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THERMODYNAMICS OF NON-BRIDGING OXYGEN IN SILICA BIO-COMPATIBLE GLASS-CERAMICS

Mimetic material for the bone tissue substitution

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Abstract

Correlations between the structural properties of Na_2O–CaO–SiO_2 glasses characterized by the activity of oxygen ions and the bioactivity were examined by comparing the compositional dependence of the structural parameters calculated on the basis of a thermodynamic consideration with that of the bioactivity. A simple model of characterizing the glass structure by considering the bridging and non-bridging oxygen ions was employed as the first step for this purpose. Further detailed thermodynamic analysis on the anionic constitution in the glass was performed and the compositional dependences of the relative proportions of bridging, non-bridging and free oxygen ions were calculated. The bioactive region corresponded to the compositional region characterized by the higher relative proportion of non-bridging oxygen ions with co-existing an appreciable concentration of bridging oxygen ions, suggesting a possible important role of the non-bridging oxygen ions on the surface chemical process of bone-like apatite layer formation.

Kevwords: bio-compatible, bone-like apatite, glass-ceramics, mimetic material, thermodynamics

Introduction

Degeneration of a human skeletal system in time results in dysfunction of bones, teeth and joints. Extensive bone defects, left after the removal of tumors, infections or as a result of injuries, are ideally replaced by autogenous bone tissue. As the amount of this material for the patient is limited and the use of allogenic bone is accompanied by biological, mechanical and also sociological difficulties, there is a great need for alternate non-human synthetic sources.

Merely four decades ago it was considered inconceivable that a man-made material could bond to living tissues in view of the deep-rooted experience that it would result in a

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foreign body reaction and the formation of non-adherent scar tissue at the interface with inserted material. This understanding was irreversibly altered when a special composition of soda-lime-phosphate-silica glass was synthesized by Hench [1] and successfully implanted in the femurs of rats. About 6% of P_2O_5 was added to simulate the Ca/P constituents of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, that is the inorganic mineral phase naturally existing in bones. Therefore the bone-like apatite formation on the surface of implant is of a key importance during the physical and chemical processes leading to the formation of an enough firm connection between the implanted material and the newly formed bone tissue [2–6]. The bioactivity leads to both the osteoconduction and osteoproduction as a consequence of rapid reaction on the bioactive glass surface. The surface reactions [7–16] involve ionic dissolution of calcium and sodium ions, phosphates and hydrated silica that give rise to both the intercellular and extracellular responses at the interfaces of the glass with its physiological environment. The smartness of such a mimetic process is likely hidden in the activity of oxygen characterized by the action of silanole groups (Si–OH). They likely serve as the nucleation sites for the bio-compatible interface formation capable to coexist between the original tissue and the implants which can be expediently made from glass, glass-ceramics, ceramics, cements and other composites as well as from certainly treated metals (etched titanium) respecting the set-in condition of its suitable surface reactivity.

We have taken part in the research progress of bioactive materials since early eighties [17–22]. This matured in their actual appliance in practical implantology under the trademark IMPLADENT- (a system for oral implantology produced by LASAK, Co. Ltd) and BAS-O, BAS-HA, BAS-R-bioactive bone tissue substitutes [23]. Figure 1 illustrates the bone-bonding ability of BAS-O which is based on inorganic, polycrystalline material prepared by controlled crystallization of glass, whose main components are CaO, P_2O_5, SiO_2 and MgO. During the crystallization process, the glassy material is converted to a glass-ceramic material whose main crystalline phases are apatite and wollastonite. BAS-O granules and ground material are used to fill cysts, defects left by injuries, defects left by excochleation of benign tumors, and can be of help to reconstruct extensive acetabular defects. Compact, wedge-shaped blocks (with various heights and surfaces) became useful for, e.g., condyl elevation. Individually shaped implants can be used in neurosurgery to cover defects left from cranial trepanation and as onlays in plastic surgery. In Fig. 2, there is revealed another case of biomaterial BAS-HA (hydroxyapatite) which is synthesized from aqueous solutions under precisely defined pH, temperature and other physical parameters, which ensure reproducible preparation of a highly pure, crystallographically defined product, which does not contain any unwanted calcium phosphates. Its structure and composition are similar to bio-apatite, which is the main inorganic component of living bone tissue. Implants form a strong bond between the bone tissue and the implant material without any intermediate fibrous layer. Final product is the BAS-R, which is the surface bioactive, resorbable, inorganic, crystalline material based on tricalcium phosphate.

