

## Novel alkali borosilicate glasses: Preparation, structural investigation and thermal study

Amina Gharbi<sup>\*,\*\*</sup>, Hafed El Feki<sup>\*\*</sup>, and Hassane Oudadesse<sup>\*,†</sup>

<sup>\*</sup>University of Rennes 1, ISCR, UMR CNRS 6226, 263 av. du Général Leclerc, 35042 Rennes, France

<sup>\*\*</sup>Faculty of Sciences of Sfax, Materials Science and Environment Laboratory, Sfax 3018, Tunisia

(Received 4 September 2015 • accepted 16 December 2015)

**Abstract**—Bioactive glasses are indicated for use as bone substitutes in orthopedic or dental surgery because of their high reactivity once in contact with the biological medium. Boron is known as a glass network former and an activator of the glasses bioactivity. In this work, bioactive glass was doped by 5, 10 and 20 wt% of B<sub>2</sub>O<sub>3</sub> according to the melting process. Adding boron oxide with high content enhances glass materials' bioactivity. Likewise, thanks to their solubility, borate-containing bioactive glasses were fluently used as orthopedic implants. The aim of our study was to investigate of boron effect on the thermal characteristics of our bioactive glass to better understand their proprieties in order for use as bone biomaterial. The obtained results proved that the more the boron content in the glass network increases, the more the melting temperature decreases and the more the thermal stability increases.

Keywords: Bioactive Glasses, Melting, Thermal Proprieties, Biomedical Applications

### INTRODUCTION

Bioactive glasses (BG) of specific compositions were studied for applications as biomaterials. The melt-quenching CaO-SiO<sub>2</sub>-Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> system (e.g., Bioglass® 45S5) was proved to be able to bond to bone mineral [1]. They form this integrated bond with living bone via formation of a hydroxyapatite (HA) layer on their surface when immersed in physiological solutions. This HA layer is generally shown to facilitate proteins attachment, allowing the formation of an intimate bond to bone [2,3]. Bioactive glasses have found application in orthopedics surgery as a suitable implant for bone substitution and reconstruction [4,5]. The originality of this work is the study of the effect of substitution of silicium (Si) by boron (B) in the glass network in order to better understand the thermal characteristics of these materials so that they can be adapted to different patients' needs. Some kinds of glasses in the borosilicate glasses compositions were studied [6]. Xianyan et al. evaluated the effect of boron- and aluminum-doped phosphosilicate glasses [7]. Saranti et al. reported that the boron in the glass network of CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system had a catalytic effect on favoring bioactivity of the other calcium phosphate glasses [8]. When boron was added to 46S6 bioactive glass, the rate of HA formation on the surface of this glass increased. As a result, the glass showed an increase in the cellular bioactive behavior [9,10]. Indeed, this chemical element (B) presented interesting physiological properties. However, the addition of large quantities of boron to this glass certainly resulted in a decrease of proliferation of osteoblastic - like cells in

culture medium [11]. Thereby, boron induced an increase of the extracellular matrix turnover [12] and played a role in bone physiology [13]. In the structural hand, earlier studies showed that doping with B<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub> favored densification of glass powder compacts with similar chemical compositions [14]. Jae et al. evaluated a novel CaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass-ceramics as a new bone replacement material [15]. They reported that the mechanical proprieties and the bioactivity of the borosilicate glasses were much greater than that of HA. To better understand the thermal behavior of borosilicate glasses, one needs to understand the direct effect of the introduction of this element on the thermal conductivity and its effect on the heat transfer mechanism between the chemical bonds in the glass network. It is known that glass is an amorphous system with an unordered structure composed forming network (B, Si), modification (Na, K), and intermediate oxides (Zn, Cu, Ti) [16]. Network forming oxides are the oxides composed of metalloid elements. Therefore, the introduction of metalloid element in the glass caused specific changes in thermal characteristics [17]. Nevertheless, the presence of B<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub> had a negligible influence on the assemblage of the crystallized phases. Yet, it caused a crystallization temperature reduction [17]. Recent studies have shown that the increase of zinc oxide in the glass matrix reduces these characteristics' temperature [18]. The addition of zinc ions to silicate and borosilicate glass improves the thermal proprieties [19]. Indeed, the lithium borophosphate are glasses which show the effect of mixed formatters on vitreous network, a very interesting fact to a solid as it leads to a simultaneous increase in the thermal stability and ionic conductivity of the glasses [20]. In this way, Wers et al. proved that the adding of titanium or argen in the glass network had an effect on the glass transition, crystallization and fusion temperatures [21]. It is generally accepted that the crystallization, the microstructure,

<sup>†</sup>To whom correspondence should be addressed.

