

Effect of biomass ash on elastic and structural properties of Zinc-borate glass system.

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Abstract:

Biomass ash generated in thermal power plants as a material, could be a valuable supply of many oxides like SiO₂, Al₂O₃, Fe₂O₃ and CaO. These oxides will function a helpful preliminary supply for glass production. The glass system ready during this project is Borate-Zinc-Biomass ash (BZB) and Borate-Zinc-Rice husk ash (BZR) glass by exploring biomass ash as glass former. The progressive addition of biomass ash to the current system of glass was created to study its effect on the chemical and physical properties of the parent glass. Ultrasonic measurements were performed by pulse-echo method. The densities of the ready samples were measured to justify the packing arrangements of the constituent chemical compound. The variations in densities and ultrasonic velocities of the ready samples containing progressive fly ash contents were correlate and mentioned. The values of elastic moduli (including Young's modulus, coefficient of elasticity, shear modulus and Poisson's ratio) were compared with those on paper calculated.

Keywords: Biomass fly ash, borate glasses, elastic properties.

Introduction:

In current scenario the issue of waste product like fly ash getting the attention of scientist community. The burning of biomass such as sugar cane bagasse and rice husk in biomass run thermal power plants produce significant amount of ashes. A number of recycling treatment and experiments were carried out to minimize the harmful effects of oxides in biomass ash generated during combustion in thermal power plants [1]. However the use of fly ash in cement is not only the solution as fly ash contain heavy metals which can cause secondary pollution[2]. The coal fly ash contain near about 60% of silica and can be used as glass former in place of silica[3]. Since coal ash contain large amount of transition oxide which produced opaque glass having high intensity colour which is not so much useful for practical application [4]. In Central India large amount of agricultural waste is produced from harvesting, sugar factories and rice mill. This agro waste is like sugarcane Bagasse, rice husk further used as fuel in thermal power plant [5]. Biomass ash and rice husk ash is natural and immense source of silica and can be used as a raw material for glass formation [6]. Biomass ash has potential to be used as glass former. Silica contain in both biomass ash, sugarcane bagasse ash and rice husk ash has more than 50% of amorphous silica contain [7]. Glasses having high transparency, optical property and electrical property attract for more scientific uses. Rowero M. et al has tried to crystallize SiO₂-CaO-N₂O glass from sugarcane Bagasse bottom ash and investigate the feasibility of glass and glass ceramic formation from sugarcane bagasse ash [8].

While Teiveira S. et al studied glass ceramic material from SiO₂-Al-CaO system using sugarcane bagasse ash [9]. Physical and mechanical properties of glass-ceramics fabricated from thermal power plant fly ash were analysed and compared with a temperature-time-mechanical (T-T-M) diagram by Myungkim J et al [10]. A. Jabar et al prepared the zinc silicate glass from rice husk and studied its properties [11]. Ruangtawee et al prepared rice husk glass doped with other oxides. The study gives result that the RHA can be used for glass production. The properties of prepared glass compared with SiO₂ glass [12]. Singh et al explore the fly ash as glass modifier [13]. Sristipokakun et al studied the CuO MnO₂ and Fe₂O₃ doped biomass ash glass [14]. Silvio Rainho Teixeira et al. studied the glass and glass ceramic formation of bagasse ash [15]. Peng f et al Investigate the

Nano composite glass ceramic formed using coal fly ash [16]. With the formation of glass using biomass ash and rice husk ash it also important to study it's physical and elastic properties of glass. The ultrasonic testing is one of the non-destructive testing used for the structural investigation of glass. The elastic moduli of glasses are influenced by many physical parameters, which may in turn be studied by measuring the ultrasonic velocities [17]. SaddeekY et al study the effect of Coal fly ash on the elastic behaviour of glass [18]. Ultrasonic study of some zinc borate glass were studied by S.Thirumaranand et.al [19]. A. Kannappan et al evaluated acoustical, elastic, and mechanical properties shows the compactness and rigid network with the doping of ZnO and PbO the structural properties of glass investigated shows the rigidity of glass [20]. P.Vastharani et al investigate the ultrasonic and structural studies of lead sodium borate glasses doped with ZnO [21]. The present work aims to prepare glass sample using biomass ash and to observe the effect of biomass on elastic properties of glass prepared from biomass ash and rice husk ash as glass former.

