

## Effect of barium on diffusion of sodium in borosilicate glass

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### Abstract

Diffusion coefficients of sodium in barium borosilicate glasses having varying concentration of barium were determined by heterogeneous isotopic exchange method using <sup>24</sup>Na as the radiotracer for sodium. The measurements were carried out at various temperatures (748–798 K) to obtain the activation energy ( $E_a$ ) of diffusion. The  $E_a$  values were found to increase with increasing barium content of the glass, indicating that introduction of barium in the borosilicate glass hinders the diffusion of alkali metal ions from the glass matrix. The results have been explained in terms of the electrostatic and structural factors, with the increasing barium concentration resulting in population of low energy sites by Na<sup>+</sup> ions and, plausibly, formation of more tight glass network. The leach rate measurements on the glass samples show similar trend.

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### 1. Introduction

Management of high level radioactive liquid waste (HLW) generated during reprocessing of spent nuclear fuel is one of the major challenges being faced by the nuclear scientists today. The radionuclides of major concern present in the HLW are the minor actinides, such as, <sup>237</sup>Np, <sup>241,243</sup>Am, <sup>245</sup>Cm, etc., and long lived fission products, such as, <sup>99</sup>Tc, <sup>129</sup>I, <sup>135</sup>Cs, etc. Though transmutation of these radionuclides in the accelerator driven sub-critical system (ADS) is being suggested, it may take quite some time before any progress is made in this direction. On the other hand, vitrification of HLW in suitable matrix, such as, borosilicate glass, synroc, etc. is being practiced worldwide [1]. Borosilicate glass has been one of the most widely used matrices for vitrification of HLW. The composition of the final glass matrix varies depending upon the nature of the waste. One of the most important aspects of the waste immobilization process is the leaching of the long lived radionuclides from the

glass matrix to human environment which may be due to the diffusion under thermal gradient in the glass matrix owing to the decay of radionuclides as well as dissolution of the glass upon contact with the ground water. Thermal gradients may develop in the waste glass during the production and storage of high activity radioactive waste form and certain elements are susceptible to migration under these thermal gradients. Modeling of leaching of long lived radionuclides from the glass matrix requires the data on their diffusion. Diffusion coefficients can also be determined by leach rate measurements. However, the diffusion coefficients obtained from leach rate measurement have been found to be 500–2000 times higher than bulk diffusion data [2]. It is therefore important to study the diffusion of long lived radionuclides in the glass matrices so that the long term assessment of the performance of the waste form may be achieved.

Diffusion in borosilicate glasses has been studied using various methods, such as, radiotracer method [3], concentration couple method [4], Rutherford backscattering spectrometry (RBS) [5] and heterogeneous isotopic exchange method [6]. In the radiotracer method the radiotracer is deposited on one surface of the sample which is then annealed at a specific temperature.

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The depth profile of the radiotracer is obtained by sectioning of the sample and measurement of the activity of radiotracer removed. In the concentration couple method, two segments of the glass samples, one with the element of interest and the other without it, are prepared in thermodynamic equilibrium. During the annealing the diffusion of the element from the concentrated side to the other side takes place which is monitored by scanning electron microscopy and X-ray microanalysis. RBS method directly gives the depth profile of the element diffused from the surface to the bulk of the sample. Heterogeneous isotopic exchange method is based on the isotopic exchange between the radiotracer in the small glass sample having high surface area to volume (SA/V) ratio and a salt melt containing the element of interest. This method was proposed by Lagerwall and Zimen [7] for studying the diffusion of rare gases in solids. The method requires samples with large surface area to volume ratio so as to achieve measurable diffusion of the radionuclide from the glass sample into a salt melt containing the stable ion.

Most of the diffusion studies on borosilicate glasses have been carried out on sodium, as its diffusion coefficient is much higher than other elements and hence the measurements can be made in a reasonable length of time.  $^{24}\text{Na}$  has been used as a radiotracer for measurement of diffusion coefficient of sodium in borosilicate glass matrices by Ivanov et al. [8] and Thomas and Matzke [9]. Malow and Lutze [10] used the heterogeneous isotopic exchange method using  $^{24}\text{Na}$  as a radiotracer for sodium, to determine the diffusion coefficient of sodium in borosilicate glass.

