<sub>2</sub>O and

B<sub>2</sub>O<sub>3</sub> (Aldrich Chemical Company) having 99.99% purity level were used as starting materials. Fly ash used in present work was obtained from National Fertilizers Limited, Bathinda, India and its chemical composition is listed in Table 1.

Table 1. Chemical composition of fly ash wt.%.

Compound	wt.%	Compound	wt.%
SiO <sub>2</sub>	56.78	TiO <sub>2</sub>	3.92
Al <sub>2</sub> O <sub>3</sub>	26.09	K <sub>2</sub> O	2.61
FeO	8.79	MgO	–
CaO	1.80	SO <sub>3</sub>	–
Na <sub>2</sub> O	–	Unburnt C	–

Appropriate amounts of oxides were weighed using an electronic balance having an accuracy of 0.001 g. The chemical compositions of all these glasses are shown in Table 2.

Table 2. Composition Mole fraction of glass samples.

Sample No.	K <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	PbO	Fly ash
K <sub>1</sub>	0.10	0.90	–	–
K <sub>2</sub>	0.10	0.85	0.05	–
K <sub>3</sub>	0.10	0.85	–	0.05

The chemicals were then mixed in a pestle mortar for half an hour. After that the crucible containing the batch was placed in an electric furnace capable of reaching a maximum temperature of 1400 °C. It was heated at a temperature of 900 °C for half an hour under normal atmospheric conditions and then dry oxygen was bubbled through it using a quartz tube to ensure homogeneity of the glass melt. The heating was performed for a longer period of time. The homogeneous glass melt was poured into a cylindrical graphite mould. The glass samples were then annealed in a separate annealing furnace for twelve hours. The samples were grounded with the help of an electric machine using different grades of SiC abrasives and aluminium oxide with machine oil by setting the sample in a specially designed holder maintaining the two faces parallel. The polishing was done with cerium oxide to obtain flatness. 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-K $\alpha$  line of wavelength  $\lambda = 1.5418 \text{ \AA}$  at the scanning rate of 2°/min and 2 $\theta$  was varied from 10° to 80°.

**Optical measurements.** The optical measurements were made using a UV-VIS spectrometer (Shimadzu, Japan), with a dual light source capable of outputting ultraviolet as well as visible light. Working in the wavelength range 200 – 900 nm, the percentage transmission spectra was calculated using air as the reference and 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 [21]. According to this model, the absorption coefficient  $\alpha$  varies with the angular frequency  $\omega$  in the following manner:

$$\hbar\omega\alpha(\omega) = B[\hbar\omega - E_0]^2, \quad (1)$$

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.

Infrared absorption spectra of powdered glass samples were recorded using KBr technique in the range 400–4000  $\text{cm}^{-1}$  at room temperature. A recording spectrometer of Perkin Elmer–1600 type was used. Corrections for the dark current noise and background were done for the spectra using a two point baseline correction. The spectra were normalized by making absorption of any spectrum varying from 0 to 1 with arbitrary units.

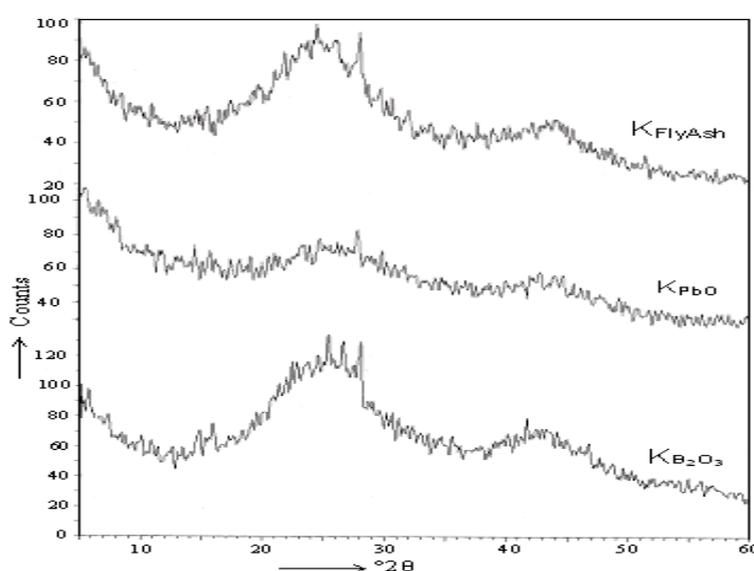
**Density measurements.** The density was obtained from Archimedes' principle using benzene as buoyant and it was determined by employing the following relation

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b, \quad (2)$$

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

### 3. Results

Figure 1 shows the X-ray diffraction spectrum of prepared glass samples.



