

# *In vitro* bioactivity of soda lime borate glasses with substituted SrO in sodium phosphate solution

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# Abstract

Borate glasses with the basic composition  $0.6B_2O_3 \cdot 0.2Na_2O \cdot 0.2CaO$  and SrO progressively substituting CaO were prepared and characterized for their bone-bonding ability. The obtained glasses were thermally treated and converted to their glass-ceramic derivatives. In this study, FTIR spectral analyses were done for the prepared glasses and glass-ceramics before and after immersion in a sodium phosphate solution for extended times. The appearance of two IR bands within the spectral range  $550-680 \text{ cm}^{-1}$  after immersion confirms the formation of hydroxyapatite. X-ray diffraction studies and scanning electron microscope analysis supported the obtained infrared spectroscopy results. The solubility test (measurements of the weight loss in aqueous sodium phosphate solution) was conducted for measuring the dissolution of both glassy and crystalline derivatives to find out the role of SrO. The corrosion behaviour of the glasses and glass-ceramics indicate the increase of weight loss with the increase of SrO content. Different suggested proposals were introduced to explain this abnormal behaviour.

Keywords: borate glass, SrO, bioactivity, phosphate solution, structural characterization

# I. Introduction

Several glass compositions have been developed and demonstrated to be bioactive [1], a property that can be assessed by analysing the formation of hydroxyapatite (HA) layer on the glass surface upon immersion in relevant physiological fluids. The apatite layer bridges chemically the host tissue and implant materials. The demand for variable bioactive material is essentially in the need to fill bone defects, augment weak osteoporotic bones and fix features. The desirable bioactive materials should be structurally and mechanically compatible with bone tissue, and have potential eventually to be replaced by new bones. In addition, they require a highly reactive surface to form a continuous interface with the surrounding bone tissue and further abundant bone formation.

Most of the studied bioactive glasses that contain  $SiO_2$  as the main constituent, and even binary  $CaO \cdot SiO_2$  and  $Na_2O \cdot SiO_2$  glasses, are capable to form an apatite layer on their surfaces when exposed to simulated body fluid (SBF) or calcium phosphate solutions [2,3]. How-

ever, the degradation of silicon based glasses is highly time dependant, which could limit their implantation in human body [4]. Also, it is a fact that bones did not contain silicon ions in their constitutions [5]. As a result, borate glasses show potential in bone bonding ability as their corrosion reactions are similar in nature to those proposed for the Hench's patented bioglass having modified soda lime silica compositions [6–10]. The boron element is assumed to be necessary for the health of some mammals and beneficial for many life processes including embryogenesis, bone growth and maintenance, immune function and psychomotor skills and therefore boron containing glasses are of special interest [11].

Because of low mechanical strength, the application of borate based glass with the different chemical compositions has been continuously investigated. The main goal was preparation of suitable bioactive glasses or glass-ceramics with controllable degradation and bone bonding ability. Some borate glasses were investigated to find out invitro bioactivity in relation to compositional dependence through introducing  $P_2O_5$ , Li<sub>2</sub>O, K<sub>2</sub>O or Al<sub>2</sub>O<sub>3</sub> [9,10,12]. In addition, some recent studies have

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investigated the modified biomaterials obtained by replacement of calcium or magnesium ions with strontium ions in borosilicate glasses [13–16]. The interest in strontium comes from its dual anti-respective and anabolic differentiation, inhibited osteochast function. Due to the bigger ionic radius of strontium, it is expected that strontium ions inhibit the movement and release of other ions from the glass network, thus reducing the dissolution rate of borate glass.

