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To Prepare Silica Soda Borate Glass from Biomass Fly Ash and Study its Optical Properties

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Abstract.- **We have prepared alkali borate glass with Biomass fly ash as a network modifier (upto 5 mole %). Structural changes induced by addition of fly ash have been investigated by UV-VIS and FTIR spectroscopy, XRD ,density measurements and molar volume. This work can lead to future application of utilization and characterization of fly ash in glass forming materials. The optical properties of the glasses were studied. The heaps of BMA can be converted into a value added product in a sustainable way.**

Key words- Silica, Biomass fly ash (BMA), glasses, boric oxide, NaCl, optical properties, density

1. INTRODUCTION

Glass is a non-crystalline amorphous solid that is often transparent and has widespread practical, electrical, technological and decorative usage. Glasses have been an integral part of our life and glass making techniques were very well known from the ancient times around 3500 B.C[1]The making of glass involves three basic types of ingredients. They are a glass former, a flux, and a stabilizer. Silica is the main ingredient of glass, which is a glass former compound. It is found that fly ash contains large amount of silica. But utilization of biomass fly ash produced during combustion biomass, rice husk is a global problem. Biomass Fly ash as a resource in cellular concrete blocks, road construction, land fill application, paint and plastic industry have beenwell reported [2],[3],[4],[5],[6],[7],[8],[9],[10]but still its use is at small scale. In the past decade, the development of glass and glass ceramic from fly ash has acquired particular importance. [11], [12], [13], [14], [15], [16],[17][18],[19]. In this work for preparing the glasses, biomass ash was used in place of silica since it contains silica. Earlier also attempts were made by different workers to use the fly ash in the preparation of glass ceramics [20] since silica content of the fly ash was very high In this work for preparing the glass ,biomass ash was used in place of silica. earlier also attempts were made by different workers to use the fly ash in the preparation of glass ceramics [21] Fly ashes in each source have different composition. Silicates, carbonates, clays, sulfates and oxides dominate the mineral matter in coals [22],[23][24]. Due to the purification of fly ash and the silica contents is not much, so it is not likely to be the main agent in the formation of the glass. But it can be used as fill material by the addition of a glass former, such as boron trioxide (B2O3) system [25]. Besides the above compounds, fly ashes also contain other transition metals compound, Fe2O3, TiO2, MnO, etc., and these elements affected to glass colors [26],[27] Here in this work biomass fly ash which is used in place of silica was produced after combustion of biomass such as plant stalks in a small scale thermal power plant. This is an attempt of recycling of the waste product obtained after burning of the biomass. The BMA used here contained large percentage of silica (53%).The other oxides present in the BMA were Alumina-14%,Iron oxide-7.8%,Calcium Oxide-3.3%,Pootassium oxide-4.7%,magnesium oxide-1.7%,and traces of Titanium dioxide, Manganese 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.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

The BMA used here was procured from a sugar factory with a small thermal power plant running on biomass fuel , 'Purti Power and Sugar Limited', Bela, District Nagpur (MS) Inddia. The ash was subjected to chemical analysis to confirm the presence of silicates alumina and other fly ash components as listed bellow

Sr.No.	Parameter	Percentage
1	Silicates	52.64%
2	Alumina	14.05%
3	Iron oxide (7.80%)	7.80%
4	calcium oxide (3.31%)	3.31%
5	Magnesium oxide (1.72%)	1.72%
6	Potassium oxide (4.74%)	4.74%
7	Titanium dioxide (0.22%)	0.22%
8	Manganese oxide (0.20%)	0.20%
9	Sodium Oxide (0.48%)	0.48%

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The glasses were prepared by using BMA, Sodium Chloride and Boric Oxide (AR grade). The molar composition of the glass was $50B_2O_3$ – (50 - Z) NaCl- Z BMA; where Z = 2,4,6,8,10 . The powders were weighed on a digital balance and mixed for 30 minutes in an aget mortar with the help of pestle. Then powders were fired at 1000^0C in a furnace. The melt was cast in a steel mould kept at room temperature and the glasses were prepared by the melt quench method. The glasses were immediately transferred to annealing furnace maintained at suitable temperature in order to remove mechanical stresses produced during quenching. The glasses thus prepared were named as N_1, N_2, N_3, N_4, N_5 for Z = 2, 4, 6,8,10 respectively.

The glasses were subjected to XRD study for confirming amorphous nature of glasses(fig-1). FTIR of three samples N_2, N_3 N_4 was studied for confirming the presence of silica alumina in the glasses (fig 2).

