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Effect of bioglass additions on the sintering of Y-TZP bioceramics

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ABSTRACT

The objective of this work was to evaluate the influence of bioglass additions on the sintering and mechanical properties of yttria-stabilized zirconia ceramics, Y-TZP. Samples containing different bioglass additions, varying between 0 and 30 wt.%, were cold uniaxial pressed at 80 MPa and sintered in air at 1200 °C or 1300 °C for 120 min. Sintered samples were characterized by X-ray Diffractometry and Scanning Electron Microscopy. Hardness and fracture toughness were determined using Vickers indentation method. As a preliminary biological evaluation, *in vitro* cytotoxicity tests by Neutral Red Uptake method (using mouse connective tissue cells, NCTC clone L929 from ATCC bank) were realized to determine the cytotoxicity level of ZrO_2-bioglass ceramics. The increasing of bioglass amount leads to the decreasing of relative density due to martensitic (tetragonal-monoclinic) transformation during cooling of the sintered samples. Y-TZP samples sintered at 1300 °C containing 5 wt.% of bioglass presented the best results, with high relative density, hardness and fracture toughness of 11.3 GPa and 6.1 MPa $m^{1/2}$, respectively. Furthermore, the un-cytotoxic behavior was observed in all sintering conditions and bioglass amounts used in this study.

1. Introduction

The metal-alloys have been currently used as crown or abutment materials in osseo-integrated implant fixtures like dental prostheses. The material must be compatible and must not promote plaque adherence, besides providing enough strength to endure and transmit occlusal forces to the implant, supporting the bone. Another significant factor is aesthetics, in order to replicate the visible aspect of the natural tooth. All these properties are necessary to fulfill intra-oral applications [1–3].

Within the last years, an important improvement in implant systems has been possible by the use of *all-ceramic* systems, which are attractive to the dental community because they provide higher strength and abrasion resistance, better biocompatibility and aesthetics, when compared with metal and resin restorations [2,4]. On the other hand, the applications of all-ceramic crowns and bridges have been limited by their brittle behaviour, long processing time and shrinkage problems related to the CAD/CAM machining, with necessary final sintering at high temperatures between 1500 °C and 1600 °C [5–8].

Tetragonal zirconia polycrystals (TZP) with 3 mol% of Y_2O_3 (3Y-TZP) are usually manufactured by solid-state sintering at temperatures around 1500–1600 °C [9]. However, it is an expensive fabrication method and inevitably increases the production cost, limiting its use. To decrease the sintering temperature and so the production costs, additives are deliberately introduced. Recently, studies have been reported in the literature concerning the effects of additives on sintering and mechanical properties, such as CAS-, LAS-, lanthanum oxide-glass or bioglasses [10–14].

Different techniques have been used to obtain dental-ceramic parts, among them CAD/CAM machining of ceramic blocks or glass-infiltration in porous ceramic matrix are currently the most used. Table 1 shows the mechanical properties of some commercial dental ceramics [15], in which it can be observed that the low fracture toughness of the glass-infiltrated ceramics and feldspar- or lithium disilicate-based ceramics and toughened-ZrO_2 that presents necessity of post-sintering at 1500 °C and rigorous shrinkage control between machining and sintering.

It is common knowledge that ZrO_2 additions may increase the fracture toughness of ceramic materials. This effect is based on the *tetragonal-monoclinic* ZrO_2-phase transformation, which occurs during the crack growing and generates a bulk-expansion between 3 vol.% and 6 vol.% [9]. This phase transformation generates a stress field around matrix-grains, which is difficult in the crack propagation and increases the fracture toughness. The possibility of union of mechanical and biological properties of the 3CaO P_2O_5–SiO_2–MgO bioglass system [16] beyond its thermal compatibility with the properties of the tetragonal ZrO_2, may reduce the hardness and allow the machining of this material with final dimension. As a consequence this material will be sintered at low temperatures, reducing the production costs and allowing the increase of its application field, especially as a dental material.

