



Phase Separation and Chemical Durability in the SiO₂-B₂O₃-Na₂O (SBN) Glass System

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Sodium borosilicates glasses were treated isothermally several times. In present work, the effect of phase separation on chemical durability and the electric resistivity was investigated. In addition, the effect of chemical composition and addition of calcium on the kinetics and rate of leaching of these glass materials in hydrochloric acid (3M HCl) was also investigated. The system studied exhibited phase separation starting from 550 °C. Present results showed that the chemical durability was weakened upon phase separation. On the other hand, chemical durability increased with increasing SiO₂ content and reducing the alkaline oxides (Na₂O) content. Results also showed a drastic decrease in the ionic electric conductivity (increase in resistivity) with decreasing C = (Na₂O + B₂O₃)/SiO₂ (reduction of Na₂O). The effect of chemical composition on the rate of leaching showed that boron and sodium are dissolved much more quickly than silicon. The greater the content of Na₂O and B₂O₃ in glass, the more soluble the glass becomes. However, addition of silica results a decrease in glass solubility. These results indicate that substitution of sodium by calcium induces an acceleration of the kinetics of deterioration.

Key Words: Phase separation, Chemical durability, Electric resistivity, Rate of leaching.

INTRODUCTION

The interest of the application of immiscibility in the technology of glasses is that of the synthesis of microporous glass. The most suited chemical compositions to decomposition is that of alkaline borosilicate caused by the anomaly of boron, by involving the formation of two phases, one rich in alkaline silica and the other borate rich phase. This second phase is easily dissolved under acidic conditions. The acidic medium results in a network of pores inter-connected, whereas the consolidation of microporous glass results in a vitrified structure, which approaches that of glass from silica (95 % SiO₂, 3 % B₂O₃ and 0.4 % (M₂O + MO), with traces of Al₂O₃ and As₂O₃) forming a glass known as Vycor[®] (M₂O: being an alkaline oxide and MO: alkaline earth oxide).

Fig.1 illustrates the gaps of immiscibility in systems of alkaninoborosilicate glass². The ternary system SiO₂- B₂O₃-Na₂O (SBN) selected is sodium borosilicate glass system, which presents an interesting gap of immiscibility for manufacture of Vycor[®] glass.

In the system (SBN), homogeneous original glass separates in several phases for the following reasons: 1) SiO₂ and B₂O₃ form binary glass. B (III) is more electronegative than Si (IV) (more acid); 2) The formation of metaborate in the area of phase separation is related to the largest reduction in free energy, compared with the formation of silicates; 3) The difference in

surface tension between the two phases, because the Na migration in the B₂O₃ phase decreases the surface tension compared to that of the silicates phase, which is one of the reasons for the resulting morphological differences^{3,4}.

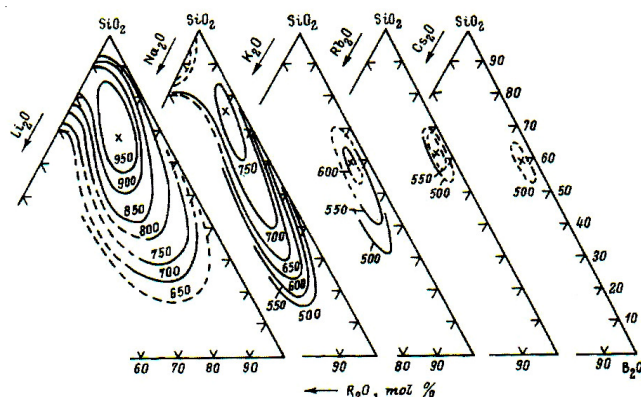


Fig. 1. Immiscibility gaps in alkaninoborosilicate glasses²

For glass with less than 50 mol % in SiO₂, the properties of the phase borate resemble those of binary alkaline borate glass and its structure will be determined by the Na₂O/B₂O₃ ratio. With the lower part of 50 mol %, silica is dispersed in all the phase borate whereas conversely, above 50 mol %, the phase borate is dispersed through the phase silicates.

Content between 2 and 3 mol % of Na₂O is favored for a technical phase separation⁵. The presence of Al₂O₃ eliminates diffusion and slowed down the process of leaching. For the separation of phases, the following molar ratios are important²: a) Na₂O/ B₂O₃ ; b) B₂O₃/ SiO₂

In the ternary system soda-borosilicate, Nordberg and Hood⁴ defined the optimal line of glass lixiviated for the industry of Vycor®, which can be expressed by the following simple equation:

$$\text{Na}_2\text{O} = 10 - 0.1 (\text{SiO}_2 - 55) \dots (\% \text{weight}) \quad (1)$$

The following are the molar ratios parameters of calculation:

$$K = \text{Na}_2\text{O}/\text{B}_2\text{O}_3 \quad (2)$$

$$R = \text{SiO}_2/\text{B}_2\text{O}_3 \quad (3)$$

$$C = (\text{Na}_2\text{O} + \text{B}_2\text{O}_3)/\text{SiO}_2 \quad (4)$$

In the present work, the study of phase separation was made in sodaborosilicate glass of meadows chemical compositions of the optimal line of the manufacture of Vycor® glass. The chemical attack of the samples in the various media including acidic, neutral and basic were given before and after phase separation. In addition, the electric conductivity of the various samples was measured after phase separation. In parallel, the leaching kinetics in the various vitreous compositions as well as the influence of the addition of calcium in the leaching speed were also investigated.

