A new glance at physico-chemical comportments of silicate bioactive glasses: influence of partial substitution: borosilicate versus fluorosilicate glasses

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Abstract—Two new glasses with compositions based on the SiO_2-Na_2O-CaO-P_2O_5 system; B_2O_3 and CaF_2 were added separately in increasing amounts (from 0 to 20 wt. %) were produced according to the melting process. The present study allows us to understand the properties of these glasses which could have an influence on their chemical reactivity and their bioactivity. Fluorine released from implant materials might result in the formation of fluorapatite, and this reduces both solubility and acid produced by bacteria. Addition of B_2O_3 generally increases glass materials bioactivity. In addition, borate based glasses were also used as orthopedic implants thanks to their solubility. X-ray analysis showed that the introducing of these elements in the chemical composition does not affect the amorphous character of glasses. The FTIR spectra revealed that the main structural units in the glass network were predominantly silicate species. The presence of phosphate and borate units in the structure of the glasses was also evident in these spectra. The presence of fluorine is assigned to the displacement in infrared spectra of the Si-O vibration mode. These results were confirmed by EDS spectra. SEM images show the similar morphological aspects of fluoride glasses versus borate glasses surface. A significant difference in thermal behavior between the two types of glasses was approved. This study allows the tailoring of novel fluoride and borate-containing bioactive glasses to address orthopedic needs.

Index Terms—Bioactive Glasses, Boron, Fluorine, Physical and Chemical Characteristics.

I. INTRODUCTION

Bioactive glass (BG) forms a double layer on the surface composed of calcium phosphate and silica-rich layers when it is immersed in a Simulated Body Fluid solution (SBF) or implanted into living tissues [1].The formation of the calcium phosphate layer that bonds with the surrounding tissue is proved to be an attractive scaffold in regenerative medicine. Recently, bioactive glasses have found applications in orthopedics as a suitable implant for bone substitution and reconstruction[2].CaO–SiO_2–Na_2O–P_2O_5systemincorporated with ZnO, MgO, and SrO as network modifiers demonstrated the effect of slowing down the degradation of the material [3]. However, some drawbacks can be found in several families of silicate bioactive glasses such as high liquidus temperature (> 1200 ° C) and high brittleness [4]. It is believed that the

bioactive behavior is related to the initial composition of the bioactive glass (BG) [5]. In fact, crystallization, microstructure and dissolution rates can be commanded by settling the composition of BG to suit with their end applications [6]. Saranti et al. signaled that the boron (B) in the glass network of CaO–B_2O_3–P_2O_5 system has a catalytic effect that favors their bioactivity [7]. Recently, Lee et al. reported that this ternary system was bioactive, and might be favorable as orthopedic implants thanks to its suitable chemical durability in physiological fluids [8]. When borate is incorporated in 45S5 BG network, the rate of hydroxyapatite (HA) formation on the surface of this glass increases. Consequently, the glass shows an increased cellular bioactive performance [9]. Yet, the addition of large quantities of boron to this glass induces a decrease of proliferation of osteoblastic like - cells in culture medium [10]. Moreover, borate-based bioactive glass presents a low mechanical strength which might delay the repairing defects especially in load-bearing bones [11]. In recent years, several trials have been made to tailor the degradation rate and ameliorate the mechanical strength of bioactive glasses through the addition of other oxides like MgO, SrO, ZnO, CaF_2 and B_2O_3 into bioactive glass network [12]. On the other hand, many studies proved that doping with B_2O_3 or CaF_2 favors densification of glass powder with similar chemical compositions [13]. In this respect, the presence of B_2O_3, Na_2O, and CaF_2 caused a reduction of crystallization temperature compared to similar glasses of the CaO–MgO–SiO_2 system [14].Nevertheless, the composition based on the SiO_2-CaO-MgO-P_2O_5 system with additives of B_2O_3, Na_2O, and CaF_2, has vitro bioactivity features. The formation of microcrystallites at the surface of these glasses was proved from the very beginning of immersion in SBF. Glass surfaces were completely covered with HA layer after 3 weeks in SBF [15]. For orthopedic and dental applications, it would be desirable to form fluorapatite (FA) rather than HA as FA is more chemically stable [16].In addition, fluorine (F) is also known to preclude dental cavities by inhibiting enamel and dentine demineralization, enhancing demineralization and blocking bacterial enzymes [17]. The use of fluoride-containing glasses would be beneficial for implantation. However, it is also known that fluorine losses