In vitro tests may not represent the real situation of an implant. However, they can provide fast results regarding the material's

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Table 1
Some properties of the ceramics used as dental material [15].

Material	Vickers hardness (GPa)	Fracture toughness (Mpa $m^{1/2}$)
Porcelain aluminized	4.3	2.0–2.9
Ceramized glass reinforced with leucite	6.5	1.0–2.0
Ceramized glass reinforced with lithium disilicate	6.7	3.4
Glass infiltrated-spinel	10	2.7
Glass infiltrated-alumina	13	4.4–4.8
Glass infiltrated-alumina-zirconia	11	6.8
Alumina	16	3.8–4.5
Yttria stabilized zirconia ceramics	13	9–10

interactions in biological media, thus helping to minimize testing on animals. *In vitro* tests have been used to evaluate the biocompatibility of materials for over two decades and they are widely used today due to the easy availability of cell strains on the market. Moreover, there is a wide range of repeatable and reproducible methods, which are regulated by national and international standards for commercial use and for the scientific development of new materials and products. In this study the cytotoxicity test will be used based on the Neutral Red Uptake method using mouse connective tissue cells, NCTC clone L929 from ATCC bank.

In this work, the influence of the 3CaO P_2O_5–SiO_2–MgO bioglass addition on the sinterability and mechanical properties of ZrO_2–(Y_2O_3) ceramics were investigated, aiming the development of ceramics for bio-applications as dental materials. A preliminary biological evaluation to determine the cytotoxicity level of ZrO_2-bioglass ceramic was also realized.

2. Experimental procedure

2.1. Processing

High-purity Y-TZP commercial 3 mol%Y_2O_3–ZrO_2 powder (Tosoh inc. Japan) and bioactive 3CaO P_2O_5–SiO_2–MgO bioglass powder were used as starting powders.

The bioglass was obtained using $Ca(H_2PO_4)_2H_2O$, $CaCO_3$, SiO_2 and MgO reagent graded. The glass composition is based on 52.75 wt.% of 3CaO P_2O_5, 30 wt.% of SiO_2 and 17.25 wt.% of MgO. The bioactivity of this composition was studied by Oliveira et al. [16,17]. $Ca(H_2PO_4)_2H_2O$, $CaCO_3$, SiO_2 and MgO powders were mixed/homogenized thoroughly, pre-calcined and then melted in Pt-crucible at 1550 °C for 2 h. The glass was obtained after quenching in cold distilled water and powered to a final maximum size of 32 μm.

The Y-TZP and bioglass powders were mixed by ball milling in ethanol, for 4 h, using high-purity ZrO_2 sintered balls, then dried and sieved through 32 μm screen. The ZrO_2-bioglass powder mixtures were coded as 100-00, 95-5, 90-10, 80-20 and 70-30, for ZrO_2 samples containing 0, 5, 10, 20 and 30 wt.% of bioglass, respectively.

The mixtures were compacted into cylindrical pellets of 15 mm-diameter by cold uniaxial pressing at 80 MPa. The compacts with relative green density near to 55% of theoretical density were sintered at 1200 °C or1300 °C, in a $MoSi_2$ furnace for 2 h, with heating and cooling rate of 10 °C/min.

2.2. Characterization

Bulk density was measured by the Archimedes' method using distilled water. Furthermore, the crystalline phases were determined by X-ray diffractometry (XRD) using Cu-kα radiation in the 2θ range of 20 to 80°, with a step width of 0.05° and 3 s of exposure time per position. The monoclinic-ZrO_2 phase fraction, X_m, was calculated using the method proposed by Garvie and Nicholson [18]:

$$X_m = \frac{I_{m(\bar{1}11)} + I_{m(111)}}{I_{m(\bar{1}11)} + I_{m(111)} + I_{t(101)}} \quad (1)$$

where, I_t and I_m represent the integrated intensity (area under the peaks) of the tetragonal (1 0 1) and monoclinic (1 1 1) and ($\bar{1}$ 1 1) peaks. The monoclinic volume fraction, V_m, is then given by Toraya et al. [19]

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (2)$$

The polished surface of the sintered samples was thermally etched at 1400 °C–15 min, with heating rate of 25 °C/min and examined by scanning electron microscopy (SEM), using a LEO-1450VP microscope.