**Fig. 1.** XRD pattern of  $K_1$ ,  $K_2$ ,  $K_3$  glasses.

The absence of sharp peaks and the presence of broad humps confirm amorphous nature of glasses. In glasses, the atoms are neither regularly spaced nor uniform as in the case of crystals. Because of variations in the interatomic distances of glasses, the peaks get broader. The calculated values of optical band gap and density for  $K_1$ ,  $K_2$  and  $K_3$  are listed in Table 3.

**Table 3.** Optical and physical data of prepared glasses.

Sample No.	Thickness (cm)	Density ( $\text{g}/\text{cm}^3$ )	Optical Band Gap (eV)
$K_1$	0.762	2.06	3.03
$K_2$	0.799	2.42	3.10
$K_3$	0.851	1.47	2.74

It is observed that the optical band gap and density of  $K_3$  is less than that of  $K_1$ . Figure 2 shows the infrared absorption spectra for  $K_1$ ,  $K_2$  and  $K_3$  glasses. The spectra have bands at about 680  $\text{cm}^{-1}$ , prominent bands centred around 1050, 1210, 1350, 1410  $\text{cm}^{-1}$ . The position of these peaks varies with change in composition and a significant change is observed in spectra of sample  $K_3$  (doped with fly ash). For  $K_3$  glass, the bands at 680  $\text{cm}^{-1}$ , at 951  $\text{cm}^{-1}$  with a shoulder at 816  $\text{cm}^{-1}$  and a prominent one at 1365  $\text{cm}^{-1}$  are observed. The relative area

of each band is considered proportional to the concentration of the structural group, which produces a particular band.

#### 4. Discussion

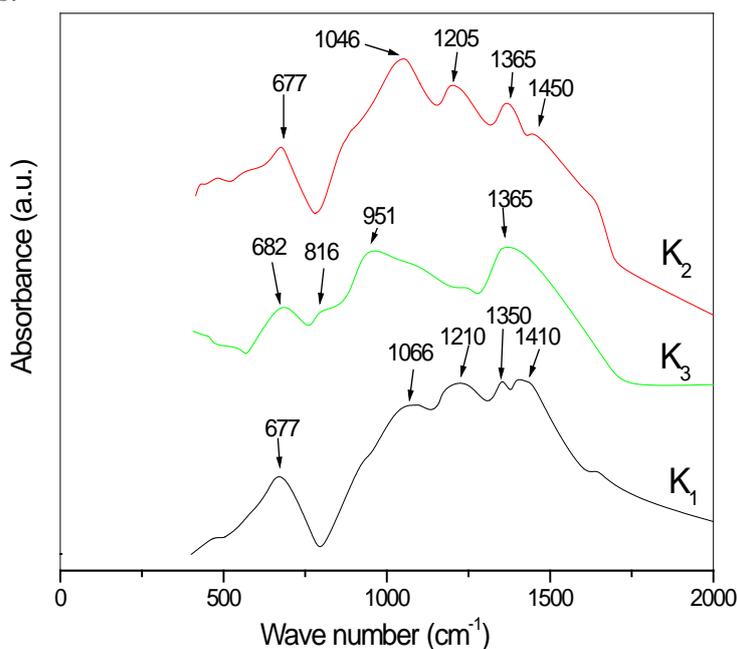
**Infrared studies.** To identify the structure of oxide glasses the following information is required [22]:

(i) the coordination number of the compound with respect to oxygen, especially of network formers, and the type of the bridging bonds of oxygen which link the coordination polyhedra of framework and the composition of chemical inhomogeneities in the structure of glass;

(ii) the change in oxygen bonds of the framework, induced by the cations modifiers which combine with those bonds.

Information on this subject is also provided by vibrational infrared spectroscopy. Vibrational spectra of glasses are generally interpreted by considering the vibrations of structural fragments from which the glass network can be built [23]. Borate glasses provide an ideal case, in comparison to other glass forming systems, to demonstrate the effectiveness of infrared spectroscopy in glass science [24]. Boron has smallest mass as compared to the other network forming elements, and thus the main vibrational modes associated with the glass network appear well above  $500\text{ cm}^{-1}$  (in the mid-infrared region) [25]. These network modes are well separated from the metal ion site vibrational modes which are active in the far infrared region [26–28]. The ability of boron to change its coordination number with oxygen between three and four provides a range of anionic environment that can coordinate the modifying metal ions. The main IR-absorption peaks in  $\text{B}_2\text{O}_3$  containing glasses lie at  $710$ ,  $1260$ , and  $1420\text{ cm}^{-1}$ . According to Krogh–Moe [29–30], the  $1420\text{ cm}^{-1}$  peak is due to the ring stretching of the boroxol groups, and the  $1260\text{ cm}^{-1}$  vibration is due to the B–O–B bond constituting the linkage of boroxol groups to neighbouring group.