EXPERIMENTAL

Table-1 presents the chemical compositions chosen expressed in percentages and the calculated molar parameters K, R and C in the (SBN) system.

Sample	SiO ₂	B ₂ O ₃	Na ₂ O	K	R	C
SBN1	55.00	35.00	10.00	0.32	1.85	0.72
SBN2	60.00	30.50	09.50	0.34	2.32	0.59
SBN3	65.00	26.00	09.00	0.38	2.63	0.47
SBN4	70.00	21.50	08.50	0.44	3.84	0.38

Borosilicate glass (SBN) selected were prepared starting from the following reagents: local sand of Blida (Blida-Algeria) (SiO₂:99.53 %), boric oxide B₂O₃ (99.99 %), boric acid and sodium carbonate, in stoichiometric proportions. The probable losses in B₂O₃ during fusion were compensated by an excess of this oxide (6 % in mass) introduced into the starting material. A catalytic amount of lithium sulfate was added to facilitate fusion and to accelerate the later phase separation.

The finely crushed mixture was then placed in a platinum crucible and transferred to an electric furnace. The temperature was gradually increased to 1650 °C with a stage of 2 h. The liquid was then cast in a graphite mold preheated to approximately 250 °C to limit the thermal shocks during hardening.

The obtained glasses were perfectly transparent and colourless. After the development of glass initial borosilicate, the material was finally treated isothermally throughout the heating time period for the creation of a phase separation

starting from the homogeneous initial matrix. The thermal program was selected for 4 alternatives samples (SBN1, SBN2, SBN3 and SBN4) as illustrated in Table-2.

Sample	Temperature (T °C)	Time (t, h)
A	550	8
B	550	16
C	550	24
D	550	32
E	600	8
F	600	16
G	600	24
H	600	32
I	650	8
J	650	16
K	650	24
L	650	32
M	700	8
N	700	16
O	700	24
P	700	32

Fig. 2 shows the physical aspect of the SBN1A sample (of rectangular form) before and after phase separation (the annealing was carried out at 550 °C for 8 h).

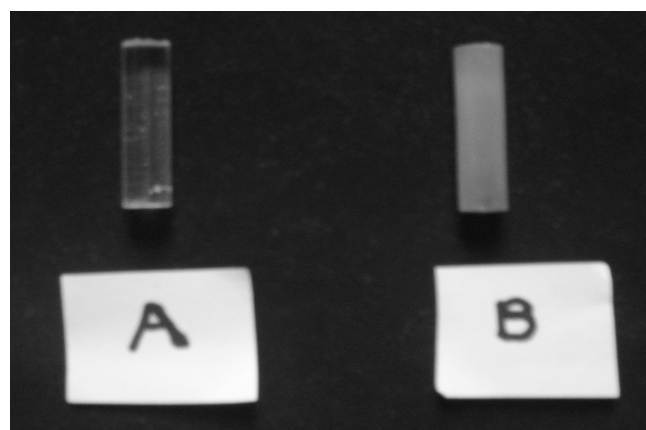


Fig. 2. SBN1A sample: A: before annealing; B : after annealing

The expansion curve was determined of SBN1 sample using a dilatometer DIL 402C [Materials Mineral Composite Laboratory (MMCL - Boumerdes- Algeria)] at an average speed of heating of 5 K min⁻¹. The sample had a rectangular shape with an 8 mm width and a 20-25 mm length.

The glass transition temperature was determined from the expansion curve using the interception method, whereas the dilatometric temperature was determined by the maximum temperature of expansion curve.

Diffraction XRD was measured at room temperature using radiations CuK_α (Solids, Surfaces and Interfaces Laboratory (SSIL) -Reims- France).

The ionic test of conductivity was carried out on samples of spherical shapes having a thickness of approximately 1-2 mm. The apparatus used was the Picoampèremètre HP 4140B with a resolution⁶ of 10⁻⁵. The distance between the two points was of approximately 3.5 cm.

RESULTS AND DISCUSSION

After the annealing heat treatment mentioned in Table-2, all the samples turned opal (Fig. 2), this indicates that the development of the phase separation, which caused micro-heterogeneities within the initial transparent and homogeneous glass. According to the dilatation thermal curve recorded on (SBN1) glass sample represented in Fig. 3, the temperature of vitreous transition T_g was *ca.* 480 °C and that the dilatometer was *ca.* 506 °C.