2.3. Mechanical properties

Microhardness and fracture toughness, K_{IC}, were determined using the Vickers Indentation method. In each sample, 10 indentations imprints were measured, under a load of 2000 gf for 30 s. The fracture toughness has been calculated by measurement of the relation between cracks length (c) and indentation length (a), using the relation proposed by Niihara et al. [20], valid for Palmqvist crack types, which present a c/a relation <3.5.

2.4. Cytotoxicity procedure

The *in vitro* biocompatibility of the ceramics was evaluated by cytotoxicity assay as described following. These tests were performed in the sintered samples (CPCp) according to ISO 10993-part 5, by neutral red uptake methodology [21–24].

2.4.1. Preparation of CPCp (ZrO_2-bioglass) extracts

Samples of CPCp gamma sterilized were added to Eagle's minimum medium (MEM) in a proportion of 1 cm^2/mL and incubated for 48 h at 37 °C. Serial dilutions were made of extracts from the CPCp samples, the Al_2O_3 (negative control) and the 0.02% phenol solution (positive control).

2.4.2. Preparation of the cell suspension

The cell line NCTC clone L929 used was acquired from the American Type Culture Collection (ATCC) bank and were maintained in MEM supplemented with 10% fetal calf serum, 20 mM glutamine and 1% non-essential amino acids (complete MEM) in a humidified incubator with 5% CO_2 at 37 °C. The cells were detached by trypsin, washed twice with calcium and magnesium free phosphate buffer solution and the cell suspension adjusted to about 2.5×10^5cell/mL.

2.4.3. Cytotoxicity assay

0.2 mL of the cell suspension was seeded in flat-bottomed 96 micro-plate wells (Costar, Cambridge, MA, USA). The micro-plate was incubated for 24 h at 37 °C in a CO_2 humidified incubator. After this period the medium of the plate was discarded and replaced with 0.2 mL of serially diluted extract of each sample (100, 50, 25, 12.5, and 6.25%). Control of cell culture medium was replaced with complete MEM. In the same micro-plate it was run on positive control (0.02% Phenol solution) and negative control (atoxic Tin stabilized poly vinyl chloride). Samples and controls were tested in triplicate. The plate was incubated again for 24 h in the same conditions.

After 24 h the culture medium and extracts were discarded and replaced with 0.2 mL of 0.005% neutral red diluted in MEM. After 3 h of incubation at 37 °C the dye medium was discarded and the micro-plate was washed twice with phosphate-saline buffer. The cells were

washed with a solution of 1% $CaCl_2$ in 0.5% formaldeid. The rupture of cells and neutral red release was obtained by the addition of 0.2 mL/well of extractant solution contained 50% ethanol in 1% acetic acid. The absorbances were read in 540 nm filter on a RC Sunrise model – Tecan spectrophotometer for ELISA.

2.4.4. Cytotoxicity determination

With the average of optical density of each extract dilution of samples, negative and positive controls the cell viability percentage were calculated in relation to cell control (100%) and plotted in a graphic against extract concentrations.

The cytotoxicity potential of the investigated materials was expressed as a cytotoxicity index ($IC_{50(\%)}$) and can be obtained in this graphic. $IC_{50(\%)}$ is the concentration of the extract which injures or kills 50% of cell population in the assay due to toxic elements extracted from tested sample.

3. Results and discussion

3.1. Bioglass characterization

Fig. 1 shows XRD pattern and SEM micrograph of the bioglass.

