



## The Influence of Alkali Oxide content on the Properties of Sodium Borosilicate glasses

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### ABSTRACT

Glasses in the system  $x\text{Na}_2\text{O}-10\text{B}_2\text{O}_3-(90-x)\text{SiO}_2$  (where  $x= 0, 10, 20, 30\dots$ ) were prepared by conventional melt quench technique and studied their densities, UV-Visible spectra, IR spectra, transition temperature, electrical conductivity and chemical durability. The XRD patterns confirm the glassy nature of the sample. As increasing the  $\text{Na}_2\text{O}\%$  the UV cut off is shift towards higher wavelength. The electrical conductivity increases up to 30% of  $\text{Na}_2\text{O}$  beyond 30% conductivity decreases it suggests that the mobility of  $\text{Na}^+$  is restricted by increasing the concentration of  $\text{Na}_2\text{O}$ . The investigated glass sample improved the chemical durability of the investigated glass in acidic as well as in alkaline medium.

**Keywords:** Borosilicate glasses, Electrical conductance, Optical properties, Chemical durability Alkali oxide.

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### INTRODUCTION

Borosilicate glasses are of technological interest because they have various applications in laboratory glassware, household cookware, industrial piping, bulbs for hot lamps, optical windows and various glass-to-metal (GM) seals. They generally have a lower thermal expansion than soda-lime silica glasses have good chemical resistance, high dielectric strength and a higher softening temperature than soda-lime silica glasses. They are also considered to be one of the most suitable materials for immobilization of high level radioactive waste generated during the reprocessing of the spent nuclear fuel [1]. For these applications, glasses with lower processing temperatures, higher activation energy for chemical dissolution may be required or glass with an expansion coefficient matching with that of the metal are used. Some other applications may require glasses having higher densities or refractive indices. Such glasses are prepared by modifying physico-chemical properties of silica glass through introduction of a large number of other metal oxides into random network of silica, which may act as network modifiers or network formers [2]. Borosilicate glasses formed by adding  $\text{B}_2\text{O}_3$  in silica network with alkali and mixed alkali oxides as modifiers. Addition of alkali oxides to these silicate glasses lowers its melting point. This also results in variation of various physical properties like mechanical strength, electrical and thermal conductivity etc. the information about the structural units, present in these glasses helps in predicting and understanding the

change in physical properties. Besides the X-ray diffraction methods, the infrared absorption (and reflection) spectrometry is also one of the most promising tools in structural investigations of silicates.

In this paper, the preparation and thermo-physical, electrical, structural properties of borosilicate glasses are discussed. Chemical durability studies on these glasses were also carried out in acidic and alkaline medium. The dissolution behavior was studied at room temperature. Shibata et al. [3] and Lim et al [4] studied and formulated expressions for the density of alkali borate glasses and sodium borosilicate glasses in relation to the atomic arrangements. Abe et al [5] suggested that in borosilicate, the anomalous property variation at a Na : B ratio of 0.2 corresponded to a maximum in the number of  $\text{BO}_4$  groups.

## MATERIALS AND METHODS

Borosilicate glasses having the following compositions  $X \text{Na}_2\text{O} - 10 \text{B}_2\text{O}_3 - (90-X) \text{SiO}_2$  were prepared using analytical grade compounds as the starting materials by conventional melt quench method. The initial constituents used were of 99.5% purity. These chemicals were thoroughly mixed and ground for 30-40 min in a mortar pestle followed by grinding in planetary ball mill at a rotating speed of 300 rpm. The charge (25g) was then melted using muffle furnace in alumina crucible. The melting temperature and dwell time were optimized in the temperature range of  $1300^\circ\text{C} - 1500^\circ\text{C}$  and 4 h. respectively. Under these conditions the melt was thoroughly homogenized and attained desirable viscosity for pouring. The pouring was done on metallic plate. The glass was annealed at appropriate temperatures. The optimized annealing temperature was found to be  $450^\circ\text{C} - 500^\circ\text{C}$  and dwell time was to about 4-5 h, for the present series of glass samples. For a lesser annealing temperature and dwell time, cracking of the glass was observed.