Bioactivity has since attracted increased attention being aimed to further molecular manipulation (doping surfactants, micro-additives of various organic molecules such as proteins, glyco-proteins and polysaccharides, useful in easier mine-realization) which in-

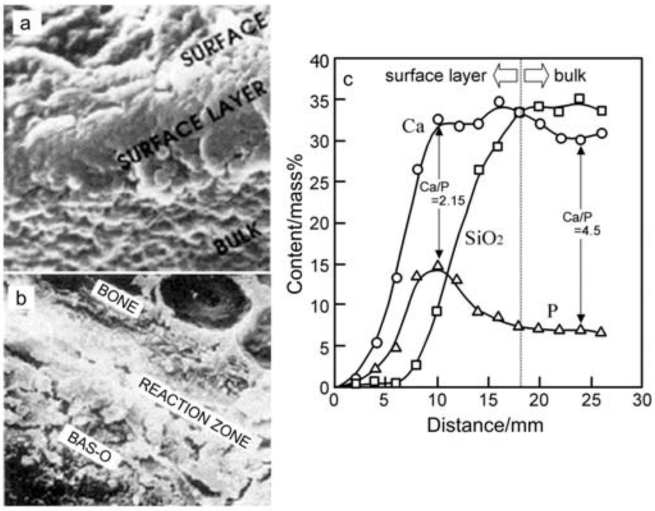

Fig. 1 Surface layer formed on a BAS-O implant after exposure in a simulated body fluid for 28 days (a) and the cross section of the actual body implant (c): a – View of the surface layer formed on the BAS-O material after exposure in SBF (SEM 1000×, fracture), b – Content of elements (P, Ca and SiO_2) in the surface layer, and c – Detail of the interface of the bone tissue with a BAS-O implant 6 months after implantation (SEM 1200×)

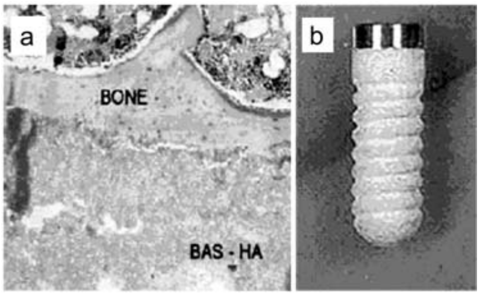

Fig. 2 a – Direct contact between the BAS-HA implant and bone tissue, 2 months after implantation. BAS-HA material is a very dense ceramics with apparent porosity of 1.7%. The Ca/P molar ratio is 1.66. The material exhibits a bending strength of 60 MPa and compression strength of 200 MPa. The strength of the junction with the bone tissue measured by the push-out test (shear stress) is equal to 19 MPa (two months after implantation) and 29 MPa (4 months after implantation). b – Dental implant ('Impladent') with hydroxyapatite coating

telligent response by host organism is evaluated in order to achieve well-tailored implants. Bio-glass-ceramics that activate genes offer the possibilities of repairing, or perhaps even preventing, many disease states, such as osteoporosis, in which a large fraction of women lose a substantial amount of bone mass as they age. They can be also used as a second phase in a composite that mimics the structure and properties of bone. In future the implication of glass activation of genes it may be possible to design therapeutic treatments or food additives that will inhibit the deterioration of connective tissues with age. Further understanding bioactivity may even help in better perception of the creation of life [24–26]. It shows a great variability in the application of different glasses and amorphous materials in many fields of human activities [23, 27–31].