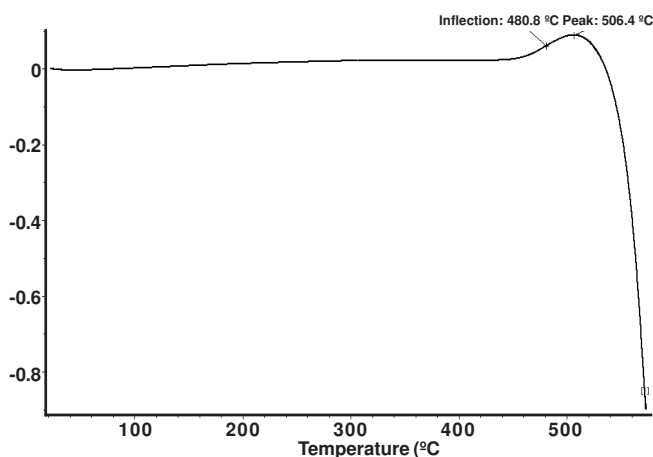


Fig. 3. Dilatation thermal curve of SBN1 sample

The starting of phase separation was generally observed at a temperature defined as follows:

$$T(\text{separation}) \text{ defined}^1 \text{ as: } T(\text{separation}) = T_g + 40^\circ\text{C}$$

$$\text{In the present study, } T(\text{separation}) = 480 + 40 = 520^\circ\text{C}$$

This temperature was reached once separation was initiated at *ca.* 550 °C.

Patterns of XRD recorded on not annealing samples SBN were represented at Fig. 4, which show the amorphous aspect (not apparent peak). All spectra obtained for (SBN) samples with the program (B, C....) were also amorphous however starting from the modes O and P, spectra XRD with the appearance of peak characteristics of crystallization were obtained.

From the mode O, XRD spectra contained significantly apparent peaks indicating that after 24 h at 700 °C, crystallization started and continued to develop with time (mode P: 32 h at 700 °C). The appearance of the cristobalite, diomignite (Li₂B₄O₇) and the lithium hydroxide salt of boron crystals became noticeable over time and temperature of the heat treatment of all samples SBN1, SBN2, SBN3 and SBN4.

To investigate the formation of crystallization according to depth of the vitreous reheated samples. Samples (SBN3O) were cut out in the medium and polished prior to analyzing the XRD spectrum of the two faces at various angles of incidences. Results showed that the diffraction varied with the sample's thickness, leading to stronger signals that were significantly greater at the surface of the sample. These results can be due to the fact that the surface layer crystallizes more rapidly than the internal layer, which can explain the fact that our glass materials, which contain boron, originating from the boric acid that is characterized by its hydration upon direct contact with the atmosphere. This hypothesis is supported by the rapid formation of crystals on the external layer of our samples. Moreover a slight change in colour was observed for the external part of samples. The two faces of the material analyzed did not present same XRD spectra. Results showed that there was a slight difference caused by the irregularities in surfaces (roughness). On the other hand, the closer we approached the center of the sample, the greater became the change in the

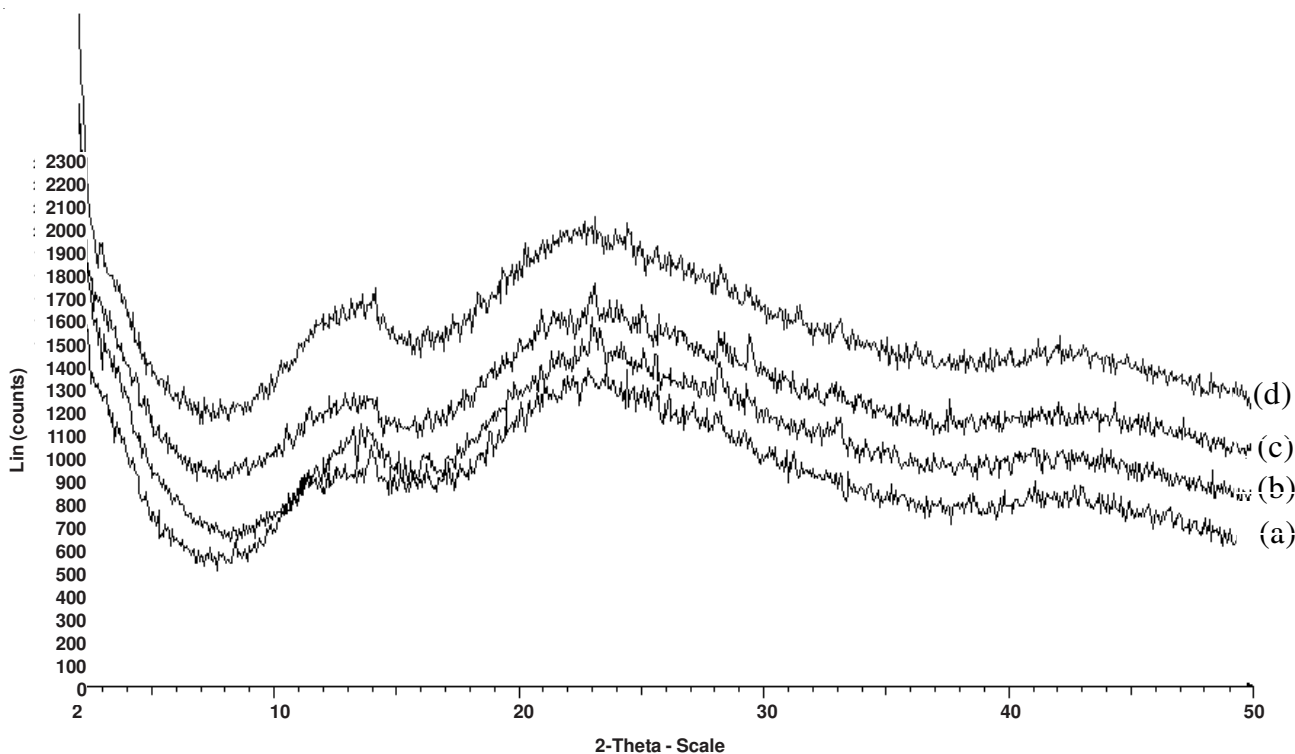


Fig. 4. XRD pattern of samples; (a) SBN1, (b) SBN2, (c) SBN3 and (d) SBN4

aspect XRD resulting in a more amorphous materials (the smaller the angle of incidence, the weaker the signals).