2 Materials and methods:

The sugarcane bagasse ash (BA) and Rice husk ash (RHA) used here was procured from thermal power plant running on biomass fuel, 'Purti Power and Sugar Limited', Bela, District Nagpur (MS) India. The ash was subjected to chemical analysis to confirm the presence of silica form ANACON LAB Nagpur. The percentage of silica, alumina and other fly ash components is as listed in Table1.

Table-1 Chemical analysis of biomass ash (BA and RHA)

Sr.No.	Parameter	BA	RHA
1	Silica	52.64%	62.74%
2	Alumina	14.05%	14.06%
3	Iron oxide	7.80%	14.70%
4	Calcium oxide	3.31%	1.61%
5	Magnesium oxide	1.72%	1.57%
6	Potassium oxide	4.74%	3.74%
7	Titanium dioxide	0.22%	0.28%
8	Manganese oxide	0.20%	0.24%
9	Sodium Oxide	0.48%	0.46%

The glasses were prepared by using BA and RHA, Zinc oxide and Boric Oxide (AR grade). The molar composition of the glass sample (with increasing percentage of biomass ash and rice husk ash) was taken. The powders were weighed on a monopan K Roy balance digital balance having accuracy 0.0001gm. The powder were mixed for 30 minutes thoroughly by repeated grinding in an agate mortar and pestle. Then mixture was transfer in a fire clay crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1000°C for 3 h to homogenize the melt. The melted mixture was poured on 2×1 cm² stainless-steel mould to form bulk glass. The glasses were prepared by the melt quench method. The chemical composition of glass sample is given in Table-2

Table-2 Glass composition

SR.No.	Glass composition	Composition in mole percent (%)
B₂O₃-Zno-BMA		
1	BZB-1	60-40-0
2	BZB-2	60-35-5
3	BZB-3	60-30-10
4	BZB-4	60-25-15
5	BZB-5	60-20-20
B₂O₃-Zno-RHA		
1	BZR-1	60-40-0
2	BZR-2	60-35-5
3	BZR-3	60-30-10
4	BZR-4	60-25-15
5	BZR-5	60-20-20

The quenching rate is 900°C/minute the glasses were immediately transferred to annealing furnace maintained at 323°C for 1 hour. The glass sample polished to form parallel faces to study ultrasonic properties. The density of the glass samples were measured using Archimedes' principle. Ultrasonic longitudinal and shear velocities of the specimen were determined by using Pulse-Echo method by using X-cut and Y-cut quartz transducers having the fundamental frequency of 30MHz was used for the generation and detection of the longitudinal ultrasonic waves. The transducer was coupled to one of the faces of the specimen with a good acoustic couplant (SnotracG-1) to avoid any air gap between the transmitted pulse and the specimen. The acoustic couplant provide a better impedance matching between the transducer and specimen as well as reduces the coupling losses. An echo was registered each time, when the transmitted pulse were received by the same transducer after travelling a distance d in the specimen. The amorphous nature of glass sample confirmed by XRD spectra. FTIR of glass samples were studied for confirming the presence of silica and alumina in the glasses.

3. Theoretical calculation:

All the equations to find out the Ultrasonic velocity and elastic constant are given below [22],

The ultrasonic velocity of glass sample was obtained using

$$U = \frac{2d}{t} \text{ ---- (1)}$$

at room temperature.

Where d is width of the sample and t is time.

The two type of velocities, longitudinal velocity (U_l) and shear velocity (U_s) were obtained by using equation 1.

The elastic modulus were obtained by measuring density (ρ) of the glass sample.