Barium borosilicate glass is being used for vitrification of sulphate bearing HLW generated at Bhabha Atomic Research Centre, Trombay, India [11]. The structural aspects of these glasses have been studied earlier by  $^{29}\text{Si}$ ,  $^{11}\text{B}$  NMR and IR spectroscopy [12]. This study showed existence of  $\text{Q}^2$  and  $\text{Q}^3$  structural units of Si with no direct interaction between  $\text{Ba}^{2+}$  and boron structural units. In the present work, we have used heterogeneous isotope exchange method for the study of diffusion of sodium in barium borosilicate glass. The aim of the study was to investigate the effect of barium on the diffusion of sodium which is considered as an analogue of cesium.

## 2. Experimental

Four barium borosilicate glasses of varying mole percent of barium oxide (0–11.7%) were prepared by the standard method described below.

The glass forming chemicals, viz.,  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{NaNO}_3$  and  $\text{Ba}(\text{NO}_3)_2$  were mixed in the proportion corresponding to desired oxide composition. The homogenized mixture was charged in the siliminite crucible and calcined in the refractory furnace at 973 K. Subsequently, the calcined mass was fused and refined at 1273 K. After adequate soaking to have homogenization of the vitreous melt, it was poured on a stainless steel tray. Small piece of the glass sample was powdered and the glass transition temperature ( $T_g$ ) was measured by differential scanning calorimetry (DSC).

Glass transition studies were carried out using a heat flux type differential scanning calorimeter, DCS131 supplied

by SETARAM Instrumentation, France. Temperature calibration for the calorimeter was carried out using the phase transition temperatures of NIST reference materials (indium;  $T_{\text{fus}} = 429.748$  K, tin;  $T_{\text{fus}} = 505.078$  K, lead;  $T_{\text{fus}} = 600.600$  K). Analytical reagent (AR) grade samples of potassium nitrate ( $T_{\text{fus}} = 400.850$  K) and silver sulfate ( $T_{\text{fus}} = 703.150$  K) were also used to perform temperature calibration of the DSC. Heat flow measurements of the glass samples were carried out by taking about 300 mg of the sample in stainless steel crucible (100  $\mu\text{L}$ ) in argon carrier gas with a flow rate of 2  $\text{dm}^3 \text{h}^{-1}$  and at a heating rate of 10  $\text{K min}^{-1}$ . The glass transition temperature was evaluated from the heat flow versus time curve with the help of the software provided along with the instrument.

For diffusion study, cuboidal glass samples having each side around 2 mm were cut from bigger pieces. These samples weighing around 50 mg were irradiated in the APSARA reactor, at Mumbai having neutron flux about  $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  for a time period of 2 h to produce  $^{24}\text{Na}$  activity. The irradiation in the reactor ensures uniform concentration of  $^{24}\text{Na}$  atoms throughout the glass sample. After a delay time of about 20 h, the samples were annealed in a furnace at varying temperatures in the range of 748–798 K. The samples were kept in a melt of  $\text{NaNO}_3$  kept in a platinum crucible and were removed from time to time to measure the activity of the  $^{24}\text{Na}$  left in the sample. Here it has been assumed that the diffusion at the glass–melt interface is very fast compared to that in the glass sample. Further, the compositional and structural changes likely to occur during isotopic exchange have been assumed to be negligible.

The sample was counted for a period of 100–200 s on a 60cc HPGe detector coupled to a 4 K channel analyzer in live time mode. The sample was kept in a standard geometry such that the dead time was less than 20%. The peak area due to the 1368 keV gamma ray of  $^{24}\text{Na}$ , obtained by linear subtraction of the Compton background, was used for determining the fraction of  $^{24}\text{Na}$  released from the glass into the salt melt. The peak area was calculated by linear subtraction of the Compton background, as the spectrum was not complex. The total time of annealing was around 20 h.