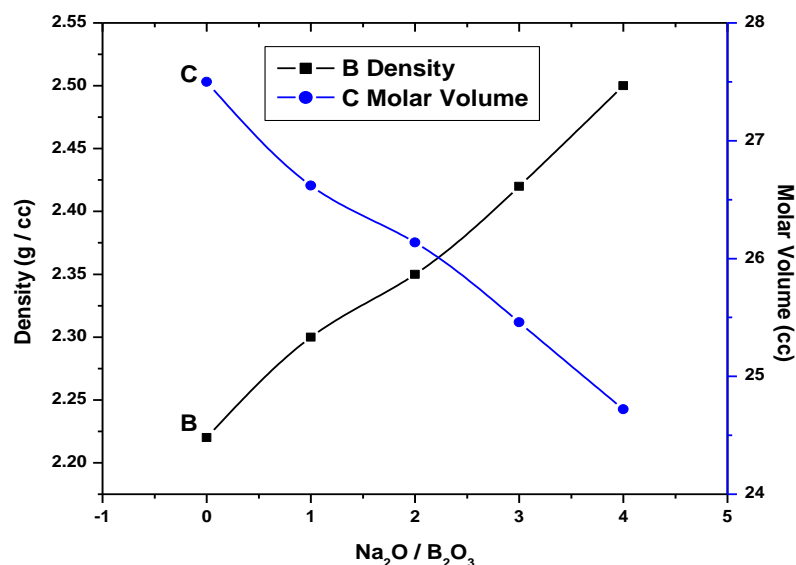
**Characterization:** Density was measured for all borosilicate glass at room temperature using xylene as immersion liquid. XRD patterns for the glass powders were recorded in the  $2\theta$  range  $10^\circ - 80^\circ$  on computer controlled X-ray diffractometer (PW 3710) with  $\text{Cu K}_\alpha$  source. The UV visible optical transmission for glass samples were measured by using double beam spectrophotometer covering the range 200-1100nm. The infrared absorption spectra of the glasses were measured at room temperature in the wave number range  $400 - 4000 \text{ cm}^{-1}$  by Fourier Transform computerized infrared spectrometer. Glass powder mixed with KBr then to produce clear homogeneous discs, mixture is subjected to a pressure of 5 tones  $/\text{cm}^3$ . The infrared absorption was measured immediately after preparing the required disc. Thermal expansion coefficients ( $\alpha$ ), glass transition temperature ( $T_g$ ) were measured using a Dilatometer. Chemical degradation studies of the glass samples were carried out in 10% HCl & 10% NaOH. The weight loss was monitored after 72 h of exposure.

## RESULTS AND DISCUSSION

**Density measurements:** The density and molar volume observed for borosilicate glasses are shown in table 1. When R ( $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ) is increased in the range 0.0 to 4, the density of glass increases from 2.22 to  $2.5 \text{ g cc}^{-1}$  and molar volume decreases from 27.50 to  $24.72 \text{ cc}$  as shown in figure.1. Sodium borosilicate glasses with R (molar ratio  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3 \leq 4$ ) are composed of  $\text{BO}_3$  triangles and  $\text{BO}_4$  tetrahedra in the silica network. These structural units are connected through bridging oxygen ions. In  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  glasses with K (molar ratio of  $\text{B}_2\text{O}_3$  to  $\text{SiO}_2 \leq 0.2$  and  $R \leq 4$  which is the present case, there are two networks, a sodium borate network and a  $\text{SiO}_2$  network [6]. This increase in density is attributed to the increase of the fraction of  $\text{BO}_4$  tetrahedra in the glass which contracts the network [7-8].