E-mail: hassane.oudadesse@univ-rennes1.fr

Copyright by The Korean Institute of Chemical Engineers.

and even the dissolution rates could be governed by adjusting the compositions of the bioactive glasses [22]. There are several ways to reduce the sintering temperature of advanced glass [23]. It is vital to note that the melt-quenching involved a high-temperature process leading to the volatilization of the oxides with low-melting points, such as  $B_2O_3$ . Thus, it becomes difficult to get the desired composition of those oxides [7].

Generally, the study of the vitreous state is an approach to describe its disordered structure. In this study, we developed a new  $B_2O_3$ -substituting  $SiO_2$ - $Na_2O$ - $CaO$ - $P_2O_5$  system (BG- $B_x$ ) prepared by the melting process where  $x$  is the amount of  $B_2O_3$ . After understanding the chemical and thermal characteristics of borosilicate glasses, we could suit these materials to the different orthopedic needs. According to the literature about the effect of incorporating boric oxide to biomaterials, boron has well-defined thermal effects on the thermal characteristics such as ( $T_g$ ,  $T_c$  and  $T_f$ ). These thermal parameters were evaluated and studied in function of the amounts of  $B_2O_3$  in bioactive glass matrix.

## EXPERIMENTAL

### 1. Glasses Elaboration

The chemical compositions of the investigated glasses are based on the fixed  $CaO$ ,  $Na_2O$  and  $P_2O_5$  system. Content of  $B_2O_3$  and  $SiO_2$  varies from 0 to 20 wt% and 46–26 wt%, respectively. The details of the composition of the used glasses are furnished in Table 1. The first studied composition was pure bioactive glass 46S6 [24]. It was used as a reference composition to validate our experimental procedure. Appropriate amounts of sodium metasilicate pentahydrate ( $Na_2SiO_3 \cdot 5H_2O$ ), boron oxide ( $B_2O_3$ ), calcium metasilicate ( $CaSiO_3$ ), sodium metaphosphate ( $Na_3P_3O_9$ ) and calcium carbonate ( $CaCO_3$ ) were thoroughly mixed in a polyethylene bottle, during 45 min. The powder mixture was heated in a platinum crucible at  $1,350^\circ C$  during 3 h. The molten glass was then poured into pre-heated molds and annealed for 4 h at a temperature near to that of glass transition.

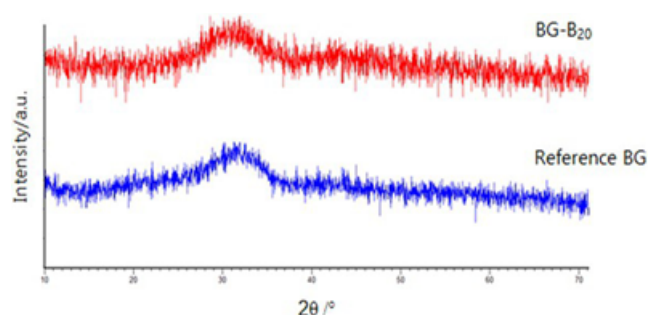
### 2. Thermal Analysis

Thermal characteristics of different glasses--vitreous transition ( $T_g$ ), crystallization ( $T_c$ ), fusion ( $T_f$ ) temperatures and onset temperatures of crystallization ( $T_{onsetc}$ ), which represents the beginning of the crystallization--were determined. Each composition was studied by thermal analysis, in the range of  $25$ – $1,400^\circ C$ , with a heating rate of  $5^\circ C \cdot min^{-1}$ , under nitrogen atmosphere (Labsys 1600TG-DTA/DSC, Setaram, France). The thermal stability (TS) of bioactive glass was expressed by the difference between vitreous temperature  $T_g$  and  $T_{onsetc}$  introduced by Dietzel [25]:

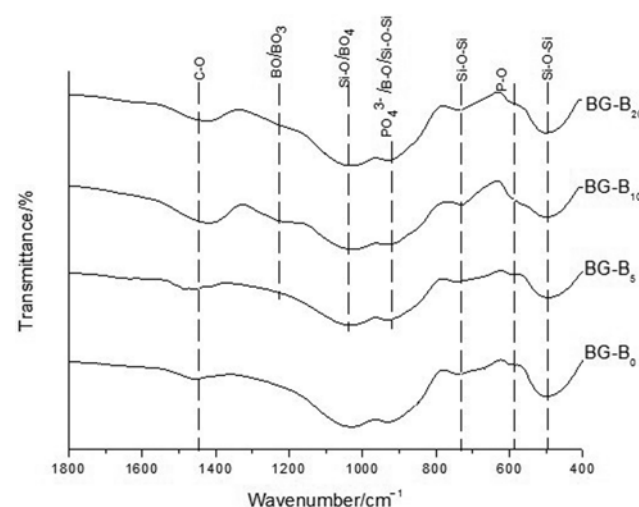
$$TS = T_{onsetc} - T_g \quad (1)$$

**Table 1. Details of the chemical composition (in mass %) of the glasses**

	$SiO_2$	$CaO$	$Na_2O$	$P_2O_5$	$B_2O_3$
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