occur during melting of silicate glasses in the shape of SiF_4 or hydrofluoric acid (HF) [18]. Thus, glasses properties can be changed. In this context, bioactive glasses have a disrupted glass structure [19] with a large number of non-bridging oxygens (NBO; *i.e.* $Si-O^-$ alkali$^+$ bonds). Well known fluorine has a lower affinity for oxygen than for silicon; hence we can consider that fluorine loss would not significantly modify the glass composition, and the present study is based on this hypothesis. Goal et al. have also widely studied the influence of SrO on the structure, the apatite-forming ability, the degradation and the sintering behavior of $CaO–MgO–P_2O_5–SiO_2–CaF_2$ glasses [20].Recently, the formation of fluoride apatite layer after a 15 - day immersion in DMEM has been observed by Lusvardi et al. when CaF_2 is introduced in 45S5 glasses network. They have reported that infrared spectroscopy technique is more significant than XRD to characterize this layer [21]. In this study, two novel bioactive glasses were elaborated: B_2O_3 and CaF_2-substituting $SiO_2–Na_2O-CaO–P_2O_5$ system, BG-B_X and BG-F_X (x from 0 to 20 wt. %) respectively. On the other hand, authors showed that fluoride-containing bioactive glasses alter in properties due to structural changes [22].

Thus, the objective of the current study is to understand the structural difference between BG-B_X and BG-F_X and to adapt their use according to the different patients' needs.

II. MATERIELS AND METHODES

A. Glasses elaboration

The chemical compositions of borosilicate glasses, chosen following the contents of CaO, Na_2O and P_2O_5, remain constant while the contents of SiO_2 are substituted by 5; 10 and 20 wt. % of B_2O_3. CaF_2 was incorporating in fluoride glasses network, from 5 to 20 wt. %. The details of the chemical compositions of the two glasses types are furnished in Table 1 and Table 2 respectively. Both of these glasses are elaborated according to the melting method by mixing appropriate amounts of calcium metasilicate $CaSiO_3$ (reagent grade, Alfa-Aesar), dehydrated sodium metasilicate from Na_2SiO_3, $5H_2O$ (97%, Sigma), sodium metaphosphate $Na_3P_3O_9$ (95–97%, Sigma), silicon dioxide SiO2 (99%, Pro-labo), CaF_2 (Sigma-Aldrich, Gillingham, UK), and B_2O_3 (99.99%) (High Purity Chemicals), using a planetary mixer, during 45min. The powdered mixture for each BG-F_X and BG-B_X glasses was then heated in a platinum crucible at 1350 °C for 3 h, poured into preheated mold and annealed for 4 h at a temperature close to that of glass transition [23].

Table 1: Details of the chemical compositions (in mass %) of BG-B_X glasses.

Glass	SiO$_2$	CaO	Na$_2$O	P$_2$O$_5$	B$_2$O$_3$
BG-B$_0$	46	24	24	6	0
BG-B$_5$	41	24	24	6	5
BG-B$_{10}$	36	24	24	6	10
BG-B$_{20}$	26	24	24	6	20

Table 2: Details of the chemical compositions (in mass %) of the BG-FX glasses.

Glass	SiO$_2$	CaO	Na$_2$O	P$_2$O$_5$	CaF$_2$
BG-F$_0$	46	24	24	6	0
BG-F$_5$	46	22	23	4	5
BG-F$_{10}$	45	21	22	2	10
BG-F$_{20}$	41	18	20	1	20

B. X-ray diffraction

Phase compositions were identified by X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) with a CuKα radiation (λ=0.154 nm, filter: Ni, voltage=40 kV and current=30 mA).