The main aim of this work is therefore to study the role of SrO, which successively replaces CaO in ternary soda lime borate glass, on their bioactive potential. The work includes detailed structural FTIR investigations of the prepared glasses before and after being immersed in a dilute sodium phosphate solution. The same measurements have been extended to the corresponding glassceramic derivatives prepared by controlled heat treatment process. The work also includes X-ray analysis of the crystalline species separated during the conversion to the glass-ceramic derivatives and after immersion in the sodium phosphate solution. Further, scanning electron microscope studies accompanied with EDX analysis were performed to follow up the textural features formed upon conversion of the glasses to their glassceramics and to characterize the changes exhibited after immersion in the dilute phosphate solution.

# **II. Experimental**

# 2.1. Preparation of glasses and glass-ceramics

The soda lima borate glasses (G-1 to G-5), with the chemical compositions shown in Table 1, were prepared from chemically pure grade reagents. The chemicals included orthoboric acid ( $H_3BO_3$ ) for  $B_2O_3$ , while Na<sub>2</sub>O, CaO and SrO were introduced in the form of their respective anhydrous carbonates. The weighed batches were melted in platinum crucibles at 1050 °C for 2 hours. The melts were stirred for 30 minutes to achieve acceptable homogeneity of the melts. The melts were poured into warmed stainless steel molds of the required dimensions. The prepared samples were immediately

transferred to a muffle furnace regulated at 400 °C for annealing and removing thermal stresses. The muffle was switched off after 1 hour and left to cool to room temperature at a rate of 25 °C/h.

The obtained bioactive glass samples were thermally treated using a two-step regime, as deduced from DTA measurements. Each bioglass was heated slowly (5 °C/min) to the first nucleation temperature for the formation of sufficient nuclei sites. After soaking for a defined period of time, the specimen was then further heated to the second higher temperature for performing crystal growth process. After the second soak for the specified time, the specimen was left inside the heating muffle and left to cool to room temperature at a rate of 25 °C/h.

#### 2.2. Structural characterization

Differential thermal analysis (DTA) investigations were carried out on the powdered bioglass samples which were examined up to  $1000 \,^{\circ}$ C using powdered alumina as a reference material. The heating rate was adjusted to be  $10 \,^{\circ}$ C/min. The data obtained are given in Table 2 which indicates the proper temperatures for conducting thermal treatment of the glasses at the glass transition or nucleation temperature and the onset of completing crystallization process for the parent glasses.

Fourier transform infrared (FTIR) absorption spectra of the prepared borate glasses and their glass-ceramic derivatives were measured at room temperature in the wavenumber range 4000–400 cm<sup>-1</sup> using a FTIR spectrometer (type Matson 5000, USA). Fine powder of the samples was mixed with KBr in the ratio 1:100 for quantitative analysis and the mixture was subjected to a load of 5 tons/cm<sup>2</sup> in an evocable die to produce clear homogenous discs. IR absorption spectra were immediately measured after preparing the discs to avoid moisture attack. The measurements were taken before and after immersion of the samples in the phosphate solution and were repeated twice to confirm the positions of the IR peaks.

Glass	B <sub>2</sub> O <sub>3</sub> [mol%]	Na <sub>2</sub> O [mol%]	CaO [mol%]	SrO [mol%]
G-1	60	20	20	0
G-2	60	20	15	5
G-3	60	20	10	10
G-4	60	20	5	15
G-5	60	20	0	20

Table 1. Chemical compositions of the prepared glasses

			-	
Class coromia	Temperature of	Duration time	Temperature of crystal	Duration time
Glass-cerainic	nucleation [°C]	[h]	growth [°C]	[h]
GC-1	500	6	650	2
GC-2	510	6	660	2
GC-3	520	6	670	2
GC-4	525	6	675	2
GC-5	525	6	675	2

 Table 2. Thermal treatment regime

Scanning electron microscopic (SEM) investigations were carried out on glass and glass ceramic samples at room temperature using an SEM model Philips XL30 attached with EDAX unit, accelerating voltage 30 kV. All studied samples were coated with gold for morphological investigations of the textures of the surfaces.