**Fig. 1. X-ray diffraction data for reference bioactive (BG) and bioactive doped with  $B_2O_3$  at 20% (BG- $B_{20}$ ).**



**Fig. 2. IR spectra of 46S6 and substituted glasses BG- $B_x$  ( $5 < x < 20$ ).**

## RESULTS AND DISCUSSION

### 1. Characterization of Alkali Borosilicate Glasses

#### 1-1. X-ray Diffraction

Phase compositions were identified by X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) with a  $Cu K\alpha$  radiation. Fig. 1 shows similar XRD data for BG-20%  $B_2O_3$  and pure bioactive glass used as reference. Similar diagrams were obtained for all compounds BG- $B_x$  ( $0 < x < 20$ ).

#### 1-2. Infrared Studies

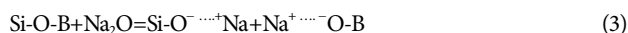
Fourier transformed infra-red spectroscopy (FTIR) (BRUKER EQUINOX 55) was used to highlight the structural analysis. Fig. 2 shows the FTIR spectra of reference glass and substituted glasses. The spectrum of reference confirmed the presence of Si-O-Si chemical bond at  $1,033$ ,  $924$ ,  $728$  and  $492\text{ cm}^{-1}$ . The mode at  $1,442\text{ cm}^{-1}$  is assigned to the vibration of C-O unit [21]. The change at  $578\text{ cm}^{-1}$  reveals the decrease of the intensity of P-O shoulder due to the substitution of 10 and 20 mass% of  $B_2O_3$  [26]. Indeed, the appearance of mode at  $1,237\text{ cm}^{-1}$  (from 5 mass% of  $B_2O_3$ ) corresponds to the formation of a B-O bond stretching of  $BO_3$  units [27]. The experimental results of FTIR measurements for BG- $B_x$  ( $5 < x < 20$ ) glasses exhibit vibrational modes at around  $1,038\text{ cm}^{-1}$  (Si-O stretching/ $BO_4$  vibrations) [28], and a large bond at  $918\text{ cm}^{-1}$  ( $PO_4^{3-}$  groups/B-O stretching in  $BO_4$  units/Si-O-Si stretching) [29].

## 2. Structural Approach

Based on the literature, we propose a structural approach to these bioactive glasses that clarifies the heat repartition into the borosilicate network. The structure of alkali borosilicate glasses was studied by infra-red, Raman and NMR spectroscopy, e.g., [30].  $^{11}\text{B}$  NMR spectroscopy was particularly useful to determine the proportion of B in trigonal- $\text{BO}_3$  ([trigonal $^{(3)}$ ]B) and in tetrahedral- $\text{BO}_4$  [tetrahedral $^{(4)}$ ]B in coordination with oxygen. Bray and co-workers [31] showed that the glass structure changed systematically with variation in composition. Addition of small amounts of  $\text{Na}_2\text{O}$  ( $0 < [\text{Na}_2\text{O}/\text{B}_2\text{O}_3]_{\text{molar}} < 0.5$ ) converted symmetrical trigonal B to tetrahedral B within borate entities where components of polymerized units were enclosed in square brackets, as indicated below:



Sitarz and his group [29] carried out extensive studies on bioactivity of  $\text{B}_2\text{O}_3$  mixed  $\text{NaCaPO}_4$ - $\text{SiO}_2$ - $\text{PO}_4$  glasses using SEM, EDAX, MIR and NMR spectral techniques. The authors concluded that the boron ions in this glass network participated in the form of  $\text{BO}_4$  and  $\text{BO}_3$  structural units with the dominance of the latter. They also found that boron ions homogenized the microstructure of the glass and produced domain structure that is close to the corresponding crystalline phases [29]. For our study, in borosilicate network, the formers were compound with covalent and semiconductor character. These are easily verifiable elements. Their structure is composed of tetrahedral or trigonal chains. Modifiers cations ( $\text{Na}^+$ ,  $\text{Ca}^{++}$ ) provide the ionic conduction phenomenon in the glasses. The chemical reaction results are the breakdown of oxygen bonds connecting two formers, and the creation of ionic bonds  $\text{O}^{\cdots}\text{Na}$  or  $\text{O}^{\cdots}\text{Ca}$  according to the schematic reaction:



In this respect, the number of bridging oxygens which perform network rigidity decreases with the addition of modifiers. This is reflected by changes in properties of the glass (for example reduction of  $T_g$ ) [32]. Pentavalent phosphorus ( $\text{sp}^3$  hybridation) adopts a tetrahedral conformation. The  $\text{PO}_4$  tetrahedral units are linked together with covalent liaison in chains or rings by bridging oxygens [33]. For our glasses,  $\text{P}_2\text{O}_5$  intervenes in the network as a modifier. Phosphorus is preferentially surrounded by cations which possess three positive charges such as  $\text{B}^{3+}$  (weak bond  $\text{P-O}^{\cdots+}\text{B}$ ). Consequently, boron could be easily integrated into a network phosphate.