Determination of chemical durability: The chemical treatment of the samples under the various conditions (neutral, acidic and basic) were carried and the weight loss of samples was determined before and after annealing (during 3 h).

Durability of the samples prior to annealing: Results illustrated in Table-3 showed that the samples exhibited high durability under the three media conditions studied (neutral, acidic and basic). These samples are borosilicate glasses samples, which are known by their high chemical stability because of the rigid structure of the vitreous network composed of tetrahedrons of silica and boron and of the rigidly dependant boron triangles with bridging oxygen molecules¹.

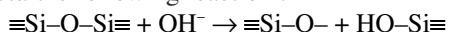
TABLE-3
CHEMICAL DURABILITY OF SBN SAMPLES
PRIOR TO ANNEALING

Samples	($\Delta M/M_0$) % in neutral medium	($\Delta M/M_0$) % in acidic medium (HCl)	($\Delta M/M_0$) % in basic medium (NaOH + Na ₂ CO ₃)
SBN1	0	0	0.67
SBN2	0	0	0.63
SBN3	0	0	0.59
SBN4	0	0	0.56

The chemical attack in basic medium decreases with increasing the silica content. The attack by water and acid is relatively weak.

The reactions between the H⁺ ion and the acid network can be neglected since the components are packed too strongly to allow for any possibility of migration in the network to take place. On the other hand, the network modifiers have a certain freedom of displacement through vacuum and also the ability to pass through the solution that surrounds them if this vacuum borders the solution. By reduction the amount of modifier and B₂O₃ and the content of silica increase, no attack was observed after 3 h of reaction time.

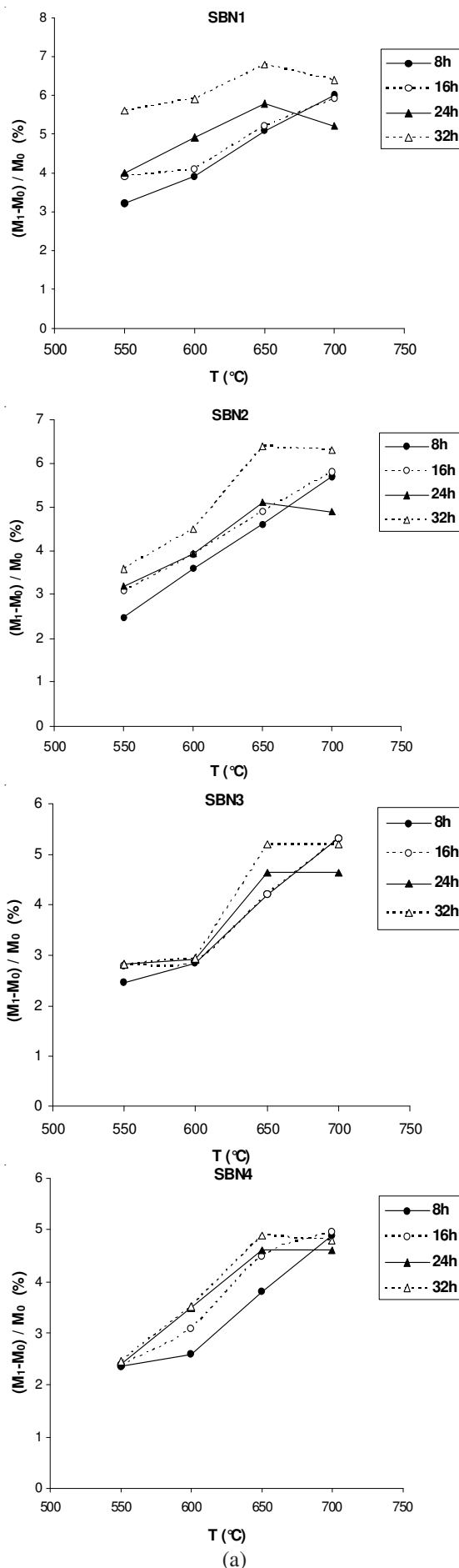
The attack by the alkaline solutions on the other hand is governed by another mechanism. The OH⁻ ion is in the case the determining factor, because its ability to react with the network *via* the following reaction¹.



As a consequence, it appears that this result in a network division, which under certain conditions can result a complete dissolution of glass. It also appears that the solubility of glass increases under basic pH conditions.

When comparing the ratio of attack by acid *versus* water, this attack decreases with decreasing Na₂O content and increasing the SiO₂ content, which also reinforced the structure and reduces the chance of network division and destruction.

Durability of the samples post the heat treatment of annealing: The results presented in Fig. 5 show the chemical durability of the samples following their annealing. These results show that there is a significant difference in durability prior and post annealing. Prior to annealing, the attack seems to be more pronounced in the three media of attack. This attack is the first index on the more loosened structure; where the phase separation weakens the structure of the vitreous network as result of the ease in the ionic exchange between the glass components and those of the mediums of attack.



