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## Y-TZP ceramic processing from coprecipitated powders: A comparative study with three commercial dental ceramics

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### ABSTRACT

**Objectives.** (1) To synthesize 3 mol% yttria-stabilized zirconia (3Y-TZP) powders via coprecipitation route, (2) to obtain zirconia ceramic specimens, analyze surface characteristics, and mechanical properties, and (3) to compare the processed material with three reinforced dental ceramics.

**Methods.** A coprecipitation route was used to synthesize a 3 mol% yttria-stabilized zirconia ceramic processed by uniaxial compaction and pressureless sintering. Commercially available alumina or alumina/zirconia ceramics, namely Procera AllCeram (PA), In-Ceram Zirconia Block (CAZ) and In-Ceram Zirconia (IZ) were chosen for comparison. All specimens (6 mm × 5 mm × 5 mm) were polished and ultrasonically cleaned. Qualitative phase analysis was performed by XRD and apparent densities were measured on the basis of Archimedes principle. Ceramics were also characterized using SEM, TEM and EDS. The hardness measurements were made employing Vickers hardness test. Fracture toughness ( $K_{IC}$ ) was calculated. Data were analyzed using one-way analysis of variance (ANOVA) and Tukey's test ( $\alpha = 0.05$ ).

**Results.** ANOVA revealed that the Vickers hardness ( $p < 0.0001$ ) and fracture toughness ( $p < 0.0001$ ) were affected by the ceramic materials composition. It was confirmed that the PA ceramic was constituted of a rhombohedral alumina matrix, so-called  $\alpha$ -alumina. Both CAZ and IZ ceramics presented tetragonal zirconia and  $\alpha$ -alumina mixture of phases. The SEM/EDS analysis confirmed the presence of aluminum in PA ceramic. In the IZ and CAZ ceramics aluminum, zirconium and cerium in grains involved by a second phase containing aluminum, silicon and lanthanum were identified. PA showed significantly higher mean Vickers hardness values ( $H_V$ ) ( $18.4 \pm 0.5$  GPa) compared to vitreous CAZ ( $10.3 \pm 0.2$  GPa) and IZ ( $10.6 \pm 0.4$  GPa) ceramics. Experimental Y-TZP showed significantly lower results than that

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of the other monophasic ceramic (PA) ( $p < 0.05$ ) but it showed significantly higher fracture toughness ( $6.0 \pm 0.2 \text{ MPa m}^{1/2}$ ) values when compared to the other tested ceramics ( $p < 0.05$ ). *Significance.* The coprecipitation method used to synthesize zirconia powders and the adopted ceramic processing conditions led to ceramics with mechanical properties comparable to commercially available reinforced ceramic materials.

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## 1. Introduction

Recent improvements in mechanical properties of structural alumina and/or zirconia ceramics have enlarged their application in the dental field. In addition, ceramic restorations present superior aesthetics and biocompatibility compared to metallic frameworks for fixed-partial-dentures (FPD) that do not allow light transmission, reducing the ability of mimicking the natural appearance of the tooth structures [1–3].

Alumina and zirconia ceramics have better mechanical properties compared to feldspath ceramics due to their increased crystalline content, chemical composition, and microstructure [1–3]. In this context, all ceramic systems, where a high toughness ceramic core is veneered with a traditional feldspath ceramic, have been developed in order to achieve improved aesthetic appearance without compromising the mechanical properties [3].

Pure zirconia has three polymorphic forms at atmospheric pressure: monoclinic from room temperature until  $1170^\circ\text{C}$ , tetragonal ( $1170$ – $2370^\circ\text{C}$ ), and cubic ( $2370$ – $2680^\circ\text{C}$ ). The tetragonal  $\rightarrow$  monoclinic phase transformation is associated with volume expansion of approximately 3–4%, originating cracks during cooling from sintering temperature. To inhibit these phase transformations, the addition of stabilizing oxides such as CaO, MgO, CeO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub> is recommended and three classes of zirconia materials can be obtained: Cubic stabilized zirconia (CSZ), Partially stabilized zirconia (PSZ), which is a mixture of cubic and tetragonal/monoclinic phases, and Tetragonal zirconia polycrystals (TZP) [4,5].

TZP materials are extensively used for biomedical applications since they possess improved fracture toughness and mechanical strength, especially when 3 mol% yttria is used as dopant. Such behavior is related to the greater extent of yttria solubility in tetragonal zirconia solid solution, when compared to others dopants [1,3,4]. At this condition, 3 mol% yttria-stabilized zirconia (3Y-TZP) exhibits a very important feature, related to the polymorphic transformation for monoclinic phase when a mechanical stress is applied. This phenomenon, known as transformation toughening, can prevent crack growth resulting in a material with high toughness and mechanical strength, but having lower hardness than alumina [4,5]. On the other hand, ceramic bodies made of pure alumina exhibit high hardness but lower toughness [6]. Since zirconia and alumina have low mutual solubility (<1 wt%), even at high temperatures [5], it is possible to tailor a ceramic composite, comprising the mechanical properties of both [6,7]. The mechanisms involved include the inhibition of grain growth during sintering and formation of microcracks [7]. However, it should be noted that the mechanical properties of 3Y-TZP depend on the grain size [8,9]. Above

a critical grain size, the 3Y-TZP ceramic is more susceptible to a spontaneous tetragonal  $\rightarrow$  monoclinic transformation, whereas a smaller grain size (<1  $\mu\text{m}$ ) is associated with a lower transformation rate [10]. Moreover, in this case the tetragonal  $\rightarrow$  monoclinic phase transformation is increased when stress is applied [5]. The maximum benefits of transformation toughening mechanism are attained by the control of ceramic grain size and matrix homogeneity [8–10], which are related to powder synthesis and the ceramic processing conditions. The consolidation of loosely agglomerated powders is expected to result in better sintering properties at lower temperatures, avoiding the use of sintering aids [11].