Structural parameters of the soda-lime-silica glasses and bioactivity

It is generally accepted that the bioactivity of glass and glass-ceramics is closely connected with the surface chemical reactions of formation of a bone-like apatite layer that bonds to the bone [2–6]. Very important is systematic understanding on mechanisms and kinetics of the reactions that occur at the surface of glassy implants of silica-specialized composition. The early stages of the bone-like apatite formation on a surface of bioactive glass have been studied systematically [7–16] and summarized as follows [16]. The alkali ions in the bioactive glass are rapidly exchanged by hydrogen ions in the surrounding solution, e.g., body or simulated body fluids (SBF), and the network dissolution rapidly reduce the amount of the Si–O–Si and Si–O–Ca modes and replace them with Si–OH bonds at the glass-solution interface. Single non-bridging oxygen modes of Si–OH are then gradually replaced by more spherical OH–Si–OH and the condensation and repolymerization of a SiO_2-rich layer take place on the surface. An amorphous $CaO–P_2O_5$-rich film is produced on the top of the SiO_2-rich layer by incorporating soluble calcium and phosphate from solution. The characteristic double layer composed of a SiO_2-rich layer and a mixed crystalline layer of hydroxy carbonate apatite and/or hydroxyl fluorapatite results from the crystallization of the amorphous $CaO–P_2O_5$-rich film by incorporating OH^-, CO_3^{2-}, or F^- anions from the surrounding solution.

The rates of consecutive and/or concurrent chemical processes of bone-like apatite formation on the glass surface depend largely on the composition of glass or glass-ceramics and on the associated physico-chemical properties of these materials such as solubility, volumetric ratios of glass phase and so on [7–16]. An evaluation of the correlation of the bioactivity with the structure of glasses is thus of interest, as have been the cases of the compositional dependence of all physico-chemical properties of glass, such as viscosity, electrical properties, immiscibility, glass formation region, nucleation, crystallization, phase separation, and so on [23, 27, 28, 32–40]. The constitution of bridging and non-bridging oxygen ions in glasses [23] is one of the most frequently used concept for characterizing the glass structure. Various physico-chemical properties have been correlated to the chemical composition in view of the thermodynamic state of oxygen ions. Although there are various different theories on evaluating the constitution of bridging and non-bridging oxygen ions in glasses [41–45], earlier we evaluated the state of oxygen ions in an iron-rich borate glasses [46] according to the model proposed by Toop and Samis [42]. In the present case of bioactivity, the state of oxygen ions is also likely important in relation to the chemical processes of the early stage of the bone-like apatite formation, especially in the dissolution process of Si–O–Si mode with bridging oxygen and intermediate formation of Si–OH with non-bridging oxygen. Previously, one of the present authors was evaluated the correlation of the bioactivity of $Na_2O–CaO–SiO_2–P_2O_5$ and $CaO–MgO–SiO_2–P_2O_5$ glass-ceramic systems with the structural parameter related to the bridging oxygen [17] using the Stevels model [41].

The Stevels's parameters [17, 41], i.e., X and Y, can be correlated to the mean number of non-bridging (O^-) and bridging (O^o) oxygen ions per polyhedron in the glass lattice, respectively, and calculated from the molar composition of glass according to the following equations.

$$X=2R-Z$$

$$Y=2Z-2R$$

where Z is the mean number of all types of oxygen ions per polyhedron, i.e., the mean coordination number of the glass-forming cations and R is the ratio of the total number of oxygen ions to the total number of glass-forming cations in glass. The parameters (X, Y) vary from (0, 4) for, e.g., the pure silica glass, to (1, 3) for, e.g., $Na_2O·2SiO_2$ glass, and to (2, 2) for, e.g., $CaO·Na_2O·2SiO_2$ glass. When $X>2$ and $Y<2$, the glasses are called as invert glasses. Having the same values of (X, Y), these glasses are characterized as structurally similar.