Fig. 1a shows a diffractogram with amorphous characteristics, typical of the glassy material, while SEM micrograph, presented in Fig. 1b, shows particles with high agglomeration degree. Despite of this material, previous works [14,16] show that this bioglass present coefficient of thermal expansion (CTE) of $10.2\times10^{-6}/°C$, indicating thermal compatibility with $ZrO_2(Y_2O_3)$ ceramic ($CTE = 10.7\times10^{-6}/°C$).

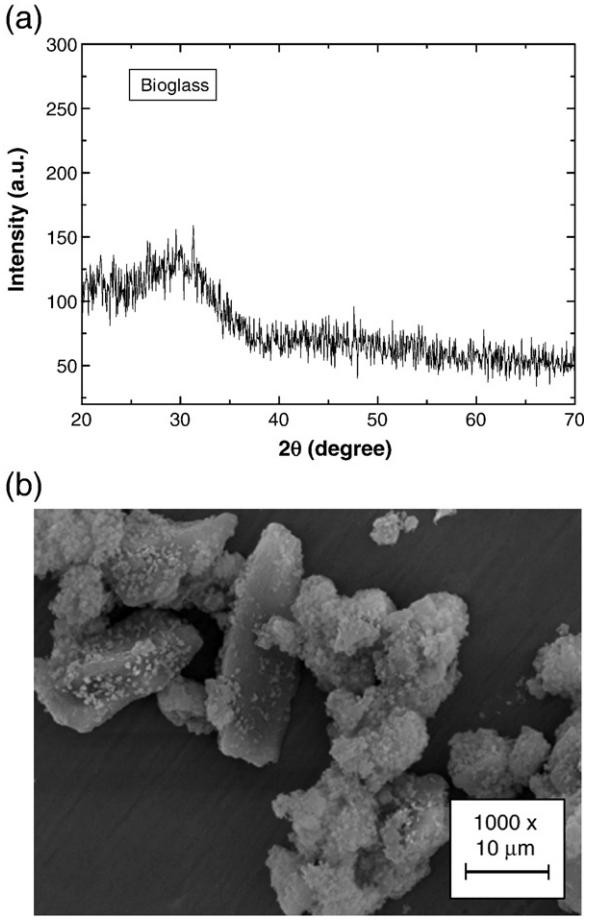

Fig. 1. a) XRD patterns and; b) SEM micrograph of the V4-bioglass particles.

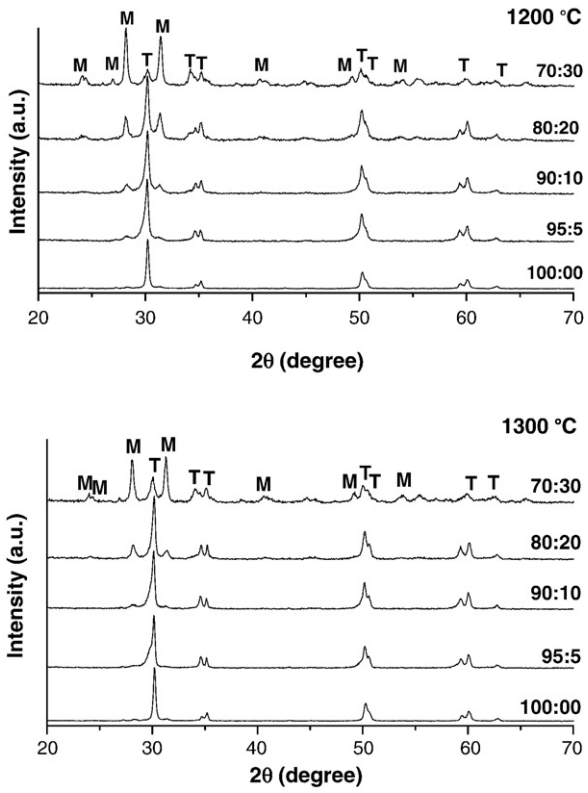

Fig. 2. X-ray diffractogram patterns of the sintered ZrO_2 samples with different bioglass contents (T – tetragonal; M – monoclinic).