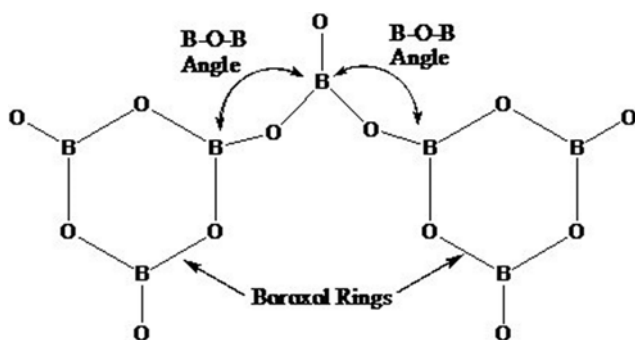


Fig. 3. The sequence  $[\text{BO}_3]$  possible entities in a borosilicate glass.

It is evident that  $\text{B}_2\text{O}_3$  is a well-known glass former that participates in the glass network with trigonal boron oxygen units mostly condensed as boroxol rings  $(\text{B}_3\text{O}_6)^{3-}$  as shown in Fig. 3.

This planar geometry of  $\text{BO}_3$  leads the glass to be more fragile. Evidently, the transition temperature of vitreous  $\text{B}_2\text{O}_3$  is much lower than the one of the vitreous  $\text{SiO}_2$  glasses ( $T_g(\text{vitreous } \text{B}_2\text{O}_3) = 260^\circ\text{C}$ , when  $T_g(\text{vitreous } \text{SiO}_2) = 1,100^\circ\text{C}$ ) [20].

Raman spectroscopy measurements made on  $\text{SiO}_2$ - $\text{B}_2\text{O}_3$  supercooled liquids [34], which showed that the proportion of boroxol rings decreased with increasing temperature. This result is explained by the disproportion of boron to non-ring positions which induce the increase of the entropy, according to Le Chatelier's principle as applied to such a temperature-induced transformation [35]. A part of boron is transformed into tetrahedral coordination in the presence of other glass formers and modifiers [36] like  $\text{Na}^+$  and  $\text{Ca}^{++}$ . Different structural intermediates are formed successively during this change of coordination number [37]. With the addition of alkali, the boroxol units are first converted to tetra-borates  $(\text{B}_4\text{O}_6)^{6-}$  units, then di-borates units  $(\text{B}_2\text{O}_5)^{4-}$ . The  $\text{BO}_4$  tetrahedral has a negative charge and therefore needs a load compensator, which is the role of the alkali cation. Whenever the addition of alkali is higher than 25 mole%, the appearance of non-bridging oxygens in the glass leads to further structural entities formed both  $\text{BO}_3$  and  $\text{BO}_4$  containing one or more non-bridging oxygens [38].

$\text{SiO}_2$  is another glass former that participates in borosilicate network with tetrahedral units and all the four oxygens in  $\text{SiO}_4$  tetrahedron are shared in absence of  $\text{Na}^+$  and  $\text{Ca}^{++}$ . The Si-O linkages normally are broken by the addition of  $\text{Na}_2\text{O}$  and  $\text{CaO}$ . The depolymerization results in the formation of orthosilicates indicated in Fig. 4, metasilicates and other forms as:  $[\text{SiO}_4]$ ,  $[\text{SiO}_4]^-$ ,  $[\text{SiO}_4]^{2-}$ ,  $[\text{SiO}_4]^{3-}$ , and  $[\text{SiO}_4]^{4-}$  which are designated as  $\text{Q}^4$ ,  $\text{Q}^3$ ,  $\text{Q}^2$ ,  $\text{Q}^1$ , and  $\text{Q}^0$ , respectively [39].

With the presence of  $\text{BO}_3$ ,  $\text{BO}_4$ ,  $\text{SiO}_4$  and  $\text{PO}_4$  units,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions occupy the interstitial positions, while the oxygens of these oxides break the local symmetry and introduce co-ordinate defects known as dangling bonds along with non-bridging oxygens [40]. Thus, from arguments based on the literature, it is assumed that  $\text{B}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{CaO}$ - $\text{Na}_2\text{O}$ - $\text{P}_2\text{O}_5$  glass network is composed of three dimensions: borate, phosphate and silicate structural units. According to the Krogh-Moe model states [41], pure  $\text{B}_2\text{O}_3$  glass consists mainly of boroxol ring. With the addition of one  $\text{Na}_2\text{O}$  and one tetraborate containing, two  $\text{BO}_4$  units are formed. Diborate units are assumed not to have enough acidity, unlike boroxol

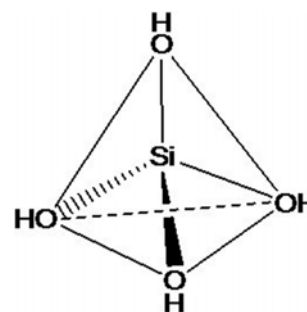


Fig. 4. Structure of the  $[\text{SiO}_4]$ .