In the previous work on the $Na_2O–CaO–SiO_2–P_2O_5$ and $CaO–MgO–SiO_2–P_2O_5$ glass-ceramic systems [17], the bioactivities of these systems evaluated by in vitro test of mutual bonding after soaking in SBF and by in vivo test of implantation in dog tibia were correlated to one of the Stevels's parameter Y, i.e., mean number of bridging oxygen ions. It was found that the Y value of the residual glass phase in the glass-ceramic system to be close to 2 is the suitable condition for the higher bioactivity. When $Y>3$, the glass loses its bioactivity.

In the present study, the attention was turned to the non-bridging oxygen ions in the glass as expressed by the Stevels's parameter X. In order to correlate the structural parameter X of a glass with its bioactivity, we focused on an empirical index of bioactivity, I_B, introduced by Hench [47] as $I_B=100/t_{0.5bb}$, where $t_{0.5bb}$ is the time for more than 50% of the implant interface to be bonded to bone. The compositional dependence of I_B in the $Na_2O–CaO–SiO_2$ system containing 6 mass% P_2O_5 has been clearly represented by Hench [2, 16, 47, 48] and employed usefully to discuss the bioactivity of the glass with a certain composition. By reading the values of I_B at various typical points of glass composition from the reported Iso I_B plots in the $Na_2O–CaO–SiO_2$ ternary system [2, 16, 47, 48], we calculated the structural parameters (X, Y) from the molar composition and relations of these structural parameters and the value of I_B were examined. Figure 3 shows the correlation between the calculated structural parameter X and the value of I_B for the $Na_2O–CaO–SiO_2$ ternary system containing 6 mass% P_2O_5. When $X<1.5$ ($Y>2.5$), the glass looses its bioactivity and bioactivity index, I_B~0. The value of $X>1.5$ (and $Y<2.5$) indicates the range of bioactive glasses, $I_B>0$. Essentially a linear dependence with negative intercept has been found between the mean number of non-bridging oxygen ions and bioactivity index.

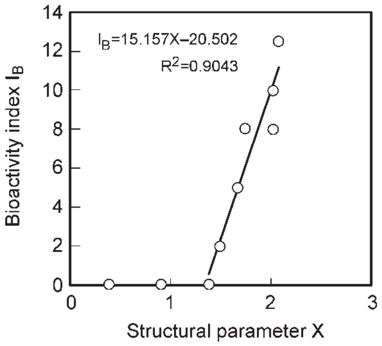

Fig. 3 Bioactive index I_B as a function of mean number of non-bridging oxygen ions X, calculated using the data of compositional dependence of I_B in the soda-lime-silica system containing 6 mass% P_2O_5 reported by Hench [2, 16, 47, 48]

Anionic constitution in the soda-lime-silica glass-forming melts and bioactivity

Since the Stevels model considers only non-bridging and bridging oxygen ions, it cannot hold in the more basic regime (X>>2) where free oxygen ions reach an appreciable concentration. Therefore, after Fincham and Richardson [49], one can propose the dominant reaction in the formation of silicate solution (glass): $O^o+O^{2-}=2O^-$ where O^{2-} refers to the free oxygen ions. The compositional dependence of relative proportion of non-bridging oxygen ions $[O^-]$ in the soda-lime-silica system has been also calculated applying methods currently used in the chemistry of organic polymers.