3 RESULT AND DISCUSSION:

The optical spectrum of the glasses was studied in ultra violet and near visible frequency range constant and optical band gap was calculated using Tauc-plot method for allowed and direct transition.Urbeach energy was calculated using urbeach plot The density was obtained from Archimedes' principle using distilled water as buoyant and molar volume was calculated

3.1- XRD

The glass samples appeared light greenish yellow in colour and can be used as show pieces.

The XRD graphs for all glass samples

Wavy XRD patterns were obtained for all five samples which confirmed that the samples are amorphous and absence of crystalline structure shown in fig-1

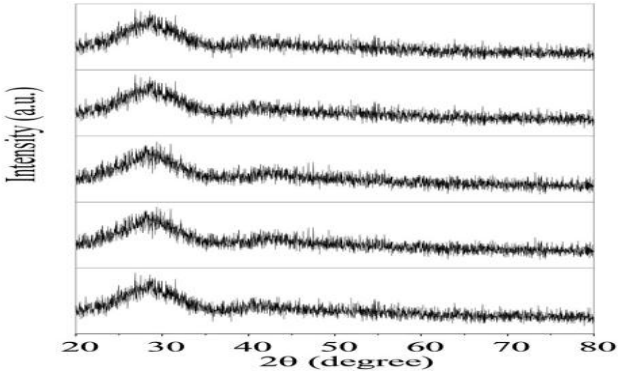

Fig-1 XRD

3.2 – FTIR

Figure 2 shows the FTIR graphs of three glass samples N_2, N_3, N_4. The FTIR graphs were done to confirm the presence of silica and alumina in the BMA. The absorption peak for all samples at 1000cm^{-1}confirmed the presence of stretched Si-O bond (.Musić S, 2011). The O-Al deformation linked to Al is evident from the absorption peak obtained between 500 - 600 cm^{-1}1 . The characteristic absorption peaks at 900 to 1000cm^{-1} are due to stretching and vibration of borate unit (Silim 2006).

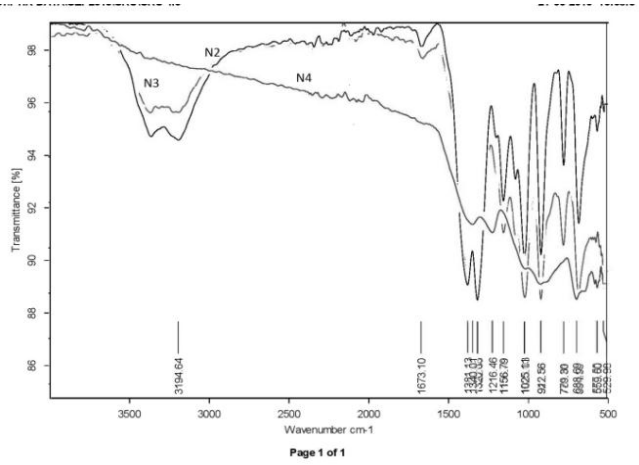

Fig-2 FTIR

3.3 Density and Molar mass

Density was determined by employing the following relation

$$\rho = \frac{w_a}{w_a - w_b} x\rho_b \qquad (1)$$

where w_a-weight of sample in air,w_b-weight of sample in buoyant ρ_b-density of buoyant.

Molar volume calculated using formula

The molar volume (V_m) of each glass sample was calculated using the formula [28]

$$V_m = \sum \frac{x_i M_i}{d} \qquad (2)$$

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 [29]. Density of sample decreases with increasing percentage of fly ash. It was found that when we added alkali metals oxides to the borate glass matrix it results in network formation or modification [30].It gives rise to different non-linear optical properties making these glasses suitable for optoelectronic application. The increasing molar volume Vm may be due to conversion of bridging oxygen atoms into non-bridging atoms. These results are also supported by the density variation.

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3.4 Optical band gap measurement

The optical absorption spectra for all the samples recorded at room temperature, are shown in Fig 3