### 2.1. Leach rate studies

Chemical durability of glasses was evaluated using standard test methods, following the procedure of product consistency test—ASTM C1285-02. The surface area of glass sample to leachant volume ratio taken was  $1.9427 \text{ m}^2 \text{ L}^{-1}$ . This test method is a 7-day chemical durability test performed at  $90 \pm 2^\circ\text{C}$  with de-mineralized water (DM) as leachant. The test method is static and conducted in stainless steel vessels inner lined with Teflon. This test method is used to evaluate, whether the chemical durability and element release characteristics of nuclear waste forms have been consistently controlled during production. Normalized leach rate of the waste form on sodium release basis is given by the equation,

$$R_{\text{Na}} = \frac{C_{\text{Na}}}{f_{\text{Na}}(\text{SA}/V)t} \quad (1)$$

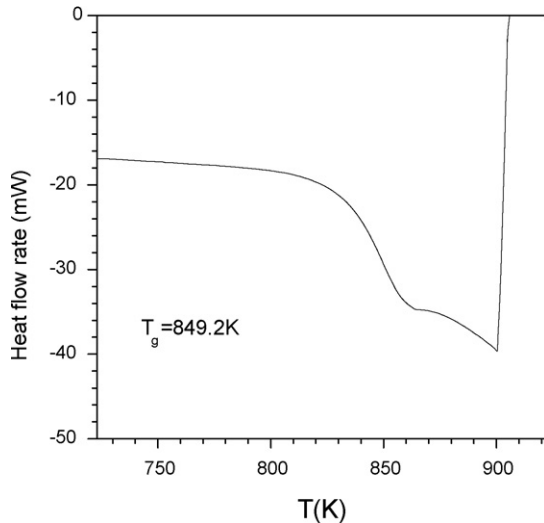


Fig. 1. Differential scanning calorimetry scan of glass sample C.

where  $R_{Na}$  is the normalized leach rate on sodium release basis ( $\text{g}_{\text{waste form}} \text{m}^{-2} \text{day}^{-1}$ ),  $C_{Na}$  is the concentration of sodium in the leachant solution ( $\text{g L}^{-1}$ ),  $f_{Na}$  is the fraction of sodium in the unleached waste form,  $SA/V$  is the surface area of the waste form divided by the leachant volume ( $\text{m}^2 \text{L}^{-1}$ ) and  $t$  is the duration of test in days.

### 3. Results

The nominal composition of the four glass samples having different barium content is given in Table 1 along with their glass transition temperatures ( $T_g$ ). All the glass samples were thoroughly characterized by X-ray diffraction (XRD), electron probe micro analyzer/wavelength dispersive X-ray spectroscopy (EPMA/WDS). The glasses were found to be homogeneous and no phase separation was observed. Fig. 1 shows a typical DSC scan of a borosilicate glass sample. Fig. 2 shows a typical gamma ray spectrum of the glass sample measured before the annealing was started. The gamma ray spectrum contains the peaks due to  $^{24}\text{Na}$  alone (1368 and 1720 keV) with those to  $^{139}\text{Ba}$  (166 keV) having decayed before the annealing was started. The fraction of  $^{24}\text{Na}$  released from the glass sample into the melt ( $F$ ) was calculated using the formula,

$$F = A(t) \frac{e^{\lambda t}}{A_0} \quad (2)$$

where  $A_0$  and  $A(t)$  are the count rate of  $^{24}\text{Na}$  in the sample at zero time and at time  $t$ .  $\lambda$  is the decay constant of  $^{24}\text{Na}$ .

Table 1  
Composition (mol%) of glass samples, their  $T_g$  values and activation energy

S. no.	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	BaO	Cs <sub>2</sub> O	$T_g$ (K)	$E_a$ (eV)	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )
A	53.42	30.03	16.09	0	0.46	840.3	$0.78 \pm 0.14$	$8.22\text{e-}08$
B	51.26	28.81	15.96	3.49	0.48	847.9	$0.96 \pm 0.16$	$1.10\text{e-}06$
C	49.42	27.78	14.89	7.39	0.52	849.2	$1.22 \pm 0.22$	$6.219\text{e-}05$
D	47.10	26.47	14.19	11.70	0.54	848	$1.07 \pm 0.24$	$1.86\text{e-}06$