For samples  $\text{K}_1$ ,  $\text{K}_2$  and  $\text{K}_3$  (Fig. 2) the bands at  $680$  and at  $\sim 1350\text{ cm}^{-1}$  can be attributed to bending vibrations of  $\text{BO}_3$  triangles and stretching vibrations of  $\text{BO}_3$  units with non-bridging oxygens (NBOs) respectively [31–34]. For  $\text{K}_1$  glass, a shoulder in the band at  $1066\text{ cm}^{-1}$  is observed which can be attributed to B–O bond stretching vibrations from tri, tetra and pentaborate groups.



**Fig. 2.** FTIR spectrum of  $\text{K}_1$ ,  $\text{K}_2$  and  $\text{K}_3$  glasses.

Whereas for  $K_2$  glass a prominent band can be observed at around  $1050\text{ cm}^{-1}$ . This indicates that there is formation of four coordinated boron units with the addition of heavy metal oxide. For both  $K_1$  and  $K_2$  glasses a broad but prominent peak at around  $1210\text{ cm}^{-1}$  can be attributed to asymmetric stretching vibrations of B–O bond in metaborates, pyroborates and orthoborates.

A significant change is observed in the spectrum with the addition of fly ash (sample  $K_3$ ). At around  $950\text{ cm}^{-1}$  a prominent band appears for  $K_3$  (Fig. 2) which can be attributed to the stretching vibrations of B–O–Si linkage, as the main content of fly ash is silica. A small but clear shoulder at  $816\text{ cm}^{-1}$  can be assigned to combined stretching vibrations of Si–O–Si and B–O–B network.

**Optical band gap.** The calculated values of the band gap of  $K_1$ ,  $K_2$  and  $K_3$  glasses are listed in Table 3. It is observed that band gap energy of  $K_3$  decreases with respect to that of  $K_1$ . A possible explanation of this reduction can be given on the basis of structural arrangements in borate glasses. At low contents, PbO ( $K_2$  glass) acts as a glass modifier and enter the glass as  $\text{Pb}^{2+}$  ions, as bonding of lead is strongly ionic, and the cations enter the network in an interstitial manner. Every oxygen atom of PbO added is used to convert two  $\text{BO}_3$  units to two  $\text{BO}_4$  units [35–38]. Since the  $\text{BO}_4$  unit has tetrahedral geometry, which is more stable than that of  $\text{BO}_3$ , therefore the optical band gap of  $K_2$  is more. For  $K_3$  glass, the decrease in band gap can be attributed to formation of borate and silicate units with non-bridging oxygens. The main content of fly ash is silica and  $\text{Al}_2\text{O}_3$  and increase in NBOs is observed with addition of these oxides. This is in agreement with infrared studies which show a very prominent band at  $1350\text{ cm}^{-1}$  attributed to formation of NBOs.

**Density.** The change in geometrical configuration, co-ordination number, cross-link density and dimensions of interstitial space of glass decide the density. Therefore, density is a tool which reveals the degree of change in structure with change in composition of glasses. The density of glass is a strong function of its composition and dependent to a lesser degree on the measurement temperature and the thermal history of the sample [39]. The density of  $\text{B}_2\text{O}_3$  glasses lies in the range of  $1.802$  to  $1.840\text{ gm cm}^{-3}$ . The network formed by primary glass forming oxides contains a large number of empty interstices and with addition of network modifiers (NWM) density increases. The addition of alkalis to pure  $\text{B}_2\text{O}_3$  results in an increase of the density [40]. For present study the density of  $K_1$  glass is  $2.06\text{ g/cm}^3$ , which is in agreement with the literature. It is proposed that change in density with oxide content reflects the structural changes in the glasses and density decreases with increase in the number of non bridging oxygens [27, 41]. The decrease in density for  $K_3$  ( $1.47\text{ g/cm}^3$ ) further supports the formation of NBOs with addition of fly ash. High value of density for  $K_2$  ( $2.42\text{ g/cm}^3$ ) glass further supports increase in formation of four coordinated boron units with PbO as a network modifier.

## 5. Conclusion

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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