**Table-1:** Variation in physical properties with composition  $X\text{Na}_2\text{O}-10\text{B}_2\text{O}_3-(90-X)\text{SiO}_2$ 

Glass Code	Com position on X (mole %)	R= $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$	K= $\text{B}_2\text{O}_3/\text{SiO}_2$	Mole Wt.	Density (g/cc)	Molar Vol. (cc)
SB-1	0	0	0.1	61.04	2.22	27.50
SB-2	10	1	0.125	61.23	2.30	26.62
SB-3	20	2	0.143	61.42	2.35	26.13
SB-4	30	3	0.166	61.61	2.42	25.46
SB-5	40	4	0.23	61.80	2.50	24.72

**Fig 1.** Variation of density & molar volume with  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3$  ratio in the range 0 to 4.

The excess of oxygen from sodium oxide are used exclusively in the formation of  $\text{BO}_4$  tetrahedra. This effect is only up to 30 mole % alkali oxide. Further addition of alkali oxide results in the formation of non bridging oxygen. However the increase in the density diminishes with increase in the alkali oxide content. This is explained by assuming that the tendency to formation of  $\text{BO}_4$  units becomes less with addition of more alkali oxide [9]. The molar volume is found to decrease with R due to the contraction of the alkali borate network and not much dependent on relative concentration of  $\text{SiO}_2$  network in the glass [7]. However, the presence of  $\text{SiO}_2$  in the structure affects greatly the volumes of the  $\text{BO}_3$  and  $\text{BO}_4$  units.

**XRD:** Powder X-ray diffraction patterns of all the borosilicate glass samples showed broad peaks, characteristic of glass structure. Representative XRD pattern is shown in fig. 2, which confirms the amorphous nature of the investigated glass samples.

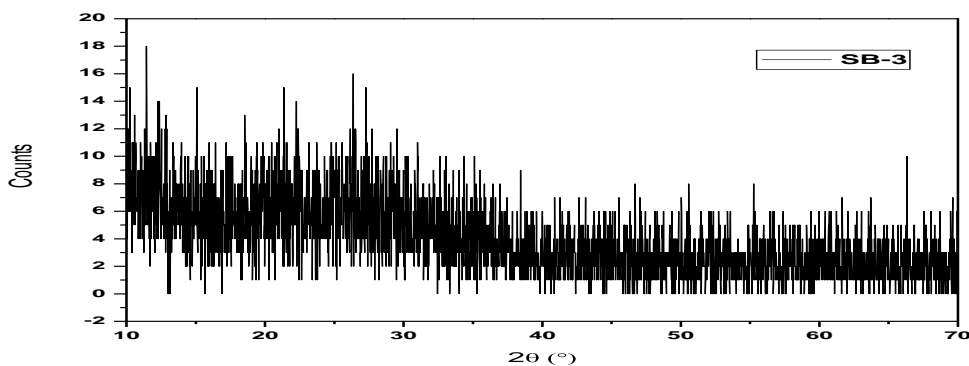


Fig 2. XRD pattern of a sodium borosilicate glass sample.

**Infrared transmission:** The transmittance spectra of the five borosilicate samples in the IR region 200 to 4000  $\text{cm}^{-1}$  are shown in fig. 3. The frequencies at 1100, 800, 480  $\text{cm}^{-1}$  correspond to the Si-O stretching and Si-O-Si bending mode ascertaining the presence of  $[\text{SiO}_4]$  tetrahedra [9]. The band around 1400  $\text{cm}^{-1}$  increases with the content of the six membered borate ring with one or two  $[\text{BO}_4]$  units.