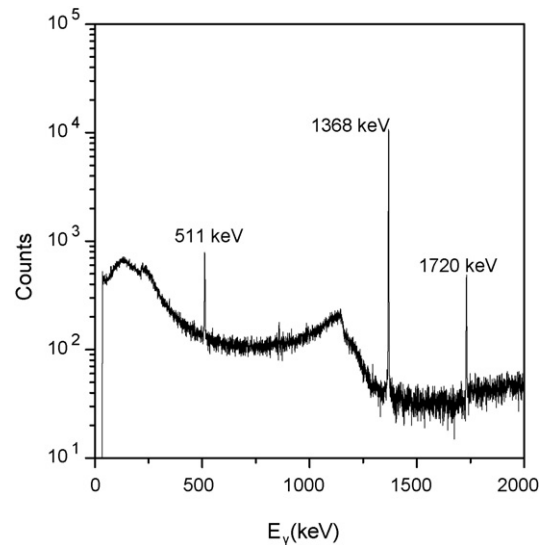


Fig. 2. Gamma ray spectrum of the irradiated glass sample.

For a rectangular parallelepiped, the fraction ( $F$ ) of the diffusion species is given by the following equation [7],

$$F = 1 - \left( \frac{8}{\pi^2} \right)^3 \exp \left[ -Dt\pi^2 \left( \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \right] \quad (3)$$

where  $a$ ,  $b$  and  $c$  are the measure of the parallelepiped.

This is the asymptotic form of the solution of the Fick's second law of diffusion for an infinitely small source, for large  $t$  values, that is,  $\alpha^2 \gg 1$ , where,

$$\alpha^2 = \frac{Dt}{q^2} \quad (4)$$

$$\text{with } q = \sqrt{\left( \frac{a}{b} \right)^2 + \left( \frac{a}{c} \right)^2} \quad (5)$$

Unique plots of  $F(\alpha^2)$  for different values of  $q$  are obtained at least for large  $F$  values. Thus, the diffusion coefficient ( $D$ ) can be obtained from the measured  $F$  values and using the plots of  $F$  versus  $\alpha^2$  for the known value of  $q$  for the sample [7].

Fig. 3 shows the plot of  $F$  versus  $t^{1/2}$ . The error on fractional release values ( $F$ ) is below 1%, as the area of the peak due to 1368 keV gamma ray was always more than 10,000. The linear relationship between  $F$  and  $t^{1/2}$  corroborates the Fickian diffusion process. The  $D$  values were deduced from the  $F$  values using Eqs. (3)–(5) and are given in Table 2 for all the samples. The diffusion coefficient were fitted into the Arrhenius equation,

$$D(T) = D_0 e^{-E_a/RT} \quad (6)$$

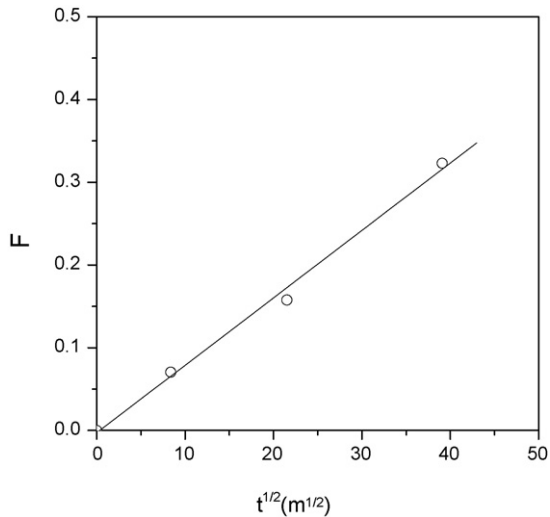


Fig. 3. Sodium isotopic exchange data for glass sample B at 773 K.

Table 2  
Measured diffusion coefficients for glass samples

Temperature (K)	Diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ) ( $\times 10^{17}$ )			
	A	B	C	D
748	4.047	3.25	1.92	1.219
773	5.31	6.07	5.25	1.682
798	8.75	8.29	6.45	3.468

Fig. 4 shows the plot of  $\log D(T)$  as a function of  $1/T$ , which gives the activation energy of diffusion ( $E_a$ ). The  $E_a$  values are given in Table 1 along with the  $D_0$  values for the four sets of samples. The error on the  $E_a$  values is the fitting error. The  $E_a$  values are lower than that observed in the case of the borosilicate glass used for immobilization of high level liquid waste at Tarapur, India [13]. This may be due to the different composition of the glass used at Tarapur, which also contains Ti and Mn as additives. The activation energy ( $E_a$ ) values for diffusion of