C. Infrared studies

The BG-B_X and BG-F_X bioactive glasses were characterized by Fourier Transform Infrared Spectroscopy (FTIR) (Bruker Equinox 55). Spectra were obtained between 2000 and 400 cm^{-1} wave number with a resolution of 2 cm^{-1}.

D. SEM-EDS analyses

The microstructure of glass surfaces was observed by Scanning Electron Microscopy (SEM) (Joel JSM 6301F) working at a 20 kV as an accelerating voltage. Chemical analysis on glass surfaces, covered by gold–palladium layer (Au — 20 wt. % Pd) to allow surface conduction, was performed using X-ray Energy Dispersive Spectroscopy (EDS) (Joel JSM 6400). SEM associated to EDS allows the determination of the surface layer nature.

E. Differential Thermal analysis

Differential Thermal Analysis (DTA) was used to measure the thermal characteristics of different bioactive glasses. The DTA principle is based on the detection of an exothermic or an endothermic phenomenon. Glass transition temperature (T_g), crystallization temperature (T_c) and fusion temperature (T_f) were recorded using a Setaram Labsys 1600TGDTA/ DSC thermal analyzer under N_2 gas atmosphere. Bioactive glasses were studied under heating rate of 5°C/min raised from room temperature to 1400°C. Each amount of the glass powder was heated in platinum crucible and another empty platinum crucible for use as control.

F. Density measurements

Experimental density was determined with a picnometer (Micrometrics, Accupyc 1330 to helium displacement (He)) at room temperature with an accuracy of 0.002 g/cm^3. Each value is an average of two independent measurements and then averaged to obtain reliable results.

III. RESULTS

A. X-ray diffraction

Fig.1 shows similar XRD data for BG-B_X and BG-F_X glasses; the final products were mainly amorphous [24]. The amorphous phases gave an indication of the formation of homogeneous silica network in the BG-B_X and BG-F_X glasses. It must be noted that no crystalline phase containing phosphorus in the BG-B_X and BG-F_X compositions can be

detected by XRD, mainly due to the limited amount of phosphate existing in the glasses matrix. These powders were compared to the documented SiO_2-CaO-Na_2O-P_2O_5 system prepared by Wers et al. [25].
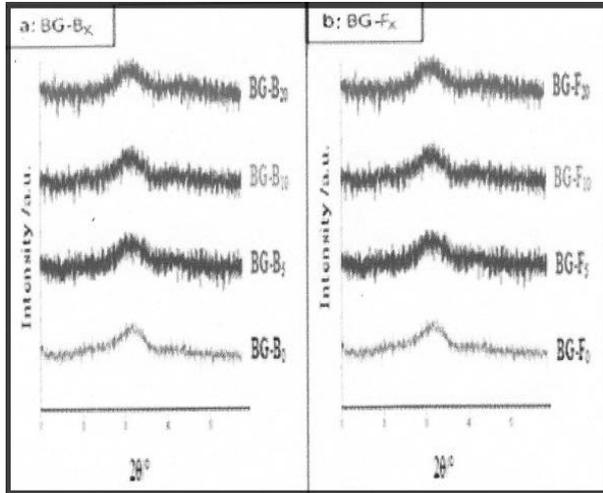