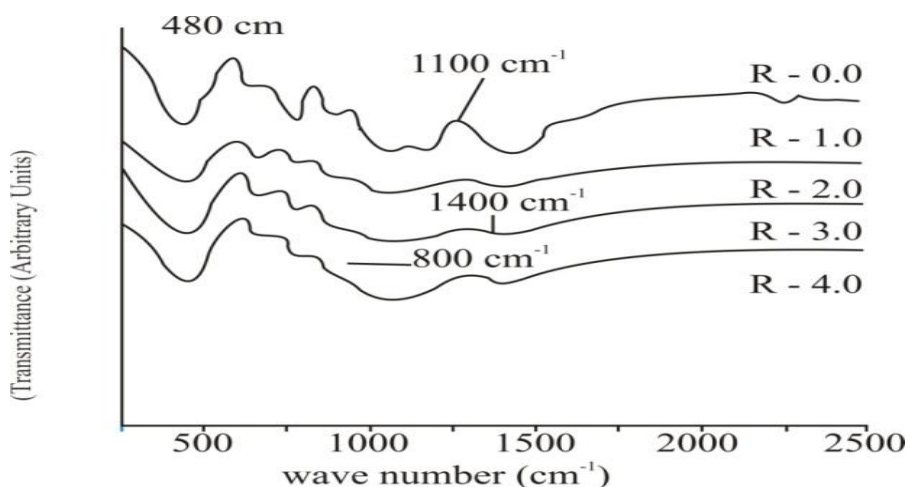


Fig.3. IR Transmission spectra of sodium borosilicate glasses.(The spectra are offset for clarity)

**Thermo-mechanical measurements:** Glass transition temperature ( $T_g$ ) and TEC of the five borosilicate samples are given table 2.

Table 2. Thermo-mechanical properties of borosilicate glass samples

Composition X (mole %)	R= $\text{Na}_2\text{O}$ / $\text{B}_2\text{O}_3$	K= $\text{B}_2\text{O}_3$ / $\text{SiO}_2$	$T_g$ $^{\circ}\text{C}$	TEC ( $10^{-6}/^{\circ}\text{C}^{\circ}$ )
0	0	0.111	480	6.46
10	1	0.125	497	5.80
20	2	0.143	517	4.72
30	3	0.166	546	4.20
40	4	0.200	574	3.68

The variation of T<sub>g</sub> and TEC with R are shown in fig 4. Addition of alkali oxide to B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems at first leads to a more coherent network [9]. This effect becomes less pronounced in presence of higher silica content in the glass.

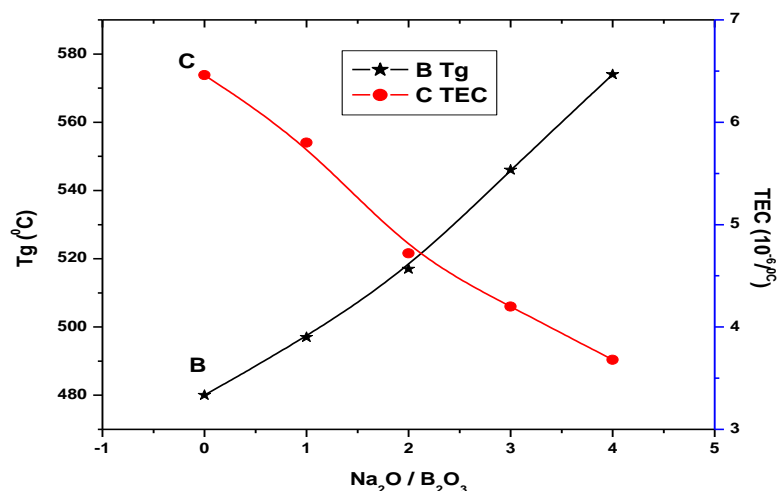


Fig 4. Variation of T<sub>g</sub> & TEC with Na<sub>2</sub>O / B<sub>2</sub>O<sub>3</sub> ratio.

This coherency is due to the mechanism of conversion of triangularly coordinated boron ions to tetrahedrally coordinated ions. Beyond certain alkali oxide content, enough non-bridging oxygen ions are formed, giving rise to a less coherent network. This is explained by taking into account the fact that the relative increase in coherency due to the formation of BO<sub>4</sub> tetrahedra will be less if more SiO<sub>4</sub> tetrahedra with bridging oxygen ions are present [9].

**UV – Visible spectroscopy:** The borosilicate glasses have been characterized with UV- visible spectrophotometer and it has shown interesting results, fig 5 represents the transmittance spectra of sodium borosilicate glass samples with different Na<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub> composition. The absorption edge cut off shift towards the longer wavelength with increase in the concentration of alkali oxide (Na<sub>2</sub>O).