According to Masson [43–45], the following assumptions were applied to derive the anionic distribution in M_2O–SiO_2 or MO–SiO_2 glass forming melts:

1) The silicate ions are presented exclusively as linear and branched chains of general formula: $Si_xO_{3x+1}^{(2x+2)-}$. These species may arise by the poly-condensation reactions expressed generally according to the following equation:

$$Si_xO_{3x+1}^{(2x+2)-}+Si_yO_{3y+1}^{(2y+2)-}=Si_{x+y}O_{3(x+y)+1}^{(2x+2y+2)-}+O^{2-} \tag{1}$$

2) The equilibrium constant k_{xy} of Eq. (1) can be approximated using that for the lowest k-members k_{11}, i.e., x=1 and y=1.

3) The Eq. (1) may be written in a more general form:

$$2O^-= O^o+ O^{2-} \tag{2}$$

where O^-, O^o and O^{2-} are the non-bridging oxygen, bridging oxygen and free oxygen ions, respectively.

4) According to the Temkin's equation [50], the activity of M_2O or MO oxides in the M_2O–SiO_2 or MO–SiO_2 binary melt a_{MO} is equated to the ion fraction of free oxide ion $N_{O^{2-}}$.

$$a_{\mathrm{MO}}=N_{\mathrm{O}^{2-}} \tag{3}$$

5) For linear and branched chains, the a_{MO} has the following relation with respect to the mole fraction of $\mathrm{SiO_2}$, i.e., for $X_{\mathrm{SiO_2}}$ it follows

$$\frac{1}{X_{\mathrm{SiO_2}}}=2+\frac{1}{1-a_{\mathrm{MO}}}-\frac{3}{1+a_{\mathrm{MO}}\left(\frac{3}{k_{11}}-1\right)} \tag{4}$$

6) Knowing the value of k_{11} for the binary system $\mathrm{M_2O{-}SiO_2}$ or $\mathrm{MO{-}SiO_2}$, the ion fraction N_{x} of any silicate ion $\mathrm{Si_xO_{3x+1}^{(2x+2)-}}$ is given by the following equation:

$$N_{\mathrm{x}}=\frac{(3x)!}{(2x+1)!x!}\left[\frac{1}{1+\frac{3a_{\mathrm{MO}}}{k_{11}(1-a_{\mathrm{MO}})}}\right]^{\mathrm{x}-1}\left[\frac{1}{1+\frac{k_{11}(1-a_{\mathrm{MO}})}{3a_{\mathrm{MO}}}}\right]^{2\mathrm{x}+1}(1-a_{\mathrm{MO}}) \tag{5}$$

7) The ion fraction of non-bridging oxide N_{O^-} in Eq. (2) is approximated by the summation of N_{x} using x up to 50.

$$N_{\mathrm{O}^-}=\sum_{\mathrm{x}=1}^{50}N_{\mathrm{x}} \tag{6}$$

8) The ion fraction of bridging oxide $N_{\mathrm{O}^{\circ}}$ is then obtained by

$$N_{\mathrm{O}^{\circ}}=1-N_{\mathrm{O}^{2-}}-N_{\mathrm{O}^-} \tag{7}$$

Taking the literature values for k_{11}=$1.6\cdot10^{-3}$ and =$8\cdot10^{-8}$ for $\mathrm{CaO{-}SiO_2}$ and $\mathrm{Na_2O{-}SiO_2}$ binary melts [51], respectively, the $X_{\mathrm{SiO_2}}$ dependence of a_{MO} can be calculated according to Eq. (4). Figure 4 shows the compositional dependence of a_{MO} for $\mathrm{CaO{-}SiO_2}$ and $\mathrm{Na_2O{-}SiO_2}$ systems. The ion fraction N_{x} is obtained according to Eq. (5). The calculated ion fractions N_{x} for $\mathrm{CaO{-}SiO_2}$ and $\mathrm{Na_2O{-}SiO_2}$ binary melts are represented in Fig. 5 as a function of mass fraction of $\mathrm{SiO_2}$. Using the compositional dependences of the activity of oxides, i.e., $N_{\mathrm{O}^{2-}}$, shown in Fig. 4 and the relative propor-