3.2. Sintering

Fig. 2 presents X-ray diffractogram patterns of different ZrO_2-bioglass samples, sintered at 1200 °C and 1300 °C.

The presence of tetragonal- and monoclinic-ZrO_2 can be observed as crystalline phases. Furthermore, an increase of the monoclinic content is observed, as function of the bioglass addition. Fig. 3 presents a specific XRD pattern of the sample sintered with high bioglass content (30 wt.%), where it can be observed that, during cooling, carried through with controlled rates, crystalline phases (apatite, diopside and altansite) were formed in intergranular phase.

The addition of bioglass phase in the ZrO_2 matrix leads to the increase of monoclinic phase content, by the undesirable martensitic transformation (tetragonal-monoclinic), during the cooling of the sintered samples. This tetragonal-monoclinic-phase transformation promotes a volumetric expansion, between 3 and 6% of the bulk [9], resulting in micro-cracking and increasing of the porosity in samples, after cooling.

This phenomenon can occur by the difficulty on the uniform spreading of the liquid phase on the ZrO_2-grains, during sintering. This difficulty can be attributed to the: 1) high agglomeration of the bioglass powder, identified in Fig. 1b, which is difficult for the homogenization of the powder mixture during milling, promoting the formation of some regions rich in glass; 2) the low sintering temperature used in this work, which is not sufficient for considerable reductions on the glass-viscosity; and 3) partial crystallization of the intergranular phases with consequence structural alterations in these regions of triple junction, that can generate considerable stress fields.

Fig. 4 shows the effect of the bioglass addition on the relative density and martensitic (t–m) transformation of the sintered samples.

The reduction of densification, related with the increase of bioglass content, is a result of phase transformation with consequent volumetric expansion, as detailed elsewhere. Furthermore, it can be observed that ceramics sintered at 1300 °C presented better

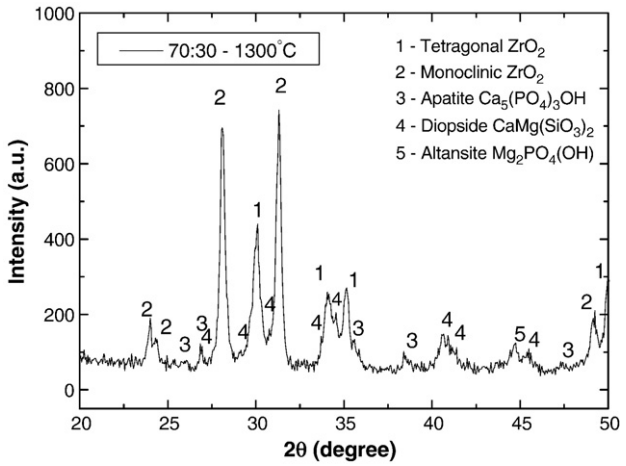

Fig. 3. X-ray diffractogram patterns of the ZrO_2 samples, sintered at 1300 °C, with 30% of bioglass.

densification than samples sintered at 1200 °C. These values are related to the liquid phase: comparatively, the increase of the sintering temperature reduce the liquid viscosity, increasing the particles attraction, facilitating partially, the spreading of the liquid around the ZrO_2-grains matrix, reducing its concentration in triple junctions and improving the densification [14,25,26].

Fig. 5 shows SEM micrographs of the etched surface of ZrO_2-bioglass ceramics sintered at 1300 °C for different bioglass contents, in which the low spreading of the glass (grey phase) around the ZrO_2 grains can be observed (white phase) and Fig. 6 shows micrographs of the surface of the ceramics sintered at 1300 °C.

The increasing of the porosity as function of the bioglass content on the mixture can be easily observed. As previously cited, the increase of the bioglass generates an increase of the martensitic transformation, resulting in pores and micro-cracking.