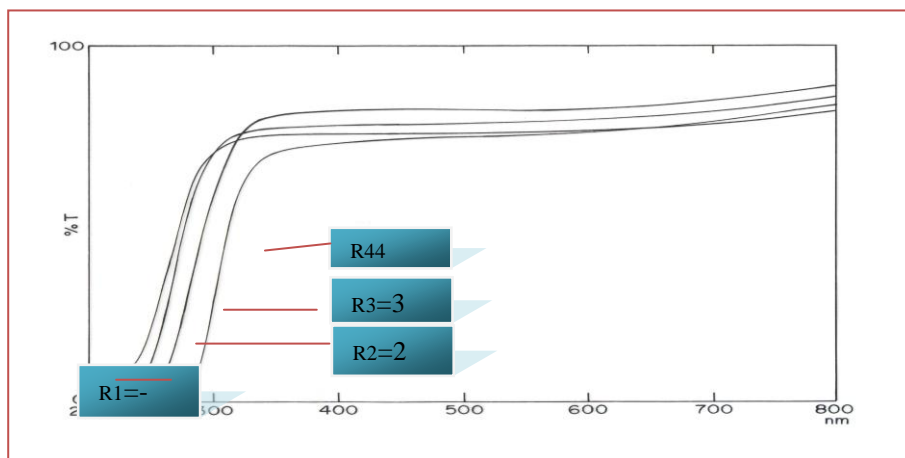


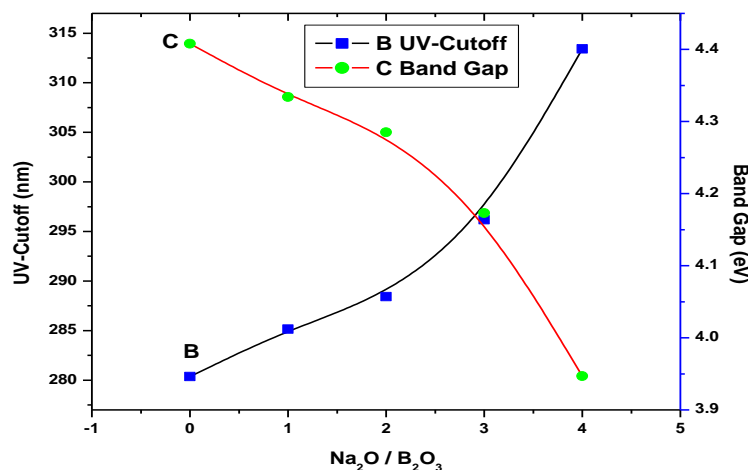
Fig 5 . UV transmission spectra of  $x\text{Na}_2\text{O}-10\text{B}_2\text{O}_3-(90-x)\text{SiO}_2$  glasses.

Band gap values at the respective UV cut offs for various sodium borosilicate glasses are summarized in table 3.

Table 3. Band gap of different Na-borosilicate glasses.

Composition X mole %	$R = \frac{Na_2O}{B_2O_3}$	UV cut off	Band Gap in eV
0	0	280.37	4.408
10	1	285.15	4.334
20	2	288.43	4.285
30	3	296.19	4.173
40	4	313.41	3.947

Fig. 6 shows the dependence of band gap on the mole% of Na<sub>2</sub>O in the glass. The graph shows that band gap decreases as per the increase in the mole% of Na<sub>2</sub>O.

Fig 6. Plot of dependence of band gap on Na<sub>2</sub>O / B<sub>2</sub>O<sub>3</sub> ratio.