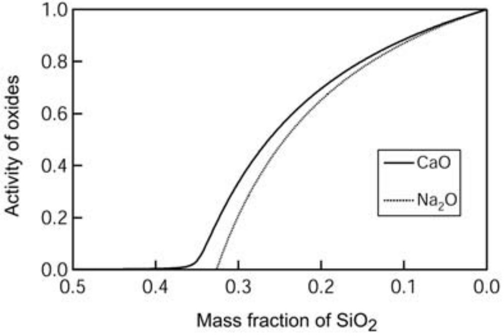

Fig. 4 The dependence of activity of sodium and calcium oxides, a_{MO}, on the mass fraction of $\mathrm{SiO_2}$ in the binary $\mathrm{CaO{-}SiO_2}$ and $\mathrm{Na_2O{-}SiO_2}$ systems

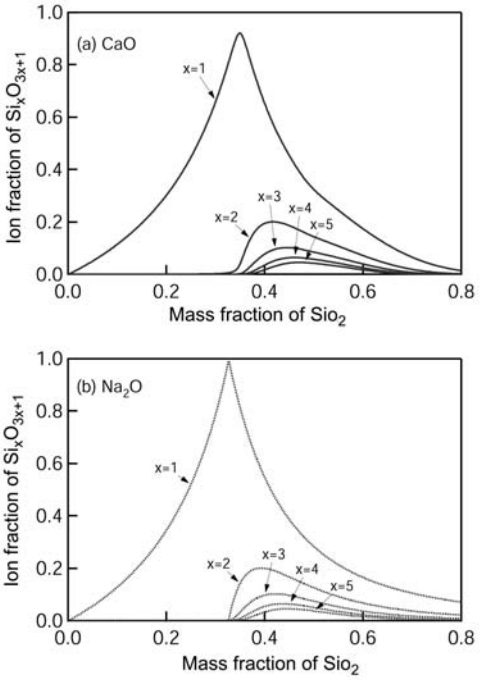

Fig. 5 The dependence of ion fraction N_x of silicate ions $Si_xO_{3x+1}^{(2x+2)-}$ on the mass of SiO_2 in the binary a – $CaO–SiO_2$ and b – $Na_2O–SiO_2$ systems

tions of O^- obtained by summing up N_x from x=1 to 50, the relative fraction of bridging oxygen ions N_{O^o} at a mass fraction of SiO_2 was calculated according to Eq. (7). Figure 6 shows the compositional dependences of the relative fractions of O^o, O^- and O^{2-} in the binary $CaO–SiO_2$ and $Na_2O–SiO_2$ systems. According to the conventional pseudo-binary assumption [52], the compositional dependence of the relative proportion of O^- in $Na_2O–CaO–SiO_2$ ternary melts was obtained using the values for the binary melts shown in Fig. 6. The compositional dependence (in mass fraction) of the calculated relative proportion of O^- in the $Na_2O–CaO–SiO_2$ ternary melts is shown in Fig. 7. These findings were compared with the compositional dependence of I_B for the system containing

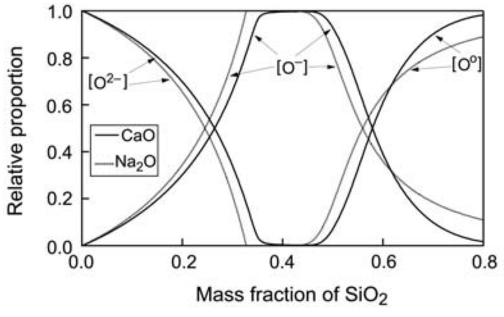

Fig. 6 The relative proportions of non-bridging oxygen ions O^-, bridging oxygen ions O^o and free oxygen ions O^{2-} in the binary a – $CaO–SiO_2$ and b – $Na_2O–SiO_2$ systems, calculated *vs*. the mass fraction of SiO_2 using the relations in Eqs (3), (6) and (7)

6 mass% P_2O_5 [2, 16, 47, 48]. The region of the remarkable high bioactivity I_B>8 can be observed in the compositional region characterized by the higher relative proportion of non-bridging oxygen ions >0.8 in the side of SiO_2-rich composition where an appreciable concentration of bridging oxygen ions exist, Fig. 7.