Fig 1: XRD patterns of glass surfaces. (a): BG-B_X and (b): BG-F_X

B. Infrared studies

Fig. 2 shows the FTIR spectra of BG-B_X and BG-F_X. The infrared spectra of BG-B_X indicate characteristic bands of the silicate vibrations: 492, 728,924, and 1024 cm^{-1} assigned to Si-O-Si bending mode, Si-O-Si symmetric stretching mode of bridging oxygen atoms between tetrahedrons, Si-O-Si stretching of non-bridging oxygen atoms and Si-O-Si asymmetric stretching of bridging oxygen atoms within the tetrahedron respectively [26]. The change at 589 cm-1 reveals the weakening of intensity of the P-O bend bond due to the addition of 10 mass% of B_2O_3 [27]. The bond at 1442 cm^{-1} is assigned to the vibration of C-O unit [28].This is in accordance with the amorphous structure observed in XRD diagram (see Fig. 1).From 5 mass% of B_2O_3, the appearance of bond at 1237 cm^{-1} corresponds to the formation of a new B-O chemical bond stretching of BO_3 units [29]. Also, the wavelength shifts observed around 904 and 1033 cm^{-1} assigned to PO_4^{3-} groups/B-O stretching in BO_4 units/Si-O-Si stretching [30], and Si-O stretching/BO_4 vibrations respectively [31]. For BG-F_X the observed bands at 728, 924, 1024 cm^{-1} are similar to those observed for BG-B_X and assigned to silicate network vibrations. The band previously observed at 492 cm^{-1} attributed to the non-substituted compound is shifted for BG-F_X to the side of the larger wavelengths at 520 cm^{-1}. Moreover, from 20 mass% of CaF_2 the substitution into the glass network by CaF_2 is proved firstly by the appearance of a band at 442 cm^{-1} corresponds to the formation of a new Si-O-Si chemical bond [32], and secondly by the shift of the absorption band of P-O.
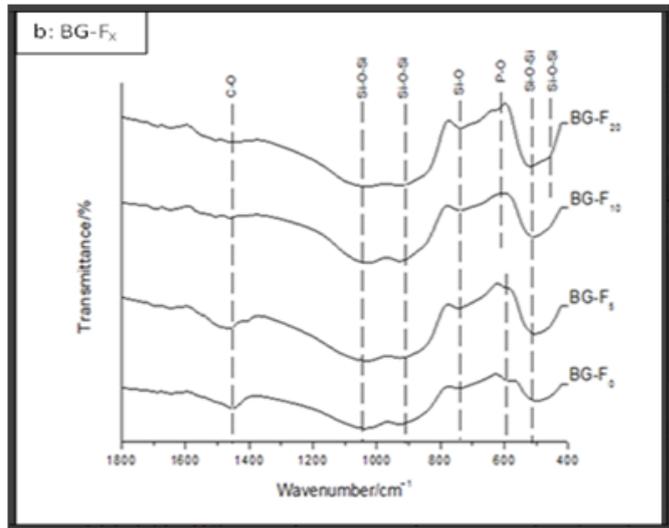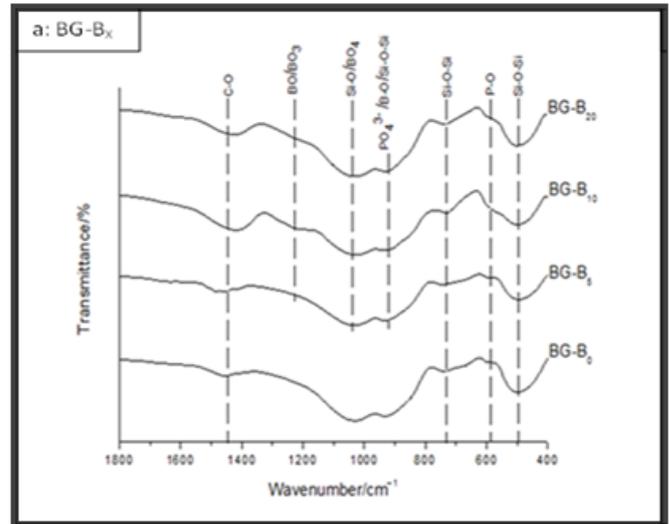

Fig 2: FTIR spectra of prepared glasses. (a): BG-B_X and (b): BG-F_X
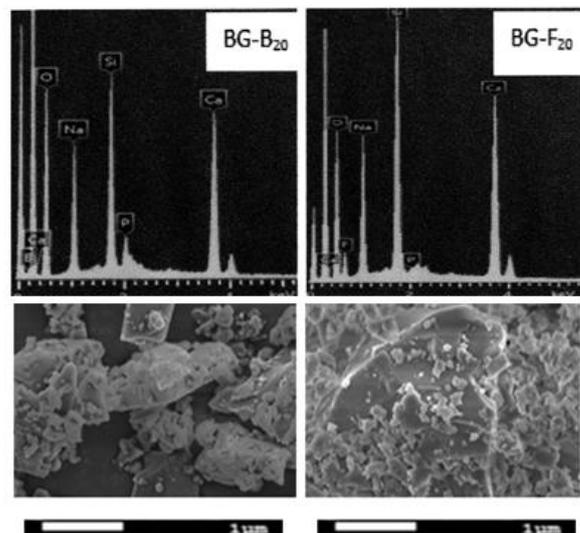
C. SEM-EDS results