3.3. Mechanical properties

Table 2 presents results of Vickers hardness and fracture toughness, K_{IC}, of samples at different sintering temperatures and bioglass contents. Samples sintered without bioglass and with 20 wt.% and 30 wt.% of bioglass, presented high porosity, disabling the mechanical properties evaluation.

It can be observed in Table 2 that samples sintered at 1200 °C presents insufficient mechanical properties as structural ceramic, with low hardness and fracture toughness, because of the high porosity.

In this way, it is noticed that bioglass-doped samples, sintered at 1300 °C, present better properties, possibly by the high relative density, which is a result of the better spreading of the liquid phase formed during the sintering as function of the viscosity reduction of the glass, around the ZrO_2 particles, which facilitates the elimination of pores and reduction of the undesirable accumulation of the glassy phase in triple junctions, promoting residual stress generation during cooling and consequent crack-propagation points. Un-doped ZrO_2 samples sintered at 1300 °C, present low relative density and consequently low mechanical properties.

The comparison of these results with commercial ceramics presented in Table 1, indicates the improvement of the fracture toughness of the ceramics obtained in this work: samples sintered at 1300 °C, with 5 wt.% of bioglass presented high fracture toughness, near to 6 MPa $m^{1/2}$ which, indicates total compatibility with reasonable values of fracture toughness in ceramic to be used as implantations, which is above 3 MPa $m^{1/2}$ [15]. These results are function of the high relative density and low monoclinic phase content, Fig. 4, and comparatively, the increase of the glass addition reduces the relative density, as previously presented. Furthermore, preliminary machining testing of this ceramic using CAD/CAM system showed high stability of these ceramics for the development of crowns and bridges.

An important property to be considered in this study is the degradation of these ceramics when submitted to the liquid environments, because monolithic ZrO_2 ceramics and different glasses present high degradation in aqueous environment [9]. On the other hand, the intergranular phase of the ceramics developed in this work, composed initially of glass, is partially converted to the crystalline phase after sintering, during cooling, Fig. 3. This partial crystallization generates higher stability of this intergranular phase. Furthermore, bioglass and/or bioactive glass-ceramic phase contained in the ZrO_2-grain boundary can form a stable bioactive phase, which is highly resistant to the degradation.

3.4. Biological evaluation

In vitro cytotoxicity tests were performed to evaluate the cytotoxicity of ZrO_2-bioglass ceramic and the cytotoxicity of possible contamination during the different steps of materials processing, i.e., grinding, pressing and sintering. Plotting the average percentage of survival of the cells as function of the concentration of the extract shows the cytotoxicity index ($CI_{50\%}$). It is known, that the negative control simulates an environment where the cell has total capacity of development and to born colonies, while the positive control simulates an environment totally adverse to its development.