The crystal phases which were formed within the glasses after thermal treatment process and that observed after immersion in the phosphate solution were identified by X-ray diffraction. The samples were ground and the fine powders were examined using a diffractometer (Philips PW 1390) adopting Ni-filter and Cu target. Computer software (Materials studio 4.4 programs) was utilized to calculate the crystalline phases within the heat treated glass samples.

#### 2.3. Solubility test

The degree of solubility of the prepared borate glasses and their glass-ceramic derivatives was obtained by measurements of their weight loss in aqueous sodium phosphate solution (0.25 wt.%) at 37 °C. The selected glass specimens were ground and polished in order to obtain dimensions of acceptable accuracy. After measuring their dimensions, the samples were placed in polyethylene beakers containing calculated volumes of the phosphate solution. The ratio of the geometric area of the samples and volume of the solutions was fixed  $0.075 \,\mathrm{cm}^{-1}$  in all samples for accurate comparison [16]. The samples were removed from the solution and excess moisture was cleaned by tissue paper at various time intervals and then reweighed. The percent changes of weight loss expressed glass solubility or corrosion. Solubility measurements were repeated twice for obtaining accurate weight loss data.

#### **III. Results**

#### 3.1. FTIR spectra of glasses before immersion

Figure 1 illustrates the FTIR absorption spectra of the studied glasses. The base soda lime borate glass (G-1) containing no SrO reveals the following IR spectral characteristics: i) four successive small far IR bands at 427, 535, 626 and 717 cm<sup>-1</sup>, ii) a strong broad band with two peaks at 872 and 1027 cm<sup>-1</sup>, iii) the second strong broad band with slight higher intensity than the preceding one and with two peaks at 1407 and 1505 cm<sup>-1</sup> followed by a band at  $1634 \text{ cm}^{-1}$ , iv) two small peaks around 2850 and 2927 cm<sup>-1</sup> and v) a strong and broad near IR band centered at  $3439 \text{ cm}^{-1}$  followed by two small peaks at 3745 and 3856 cm<sup>-1</sup>.

The following spectral features characterize the FTIR spectra (Fig. 1) of the glasses containing SrO (G-2, G-3, G-4, G-5): i) the relative intensity of the broad bands changes with addition of SrO, ii) the first far IR peak around  $427 \text{ cm}^{-1}$  disappears when all CaO are replaced with SrO and iii) the intensity of the broad band at  $3437-3455 \text{ cm}^{-1}$  decreases with replacement of CaO with SrO (G5).



Figure 1. FTIR absorption spectra of studied glass before immersion

# 3.2. FTIR spectra of glass-ceramics before immersion

Figure 2 illustrates FTIR spectra of the heat treated glass-ceramics samples (GC-1 to GC-5) before immersion in the phosphate solution. FTIR spectra reveal the following spectral characteristics: i) all the main vibrational modes (within the range 400–1600 cm<sup>-1</sup>) for the borate network reveal numerous sharp peaks representing the various crystalline borate species instead of rounded peaks in glasses and ii) the rest peaks and the broad band in the range 2000–4000 cm<sup>-1</sup> remain unchanged and the near IR broad band increases in intensity with the increasing SrO content in the glass-ceramics.

#### 3.3. FTIR spectra after immersion

Figure 3 illustrates FTIR spectra of the studied glasses after immersion in the phosphate solution for two weeks. The most distinctive spectral variations in comparison to the spectra of the glasses before immersion are summarized as follows: i) the appearance of two distinctive peaks at 570–590 and 690–710 cm<sup>-1</sup>, ii) the obvious decrease of the second broad band extending from 1250 to  $1550 \text{ cm}^{-1}$  in all samples and iii) the



Figure 2. FTIR absorption spectra of studied glass-ceramics before immersion

obvious increase of the intensity of the near IR broad band around 3440 cm<sup>-1</sup>.