Among the many ceramic processing techniques used to improve physical and chemical properties of zirconia-based materials, the synthesis of nanocrystalline powders has been considered extremely important. As an alternative to the traditional mechanical mixing procedure, chemical methods can be used to synthesize different doped zirconia ceramic powders with higher reactivity, allowing better sintering without the application of pressure [11]. Some examples of these powder preparation techniques are: sol-gel synthesis [12], polymeric precursor route [13], combustion synthesis [14], hydrothermal treatment [15] and coprecipitation from metal aqueous solutions [16–18]. From a commercial standpoint, however, coprecipitation is the most common route adopted due to the great chemical and physical homogeneity of the products, cost effectiveness and simplicity [16–18]. The coprecipitation route consists of preparing an aqueous solution with the metal ions (i.e., YCl<sub>3</sub>, and ZrOCl<sub>2</sub>), with the desirable composition and slowly mixing them with aqueous base (i.e., NH<sub>4</sub>OH), causing precipitation. The use of organic liquids to dehydrate the precipitate and wet milling to control the state of powder agglomeration have to be employed [18].

In this work, 3Y-TZP powders were synthesized via coprecipitation and then ceramic specimens were obtained by pressureless sintering with suitable properties to be used in conjunction with CAD–CAM systems in the manufacturing of dental restoration frameworks. In order to validate its possible application as a ceramic core, two mechanical properties, namely, Vickers hardness ( $H_V$ ) and fracture toughness ( $K_{IC}$ ) were measured and compared to three commercially available reinforced dental ceramic materials, which were based on pure alumina, and zirconia toughened alumina infiltrated by a glassy phase. Furthermore, apparent densities were measured and ceramic characteristics were analyzed using SEM, TEM, XRD and EDS. The hypothesis to be tested was that the processing route used to obtain the 3Y-TZP powders and consequently the 3Y-TZP ceramic produced might result in a material with superior mechanical properties when compared to the commercially available ceramics.

## 2. Materials and methods

### 2.1. Production of 3Y-TZP experimental ceramic

A coprecipitation route was used to synthesize 3 mol% yttria-stabilized zirconia powders [18]. Zirconium oxychloride purified by the basic zirconium sulphate precipitation process (99.8 wt%  $ZrO_2 + HfO_2$ —IPEN, São Paulo, Brazil) and yttrium chloride (hydrochloric acid dissolution of 99.99%  $Y_2O_3$ —Aldrich Chemical Co., Milwaukee, WI, USA) were used as starting materials. Balanced quantities of these reagents were mixed and diluted in water to achieve a solution containing 35 g/L of 3 mol% of yttria-stabilized zirconia. Coprecipitation was performed by spraying the mixed chlorides into a 3 molar ammonium hydroxide solution at a rate of approximately 50 mL/min. The reaction was carried out under vigorous stirring, maintaining the pH of the solution at 10. The gel suspension was filtered and washed with water until no residual  $Cl^-$  was present as indicated by a chemical reagent ( $AgNO_3$ ). The precipitate was washed with ethanol and treated by azeotropic distillation with butanol in order to hinder hard agglomerate formation. In this case, the azeotrope liquid containing 44.5 wt% water and 55.5 wt% *n*-butanol was first evaporated at 93 °C. Once the temperature of 117 °C was reached (boiling point of *n*-butanol), all water was removed from the gel. The distilled gel was oven-dried at 80 °C for 24 h. Calcination was carried out at 800 °C for 1 h. The ceramic aggregate was ball milled and the resulting powder was pressed by uniaxial compaction at 100 MPa in a metallic matrix (60 mm × 12 mm). The green pressed specimens were sintered in air at 1500 °C for 1 h using an electrical box furnace (Lindberg/Blue M, Asheville, NC, USA) [18]. Ceramic specimens (6 mm × 5 mm × 5 mm) were cut with a diamond wafering blade mounted on a precision saw machine (Isomet 2000, Buehler, Lake Bluff, IL, USA), and polished with 15, 6 and 1 μm ceramographic cloth and diamond suspensions (Mecapol P320, Presi, Grenoble, France). The specimens were cleaned in an ultrasonic bath (Vitasonic II, Vita-Zahnfabrik, Bad Säckingen, Germany) in acetone for 10 min.

The as-sintered ceramic densities were determined by an immersion method based on the Archimedes principle. In order to reveal the post-sintering microstructure morphology, fractured and polished specimen surfaces were analyzed under a scanning electron microscope (SEM, XL30, Philips, Eindhoven, The Netherlands). Transmission electron microscopy (TEM, JEM-200, JEOL Ltd., Tokyo, Japan) was used

for microstructural phase evaluation. Polished and TEM specimens were subjected to thermal etchings at 1450 °C for 30 min in order to reverse the tetragonal → monoclinic transformation produced during ceramographic procedures. X-ray diffraction patterns of the polished surfaces were registered (DMAX 2000, Rigaku Corporation, Tokyo, Japan). Data were collected in the  $2\theta$  range from 5 to 80°, with 0.02° step size and counting time 12 s. Quantitative phase analysis and determination of theoretical density were calculated using Rietveld refinement with DBWS9807 software (CCP14). This method is based on mathematic fitness of X-ray pattern upon a model that includes known crystallographic parameters such as unit cell dimensions and atomic positions, as well as pattern line shape, background and phase composition. These parameters are adjusted via least-squares refinement. In this work peak shapes were modeled using a Pseudo-Voigt distribution.