Longitudinal Modulus (L) can be obtained from longitudinal velocity.

$$L = \rho U_l^2 \text{ ---- (2)}$$

Shear Modulus (G) The shear modulus can be found from shear velocity as,

$$G = \rho U_s^2 \text{ ... (3)}$$

Bulk Modulus (K) which the ratio between bulk stress and bulk strain is obtained from the ultrasonic velocities as

$$K = L - \left(\frac{4}{3} \right) G \text{ (4)}$$

Young's Modulus (E) is the ratio of stress and strain which is given as

$$E = (1 + \sigma) 2G \text{ ... (5)}$$

Where σ Poisson's ratio.

Poisson's Ratio (σ) it is the ratio of lateral and longitudinal strain which is given by the relation,

$$\sigma = \left(\frac{L - 2G}{2(L - G)} \right) \text{ (6)}$$

Acoustic Impedance (Z) gives the transmission and reflection of sound energy in the glass specimen.

$$Z = U_l \rho \text{ ... (6)}$$

Micro Hardness (H) it is given by

$$H = (1-2\sigma) \frac{E}{6(1+\sigma)} \dots (7)$$

Debye Temperature (θ_D)

The Debye temperature θ_D of the sample is calculated from the relation

$$\theta_D = \frac{h}{k} \left(\frac{9N}{4\pi Vm} \right)^{\frac{1}{3}} Um \dots (8)$$

Where h, K, N and Vm are the Planck's constant, the Boltzmann's constant, the Avagadro's number and the molar volume of the sample, respectively.

The mean sound velocity Um is given by

$$Um = \left(\frac{1}{3} \left(\frac{2}{U^3_s} + \frac{1}{U^3_l} \right) \right)^{\frac{1}{3}} \dots (9)$$

Thermal Expansion Coefficient (α_P):

Thermal expansion coefficient can be obtained as

$$\alpha_P = 23.2 (U\ell - 0.57457) \dots (10).$$

4 Results and Discussion:

4.1 X-Ray Diffraction Spectra-

The amorphous nature of the glass sample were confirmed using X-Ray diffraction analysis using PW-3050/60XPRT-PRO type-0000000083005381 diffractometer and target $\text{CuK}\alpha$ radiations (Fig 1).

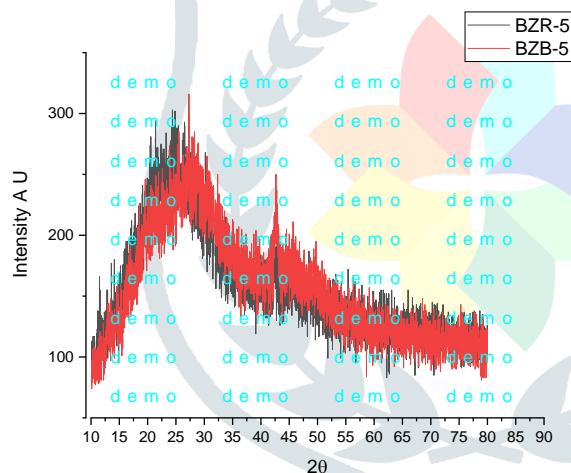


Figure-1 X-ray diffraction pattern of BZB and BZR glass sample

4.2 IR-Spectroscopy of glass sample:

The infrared spectra of glass sample BZB-5 and BZR-5 is studied in the wave number range $400-4000\text{cm}^{-1}$ on Perkin Elmer-467 IR spectrometer. Kbr technique was used. The absorption 20 peaks were obtained in BZB and 12 peaks were obtained in BZR. Details of the appeared peaks are presented in Table 2. The peak assignment is consistent with other published work [23-24]. Absence of peak around 806cm^{-1} , which is clear from the inset of Figure 5, indicate that borate network does not contain any boroxol ring[25]. The peak near 450cm^{-1} shows Si-O-Si stretching modes[26](Fig 2 and Fig-3).