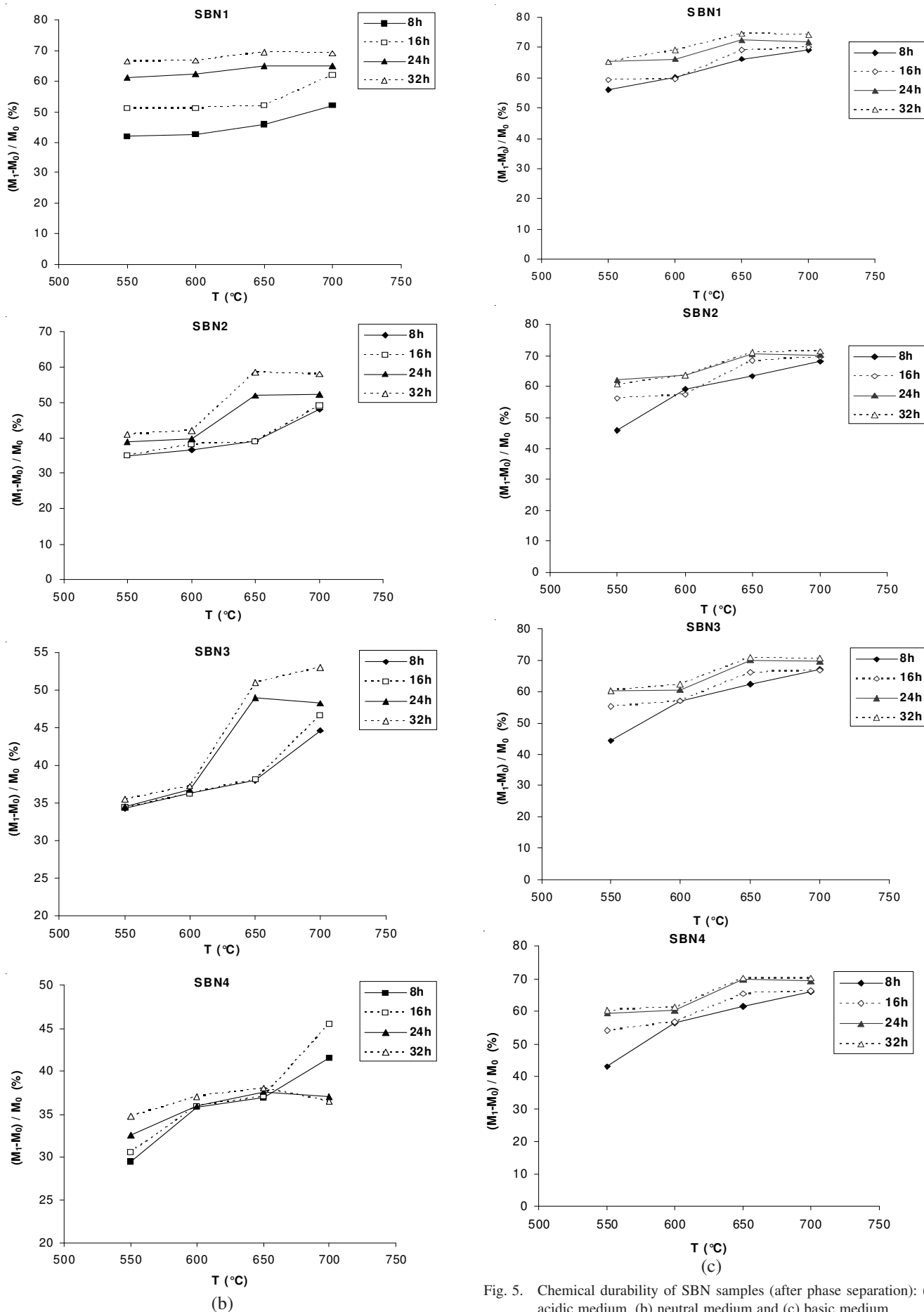


Fig. 5. Chemical durability of SBN samples (after phase separation): (a) acidic medium, (b) neutral medium and (c) basic medium

TABLE-4
CALCULATED MOLAR PARAMÈTRES

Sample	m (g/mol)	m _v (g/cm ³)	M _v (g)	C ₀ (10 ² mol/cm ³)	h (mm)	t (h)	V ₁ (cm ³)
SBN3C	62.482	2.349	1.174	0.876	0.650	1.3+0.1	0.065

Determination of electrical resistance: The ionic conductivity test was given for the spherical samples forms of the following compositions (SBNC), (SBNI) and (SBNJ) *i.e.* the samples are heated at 550 °C for 24 h and samples were heated at 650 °C for 8 h and 16 h respectively. Fig. 6 represents the variation of the log conductivity according to the C [C= (Na₂O + B₂O₃)/SiO₂] of studied glasses. The ionic electric conductivity decreases (resistivity increases) with the reduction of the ratio C (reduction in Na₂O content), this is explained by the reduction of not bridging oxygen (NBO); and since the mobility of the Na⁺ ions is a determining factor ionic conductivity, its reduction influences directly the deceleration of the ionic transfer. This mobility is the most important factor as if the bridging oxygen content is also not high, because the formation of (NBO) contributes to a relatively open structure of the vitreous network with a larger volume free what supports better a mobility of the alkaline ions. And as lithium sulfate was added to the beginning, ionic conductivity increases a little, because the Li⁺ ion has a small size and it will be able to move through the vitreous structure freely. The lithium oxide addition creates not bridging oxygen in the silica network and forms the BO₄ tetrahedrons and (NBO) ions in the borate network.