### 2.2. Processing of commercially available ceramics

Alumina or alumina/zirconia ceramics, namely Procera All-Ceram (PA), In-Ceram Zirconia Block (CAZ), and In-Ceram Zirconia (IZ) indicated for fabrication of FPD frameworks were processed either by dry pressing or slip casting according to each manufacturer's instructions. Densely sintered alumina ceramic blocks (PA) were obtained from the manufacturer. A detailed description of these materials is listed in Table 1.

All the commercially available ceramics were also cut as blocks (6 mm × 5 mm × 5 mm) with a diamond wafering blade mounted on a precision saw machine and polished with 15, 6 and 1 μm ceramographic cloth and diamond suspensions. The specimens were cleaned in an ultrasonic bath in acetone for 10 min. The polished commercial sintered ceramics were characterized by SEM and XRD ( $Cu K\alpha$ ,  $2\theta$  20–80°) in order to identify the crystalline phases. X-ray energy spectroscopy (EDS) (EDAX®, Japan) was used for qualitative chemical analysis.

### 2.3. Vickers hardness test

Hardness was determined by the Vickers hardness test (VMT-7, Buehler, Lake Bluff, IL, USA). In a preliminary investigation, loads in the range of 10–100 N were studied. The application of 60 and 30 N for 30 s was found to create cracks with a suitable shape under indentation, for Y-TZP and commercially available ceramics, respectively. In these conditions, impressions were performed at 10 regions in each one of the specimens.

**Table 1 – The codes, commercial names, ceramic forming process, ceramic matrix, and manufacturers of the ceramics used for the experiments**

Code	Commercial name	Process	Ceramic matrix	Manufacturer
PA	Procera AllCeram	Dry pressing	Alumina	Nobel Biocare, Uppsala, Sweden
CAZ	In-Ceram Zirconia Block	Dry pressing	Alumina/Zirconia <sup>a</sup>	Vita-Zahnfabrik, Bad Säckingen, Germany
IZ	In-Ceram Zirconia	Slip casting	Alumina/zirconia <sup>a</sup>	Vita-Zahnfabrik, Bad Säckingen, Germany
Y-TZP	Experimental	Dry pressing	Zirconia	Materials Science and Technology Center, IPEN-CNEN/SP, São Paulo, Brazil

<sup>a</sup> Infiltrated by a lanthanum–aluminum borosilicate glassy phase.

Vickers hardness values were calculated using Eq. (1) where “P” was the applied load (N) and “d” was the average of the diagonal length (m) and  $\alpha$  the angle between the opposite faces of the indenter ( $136^\circ$ ) [19]

$$H_v = \frac{\alpha P}{d^2} \quad (1)$$

#### 2.4. Fracture toughness test

Images and dimensions of the indentations and cracks were acquired using an optical microscope (PMG3, Olympus, Tokyo, Japan). The crack type was identified by investigating the indented surface that was polished with a  $1\ \mu\text{m}$  diamond suspension. It is important to point out that determination of the crack's type and measurement of the exact crack length is an important concern in obtaining the fracture toughness values [19].

Fracture toughness data can be obtained by using a great variety of equations. Ponton and Rawlings [20] normalized several models related to the *Palmqvist* and *radial-median* crack formation that are represented in Fig. 1A. The *Palmqvist* type cracks are generally obtained for materials that present high

fracture toughness (i.e., TZP ceramics) especially when the applied force is relatively low. Values of the  $c/a$  ratio smaller than 3 ( $c/a < 3$ ) also supports the *Palmqvist* type crack formation, where “c” is the summation of the crack length (l) and the semi-diagonal length of the impression (a).

In this study, two equations, normalized by Ponton and Rawlings [20] were used to compute the fracture toughness values: Eq. (2), proper for *Palmqvist* cracks, proposed by Shetty, Wright, Mincer, and Clauer [20] and Eq. (3), for *radial-median* cracks, proposed by Evans [20]. The cracks propagated in the Y-TZP ceramic were classified as *Palmqvist*, however, on the commercial ceramics they were *radial-median* (Fig. 1A–C)

$$K_{IC} = 0.0319 \frac{P}{a^{1/2}} \quad (2)$$

$$K_{IC} = 0.0824 \frac{P}{c^{3/2}} \quad (3)$$

where  $K_{IC}$  is the fracture toughness ( $\text{MPa m}^{1/2}$ ),  $H_v$  is the Vickers hardness (GPa), P is the applied force (N), a is the semi-diagonal impression length (m), l is the crack length (m), and  $c = a + l$  (m)