Figure 4 reveals FTIR spectra of the glass-ceramics after immersion in the phosphate solution and the spectra show the following main characteristics: i) the appearance of the characteristic two peaks at 560–570 and 708–711 cm<sup>-1</sup>, ii) lower intensity of the second broad band ( $1250-1600 \text{ cm}^{-1}$ ) in comparison to the first broad band ( $800-1200 \text{ cm}^{-1}$ ) and iii) sharp decrease in intensity of the near IR broad band around  $3450 \text{ cm}^{-1}$  with the increase of SrO.

#### 3.4. X-ray diffraction investigations

Figure 5 illustrates X-ray diffraction patterns of the glass-ceramic samples before immersion. It is obvious that the following crystalline phases are formed: i) the first precipitated crystalline phases are calcium sodium borate with two compositions  $CaNa_5O_9$  and  $CaNa_3B_5O_{10}$  which is present as main constituent in the glass-ceramics GC-1, GC-2, GC-3 and GC-4, ii) the appearance of the crystalline strontium borate phase increases and becomes prominent in the glasses-ceramics GC-4 and GC-5, and iii) crystalline sodium borate phase is also identified in the glass-ceramic GC-5, containing 20 mol% SrO.

Figure 6 reveals comparative X-ray diffraction patterns of the glasses and glass-ceramics after immersion:



Figure 3. FTIR absorption spectra of studied glass after immersion

i) the base glass with 20 mol% CaO and no SrO is found to be showing the separation of minute peaks of hydroxyapatite, ii) the glass with 20 mol% SrO and no CaO is showing some indications of sodium borate and strontium apatite, iii) the glass-ceramic with 20 mol% CaO and no SrO reveals separation of crystalline phases of sodium borate, calcium sodium borate and hydroxyapatite and iv) the glass-ceramics with 20 mol% SrO and no CaO showing crystalline phases of sodium borate, strontium apatite.

#### 3.5. Solubility of glasses and glass-ceramics

Figures 7 and 8 illustrate the weight loss (the solubility test) of the studied glasses and their corresponding glass-ceramics. The experimental data indicate the following parameters:

- The weight loss of all studied glasses is observed to increase progressively with increase of SrO replacing CaO. Each glass is observed to dissolve rapidly at first and then the increase becomes slower and attains some sort of stability at higher immersion times on reaching 360 hours.
- The weight loss of all investigated glass-ceramics has the same trend as the original base glasses, i.e. the weight loss increases with the increase of SrO content. The increase of the weight loss is higher at first and then becomes slower with time of immer-



Figure 4. FTIR absorption spectra of studied glass after immersion



Figure 5. X-ray diffraction of studied glass ceramics

sion until reaching almost constancy or stability at 360 hours of immersion.

• The quantity of weight loss is always higher for glasses in comparison to the corresponding glass-ceramics at specified time and the difference is clearly identified at the final time of immersion.



Figure 6. X-ray diffraction of G-1 (a) and G-5 (b) glasses, and glass ceramics GC-1 (c) and GC-5 (d) after immersion 2 weeks



Figure 7. Weight loss of studied glass samples



Figure 8. Weight loss of studied glass-ceramic samples

#### 3.6. pH measurements

Figures 9 and 10 illustrate the measured pH values of the glass and glass-ceramics after immersion in the dilute sodium phosphate solution. The data indicate that pH value increases with prolonged immersion time and the increase is sharper at first and then slower afterwards reaching some sort of stability or equilibrium. Also, the data indicate that the introduction of SrO replacing CaO gives progressively higher values with the SrO content.