**Electrical conductivity:** The prepared glass samples were cut and then finely polished to a uniform thickness for the measurement of electrical conductivity ( $\sigma$ ). The electrical conductivity of the glass samples were recorded from room temperature to 423<sup>0</sup>K using impedance analyzer (Agilent 4294 A) in the frequency range of 40 Hz to 20 MHz. Fig. 7 shows the temperature dependence of the conductivity ( $\sigma$ ) for sodium borosilicate glasses. The linear relationship between the logarithm conductivity and inverse of temperature for all the samples indicates that the following Arrhenius law is satisfied.

$$\sigma = \sigma_0 \exp \left( \frac{-E_a}{KT} \right) \text{----- (1)}$$

Where  $\sigma_0$  is a constant for given glass, 'K' is Boltzmann's constant and  $E_a$  is the activation energy for conduction.

The values of  $E_a$  were evaluated from the linear portion of curves (Fig 7). The calculated values of  $\sigma$  at 423<sup>0</sup>K and  $E_a$  for all the glass samples are included in Table 4. From Table 4 and Fig 8 it is observed that the conductivity increases up to 30% with an increase in temperature and it also increases with increase in Na<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub> ratio. Conductivity decreases beyond 30% of Na<sub>2</sub>O.

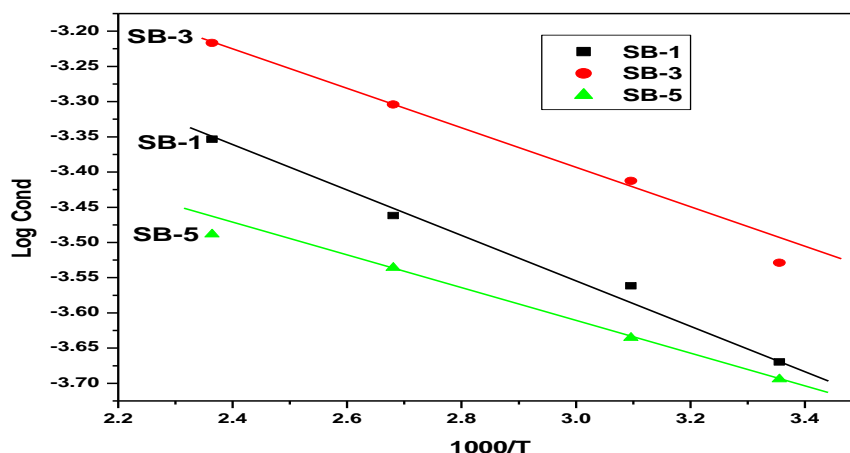


Fig. 7. Arrhenius plot for  $X\text{Na}_2\text{O} - 10\text{B}_2\text{O}_3 - (90-X)\text{SiO}_2$  glasses

Table 4: Calculated values for the activation energy & conductivity of  $X\text{Na}_2\text{O} - 10\text{B}_2\text{O}_3 - (90-X)\text{SiO}_2$  glasses at  $423^0\text{K}$  &  $20\text{ MHz}$ .

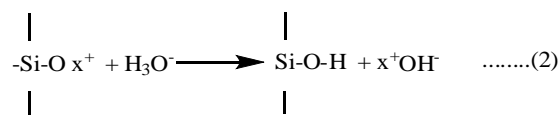
Glass Code	$\text{Na}_2\text{O} / \text{B}_2\text{O}_3$	Cond. $\sigma$	Activation energy $E_a$ (eV)
SB-1	0.0	$4.426 \times 10^{-4}$	6.2503
SB-3	2.0	$6.071 \times 10^{-4}$	4.2486
SB-5	4.0	$3.241 \times 10^{-4}$	4.4001

**Chemical degradation (corrosion) studies :** Polished samples of the sodium borosilicate glass samples of various composition  $X\text{Na}_2\text{O} - 10\text{B}_2\text{O}_3 - (90-x)\text{SiO}_2$  where  $X = 0$  to  $40\%$  were exposed to  $10\%$  HCl and  $10\%$  NaOH separately at room temperatures for  $72\text{ h}$  of exposure. The effect of glass composition and the environment (acidic or alkaline) on the degradation behavior of these glasses was studied and interpreted. The weight loss observed are plotted as a function of ratio of sodium oxide to boron oxide [ $\text{Na}_2\text{O} / \text{B}_2\text{O}_3$ ] content and are given in the table 5 and fig. 8.