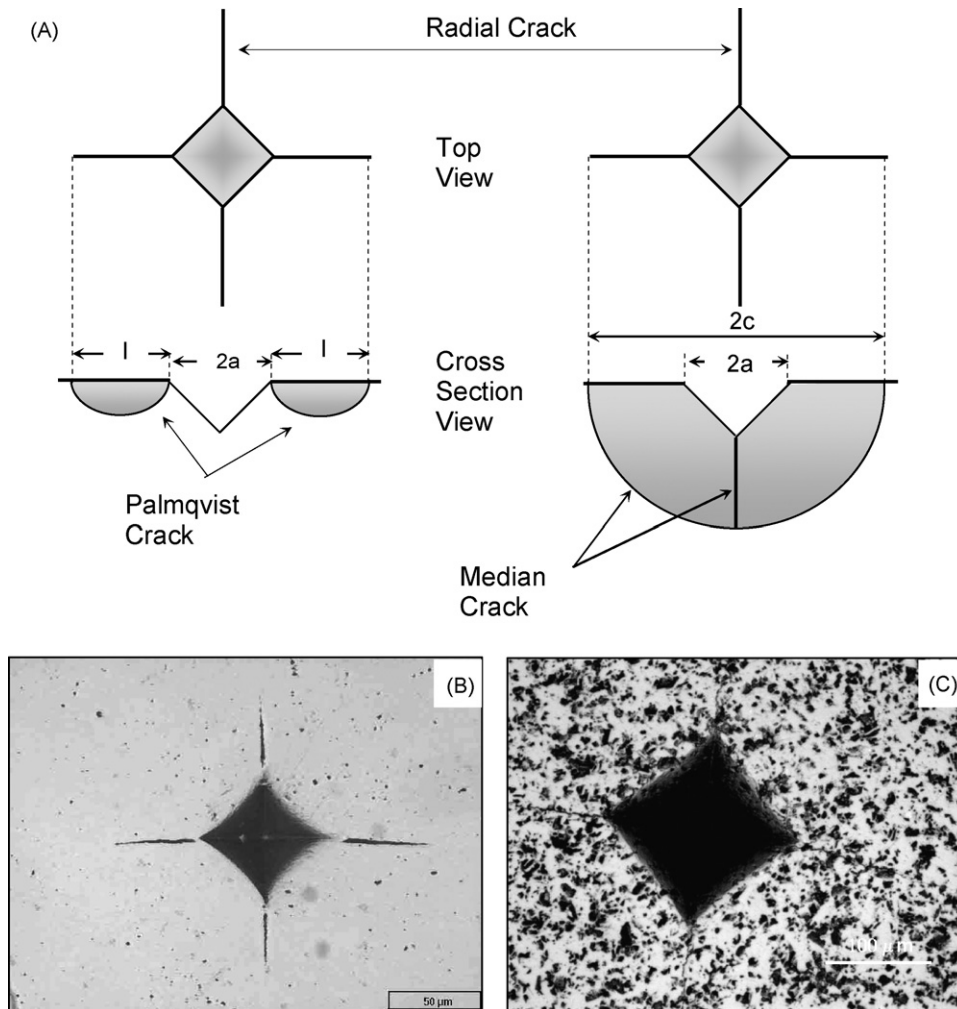


Fig. 1 – (A) Crack formation by Vickers indentation [20], (B) representative optical micrographs of the Vickers indentation impression after polishing with diamond paste from Y-TZP, and (C) IZ.

## 2.5. Statistical analysis

Statistical analysis was performed using statistical software for Windows (StatSoft Inc., version 5.5, 2000, Tulsa, OK) and statistix for Windows (Analytical Software Inc., version 8.0, 2003, Tallahassee, FL, USA). The means of each group from Vickers hardness and fracture toughness measurements were analyzed by one-way analysis of variance (ANOVA), with the test type as the dependent variable and the ceramic types as the independent factors. *p* values less than 0.05 were considered to be statistically significant in all tests. Multiple comparisons were made by Tukey's test.

## 3. Results

### 3.1. Ceramic characterization

The results of the phase fraction (Rietveld refinement) of X-ray diffraction patterns, theoretical and apparent density, Vickers hardness, and fracture toughness of as-sintered blocks of the experimental zirconia are shown in Table 2. The XRD pattern followed by Rietveld refinement showed a 96 wt% tetragonal phase content and 4 wt% of monoclinic phase.

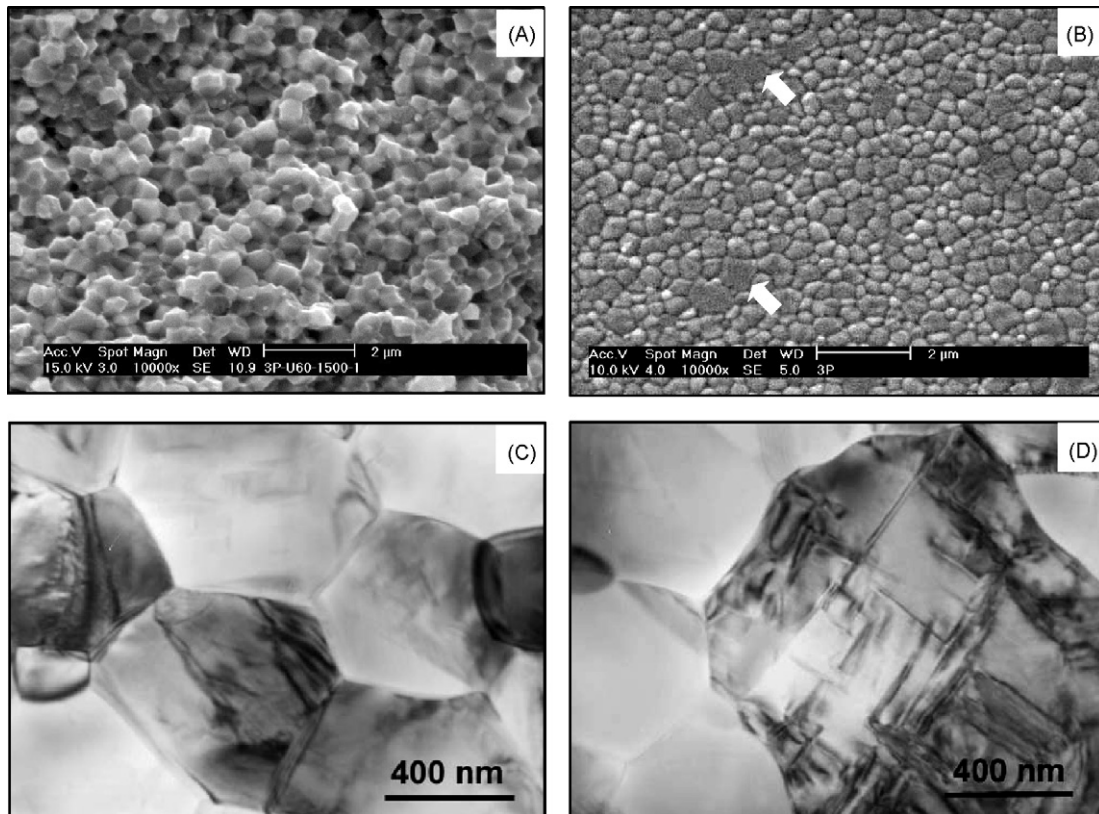
SEM evaluation of fractured surfaces of the experimental zirconia revealed that fracture was located at the intergranular regions (Fig. 2A). The grain size assessment was carried out by a computer software as suggested elsewhere