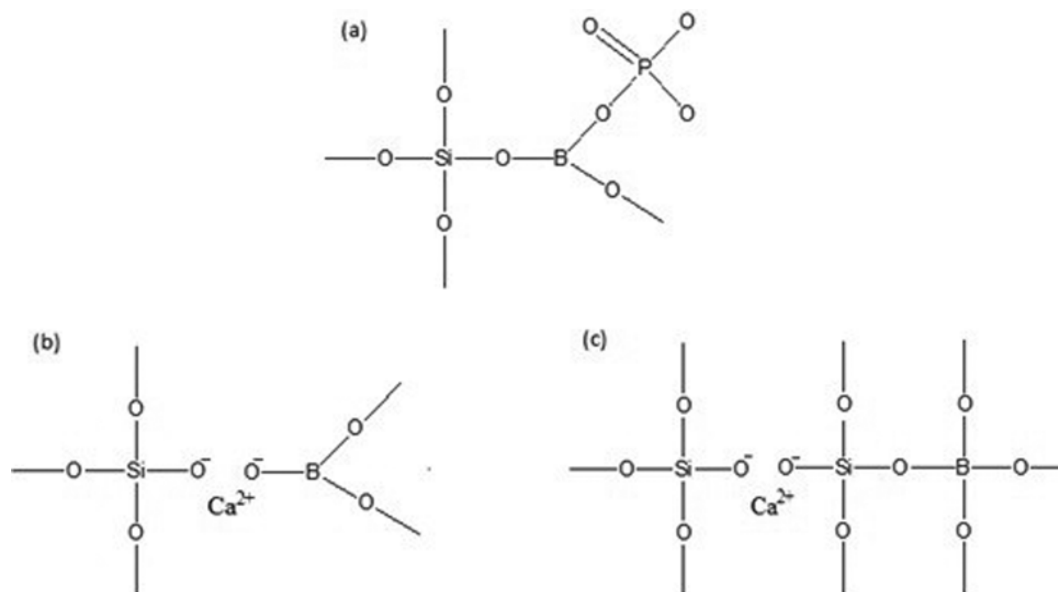


Fig. 5. Structural fragments proposed in alkali borosilicate glasses.

units, which have higher acidity than  $\text{SiO}_2$  units [42] since diborate units already contain two negatively charged  $\text{BO}_4$  units. On the other hand, the synergy between  $\text{B}_2\text{O}_3$  and  $\text{SiO}_2$  units is reported in  $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  systems [43]. This allows the estimation of a unit-like represented in Fig. 5(a). Neutral  $\text{SiO}_2$  units may react favorably with Ca to form the species in Fig. 5(c) or the high-entropy units illustrated in Fig. 5(b). The presence of species such as those in Fig. 5(b) or Fig. 5(c) is also supported by the  $^{29}\text{Si}$  MAS NMR spectra [44].

### 3. Effect of Partial Substitution of Silicon by Boron on the Thermal Properties

The  $\text{CaO}/\text{Na}_2\text{O}$  ratio was maintained equal to 1 ( $\text{CaO}=\text{Na}_2\text{O}=24$  mass%) in the alkali borosilicate glasses. DTA curves, at heating rate of  $5^\circ\text{C min}^{-1}$ , are shown in Fig. 6. All the curves present three characteristic peaks, respectively, for the glass transition, crystallization and fusion temperatures.

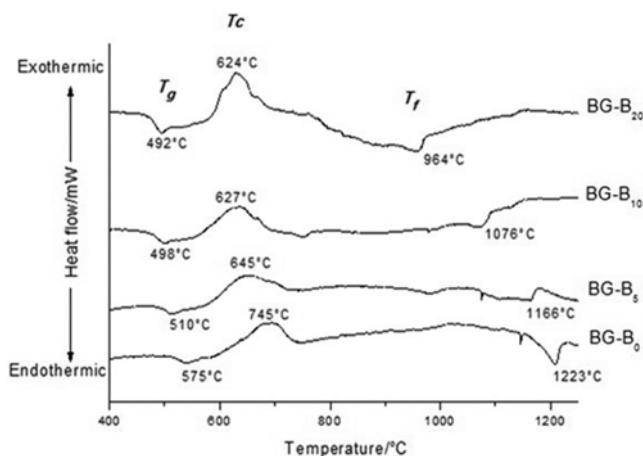


Fig. 6. Thermal curves of BG-B<sub>0</sub> and substituted glasses BG-B<sub>5</sub>, BG-B<sub>10</sub>, and BG-B<sub>20</sub>.