Figure 9. pH values after immersion at different periods of studied glass samples



Figure 10. pH values after immersion at different periods of studied glass-ceramic samples

#### 3.7. Scanning electron microscope and EDAX data

Figures 11 and 12 illustrate SEM images of the selected representative glasses (G-1 and G-5) and glassceramics (GC-1 and GC-5) containing 20 mol% CaO and 20 mol% SrO. It is evident in Fig. 11 that both the glass G-1 and glass-ceramics GC-1 reveal nodular structures after immersion and other interfering microcrystalline species. EDAX results show sharp intensity



Figure 11. SEM and EDX of: a) glass G-1 and b) glass-ceramic GC-1



Figure 12. SEM and EDX of: a) glass G-5 and b) glass-ceramic GC-5

peaks due to several elements with the main Ca, O and Na which are more pronounced in the glass-ceramics derivatives. Figure 12 shows SEM and EDAX of the glass G-5 and glass-ceramics GC-5 containing 20 mol% SrO and without CaO. The micrographs of both G-5 glass and GC-5 glass-ceramics show some microcrystalline texture with other scattered bars and rounded small crystals. EDAX result of both samples shows high intense signals for Sr, as well as elemental P, O and Na and traces of Ca.

# **IV.** Discussion

#### 4.1. Interpretation of the FTIR spectral results

Infrared spectroscopy is a very valuable analytical and descriptive technique which can be applied in many applications of glass science. It can provide useful information about structural building units in various different oxide glasses [17–19]. It is an important tool for studying the bone bonding or bioactivity behaviour of silicate, phosphate and borate glasses [9,20,21]. A further application includes confirming the type of corrosion mechanisms in glasses [22,23].

Borate glasses are very promising candidates for the application of infrared spectroscopy to determine the various structural triangular and tetrahedral borate building units. Borate glasses possess rich chemistry and specific properties which are sometimes different than the properties of corresponding silicate and phosphate glasses and these specific properties are summarized as follows which will enable for the interpretation of the FTIR spectra:

- $B_2O_3$  is accepted by most scientists [9,20,21] to have a structure consisting mostly of 3 boronoxygen triangles joined to form a structure known as boroxol rings or boroxol groups  $(B_3O_6)$ .
- The addition of alkali oxide, alkaline earth oxide or some other heavy metal oxides (PbO, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>) causes some of the borons to change at first from triangular to tetrahedral coordination. This process of the conversion of borons from 3 to 4 fold coordination ceases after reaching some critical concentration of tetrahedraly coordinated borons after which any additional mentioned oxide brings the formation of non-bridging oxygen (NBO) as it happened in silicate and phosphate glasses.
- The vibrational modes of 3 and 4 coordinated borate units are quite separated and easily followed and differentiated by infrared spectral measurements as follows: i) the B-O stretching vibrations of trigonal (BO<sub>3</sub>, BO<sub>2</sub>O<sup>-</sup>) units are specified within the wavenumbers 1200–1550 cm<sup>-1</sup>, ii) the B-O stretching vibrations of tetrahedral BO<sub>4</sub> units are centered within the wavenumbers 800–1200 cm<sup>-1</sup>, iii) the bending vibrations of various borate groups are active within the range of wavenumbers 600–800 cm<sup>-1</sup> and iv) the peaks within the range 400–580 cm<sup>-1</sup> are assumed by some authors [9,20–24] to represent vibrations of modifier cations (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Na<sup>+</sup>) in their various specific sites.

#### FTIR spectra before immersion

FTIR spectra of the obtained glasses before immersion (Fig. 1) can, thus, be interpreted as follows:

- The asymmetric stretching vibrations of tetrahedral borate units such as (diborate, pentaborate, triborate units) are seen to be active as the first broad band within the range 800–1200 cm<sup>-1</sup> is evidenced by the appearance of the strong bands at 993 and 1028 cm<sup>-1</sup> [20,21].
- The second broad and strong band with peaks at 1407–1448 and 1505–1510 cm<sup>-1</sup> are representing the high frequency absorption related to triangular borate units (BO<sub>3</sub> and BO<sub>2</sub>O<sup>-</sup>) which are absorbing in this region [20,21].
- The low frequency part of the mid region (500–800 cm<sup>-1</sup>) is dominated by the bending vibrations or deformations modes of various borate units and the bands around 709–711 cm<sup>-1</sup> represent this mode [20,21].
- The peaks observed at 427–476 cm<sup>-1</sup> are assumed to be due to vibrations of modifier cations (e.g. Ca<sup>2+</sup>, Na<sup>+</sup>) in these glasses [9,10,21].