**Table 2 – Phase fraction (Rietveld refinement), theoretical density, apparent density, Vickers hardness, and fracture toughness of the experimental zirconia tested**

Tetragonal phase content (wt%)	96
Monoclinic phase content (wt%)	4
$\rho_{\text{theoretical}}$ ( $\text{g cm}^{-3}$ )	6.07
$\rho_{\text{apparent}}$ ( $\text{g cm}^{-3}$ )	$5.92 \pm 0.03$
$\rho_{\text{relative}}$ (%)	$97.5 \pm 0.5$
Hv (GPa)	$13.5 \pm 0.3$
$K_{\text{IC}}$ ( $\text{MPa m}^{1/2}$ )	$6.0 \pm 0.2$

[21]. 3 mol% yttria-stabilization allowed the processing of microstructures with uniform grain size smaller than  $0.5 \mu\text{m}$  (Fig. 2B). Polished and thermally etched Y-TZP surfaces showed low fraction of monoclinic phase (Fig. 2B). Twinning formation was clearly observed in the larger grains [22].

The TEM micrographs (Fig. 2C and D) further confirmed the presence of a fine microstructure with little amounts of monoclinic phase, which was characterized by twinning formation due to martensitic transformation after the thermal treatment step. Amorphous phase content was not observed at the grain boundaries and triple points in the experimental zirconia specimens. The selected area diffraction (SAD) pattern identified by DIFFPAT software (Ottawa, Canada) presented in Fig. 3 corresponds to the tetragonal zirconia phase.



**Fig. 2 – (A) SEM image of the fractured surface of 3 mol% Y-TZP ceramic sintered at  $1500^\circ\text{C}$  for 1 h, (B) SEM image of the polished and thermal etched surface of the Y-TZP. Note the low fraction of monoclinic phase clearly observed in the larger grains where the twinning formation occurs (white arrows), (C) TEM surface micrograph of 3 mol% Y-TZP ceramic sintered at  $1500^\circ\text{C}$  for 1 h, showing tetragonal grains, and (D) TEM surface micrograph of 3 mol% Y-TZP ceramic sintered at  $1500^\circ\text{C}$  for 1 h, showing twin formation in monoclinic grains.**

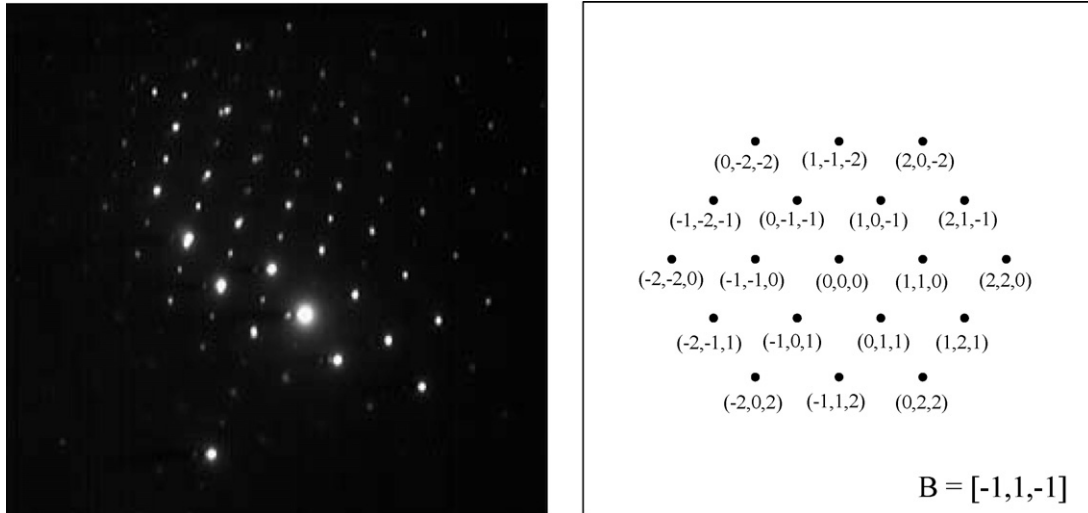


Fig. 3 – Selected area diffraction (SAD) pattern of a tetragonal grain of 3 mol% Y-TZP ceramic ( $B = [-1, 1, -1]$ ).

Fig. 4 presents the XRD patterns for the tested dental ceramics. It was confirmed that the PA ceramic was constituted of a rhombohedral alumina matrix, so-called  $\alpha$ -alumina (JCPDS 10-173). On the other hand, both CAZ and IZ ceramics presented, as crystalline phases, a mixture of tetragonal zirconia (JCPDS 17-923) and  $\alpha$ -alumina.

SEM micrographs of the resultant cracks after the Vickers hardness indentation test from the experimental Y-TZP (Fig. 5) and the other ceramics with the identified phases and elemental constituents are indicated on their respective EDS spectra (Figs. 6–8A–D). The SEM/EDS analysis showed that PA ceramic contains aluminum and oxygen as chemical constituents. Three regions of IZ and CAZ ceramics were analyzed. The first one is formed by aluminum, silicon, zirconium, cerium, and oxygen, indicating the presence of alumina/zirconia composite. The second region contains the elements of the vitreous phase (oxygen, sodium, aluminum, zirconium, calcium, lanthanum, and cerium) and the third region corresponds to alumina phase.