Fig 3: SEM micrographs and EDS spectra of BG surfaces

SEM images coupled with EDS analyses (Fig. 3) show similar morphology for BG-B$_X$ and BG-F$_X$ glasses. The results obtained show that the synthesized materials are amorphous, and homogeneous in composition. The layer thin of each powder consists of small and large spherical aggregates. Furthermore, increasing the boron or fluorine content in the glass network causes a decrease of the form of agglomerates. According to EDS results for both types of bioactive glasses, the layers are rich in silicon (Si), calcium (Ca) and sodium (Na).

**D.Influence of boron and fluorine on the thermal characteristics of bioactive glasses.**

The insertion of Na$_2$O established two bridges of oxygen in the amorphous system. The two negative charges of oxygen are balanced by the charge of Na$^+$ pair training a neutral electrostatic matrix. Thus, the network structure is amended and consequently changes the glass thermal behaviors [25]. The adding of CaO does not implicate modifications because the two positive charges of Ca^{2+} are balanced and create two tetrahedrons attached by ionic bonds [25]. The impact of boron and fluorine on the thermal characteristics was described in Fig. 4.a for B-substituted glasses and 4.b for F-substituted glasses.

Fig 4(a): Thermograms of B-substituted glasses

Fig 4(b): Thermograms of F-substituted glasses

Each thermo gram presents 3 peaks characteristics of glass: the transition, the crystallization and the fusion temperatures. The thermal characteristics of BG are summarized in Table 3.

Table 3: Glass transition, crystallization and fusion temperature (T_g, T_c and T_f °C)

Glass	T_g	T_c	T_f
B and F-free glass	575	745	1223
BG-B$_5$	510	645	1166
BG-B$_{10}$	498	627	1076
BG-B$_{20}$	492	624	964
BG-F$_5$	523	643	1210
BG-F$_{10}$	510	608	1193
BG-F$_{20}$	488	592	1162