Figure 2 represents the FTIR spectra of the glassceramics before immersion and the vibrational modes observed represent reflection or indication of the finegrained crystalline derivatives of borates in three and four coordinations. They show sharper peaks due to the marked crystallinity of the measured powder.

#### FTIR spectra after immersion

FTIR spectra of the glasses after immersion in sodium phosphate solution (Fig. 3) can be interpreted as follows:

- The decrease of the intensity of the second broad band at 1250–1550 cm<sup>-1</sup> indicates that the phases containing BO<sub>3</sub> are more soluble in the immersed phosphate solution than the phases containing BO<sub>4</sub> groups with bands at 800–1200 cm<sup>-1</sup>. This behaviour is expected as the boron in BO4 groups are bonded firmly in equal four directions and with alkali or alkaline earth cations firmly attached to compensate for the excess negative charges.
- The appearance of two peaks at about 560–586 and 708–711 cm<sup>-1</sup> confirms the formation of calcium phosphate (hydroxyapatite) (Fig. 4).

The same reasoning and interpretations can be applied to FTIR spectra of the glass-ceramics derivatives after immersion in the phosphate solution.

# 4.2. X-ray diffraction data

Figures 5 and 6 illustrate X-ray data for the heat treated glass-ceramics before and after immersion in the phosphate solution and the results can be explained as follows:

• It is accepted that the type of the separated microcrystalline phases upon the thermal treatment process adopted depend on both the type and composition of bioglass and condition of heat treatment [25–27].

- In the base soda lime borate glass and some derived SrO-containing glasses, two calcium sodium borate microcrystalline phases are formed. This result comes from the ability of Ca<sup>2+</sup> ions to participate phase separation in borate glasses according to the assumption of Hudon and Baker [28,29] regarding the readiness of Ca<sup>2+</sup> ions to nucleate and form microcrystalline phases.
- The formation of microcrystalline strontium borate phase can be recognized in the samples GC-4 and GC-5 because they contain 75% or all the CaO replaced by SrO. It is expected that  $Sr^{2+}$  ions behave like  $Ca^{2+}$  ions in promoting nucleation and crystallization of the glasses [28,29].
- It is evident that during the crystallization process of the glasses-ceramics GC-1 and GC-5, containing 20 mol% of CaO or SrO, crystalline phase of sodium borate finds the route to accompany the formed crystalline species as indication of almost complete crystallization of glass constituents.
- The formation of minute peaks in the diffraction of the base glasses immersed in phosphate solution of hydroxyapatite or strontium apatite can be explained by the ability of phosphate ions in solution to react and combine with Ca<sup>2+</sup> or Sr<sup>2+</sup> from the bioglass but with lower rate due to their relative low mobility as they possess higher charges and larger ionic radii than alkali ions during the immersion process.

# 4.3. Interpretation of corrosion weight loss data

It is generally agreed upon that the chemical corrosion of glasses depends on several parameters including the glass type and its composition, the type and concentration of leaching solution, the temperature of attack or immersion and the duration time of the corrosion process [30–34]. Therefore, the corrosion behaviour is not a simple process of dissolution as observed in many inorganic solids. In most commercial SiO<sub>2</sub>-containing glasses, the process of corrosion involves preferential ion exchange between modifier ions (e.g. alkalis, alkaline earths) and protons or hydronium ions from the leaching solution. This primary step is followed by leaching or bulk dissolution of the glass.