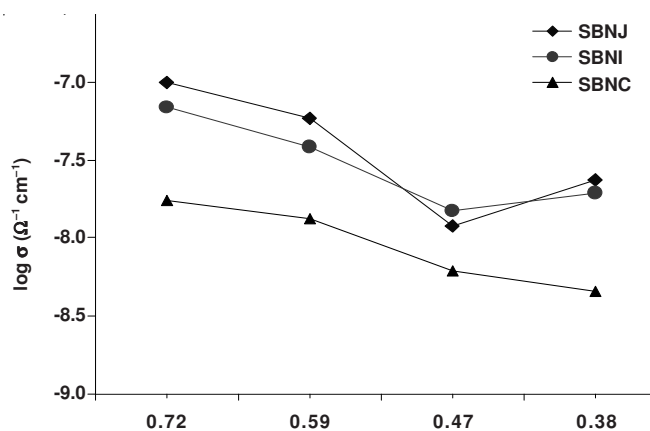


Fig. 6. Ionic measured log conductivity of SBN samples

Experimental study of leaching: Based on the results obtained, (SBN3C) samples was chosen to be leaching in acid^{7,8}. One will test after carrying out a leaching of vitreous composition in order to tackle the least stable phase: The selected samples were rectangular in shape (10 mm × 10 mm × 5 mm) and exhibited polished plane surfaces. To measure: (i) the volume of the front sample attacks in 3 M HCl; (ii) the density of glass (hydrostatic method); (iii) the sample's surface of contact with the solution lixiviating before attack (S); the sample is immersed in the solution of leaching (3 M HCl at 100 °C) (suspension by platinum wire); (iv) the volume of solution the ratio of the sample's surface of contact to the volume of solution (S/V) was of approximately 2 × 10⁻¹ cm⁻¹ (to ensure the constancy of the pH during the experiment). Initial ratio between the volume of acid and the volume of glass was of 400:1.

The leaching speed, *i.e.* the layer thickness (h) was measured after a sequence of processing time with the optical microscope (MIN-8) (a curve was plotted) and a glass sample was leached in 3 M HCl without stirring⁷. Calculation of the B₂O₃ volume concentration in the front glass attacks (C₀). The experimental quantity extracted from B₂O₃ was measured by titration with NaOH solution (error 10 %) was measured (Q_c); Calculation of the extracted quantity from B₂O₃ of glass (Q_c) with Q_c = V₁. C₀ or V₁ is the volume of glass attacked at time t (cm³) and C₀ the initial concentration of B₂O₃ in glass in (mol/cm³). The porous sample was then washed with distilled water at 20 °C during 5 days and subsequently dried at 120 °C for 1 h.

Study of the kinetics of B₂O₃ extraction with the acid solution: Calculation of the quantity extracted from B₂O₃ of glass (Q_c):

$$Q_c = V_1 \cdot C_0$$

For the calculation of C₀, the initial concentration of B₂O₃ in glass SBN3C is in (mol/cm³) the following parameters were determined in Table-4.

Molar glass mass (m), the measured glass density (m_v), sample glass mass (M_v) and V₁ (the volume glass attacked at time t (cm³) were calculated for sample SBN3C.

The thickness of the attacked layer (h) was measured at the time taken for example at approximately 1 h.

Q_c was found to be equal to 5.694 × 10⁻⁴ mol

Determination of the experimental quantity extracted from B₂O₃ of glass (Q_c): Titration was carried out (acid HCl 3 M with NaOH)⁸. The volume of the base needed to reach equilibrium was determined (neutralization of the acid by the base) The concentration of the base was determined at equilibrium

Finally Q_c was calculated to be : Q_c = 4.812 × 10⁻⁴ mol

Characterization by chemical analysis of the sample obtained after leaching: Chemical analysis on the lixiviated sample were carried out (Table-5).

TABLE-5
CHEMICAL COMPOSITION OF POROUS GLASS (WEIGHT %)

SiO ₂	B ₂ O ₃	Na ₂ O	K ₂ O
94.0	5.8	0.1	0.1

Kinetics and speed of leaching

Influence of the chemical composition on the speed of leaching: Four samples of each type of glass studied (SBN1, SBN2, SBN3, SBN4) presenting decompositions of the type inter-connected immiscibility (mode C) were chosen and the same procedure was repeated. The curve presenting the variation thickness of the layer lixiviated according to the time of various glasses as well as the speed of attack is represented in Fig. 7.