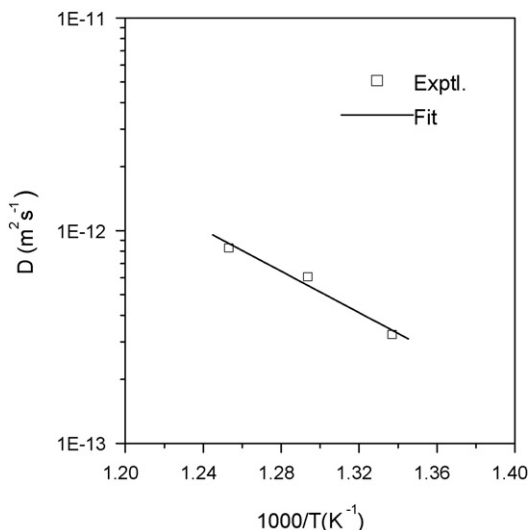


Fig. 4. Plot of  $D$  versus  $1/T$  for glass sample B.

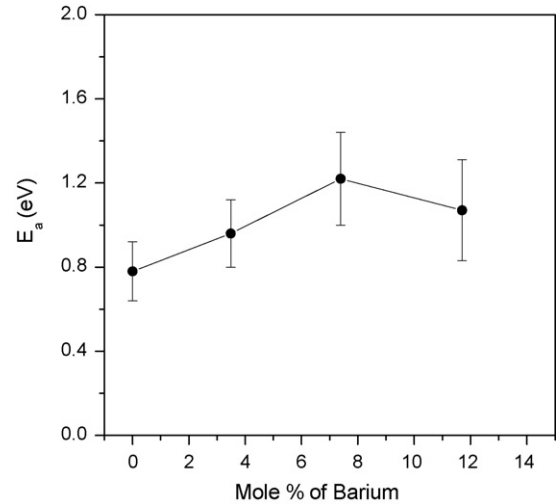


Fig. 5. Variation of activation energy with barium content of glass.

sodium in barium borosilicate glasses of varying composition as obtained from the Arrhenius plots are found to be in the range of 0.8–1.2 eV. These are in agreement with those corresponding to the diffusion of  $\text{Na}^+$  ions associates with  $\text{B}^{\text{IV}}$  [14]. Similar values are obtained by Tian and Dieckmann [15] in alkaline earth containing borosilicate glasses.

Fig. 5 shows the variation of  $E_a$  with increasing mole percent of barium. As can be seen from the figure, the activation energy of diffusion of sodium increases with increasing barium concentration of the borosilicate glass, indicating that introduction of barium retards the diffusion of sodium in the glass. The present observations are in agreement with that of Malow and Lutze [10], who observed an increase in  $E_a$  of sodium diffusion in borosilicate glass with increasing calcium content. However, at the higher concentration of barium there is a slight decrease in  $E_a$  which may be plausibly due to the value of  $(\text{Na} + \text{Ba})/\text{B}$  being more than one indicating excess network modification.

Fig. 6 shows the plot of pre-exponential factor ( $D_0$ ) versus  $E_a$  obtained from Arrhenius plots. The data fall on a linear plot

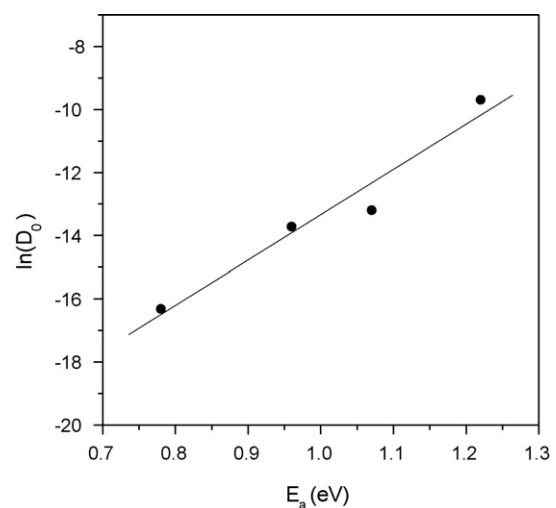


Fig. 6. Plot of pre-exponential factor ( $D_0$ ) versus activation energy for barium borosilicate glasses.

represented by,

$$\ln(D_0) = \alpha E_a + \beta \quad (7)$$

With the positive values of  $\alpha$ , this is in agreement with the Meyer Neldel (M-N) formula for solid electrolytes [15].