Knowledge of ionic mobility in glass has a great importance for a proper understanding of these metastable materials' comportment during thermal treatment. The thermodynamic characteristics of diffusion processes are related to the glass structure and chemical bonding. The nature of thermal conductivity in a multicomponent material depends on the type, number and mobility of charge carriers [45]. Characteristic temperature functions of  $\text{B}_2\text{O}_3$  content are presented in Fig. 7. It shows that when the amount of boron increases, the vitreous transition, crystallization and fusion temperatures decrease from 575 to 492 °C, from 745 to 624 °C and from 1,223 to 964 °C respectively. Consequently, TS increases from 42 to 90 °C as shown in Fig. 8. Therefore, the higher TS revealed, the lower tendency to crystallization [46].

To understand the three characteristic temperatures' decline and the heat transfer phenomenon between molecules of the glass network, we have to appeal to the diffusion mechanism proposed by

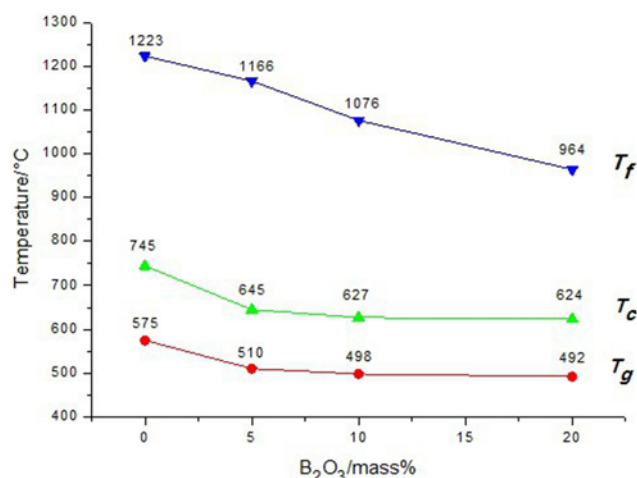


Fig. 7. Characteristic temperatures functions of the amount of  $\text{B}_2\text{O}_3$ .

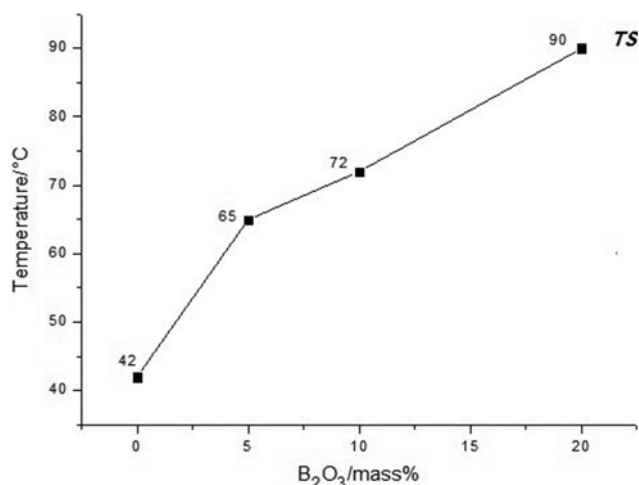


Fig. 8. Evolution of the thermal stability (TS) functions of the content of B<sub>2</sub>O<sub>3</sub>.

Souquet et al. [47] who assumes that, as for ionic crystals, Na<sup>+</sup> displacements occur by migration of interstitial pairs. In this model, when the cation leaves its 'normal position', this latter will occupy an 'interstitial position' and its previously occupied site will become a 'vacancy'. The concentration of B<sub>2</sub>O<sub>3</sub> introduced into the glass involves these defects' formation and increases the number of non-bridging oxygen. Consequently, cations move more easily and provide thermal conductivity. The formation of these pairs in the same non-bridging oxygen is thermally activated. In this context, the plane geometry of trivalent boron greatly facilitates the transfer of heat from the hot zone to the cold zone. This explains the rupture of intermolecular bonds of the network that leads to a decrease of the internal energy of the glass structure. On the other hand, the decrease of glass energy cohesion is understandable with the increase of boron content by the low contact area between a four-coordinated silicon and three-coordinated boron. This difference prevents the solubility of boron oxide in silica [45]. Fig. 9 shows the variation of the transition, crystallization and fusion temperatures versus B<sub>2</sub>O<sub>3</sub> content. The experimental data points form a straight line, as we observed. According to experimental results, we elabo-