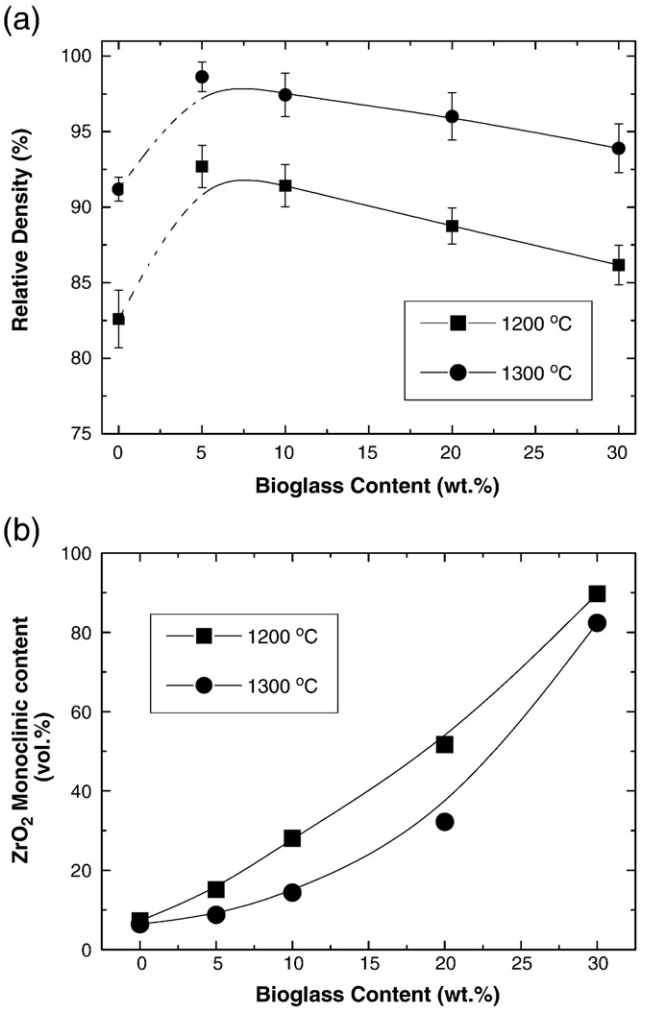

Fig. 4. Effect of bioglass addition on the: a) relative density; b) monoclinic ZrO_2-phase content.

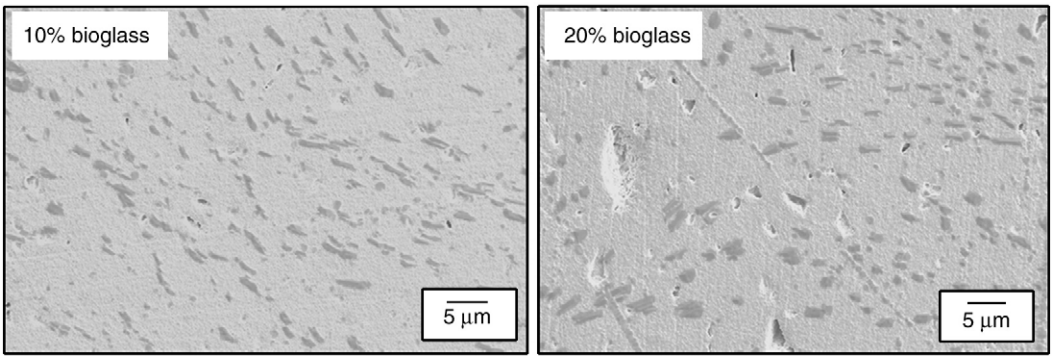

Fig. 5. SEM micrographs of the ZrO_2-bioglass ceramics sintered at 1300 °C.