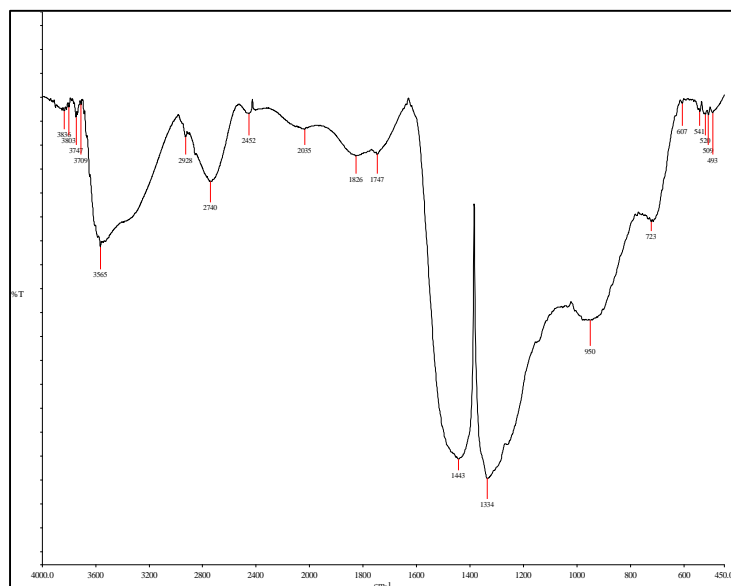


Figure-2 IR spectra of BZB-glass sample

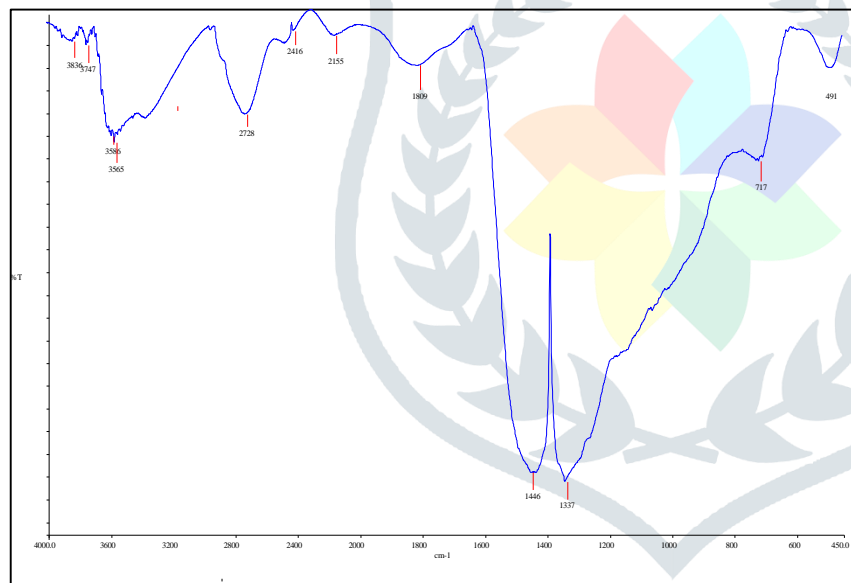


Figure-3IR spectra of BZR-5 glass sample

Table-2 FTIR analysis of glass sample

Sr.no.	Peak position	Assignments
1	440-770 cm^{-1}	B-O-B bending vibration of cations borate network
2	1330-1400	Stretching of B-O bond
3	1446-1826	Due to presence of Zn^{+2}
4	2100-2730	-OH group
5	3565-3747	Hydroxyl or water group
6	3709-3747	Suggest the ZnO bond formation
7	490 cm^{-1}	Si-O-Si

4.3 Elastic properties of glass system:

The experimental values of density (ρ), longitudinal ultrasonic velocity (U_l) and shear ultrasonic velocity (U_s) of the different glass specimen with respect to the change in the mol% of BA and RHA are listed in Table-3. The calculated longitudinal modulus (L), shear modulus (G), bulk modulus (K) and Young's modulus (E) are also reported in Table-4.