Table 5. Weight loss observed after  $72\text{ h}$  of exposure.

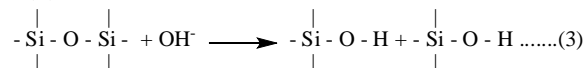
Composition X mole%	$R = (\text{Na}_2\text{O}/\text{B}_2\text{O}_3)$	Wt. loss in $10\%$ HCl ( $\text{g}/\text{cm}^2$ )	Wt. loss in $10\%$ NaOH ( $\text{g}/\text{cm}^2$ )
0	0	0.038	0.58
10	1	0.005	0.42
20	2	0.003	0.36
30	3	0.002	0.28
40	4	0.0015	0.20

The dissolution was seen to be higher in alkaline medium as compared to acidic medium. This can be explained on the basis of chemical reaction involved in respective media. In acidic medium, the hydronium ions attack the modifier ions present at the interstitials of the glass network <sup>[10]</sup> as shown in equation (2)



Where X = Na<sup>+</sup> or K<sup>+</sup> modifier cations.

The major features characterizing aqueous alteration of silicate glass are the extraction of mobile alkali cations from the glass network and their replacement by hydrogenated species. The weight loss is found to be more in alkaline medium due to the attack of the hydroxyl ions of alkaline medium on the silicate network as shown in equation (3)



The dissolution rate was seen to decrease with increase in sodium oxide content. The replacement of silica by sodium oxide results in the conversion to more stronger tetrahedral SiO<sub>4</sub> structure, thus strengthening the structure of the glass. Hence the dissolution rate in 10% HCl and 10% NaOH goes on decreasing with increasing sodium oxide content.

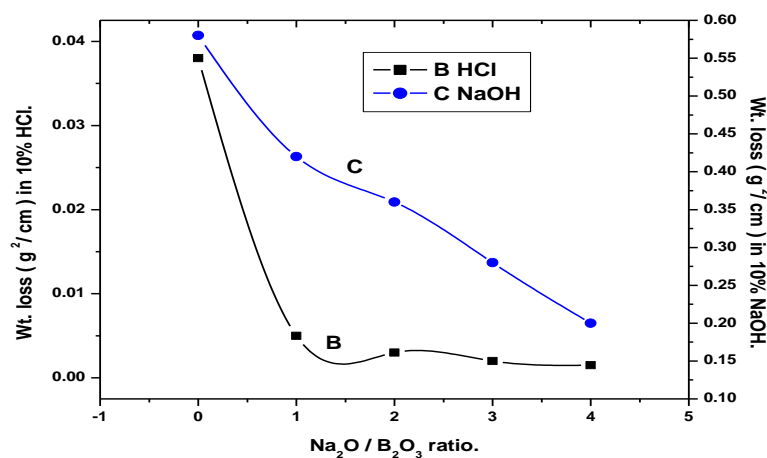


Fig 8. Plot of weight loss against Na<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub> in 10% HCl & 10% NaOH.

## APPLICATIONS

The investigated glass sample improved the chemical durability of the investigated glass in acidic as well as in alkaline medium.

## CONCLUSIONS

The investigated glass samples have been characterized to study its structural, optical, electrical and durability properties. Addition to alkali oxide to B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system leads to a more coherent network. This is due to the mechanism of conversion of triangularly coordinated boron ions to tetrahedral coordinated ions. In the present case there are two networks, a sodium borate network and a SiO<sub>2</sub> network, which resulting in strengthening of the structure. The increase in density indicates the tight packing of the atoms. The XRD patterns confirm the glassy nature of the sample. As increasing the Na<sub>2</sub>O% the UV cut off is shift towards higher wavelength. The electrical conductivity increases up to 30% of Na<sub>2</sub>O beyond 30% conductivity decreases it suggests that the mobility of Na<sup>+</sup> is restricted by increasing the concentration of Na<sub>2</sub>O. The investigated glass sample improved the chemical durability of the investigated glass in acidic as well as in alkaline medium.



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