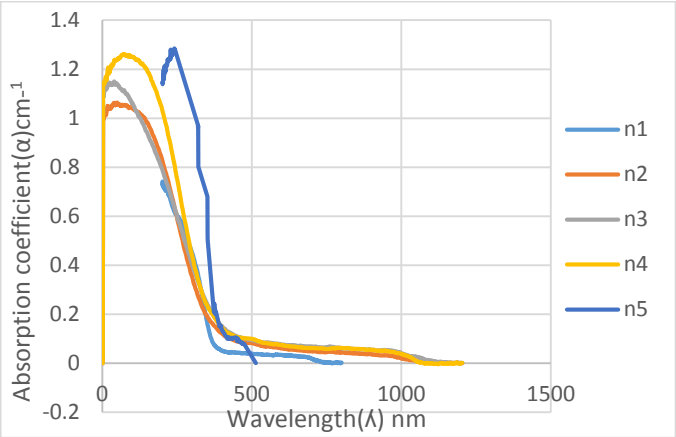

Fig-3Absorption spectra for all samples

The absorption edge as observed in UV region (Fig. 3) can be divided into two regions depending on the value of the absorption coefficient (α(ν)) for many glassy and amorphous materials. The sharp peak of sample N5 is attributed to iron oxide present in BMA where percent of BMA is maximm.The first region usually known as Urbach tail [31], which is characterized with α (ν) $<10^4$ cm^{-1} and depends exponentially on the photon energy as

$$\alpha(\nu) = C^{\frac{h\nu}{\Delta E}} \qquad (3)$$

where C is constant and 'ΔE' is the width of band tail energy. At higher value of α (ν) ($\geq 10^4$ cm^{-1}) optical absorption follows the general relation given by Davis and Mott [32]

$$(\alpha h\nu) = (h\nu + E_g)^r \qquad (4)$$

where r is the index and can takes different values i.e. 2, 3, 1/2 and 1/3 depending on mechanism of inter band transitions, B is a constant called band tailing parameter, hν is the incident photon energy and Eg is the optical band gap energy.

For amorphous materials only indirect transitions are valid [33]Tauc plots(hν vs$(\alpha h\nu)^r$) corresponds to r=2 & r=3 respectively used to calculate the optical band gap given by the intercepts of the curve on x-axis where the band tailing parsmeter (B) given by slop of linear portion of the Tauc-plots given in table1.

It is found that for r = 2, the equation (4) gives the best fit of the data as shown in Fig 4 and this corresponds to the indirect allowed transition. The same absorbance data was used in Eq. (4) for r = 3 also, to calculate the value of optical band gap (Table 1). For r = 3, the curve fitting of Fig. 5 shows some deviation from linear fit for the given data.

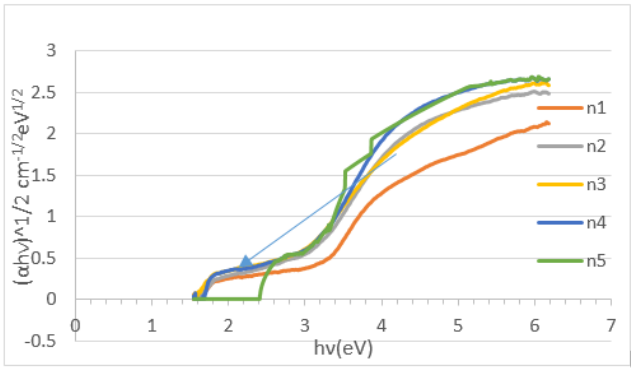

Fig-4 Tauc-plot for r=2

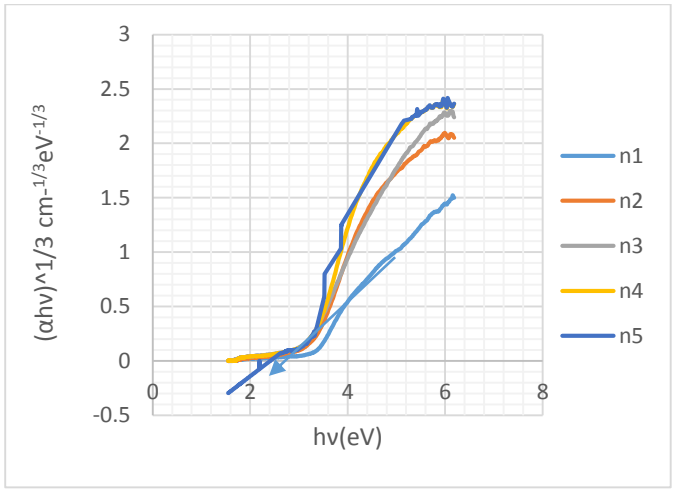

Fig-5Tauc-plot for r=3

The optical band gap for the two transitions lies between 2.2-3eV and 3.2-2.2eV for r = 2 and r = 3 respectively. On the basis of these results it is interpreted that the glass system under study behaves as indirect band gap semiconductors.

3.5 Urbach Energy- The values of Urbach energy (ΔE) are calculated from the reciprocal of the slope of ln α versus h ν curve (Fig. 6). The values of ΔE for the present glass system lie between 0.20- 0.26 eV.