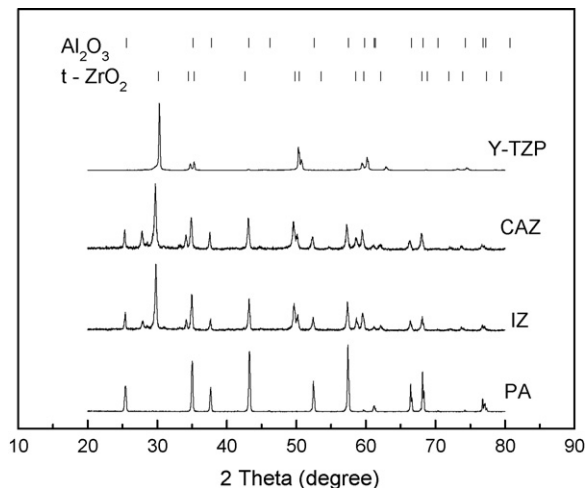


Fig. 4 – XRD patterns of the ceramics tested. Refer to Table 1 for abbreviations.

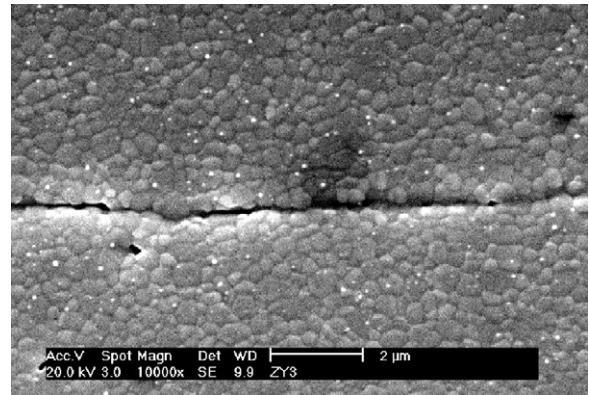


Fig. 5 – Representative SEM micrograph of the experimental Y-TZP ceramic after Vickers impression. Note the crack propagation.

### 3.2. Vickers hardness test and fracture toughness

ANOVA revealed that the Vickers hardness ( $p < 0.0001$ ) and fracture toughness ( $p < 0.0001$ ) were affected by the ceramic composition (Table 3). Materials were classified into three groups in which ceramics of the same group (indicated by superscript letter) do not show statistical difference. Con-

Table 3 – Mean Vickers hardness ( $H_v$ ) and fracture toughness ( $K_{IC}$ ) for the different ceramic materials tested

Code	$H_v$ (GPa)	$K_{IC}$ (MPa $m^{1/2}$ )
PA	$18.4 \pm 0.5^a$	$4.2 \pm 0.7^a$
IZ	$10.6 \pm 0.4^b$	$5.5 \pm 0.5^b$
CAZ	$10.3 \pm 0.2^b$	$5.2 \pm 0.4^b$
Y-TZP	$13.5 \pm 0.2^c$	$6.0 \pm 0.2^c$

See Table 1 for the abbreviations. The superscripted letters indicate no significant differences.

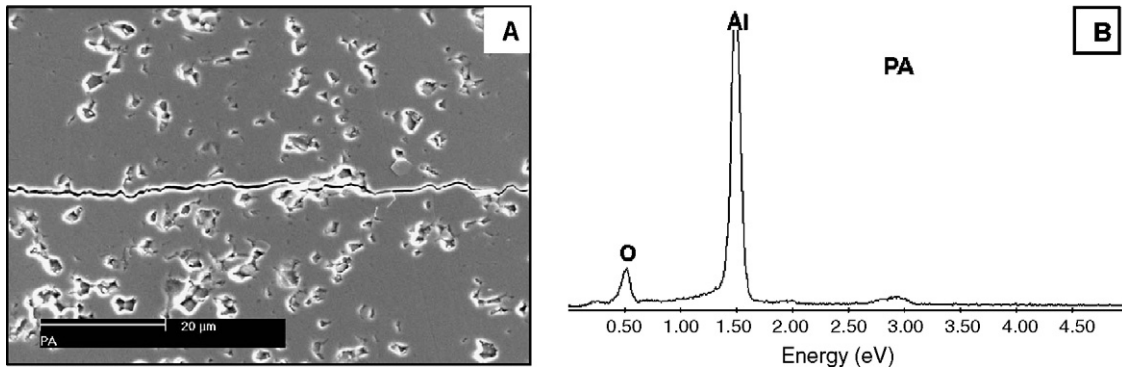


Fig. 6 – (A) SEM micrograph of the PA ceramic microstructure after Vickers impression, and (B) EDS analysis showing the high aluminum content.

cerned to hardness, high alumina content ceramic (PA) showed significantly higher mean Vickers hardness values ( $18.4 \pm 0.5$ ), compared to experimental Y-TZP ( $13.5 \pm 0.2$ ) ( $p < 0.05$ ). Lowest hardness values were obtained for glass infiltrated alumina–zirconia composites, but no statistical difference between CAZ ( $10.3 \pm 0.2$ ) and IZ ( $10.6 \pm 0.4$ ) ceramics was observed. As pointed out earlier, CAZ and IZ samples have the same chemical composition and similar microstructure, indicated by SEM micrographs (Figs. 7A and 8A). Related to fracture toughness values, materials were also divided into three groups, in the following increasing order: experimental Y-TZP ( $6.0 \pm 0.2$ ), IZ ( $5.5 \pm 0.5$ ), CAZ ( $5.2 \pm 0.4$ ), and PA ( $4.2 \pm 0.7$ ). The higher toughness value for Y-TZP ceramic is a consequence of transformation toughening mechanism. On the

other hand, the lowest fracture toughness of alumina ceramics can be improved by the addition of zirconia to the matrix, even in the presence of a vitreous glassy phase. Figs. 7A and 8A show that the presence of alumina and zirconia grains promotes the deflection of crack trajectories along the glassy matrix.