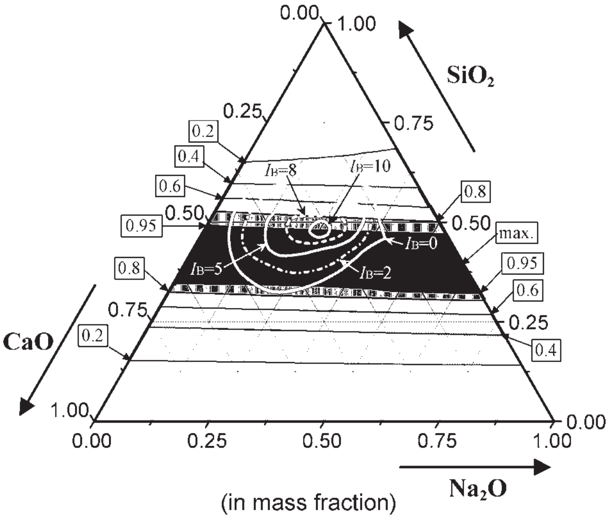

Fig. 7 A comparison of the relative proportion of non-bridging oxygen ions O^- in the Na_2O–CaO–SiO_2 ternary system calculated in the present study with the Iso I_B plots for the system with 6 mass% P_2O_5 reported by Hench [2, 16, 47, 48]

The ability to form the bone-like apatite layer after soaking P_2O_5-free Na_2O–CaO–SiO_2 glasses in SBF has been investigated experimentally by Kim *et al.* [53]. It was shown that the compositional region of the apatite layer formation on the surface of the P_2O_5-free Na_2O–CaO–SiO_2 glasses corresponds closely to the region of I_B>0 for the Na_2O–CaO–SiO_2 glasses containing 6 mass% P_2O_5. It was also pointed out that the rates of apatite formation of P_2O_5-containing Bioglass 45S5-type and a corresponding P_2O_5-free Na_2O–CaO–SiO_2 glass are comparable. Those findings indicate that the bioactivity of the glass characterized by the bone-like apatite formation depends largely on the properties of the basic P_2O_5-free Na_2O–CaO–SiO_2 ternary glass. From the present results, it is predicted that a close connection exists between the structural property of the glass characterized by the activity of oxygen ions and its bioactivity. The special notice is concerning the proportion of non-bridging oxygen ions in the glasses, where the region of remarkable high bioactivity is observed for the compositional region with the higher relative proportion of non-bridging oxygen ions >0.8, indicating a possible important role of the non-bridging oxygen ions during the course of the surface chemical processes of bone-like apatite layer formation.

Conclusions

A close correlation between the structural properties of the Na_2O–CaO–SiO_2 glasses and its bioactivity was found. Using the structural parameters X and Y related, respectively, to the mean number of non-bridging and bridging oxygen ions, the bioactive region can be correlated to the structural parameters $X > 1.5$ and $Y < 2.5$. Further detailed analysis of the anionic constitution in the glass system indicated that the remarkable high bioactive region is seen in the compositional region of higher relative proportion of non-bridging oxygen ions with co-existing an appreciable concentration of bridging oxygen ions and no significant free oxygen ions.

The structural correlations of the bioactivity shown in the present study can be used as a useful tool for designing the bioactive glass and for tailoring bioactive glass-ceramics and composites with a glass-ceramic matrix. At the same time, a possible important role of the non-bridging oxygen ions on the surface chemical processes of the bone-like apatite layer formation is expected from the close correlation of the relative proportion with the bioactivity.

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