Regarding the present studied glasses consisting of  $B_2O_3$  with  $Na_2O$  and CaO constituting the base glass, the suggested corrosion mechanism is quite different than with silicate glasses due to the following basic reasons [9,33,34]:

- Vitreous B<sub>2</sub>O<sub>3</sub> is a highly hygroscopic oxide and easily dissolves in water.
- It is accepted that there are no known boron compounds that precipitate from the solution under experimental conditions and it is therefore expected for borate glasses with alkalis and alkaline earth oxides to be quite soluble to a noticeable degree but with some variations of the degree of solubility of all constituents.

- The addition of alkali oxide to  $B_2O_3$  slightly decreases the high dissolution of pure  $B_2O_3$  because it forms tetrahedrally coordinated  $BO_4$  groups in which the boron is attached firmly in four equal directions with oxygens and with a nearby alkali borate cation strongly attached to compensate the excess negative charge. This assumption is supported by FTIR spectral measurements which indicate that  $BO_3$  phases are more soluble in aqueous media than  $BO_4$  phases [9].
- The addition of alkaline earth oxide to alkali borate glass is expected to further decrease the solubility by introducing double charged alkaline earth cations and their mixed interference during the route of solubility process within the percolation channels proposed by Greaves [34].
- It is expected that the replacement of CaO by SrO will not change the corrosion to a measurable rate, due to the resemblance of Ca<sup>2+</sup> and Sr<sup>2+</sup> in many respects as they belong to alkaline earth cations. However, the experimental weight loss data from glass and glass-ceramics reveal a measurable difference and the weight loss progressively increases at first with the SrO content but shows slower increase after some replacement and reaches some sort of constancy at full replacement of CaO by SrO.
- The weight loss data indicate that the introduction of SrO substituting CaO continuously and sharply increases the solubility and then for the samples GC-4 and GC-5 containing 15 and 20 mol% SrO the weight loss becomes slower. This data cannot be interpreted on the basis of the differences in ionic radii as Ca is (0.99 Å) while Sr is larger (1.013 Å) and according to the principle of diffusion process, the larger cations will retard the dissolution than the smaller cations. Two alkaline earth cations (Ca<sup>2+</sup> and Sr<sup>2+</sup>) are both incorporated into the network structure of glass as modifiers without any differences except that Sr<sup>2+</sup> cations are expected to expand the structural size.

The other factors which are affecting the dissolution weight loss data include the attacking sodium phosphate solution and the expected reactions or combinations of the ionized species from the solution with strontium ions within glass matrix. It has been reached by Elbadry *et al.* [23] that sodium phosphate solution is ionized into two powerful ionic species, namely phosphoric acid and sodium hydroxide which are shown to dissolve most of the modified bioglasses based on the Hench's patented composition containing SiO<sub>2</sub>, Na<sub>2</sub>O, CaO,  $P_2O_5$  and other constituents. The effects of such two component ionic species are formed to be more destructive than separate HCl or NaOH solutions. It is suggested that the sodium phosphate solution reacts with strontium cations forming strontium phosphate or the basis of crystalline strontium hydroxyapatite phase afterwards. It seems that this suggested reaction is faster than the reactions of sodium phosphate solution with calcium cations  $(Ca^{2+})$  and the observed higher weight loss at higher SrO content can be explained with the following facts:

- The lower weight loss with the increase of SrO and reaching some sort of equivalence can be related to the possibility of reaching super saturation of the dissolved constituents.
- Recent review articles on biological response to ionic dissolution products from bioactive glasses and glass-ceramics by Hoppe *et al.* [35] have indicated that Sr in biosilicate glasses can accumulate in bone by exchanging with Ca in the hydrox-yapatite crystal lattice. Also, they have mentioned that Sr has been confirmed as a promising agent in healing fractions. In phosphate bioglasses, Sr has been assumed to increase osteoblast activity. Hoppe *et al.* [35] have not mentioned in their recent review about the incorporation of Sr in borate glasses.
- Li *et al.* [36] have studied the lattice structure of bone crystal (apatite) after incorporation of Sr replacing Ca. Their results have indicated the incorporation of HPO<sub>4</sub><sup>2-</sup> in Sr-HA and not PO<sub>4</sub><sup>3-</sup> observed with Ca-HA. They have concluded that after 15% Sr incorporated the crystal size and crystallinty decrease which may be attributed to the destabilizing effect after more Sr incorporation. Li *et al.* [36] lastly added that more studies should be performed to further elucidate the effects of Sr incorporation on bone hydroxyapatite.
- It must be born in mind that the involved reactions between glasses and the leaching sodium phosphate solution does not include such reactions of the exchange of  $H^+$  (or  $H_3O^+$ ) from the solution and followed by polycondensation reactions of silanol groups as frequently happened in silicate bioglasses and leading finally to the formation and growth of calcium phosphate which will crystallize to surface hydroxyapatite. In the studied borate glasses, all the constituents are assumed to dissolve but with different degrees.
- A further assumption to explain the obvious increase of the weight loss data on replacing SrO for CaO might be related to the different reactivity of the glasses with sodium phosphate solution. There is a great affinity of calcium ions to react with phosphate ions to form a mixture of calcium phosphate including the production of both hydroxyapatite (HAP) and whitlockite ( $\beta$  tricalcium phosphate  $\beta$ -TCP,  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). The later  $\beta$ -TCP is known to be highly soluble product compared to the most insoluble calcium hydroxyapatite product possessing the solubility product of  $4.7 \times 10^{-59}$ . This assumption is supported by the work of Renadin et al. [37] on strontium substituted calcium phosphate. These authors have arrived to several important results which support

our studies and can be summarized as follows: i) the whitlockite formation is not attributed to the non-stoichiometry of the apatite structure, ii) the stabilizing effect of Sr for the whitlockite structure explains the fact that hydroxyapatite formation was inhabited when strontium was introduced and iii) easy delivery of  $Sr^{2+}$  ions in biological conditions can be related to the observed substitution of Ca for Sr in the whitlockite phase present in Srdoped ceramics, according to the high solubility product of whitlockite compared to hydroxyapatite [38].

• The corrosion weight loss data of glass-ceramics are found to be as expected lower than the weight loss data from their original glasses. This behavior is understood by referring to the presence of crystalline phases with definite structures and not loose non periodic nature in glasses [25].

# 4.4. Interpretation of pH data

The pH results can be interpreted by referring to the expected ionization of several alkali and alkaline earth ions (Na<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>) present in the form of their hydroxides which eventually lead to the increase of the pH values. The differences between the values of glasses containing SrO replacing CaO can be related to the known high insolubility of Ca-phosphate phases than Sr-phosphate phases.

# 4.5. Interpretation of SEM results

SEM micrographs obtained from two representative glass-ceramic samples (GC-1 and GC-5) are shown in Figs. 11 and 12. Textural features with numerous rounded microcrystals, characteristics for the presence of hydroxyapatite crystalline phases, can be seen in Fig. 11. In addition, small crystals which can be easy visible in SEM micrograph presented in Fig. 12 represent microcrystals of strontium phosphate (or Sr-apatite) with some other microcrystals of Ca-Na borates or Na borates.

# V. Conclusions

Borate glasses (0.6B<sub>2</sub>O<sub>3</sub>·0.2Na<sub>2</sub>O·0.2CaO) with SrO progressively substituting CaO were prepared and characterized for their bone-bonding ability. FTIR spectral analyses of the prepared borate glasses and glassceramic derivatives were carried out before and after immersion in a sodium phosphate solution for extended times. FTIR spectra reveal the appearance of characteristic IR peaks in the range 550–680 cm<sup>-1</sup> to confirm the calcium phosphate (hydroxyapatite) or strontium phosphate. X-ray diffraction studies and scanning electron microscope analysis confirm the IR spectral data. The corrosion behaviour (expressed as weight loss) of the glasses and glass-ceramics indicate the increase of weight loss with the increase of SrO content. Different suggested proposals were introduced to explain this abnormal behaviour.

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