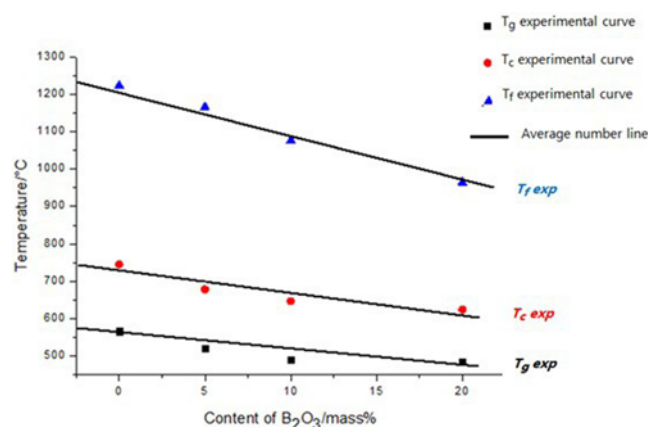


Fig. 9. Variation of the temperature functions of the content of B<sub>2</sub>O<sub>3</sub>.

rated mathematical relations between the temperatures characteristic of glasses and the content of B<sub>2</sub>O<sub>3</sub>.

$$T_g = 575 - 4.57 \cdot B_2O_3 \quad (4)$$

$$T_c = 746 - 5.79 \cdot B_2O_3 \quad (5)$$

$$T_f = 1229 - 11.69 \cdot B_2O_3 \quad (6)$$

B<sub>2</sub>O<sub>3</sub> amounts of introduced B<sub>2</sub>O<sub>3</sub> in glass.

B<sub>2</sub>O<sub>3</sub> is known to improve the hardness of silicate glasses. We demonstrate through this mathematical simulation that the more concentration of SiO<sub>2</sub> is substituted by B<sub>2</sub>O<sub>3</sub>, the more the three characteristic temperatures of glasses decrease.

## CONCLUSION

The X-ray diffraction of borosilicate glasses confirms the amorphous character of all glasses to 20% by weight of B<sub>2</sub>O<sub>3</sub> incorporated into the glass network. Moreover, substitution of silicon by boron is proved by infrared spectroscopy. The addition of boron oxide in the glass matrix involves several changes in the thermal characteristics. Vitreous transition, crystallization and melting temperatures decrease when the amount of boron oxide increases. The introduction of B<sub>2</sub>O<sub>3</sub> increases the thermal stability of the glass. These thermodynamic phenomena are explained by the structural approach of the bioactive glasses. This highlights the heat supply mechanism in the borosilicate network. Furthermore, changes in the thermal behavior of glasses have an impact on their chemical reactivity.

At the contact with the simulated body fluid solution (SBF), the kinetic of the bioactivity could be changed according to the content of doping elements. It is our task in perspective to adapt it to bone metabolism which differs from one patient to another.

## REFERENCES

1. L. L. Hench, *J. Am. Ceram. Soc.*, **74**, 1487 (1991).
2. L. L. Hench, *J. Mater. Sci.*, **17**, 967 (2006).
3. S. Jebahi, R. Nsiri, M. Boujbiha, E. Bouroga, T. Rebai, H. Keskes, A. ElFeki, H. Oudadesse and H. ElFeki, *Eur. J. Orthop. Surg. Traumatol.*, **23**, 759 (2013).
4. J. R. Jones, *Acta Biomater.*, **9**, 4457 (2013).
5. A. Hoppe, N. S. Güldal and A. R. Boccaccini, *Biomater.*, **32**, 2757 (2011).
6. G. J. Mohini, N. Krishnamacharyulu, G. S. Baskaran, P. V. Raoc and N. Veeraiah, *Appl. Surf. Sci.*, **287**, 46 (2013).
7. X. Yang, L. Zhang, X. Chen, X. Sun, G. Yang, X. Guo, H. Yang, C. Gao and Z. Gou, *J. Non-Cryst. Solids.*, **358**, 1171 (2012).
8. A. Saranti, I. Koutselas and M. A. Karakassides, *J. Non-Cryst. Solids.*, **352**, 390 (2006).
9. R. F. Brown, M. N. Rahaman, A. B. Dwilewicz, W. Huang, D. E. Day and Y. Li, *J. Biomed Mater. Res.*, **88**, 392 (2009).
10. G. Kaur, O. P. Pandey, K. Singh, D. Homa, B. Scott and G. Pickrell, *J. Biomed. Mater. Res. Part A*, **102**, 254 (2014).
11. H. Fu, Q. Fu, N. Zhou, W. Huang, M. N. Rahaman, D. Wang and L. Xin, *Mater. Sci. Eng.*, **29**, 2275 (2009).
12. M. D. Gadet, R. M. Nzietchueng, K. Hess, P. Nabet, F. Belleville