For B-substituted glasses, a decrease of T_f (from 1223 up to 964 °C), of T_c (from 745 up to 624 °C) and of T_g (from 575 up to 492 °C) was observed when the content of B increases. For F-substituted glasses, changes were observed for the three characteristic temperatures. Thereby, T_g, T_c and T_f decrease from 575 up to 488°C, from 745 °C up to 592°C , and from 1223 up to 1162 °C respectively when the content of F increases in the glass matrix. For T_g and T_f, comparable results are found in Zn-doped glasses [25]. In this respect, important variances of temperature for T_g, T_c and T_f were observed between glasses substituted with a low content of substituting element and those with a high content. In fact, for BG-B$_5$, T_f = 1166°C and for BG-B$_{20}$, T_f = 964°C i.e. a difference ΔT_f = +202°C. For F-substituted glasses, BG-F$_5$ presents a T_f = 1210°C and for BG-F$_{20}$, T_f = 1162°C i.e. ΔT_f = + 48°C. Thus, although B-substituted glasses have weaker fusion temperatures, the introduction of B decreases fusion temperatures faster than the adding of F. For glass transition temperatures, the impact of the two elements (F or B) is less pronounced. Indeed, BG-B$_5$ and BG-B$_{20}$ present a ΔT_c = +21°C while BG-F$_5$ and BG-F$_{20}$ have a ΔT_c = 51°C. Boron, unlike fluorine, does not have an important effect on the glass crystallization temperature [14].The most significant impact caused by the introduction of B or F is the reduction of the fusion temperature that is the glass synthesis temperature. The range between BG-F$_5$ and BG-F$_{20}$, ΔT_f = -48°C and for BG-B$_5$ and BG-B$_{20}$, ΔT_f = -202°C. The introduction of CaF$_2$ and B$_2$O$_3$ in the amorphous network involves the break of covalent chemical bonds Si-O-Si to create ionic bonds. As covalent bonds are energetically stronger than ionic bonds formed, modifications in the thermal behavior of glasses are proved. Indeed, the reduction of fusion temperatures for BG-B$_X$ glasses is more significant in contrast than those BG-F$_X$ glasses. The substitution of a network former element for B-substituted glasses can explain this phenomenon. These results allow the understanding of the thermal behavior of glasses. This present study can adduce indications about the glasses behavior during in vitro assays and their ability to exchange ionic elements to form hydroxyapatite layer. Therefore, we could adapt the use of F and B in the biomaterial to improve its physiological properties and to be
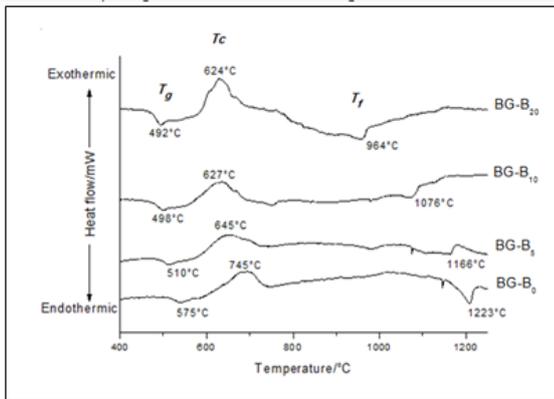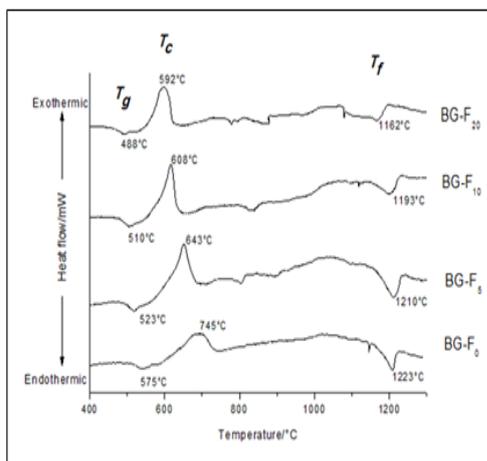
used into wider medical applications.

E. Density

The experimental density and volume values obtained using picnometer were reported in Table 4. The density data values increase linearly with substituent element concentration (Fig. 5). This behavior suggests a unique structural role for the boron or fluorine ion in the glass network in the range of concentrations allowed. Fig. 6 presents the average volume of the glasses showing a linear increase in volume with increasing CaF_2 or B_2O_3 content.

Table 4: Density (D) and volume (V) of the studied glasses

Glass	$D(g/cm^3)$	$V(10^{-1}cm^3)$
B and F-free glass	2,641	1,895
BG-B$_5$	2,662	2,296
BG-B$_{10}$	2,676	2,640
BG-B$_{20}$	2,710	3,290
BG-F$_5$	2,681	2,453
BG-F$_{10}$	2,724	2,912
BG-F$_{20}$	2,795	3,698