#### 4. Discussion

This study investigated the efficacy of an experimental Y-TZP ceramic obtained by a coprecipitation method and pressureless sintering as dental material in lieu of other commercially available ceramics.

Y-TZP ceramics are generally characterized by a fine-grained microstructure with a mean grain size lower than

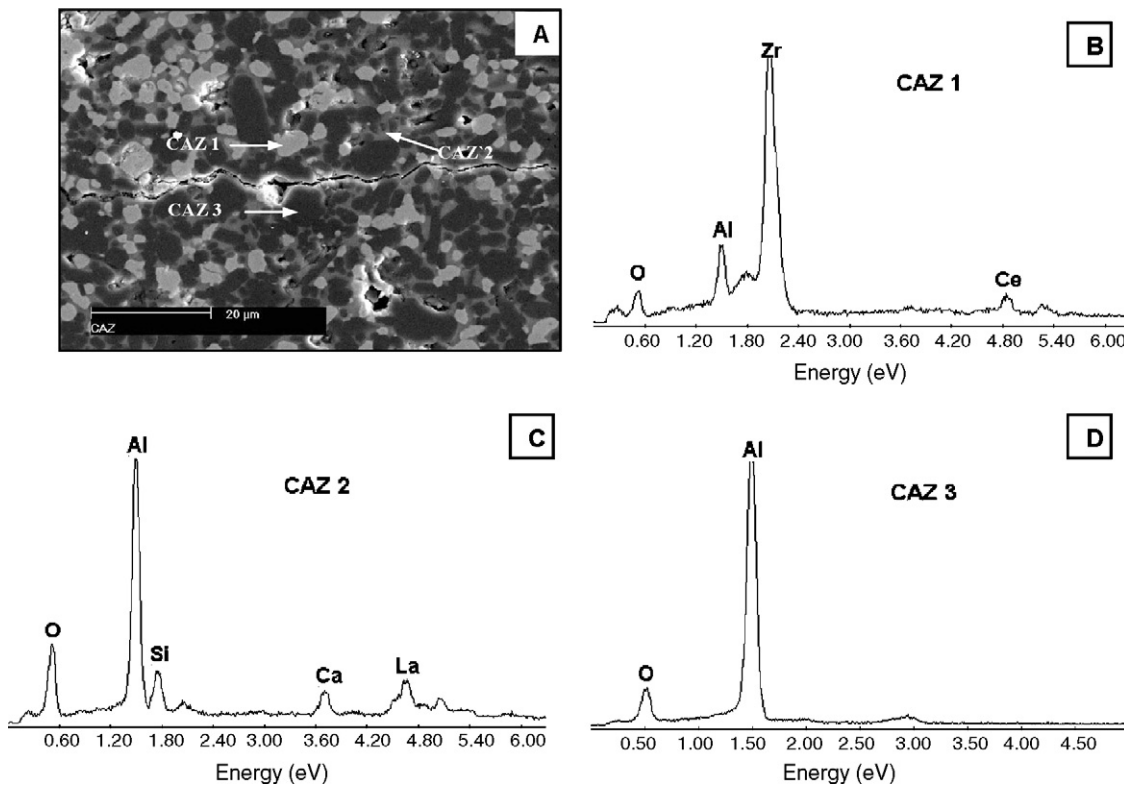
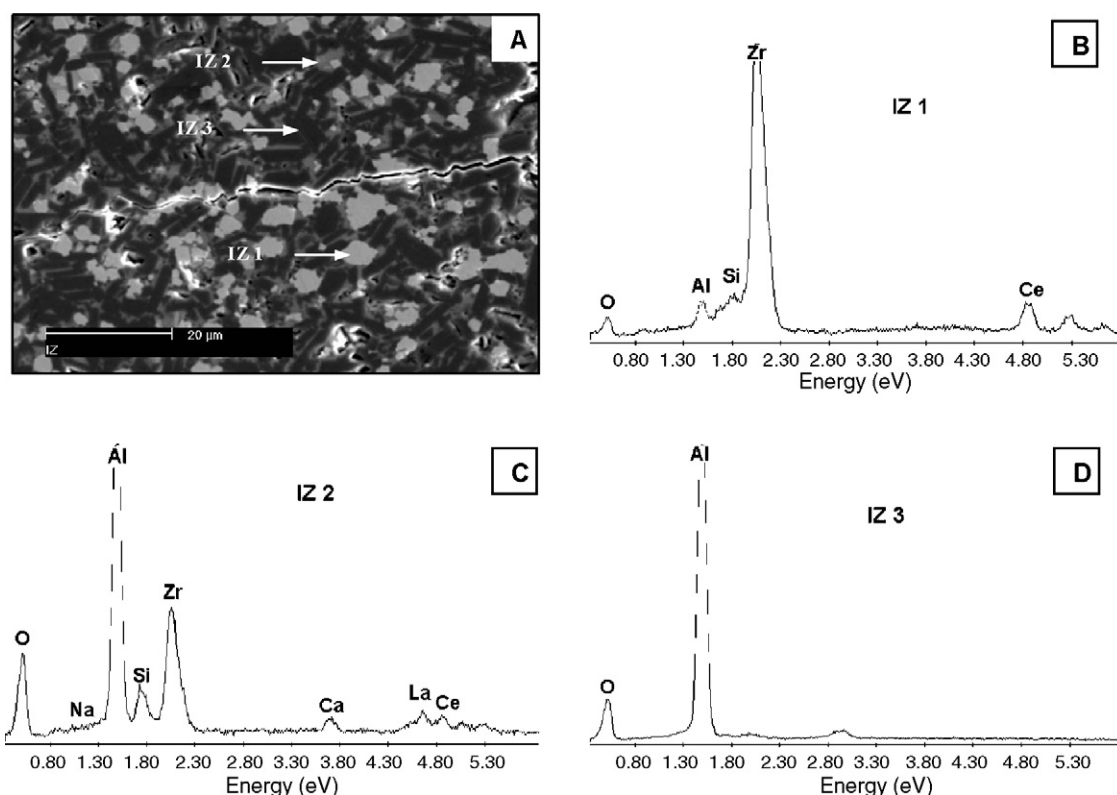


Fig. 7 – (A) SEM micrograph of the CAZ ceramic microstructure after Vickers impression, (B–D) EDS analyses showing an alumina–zirconia-based matrix.