- and B. Dousset, *Biol. Trace Elem. Res.*, **85**, 23 (2002).
13. S. S. Hakki, B. S. Bozkurt and E. E. Hakki, *J. Trace Elem. Med. Bio.*, **24**, 243 (2010).
14. F. J. Torres and J. Alarcon, *J. Non-Cryst. Solids*, **34**, 45 (2004).
15. J. H. Lee, C. K. Lee, B. S. Chang, H. S. Ryu, J. H. Seo, K. S. Hong and H. Kim, *J. Biomed. Mater. Res. A*, **77**, 362 (2006).
16. M. N. Rahaman, D. E. Day, B. S. Bal, Q. Fuc, S. B. Jung, L. F. Bonewald and A. P. Tomsia, *Acta Biomater.*, **7**, 2355 (2011).
17. S. Agathopoulos, D. U. Tulyaganov, J. M. G. Ventura, S. Kannan, A. Saranti, M. A. Karakassides and J. M. F. Ferreira, *J. Non-Cryst. Solids*, **352**, 322 (2006).
18. E. Wers and H. Oudadesse, *J. Therm. Anal. Calorim.*, **115**, 2137 (2014).
19. L. Linati, G. Lusvardi, G. Malavasi, L. Menabue, MC. Menziani and P. Mustarelli, *J. Phys. Chem. B.*, **109**, 4989 (2005).
20. B. Raguene, Thèse. Université de Montpellier II, **170** (2011).
21. E. Wers, H. Oudadesse, B. Lefeuvre, B. Bureau and O. Merdri-gnac-Conanec, *Thermo. Acta*, **580**, 79 (2014).
22. A. L. Giro, F. Z. Mezahi, M. Mami, H. Oudadesse, A. Harabi and M. Le Floch, *J. Non-Cryst. Solids*, **357**, 3322 (2011).
23. W. Huang, D. E. Day, K. Kittiratanapiboon and M. N. Rahaman, *J. Mater. Sci.-Mater. M.*, **17**, 583 (2006).
24. L. L. Hench, R. J. Splinter, W. C. Allen and T. K. Greenlee, *J. Biomed. Mater. Res.*, **36**, 117 (1971).
25. V. Kumar, S. Sharma, O. P. Pandey and K. Singh, *Solid State Ionics*, **181**, 79 (2010).
26. W. Jastrzebski, M. Sitarz, M. Rokita and K. Bulat, *Spectrochim. Acta*, **79**, 722 (2011).
27. E. I. Kamitsos, A. P. Patsis, M. A. Karakassides and G. D. Chrys-sikos, *J. Non-Cryst. Solids*, **126**, 52 (1990).
28. M. Sitarz, *J. Non-Cryst. Solids*, **357**, 1603 (2011).
29. M. Sitarz, K. Bulat and Z. Olejniczak, *Vib. Spectrosc.*, **61**, 72 (2012).
30. T. Yano, N. Kunimine, S. Shibata and M. Yamane, *J. Non-Cryst. Solids*, **321**, 137 (2003).
31. J. Zhong and P. J. Bray, *J. Non-Cryst. Solids*, **87**, 226 (1986).
32. J. Barton and C. Guillemet, *Le verre: science et technologie*, Les Ulis: EDP Sciences (2004).
33. G. L. Flower, M. S. Reddy, M. V. R. Reddy and N. Veeraiah, *A: Phys. Sci.*, **62**, 315 (2014).
34. T. Furukawa and W. B. White, *J. Am. Ceram. Soc.*, **64**, 443 (1981).
35. P. Richet, T. Atake and I. Yamashita, *J. Non-Cryst. Solids*, **352**, 3854 (2006).
36. M. A. Azooz, T. H. M. AbouAiad, F. H. El Batal and G. El Tabii, *Indian. J. Pure. Ap. Phy.*, **46**, 880 (2008).
37. P. J. Bray, Proceedings of the second international Conference on Borate Glasses, Crystals and Melts 1-20 (1997).
38. J. E. Shelby, *Royal Society of Chemistry*, **91**, 108 (1997).
39. K. J. Rao, Structural Chemistry of Glasses, 1<sup>st</sup> Ed., Elsevier Science, Amsterdam (2002).
40. M. S. Reddy, G. N. Raju, G. Nagarjuna and N. Veeraiah, *J. Alloy. Compd.*, **438**, 41 (2007).
41. J. Krogh-Moe, *Phys. Chem. Glasses-B*, **6**, 46 (1965).
42. K. Asai and T. Yokokawa, *Trans. JIM*, **9**, 571 (1982).
43. S. K. Lee and J. F. Stebbins, *Geochim. Cosmochim. Acta*, **66**, 303 (2002).
44. H. Miyoshi, D. Chen, H. Masuia, T. Yazawa and T. Akai, *J. Non-Cryst. Solids*, **345/346**, 99 (2004).
45. A. Grandjean, M. Malki and C. Simonnet, *J. Non-Cryst. Solids*, **352**, 2731 (2006).
46. I. Bardez. Thèse. Université Pierre et Marie Curie, Paris IV. Serial number D-11, 71-77 (2004).
47. J. L. Souquet, M. Duclot and M. Levy, *Solid. State. Ionics*, **105**, 237 (1998).