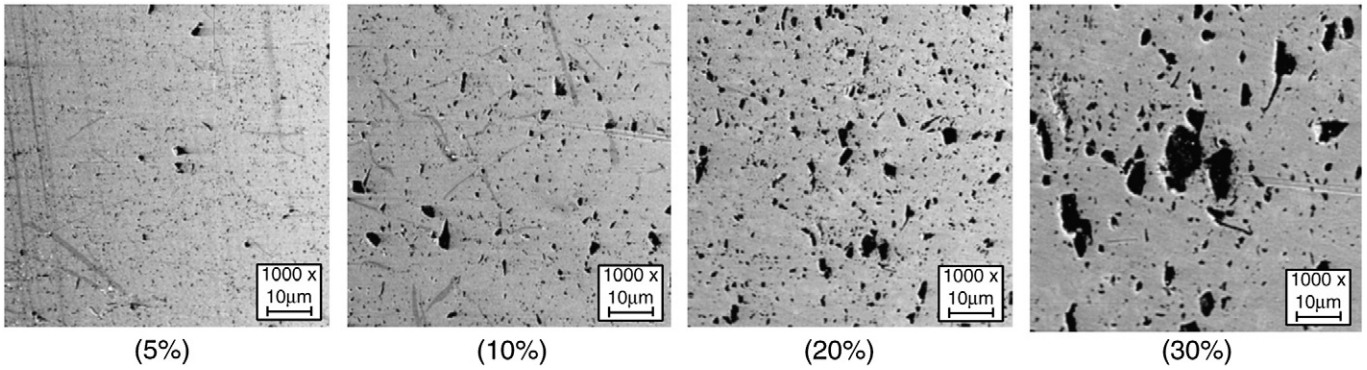

Fig. 6. SEM micrographs of the ZrO_2-bioglass ceramics sintered at 1300 °C with different bioglass additions.

Fig. 7 shows the viability curves of the four ZrO_2-bioglass ceramic compositions and positive (phenol solution) and negative (Al_2O_3) controls in the cytotoxicity assay by neutral red uptake methodology.

From these curves, it is possible to observe that the extracts even with high extract concentration do not cause death or injury of the cell population, indicating that these materials presented no cytotoxicity. All studied sintered ZrO_2-bioglass ceramics showed the same behavior as negative control. Only positive control showed cytotoxicity presenting cytotoxicity index ($IC_{50\%}$) of about 40% indicating that the extract of positive control in the concentration of 40% injured or killed 50% of cell population in the assay. Besides, the test showed that there is no contamination by the processing in significant amounts to compromise the experiment.

4. Conclusions

Dense ZrO_2-bioglass ceramics can be obtained using a limited bioglass content. High bioglass content and low sintering temperatures (1200 °C), lead to martensitic (tetragonal-monoclinic) transformation after sintering during cooling, promoting an increasing of the porosity and cracking of the sintered bulk, reducing the properties of the sintered samples. The use of higher sintering temperature, 1300 °C, reduces the viscosity of the bioglass, improving the densification. In this form, optimized samples, sintered with 5 wt.% at 1300 °C, present hardness of 11.3 GPa and fracture toughness of 6.1 MPa $m^{1/2}$, allowing its use as a reliable dental material. The preliminary biological evaluation made in this work, indicates that these ceramic can be used in bio-applications, without reduction of the peripheral cellular growth.

Table 2
Hardness and fracture toughness of the sintered samples.

Bioglass content (wt.%)	Sintering temperature			
	1200 °C		1300 °C	
	Hardness (GPa)	K_{IC} (MPa $m^{1/2}$)	Hardness (GPa)	K_{IC} (MPa $m^{1/2}$)
0	–	–	8.7 ± 0.9	4.1 ± 0.5
5	7.4 ± 0.8	3.6 ± 0.3	11.3 ± .07	6.1 ± 0.4
10	4.8 ± 0.6	3.4 ± 0.7	9.3 ± 0.4	5.0 ± 0.5

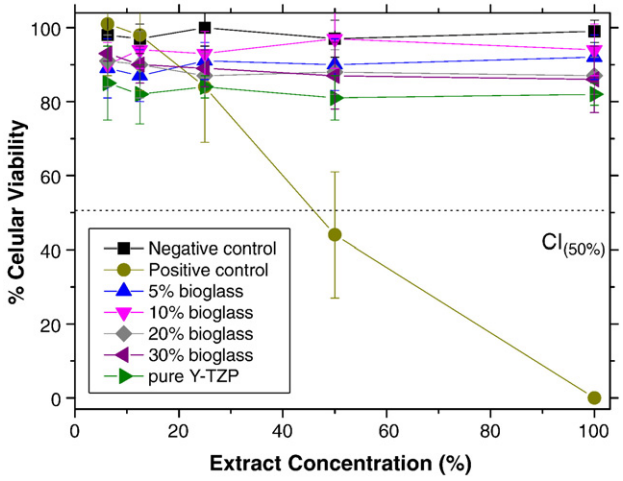

Fig. 7. Cellular viability curves of sintered ZrO_2-bioglass ceramics, in the cytotoxicity test by neutral red uptake assay.

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