Results showed that the greater the silica content, the smaller the depth and speed of leaching. The phenomena involved in the chemical attack of glass are very complex. These phenomena are mainly due to the effect of the chemical composition of glass. Glasses samples are mainly made up of the O, S, B, Na, Ca, Fe, Zn... *etc.*

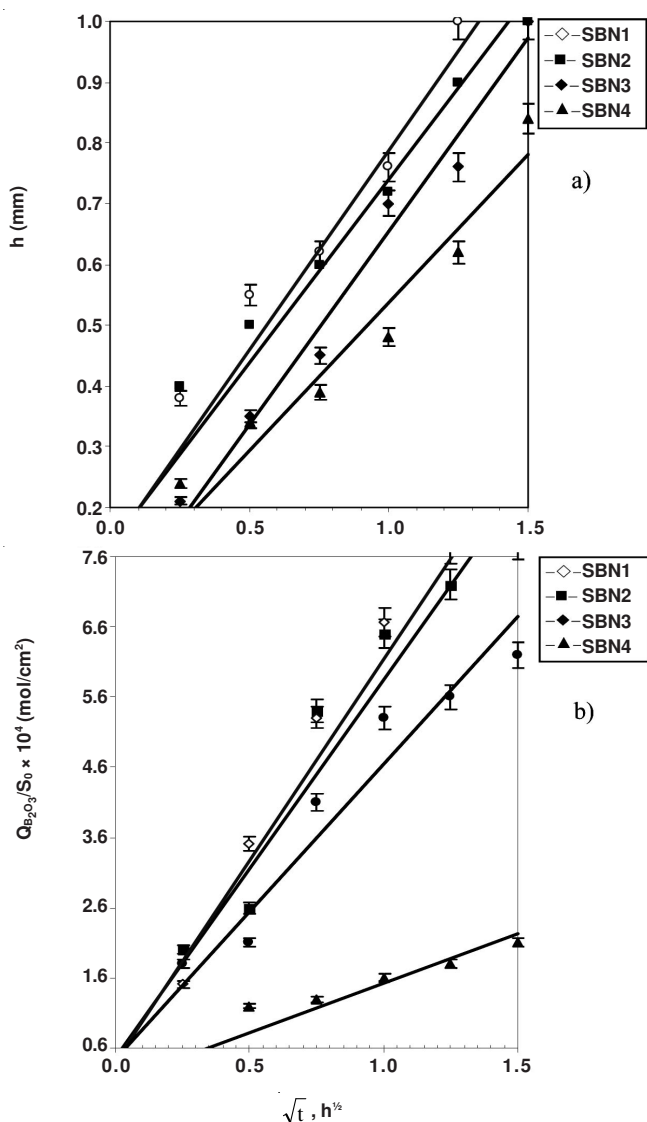


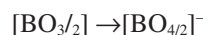
Fig. 7. (a) Thickness of the lixiviated layer (h) and (b) B₂O₃ amount (Q/S_0) extracted from glass into solution per unit surface area of (SBN) samples, plotted against the square root \sqrt{t} of the leaching time in 3 M HCl

The silicon, boron and sodium oxides represent meadows of 80 % of the total mass of glass (SBN). The speed of the mass transfer during leaching depends on the structure and the chemical properties of the solid phase⁹.

It will be a question of discussion that the influence of the initial glass composition and particularly the polymerization of the covalent network upon leaching.

Silicon is naturally in co-ordination number four in amorphous silica (3-dimensional network of deformed diamond type), boron in co-ordination number 3 in boron oxide (deformed plane triangular network). This difference in dimensionality between the 2 structures makes it difficult to dissolve boron oxide in silica¹⁰.

The miscibility of these two structures to obtain homogeneous glass borosilicate, are made possible by the ability of boron to adopt a co-ordination number four when it is put in the presence of a compensation element of load, such as sodium. Indeed, this change of co-ordination number is accompanied by a change of load of the basic unit of boron:



Therefore, the role of the compensators of load in borosilicate glass, they contribute to the solubilization of boron in the silica network *via* formation and of species $[BO_{4/2}]^-$ (which one will henceforth call B[4]).

However, the presence of sodium does not have only favourable effects on the vitreous skeleton. It proves that the transformation of trivalent boron into tetravalent boron is not complete, even in glasses where the ratio $K = [Na_2O]/[B_2O_3]$ is equal to one.

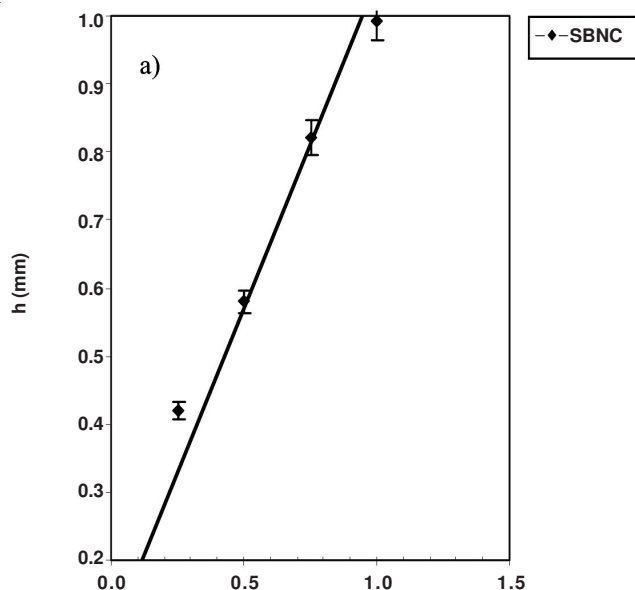
Sodium, when it is not used to form B[4], does not compensates for the oxygen bridging, which it is created by modification of the covalent network. In general, it cleaves the siloxanes bonds, which are the most numerous. Boron supports the NBO badly and prefers to minimize its total load rather while becoming again B[3] rather than to remaining in co-ordination number four with an NBO. Boron and sodium are dissolved much more quickly than silicon. The formation of NBO weakens the structure of glass and makes the species soluble and more accessible to water. The depolymerization of the silica network by the creation of NBO generates larger cavities, favorable with the invasion of water and the exit of the soluble species.