The Urbach energy was used to characterize the degree of disorderness in amorphous and crystalline solids. The materials which have large value of ΔE would have great tendency to convert weak bonds in to defects. The width of the band tails (ΔE) associated with valance and conduction bands was believed to be originated from electron transition between localized states, where the density of these localized states is exponentially dependent on energy [34],[35].

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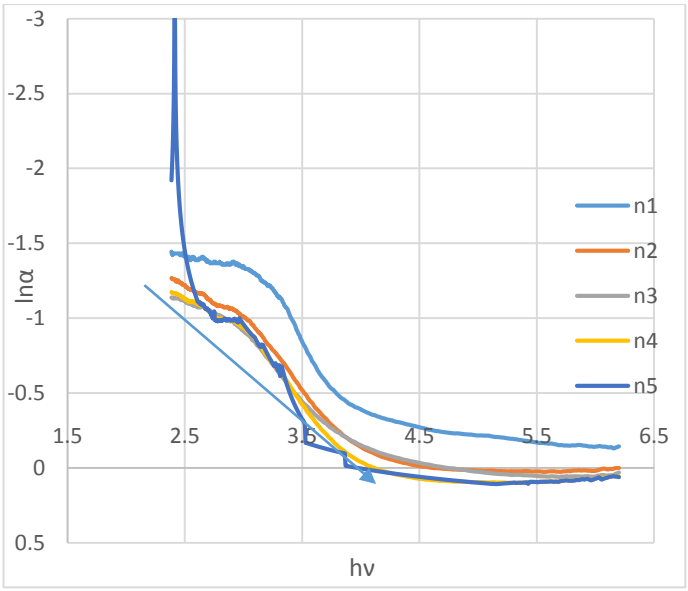

Fig-6 urbeach plot

The plots of natural logarithm of absorption coefficients ln(α) verses photon energy($h\nu$)are called Urbach plots. The values of Urbach energy (ΔE) were estimated from the reciprocals of slopes of linear regions of Urbach plots. Urbach energy (ΔE) values of the present glass samples are giveninTable1. There is an increase in the band gap values with increasing BMA content. The values of optical band gaps of present glass gives good agreement with other glass systems found in the literature [36],[37],[38]]. The variation of optical band gap with BMA content in the glass system is shown in Fig7. The Urbach energy values of the present glass varied from 0.20to 0.26eV in a nonlinear manner

With increasing BMA content in the glass.

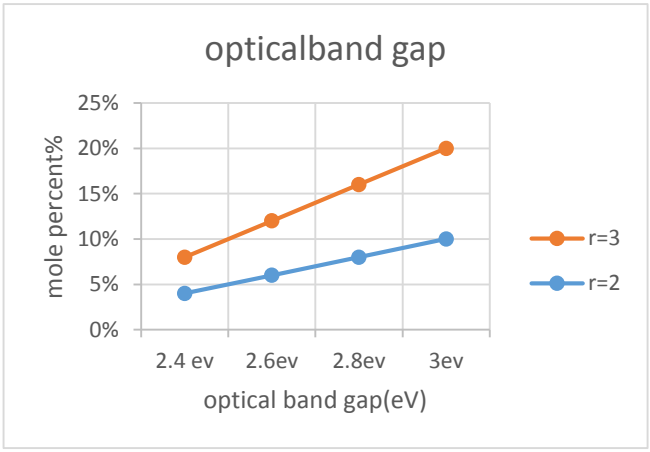

Fig-7 variation of optical band gap with mole % of BMA

It is well established that borate glasses without any modifier are found to have fairly large band gap energy (Eg) and the formation of non-bridging oxygen is blocked. The increase in BMA which contains silica, alumina and other metal oxides is related to the progressive decrease in the concentration of non-bridging oxygen, which in turn gives rise to a possible increase in bridging oxygen. As bridging oxygen are more excited than the NBOs, therefore with addition of BMA concentration Eg increases slightly.

4 CONCLUSION

Glass sample using Biomass ash was successfully prepared using melt-quench method. The physical, structural and optical properties of the glass system prepared by using biomass ash (BMA) have been studied the density increases and molar volume of all the glass samples decreases almost linearly with BMA content. This is due to the relatively lower molar mass of the BMA compared to NaCl.The values of different optical parameters i.e., cut-off wavelength, optical band gap, Urbach energy have been reported. It is observed that optical band gap increases slightly with increase in BMA content and is due to increase in BOs. From the theoretical fitting of the experimental absorption coefficients for all the glass samples, it is concluded that the present glass system behaves as an indirect band gap semiconductor and from optical band gap values it is concluded that the present glass system can be used as uv-ray absorber in paint also.

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