Table-4: Values of Density, Ultrasonic velocity, Elastic moduli for both glass sample series

Name of sample	Density $\text{kg/m}^3 \times 10^3$	ultrasonic velocity			Elastic Module		
		Longitudinal	Shear	longitudinal modulus	shear modulus	bulk modulus	young's modulus
		$U_l(\text{ms}^{-1})$	$U_s(\text{ms}^{-1})$	10^9N/m^2	10^9N/m^2	10^9N/m^2	10^9N/m^2
BZB1	4.51	3015	1700.2	40.90	13.03	23.52	32.83
BZB2	5.55	3426	1822	65.14	18.42	40.58	47.89
BZB3	6.52	3614	1850	86.46	23.65	54.92	61.96
BZB4	7.25	3812	1950	105.5	27.56	68.75	72.75
BZB5	7.82	4023	2006.1	124.9	30.97	83.60	82.38
BZR1	4.51	3015	1700.2	40.90	13.03	23.52	32.83
BZR2	5.57	3026	1741.2	51.00	16.88	28.49	42.2
BZR3	5.85	3624	1952.2	76.83	22.29	47.11	57.50
BZR4	6.1	3923	2000.01	93.87	24.44	61.12	64.52
BZR5	6.61	4152	2963.1	113.9	58.03	65.32	118.26

Density (ρ) of sample increases and molar volume decreases with increasing percentage of BA and RHA due to structural changes in glass network. The structure of glass depends on the nature of ions entering in the network and hence the density [27-28]. For BZB and BZR glasses, B_2O_3 is a well-known glass former, the network of pure B_2O_3 glass consists of three coordinated trigonal (B_3) boron atoms. In addition to B_2O_3 , SiO_2 in the form of BA and RHA also act as a glass former and all the four oxygen in SiO_4 tetrahedral are randomly connected to one, two, three or four, depending upon the other oxides present in the glass network [29-30]. The vitreous B_2O_3 consist planar $[\text{BO}_3/2]$ units. The addition of BA and RHA as silica source to B_2O_3 network creates $[\text{BO}_4/2]$ units. This leads to increase in the network dimensionality and connectivity of silver borate glass structure. Hence both ultrasonic moduli increases with the increase in BA and RHA concentration [31]. It is seen from the Table 4 that both longitudinal velocity (U_l) and shear velocity (U_s) increase almost linearly with the concentration of BA and RHA. The increase in velocity is caused by the increase in the packing density [32]. Increase in packing density responsible for the increase in ultrasonic velocity and elastic modules. Elastic constants and thermal expansion coefficient, micro hardness have increasing trend with the increasing mole percentage of BA in BZB sample and RHA in BZR sample series. Thus rigidity of sample increases. The variation of Poisson's ratio with mole percent of BA and RHA is shown in Table-5.

Table-5: Values of Poisson's ratio, Micro hardness, Acoustic Impedance, Debay Temp, Thermal expansion of BZB and BZR glass system.

Name of sample	Poisson ratio	Micro-hardness 10^9N/m^2	Acoustic Impidance $10^7 \text{kg m}^{-2} \text{s}^{-1}$	Debay Temp $(\text{K})\theta$	Thermal expansion (K^{-1})
BZB1	0.26	2.08	1.359	603.13	69934.67
BZB2	0.30	2.45	1.9014	622.26	79469.87
BZB3	0.31	2.99	2.3924	669.73	83831.74
BZB4	0.32	3.30	2.7637	715.12	88425.07
BZB5	0.33	3.5	3.1057	732.10	93320.27
BZR1	0.26	2.08	1.359	332.20	69534.07
BZR2	0.25	2.81	1.6857	362.10	70769.87
BZR3	0.29	3.12	2.120	379.12	70189.88
BZR4	0.32	2.93	2.3930	438.56	91000.20
BZR5	0.19	12.76	2.7444	452.14	96313.00

Poisson's ratio (σ) is an important tool used to explore the cross-link density of glass network, shows increasing trend with increasing concentration of ash. Generally, as the glass structure weakens, as the value of poison's ratio (σ) increases. This glass system shows the same nature [33-34]. The increase in Poisson's ratio shows that the atoms experience higher transverse contraction strain action on them and hence become more tightly packed [35]. The continuous increase in Poisson's ratio and micro hardness reveals that the addition of BA and RHA as glass former forms non-bridging oxygen and giving rise to formation of glass network (Fig-4 and Fig-5).