The most significant difference between BG-B$_X$ and BG-F$_X$ experimental values were observed in the studied glasses. Earlier studies [33] showed that doping with B_2O_3 and CaF_2 favors densification of glass powder compacts with similar chemical compositions. Recently, it has been shown that by adding fluoride (CaF_2) in this way, the network connectivity of the glass and the Q speciation (i.e. the number of bridging and non-bridging oxygen atoms per silicon atom) remained unchanged [22].
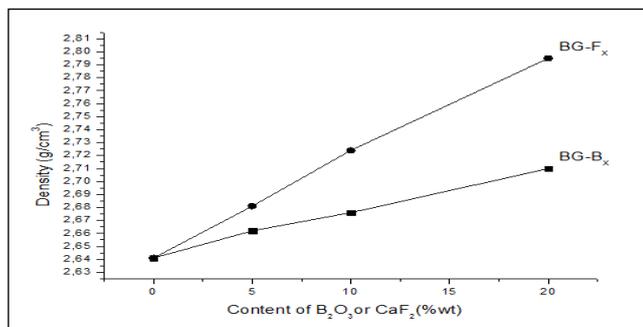
Fig 5: Experimental density as a function of B_2O_3 or CaF_2 content in the glasses.
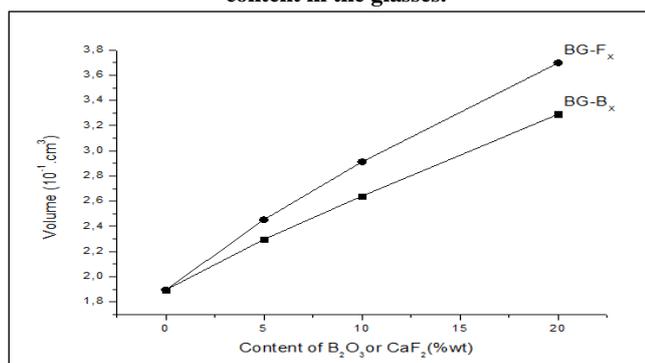
Fig 6: Average volume as a function of B_2O_3 or CaF_2 content in the glasses.

[19]F magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy also showed that fluorine did not disrupt the silicate network by forming Si-F bonds; instead it formed F-M(n) species in the glass (M: Ca or Na) [32].Based on recent findings [34], when modeling the density of the glasses, it was assumed that CaF_2 enters the glass structure in the form of CaF_4 tetrahedral. In addition, the formation of Ca-F clusters was proved, whose size increasing with CaF_2 content [34]. Formation of such clusters was also confirmed by molecular dynamics simulation [35]. D.S. Brauer et al. [36] proved that the volume of the CaF_4 tetrahedron in the glass is about 1.02% larger than in the crystalline form, the volume increase is related to the disordered nature of the glass structure. The increase in the volume of CaF_4 in the studied glasses is consistent with a slightly longer Ca-F distance in amorphous glasses [37].It must be taken into consideration that the boron ions in this glass network participate throughout BO_3 and BO_4 structural units with the dominance of BO_3 units. Moreover, boron ions homogenize the microstructure of the glass [38]. Thereby, simulations on a $70SiO_2$-$15B_2O_3$- $15Na_2O$ glass showed that without more insoluble oxides than silicon results in the porous structure hardening. These mechanisms will lead to densification of the glass powder followed by a closed porosity and a large shrinkage. This model was used to quantitatively reproduce the influence of the content of soluble elements (boron, alkali) to the alteration kinetics [39]. Both types of glasses can be considered as consisting of two matrices mixed together. The first is the silicate matrix [40] while the second is formed by CaF_4 or BO_3 units. Each of these matrices has its own properties. Following these results, it is noticeable that fluorine has a more important effect on the glass density than boron. The linear change in both D and V reveals that each of the units emerging in the structure maintains its volume constant over the investigated composition region.

IV. CONCLUSION

The X-ray diffraction of substituted bioactive glasses proved the amorphous character of all glasses up to 20 wt. % of elements added in the vitreous network. Moreover, FTIR spectra report that different chemical bonds were formed according to the substituent elements. The adding of boron or fluorine in the glass matrix induces various changes in the thermal behaviors. Elaboration temperatures decrease as a function of these elements. Variations were also observed on the crystallization and glass transition temperatures. The experimental density values show that F-containing glasses have a more important density than B-containing glasses. The presence of these elements in the glass matrix increases the density and the average volume according to the content introduced. The present study allows us to understand the physico-chemical comportments of borosilicate and fluorosilicate bioactive glasses which can have an influence on their chemical reactivity and on their bioactivity. Biomaterials can be adapted in different medical applications

by introducing chemical interesting elements having appropriate physiological properties.

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