**Fig. 8 – (A) SEM micrograph of the IZ ceramic microstructure after Vickers impression, (B–D) EDS analyses showing an alumina–zirconia-based matrix.**

0.5 μm [8]. The typical specimens processed throughout this study had uniform microstructure constituted by tetragonal grains with a mean grain size of 0.3 μm. The presence of coarser grains in the microstructure of Y-TZP ceramics is an indicator of a monoclinic phase [22], herein confirmed by the Rietveld refinement of XRD patterns. The presence of large grains with evidence of twinning shows that these grains are likely to be transformed during specimen cooling. Such a phase transformation during cooling could be attributed to localized strain at large grains, opposed to the surrounding smaller grains, likely due to thermal contraction of the TZP ceramic [5]. The tetragonal → monoclinic transformation may also occur as a consequence of polishing procedures or TEM assessment due to the effect of electron beam [23]. The small grain size observed for the specimens processed in the present study is desirable since it has been previously shown that the resistance to tetragonal → monoclinic transformation is increased by the decrease in grain size, especially in the case where density approaches theoretical values ( $d = 6.1 \text{ g/cm}^3$ ) and yttrium oxide ( $\text{Y}_2\text{O}_3$ ) content is close to 3 mol% [24]. In this work, the experimental Y-TZP also achieved apparent density around 97.5% of the theoretical value, indicating the reduction of flaws due to the presence of pores in the microstructure.

Burger et al. [25] have also reported that tetragonal phase of coprecipitated powders is already formed below the martensitic phase transformation temperature of pure zirconia (1175 °C). Additionally, these authors verified that the stabilization of tetragonal phase of ceramics obtained from yttria-coated zirconia powders is achieved only during

sintering, due to the higher rate of diffusion of yttria into zirconia. This behavior results in a heterogeneous distribution of yttria within zirconia grains and, consequently, in a greater concentration of monoclinic phase. Considering that the transformation toughening mechanism is a function of the concentration of monoclinic phase, the lower fracture toughness values of Y-TZP ceramics processed from coprecipitated powders, compared to yttria-coated zirconia, can be explained.

The hardness and fracture toughness results of the experimental Y-TZP ceramic material evaluated in this study ( $6.0 \pm 0.2 \text{ MPa m}^{1/2}$ ) are in agreement with those reported in the literature for 3Y-TZP ceramics [3,26]. Some authors [25,27,28] have showed that this value can be increased to 8–9  $\text{MPa m}^{1/2}$  modifying yttria concentration or increasing grain size by changing the conditions of powder's synthesis and sintering. However, it has to be pointed out that in these cases tetragonal → monoclinic transformation may easily occur, leading to the formation of surface flaws that could be deleterious to the *in vivo* performance of zirconia ceramics.

The 3Y-TZP specimens processed in this study presented 96 wt% of tetragonal and 4 wt% monoclinic phases. These microstructure characteristics may not be favorable for acid etching, since acidic solutions preferentially degrade vitreous phases but not the crystalline grains [29–33]. Adhesion of resin-based cements to Y-TZP has been reported to be inferior to glassy matrix ceramics. The absence of a vitreous phase, which makes adhesion of resin-based cements onto such ceramics possible, might be a limitation of this material



for its clinical use since *in vivo* predictability could not be guaranteed for minimal invasive FPD applications. *In vitro* bond strength tests are undertaken at our laboratories in order to evaluate this important issue.

The crack propagation through the PA alumina ceramic microstructure showed a more linear behavior when compared to commercial ceramics. Significantly lower fracture toughness values were obtained for the pure alumina ceramic when compared to those of the others. It can be therefore stated that the increased fracture toughness is related to the tetragonal phase of zirconia as it was evident for the CAZ, IZ, and Y-TZP ceramics. Therefore, it can also be argued whether Vickers hardness values should be taken into consideration when the mechanical aspects of the ceramic materials are compared with each other. Nevertheless, higher fracture toughness obtained with the experimental Y-TZP could indicate that this ceramic is a promising material with potential features to be used in dental applications in conjunction with CAD–CAM systems where machining techniques are required.

## 5. Conclusions

Y-TZP powders synthesized by coprecipitation route have proved to be adequate for processing of biomedical/dental ceramics with mechanical properties comparable to commercially available reinforced ceramic materials. The lower fracture toughness ( $6.0 \pm 0.2 \text{ MPa m}^{1/2}$ ), compared to some Y-TZP ceramics cited in the literature ( $8\text{--}9 \text{ MPa m}^{1/2}$ ), seems to be beneficial for *in vivo* performance. In this case, the high fraction of tetragonal phase retained at room temperature inhibits an excessive transformation to monoclinic phase due to the small grain size ( $0.3 \mu\text{m}$ ), preventing the formation of cracks on the ceramic surface. A homogeneous microstructure with high density (98% of theoretical density) was obtained by uniaxial compaction and sintering at  $1500^\circ\text{C}$  for 1 h. In order to guarantee the clinical applicability of the developed material, adhesion studies of Y-TZP ceramics to resin-based cements are in progress.

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