The results were further confirmed by another parameters like Debye temperature, obtained directly from the measured velocity. The Debye temperature (θ_D) plays an important role in solid materials in the determination of elastic constant and atomic vibrations. θ_D represents temperature at which all modes of vibrations in a solid are excited and its increase implies an increase in rigidity of glass. The increase the Debye temperature is possibly due to the charged centre coming closer than the distance required statistically achieving a more effective Colombian interaction. Such interaction can give rise to high energy vibrational modes, thereby increasing the Debye temperature [36]. This increase in Debye temperature with the addition of BA and RHA shows the glass structure strengthen. The thermal expansion coefficient increases with increase in mol% BA and RHA and hence the rigidity of the structure of the glass.

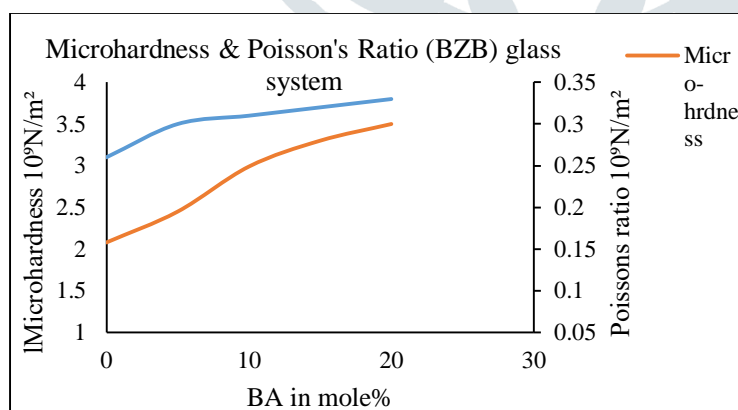


Figure-4 Variation of micro-hardness and Poisson's ratio with BA in mole %

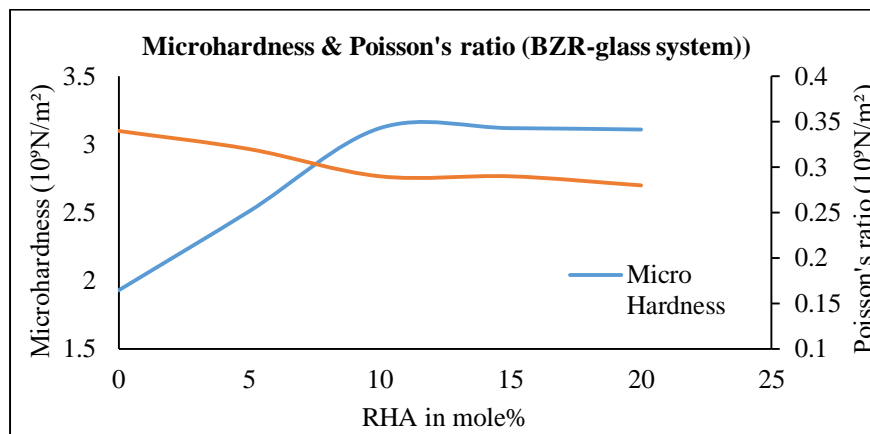


Figure 5- Variation of micro hardness and Poisson's ratio with RHA in mole%

5 Conclusion:

It is concluded that the biomass ash has significant effect on acoustical elastic and mechanical parameters of the glass specimen (BZB, BZR). Present glass system throw light on the effect of biomass ash on rigidity and compactness in structural network of glass. The BZB and BZR glass possess higher rigidity, strength and compactness in structural network with the addition of biomass ash and rice husk as silica source for glass former.

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