The leach rates of glass samples were found to be  $2.58 \times 10^{-4}$  and  $1.86 \times 10^{-5} \text{ g cm}^{-2} \text{ day}^{-1}$  for the glass without and with 11.2 mol% barium oxide, respectively.

#### 4. Discussion

Addition of sodium in borosilicate glass helps in increasing the miscibility of  $\text{B}_2\text{O}_3$  and  $\text{SiO}_2$  by facilitating the change in the coordination of boron from three ( $\text{B}_2\text{O}_3$ ) to four ( $\text{BO}_2^-$ ). At lower mole fraction ( $\text{Na/B} < 0.5$ ), sodium merely acts as a charge compensator for  $\text{BO}_2^-$  group in the borosilicate glass. As the concentration of sodium ion increases it modifies the glass network by breaking Si–O–Si and Si–O–B bonds, thereby creating non bridging oxygen (NBO). In the present case the Na/B ratio is around 0.5–0.6 and hence it is expected that sodium acts as a charge compensator.

Three mechanisms have been proposed to explain the alkali ion diffusion in borosilicate glass [16]. (i) Direct Coulomb interaction forces between alkali cation and the non bridging oxygen, (ii) a broad distribution of cation site energies arising from structural and/or Coulomb disorder and (iii) network density of oxygen atoms. The increase in  $E_a$  with increasing barium concentration can be explained as follows.

Alkali ion diffusion is known to depend on the ratio of the ionic radius of the alkali and alkaline earth ions present in the ternary glasses of type  $\text{A}_2\text{O BO SiO}_2$ , where A and B represent the alkali and alkaline earth ions, respectively [16]. The  $E_a$  value is minimum for  $r_B/r_A = 1$  and increases with the increase or decrease in the value of this radius ratio. For  $r_B/r_A > 1$  (as in the case of present glass systems) the larger cations ( $\text{Ba}^{2+}$ ) occupy sites wherein they are located further apart from the oxygen anions, while the smaller cations occupy sites with a smaller distance to the anion. Thus with increasing  $\text{Ba}^{2+}$  concentration more and more  $\text{Na}^+$  ions will occupy the strong binding sites close to  $\text{BO}_4^-$  resulting in higher  $E_a$ . The preferential interaction of  $\text{Na}^+$  ion with boron structural units in  $\text{SiO}_2\text{--B}_2\text{O}_3\text{--Na}_2\text{O}$  glass system is reported based on  $^{17}\text{O}$  NMR studies [17].

Another mechanism is based on Dietzel's structural field strength theory according to which the large difference in the field strength ( $\Delta F$ ) values between alkali and alkaline earth ions result in more tightly bonded glass network than that in the absence of alkaline earth ions [18]. Thus both the factors, that is, the electrostatic and structural factors favour decreased mobility of  $\text{Na}^+$  ions in the barium borosilicate glass explaining the increase in  $E_a$  with barium content.

The leach rate decreases with increasing barium content of the glass, which is in conformity with the results of diffusion coefficient. Though the leach rate also depends upon other factors, such as, inter-diffusion between  $\text{H}^+$  and  $\text{Na}^+$  ions at the glass/aqueous solution interface, surface modification of glass

due to its dissolution and concentration gradients, the correlation between the diffusion coefficient and the leach rate suggests that the diffusion process in the glass matrix plays an important role in determining the leach rate.

#### 5. Conclusion

Diffusion of sodium in barium borosilicate glasses of varying barium concentration was studied by heterogeneous isotopic exchange method using  $^{24}\text{Na}$  as a radiotracer of sodium. The results show that the activation energy of self diffusion of sodium increases with increasing barium concentration. Similar results were shown by the leach rate studies. The results have been explained in terms of the electrostatic and structural factors, with the increasing barium concentration resulting in population of low energy sites by  $\text{Na}^+$  ions and formation of more tight glass network.

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