The greater the content of Na₂O and B₂O₃ in glass, the higher the solubility of glass. Addition of silica to glass results in a decrease of solubility and dissolution.

A comparison of Q_e and Q_c showed that $Q_e < Q_c$ wish is explained by the diffusion character of the B₂O₃ extracted from the instable phase during leaching in acid⁸.

Calcium influence: A glass of composition similar to that of glass SBN3C was prepared, where the Na was substituted with Ca (one proceeded by the same stages of annealing where glass became opal indicating its phase separation).

The same leaching procedure was repeated for the various samples leading to the following observations (Fig. 8). An increase in thickness of attack, as well as the speed of leaching with time, in comparison to the other tests.



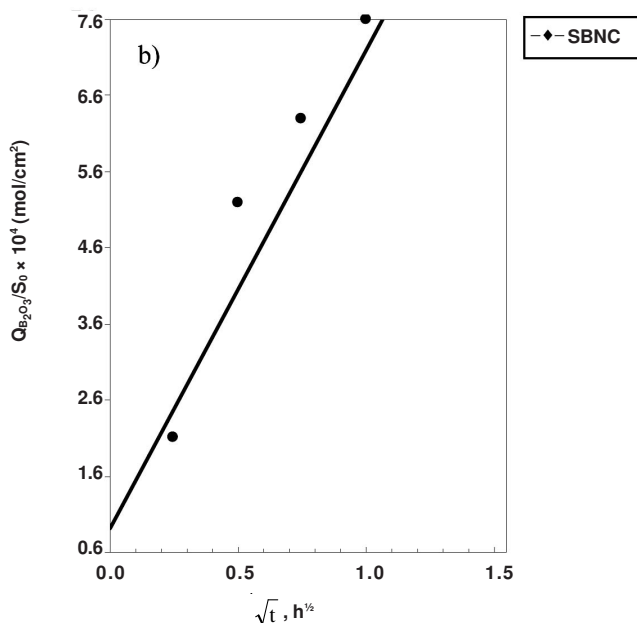
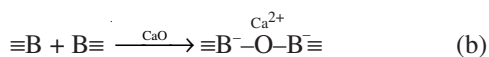
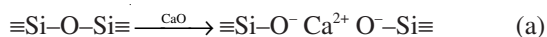


Fig. 8. (a) Thickness of the lixiviated layer (h) and (b) B_2O_3 amount (Q/S_0) extracted from SBN3C glass into solution per unit surface area of samples, plotted against the square root \sqrt{t} of the leaching time in 3 M HCl



Calcium is part of the alkaline-earth family of elements. Contrary to sodium, it carries two positive loads when it is in ionic form. It is known to be implied in ionic-covalent connections. This mixed character made not only one compensation element of load within the meaning of Zachariassen, but also a modifying element of network¹.

The equations above (a) and (b) show how calcium fits in glass. As in the case of sodium, calcium creates at the same time B [4] and NBO related to Si. Remain to be seen in which proportions. On the other hand, unlike Na, calcium cannot be used to stabilize a connection Si-O-B, since there is only one load to compensate.

Solution chemistry of calcium is complex. This one is complexes or precipitated easily with certain ions of the solution. For example, its strong affinity to carbonates present in solution has been known for a long time. It is known that calcium has a beneficial effect on deterioration of glasses, in particular when it is integrated into the borosilicate compositions conta-

ining Zr or Al, or simply present in the lixivium. In addition, it was observed that calcium accelerates the initial speed of deterioration of glass and increases the concentration with saturation of silicon, but its mechanisms of action on the gel formation and the deterioration reduction of glasses remain poorly understood. The substitution of sodium by calcium induces an acceleration of the kinetics of deterioration.

Conclusion

During the study of the phase separation in sodium borosilicate systems which presented a phase separation starting at 550 °C, it is noticed that chemical durability was weakened following phase separation and increased with increasing SiO_2 content and reducing the amount of alkaline oxides (Na_2O). In addition, the ionic electric conductivity decreased (resistivity increased) with the reduction of the ratio C (reduction in Na_2O). This is explained by the non-bridging oxygen reduction.

The pattern of XRD diffraction changes according to the depth of borosilicate glass sample one more approaches the center (volume) of the sample plus the structure is amorphous. The influence of the chemical composition on the speed of leaching shows that boron and sodium are dissolved much more rapidly than silicon. The formation of NBO weakens the structure of glass and makes the species soluble and more accessible to water.

Increasing the content of Na_2O and B_2O_3 enhanced the dissolution of glass whereas addition of silica decreases the dissolution of glass. The substitution of sodium by calcium induces an acceleration of the kinetics of deterioration.

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