

## Evaluation of Hardness and Fracture Toughness of TZP Ceramics Stabilized with Yttria Concentrates

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**Abstract.** The influence of yttria purity level on hardness and fracture toughness of TZP ceramics was investigated. Terbium, dysprosium, holmium, erbium and ytterbium were the heavy rare earths evaluated as impurities. Samples were prepared employing zirconia powders doped with 3 mol% of high purity yttria or concentrates containing 85 and 95 wt% of this oxide. Two procedures were used to obtain the concentrates: solvent extraction and mixture of purified heavy rare earth oxides. These powders were synthesized by the coprecipitation route, pressed by uniaxial compaction (100 MPa) and sintered at 1500 °C for 1 hour. Gas adsorption (BET), laser diffraction and scanning electron microscopy were the techniques used for powder characterization. The sintered pellets were characterized by X-ray diffraction and scanning electron microscopy. Apparent density values were determined by the Archimedes method. Hardness and fracture toughness were evaluated by Vickers indentation technique. It was verified that the presence of heavy rare earth oxides in yttria concentrates has no significant effect on mechanical properties of zirconia ceramics. These samples have uniform microstructure, composed by tetragonal grains smaller than 0.5 µm. Hardness and fracture toughness are around 13 GPa and 6 MPa.m<sup>1/2</sup>, respectively.

### Introduction

Yttria tetragonal zirconia polycrystals (Y-TZP) are of great interest as engineering ceramic materials due to the high values of toughness arising from the transformation-toughening phenomena [1]. However, the industrial production of these materials still involves high costs associated with the starting raw materials and their processing. The use of yttrium concentrates, as zirconia stabilizing agent, may represent a reduction in the product cost. It has been demonstrated that most of lanthanide oxides can form tetragonal solid solution with zirconia but it is not well established the influence of such elements on mechanical properties of Y-TZP [2-6].

Yttrium is chemically similar to the heavier lanthanides elements such as terbium, dysprosium, holmium, erbium and ytterbium that often occur in the same minerals represented mainly by bastnasite, monazite and xenotime [7]. As a consequence of the similar ionic radius, the separation of these elements is very difficult and needs chemical processes based on solvent extraction and on ion exchange technique [8-9].

The heavy rare earths represent 15 wt % of an yttrium concentrate prepared from the monazite ore by a liquid-liquid extraction method, using di-2-ethylhexil phosphoric acid (D2EHPA) as extractant [10]. Further purification steps employing chelating agents are required to obtain high purity yttria [11]. To verify the possibility of using this concentrate for zirconia stabilization, this work reports the effects of heavy rare earths on the microstructure, hardness and fracture toughness of Y-TZP ceramics.

### Experimental Procedure

Stabilized zirconia powders were synthesized by the coprecipitation route [12]. Zirconium oxychloride solution (IPEN, Brazil) and rare earths chlorides, prepared by dissolution of high purity oxides (Aldrich, USA) and solvent extraction [10], were the precursors used in this investigation. The chemical composition of M1 yttria concentrate prepared by solvent extraction and of coprecipitated powders is shown in Table 1 and 2, respectively.

Sample 3P was stabilized with high purity yttria. M2 concentrate is a synthetic mixture containing 95 wt% of yttria. To verify the influence of individual heavy rare earths, M3 samples simulate the 85 wt% yttria concentrate. It is important to notice that, except for sample 3M3Tb, the molar composition of these samples is very similar due to the similar molecular weight and valence of these rare earth elements. The same molar composition is provided by sample 3M4Tb that was stabilized with a mixture of 74 wt% of yttria and 26 wt% of terbia.

Table 1: Chemical composition, determined by X-ray fluorescence analysis, of M1 yttria concentrate prepared by solvent extraction.

Sample code	Composition (weight %)						
	Y <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Er <sub>2</sub> O <sub>3</sub>	Ho <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>	others
M1	84.4	8.7	4.2	1.9	0.3	0.2	0.3

Table 2: Chemical composition of rare earth oxides in stabilized zirconia powders.

Sample code	Composition (mol %)					
	Y <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Er <sub>2</sub> O <sub>3</sub>	Ho <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>
3P	3.00	—	—	—	—	—
3M1	2.72	0.18	0.04	0.04	<0.01	<0.01
3M2	2.90	0.05	0.04	0.01	<0.01	<0.01
3M3Dy	2.71	0.29	—	—	—	—
3M3Er	2.71	—	0.29	—	—	—
3M3Ho	2.71	—	—	0.29	—	—
3M3Yb	2.71	—	—	—	0.29	—
3M3Tb	2.85	—	—	—	—	0.15
3M4Tb	2.71	—	—	—	—	0.29

Calcined and ball milled powders were pressed by uniaxial compaction at 100 MPa and sintered at 1500 °C for 1 hour.

Powders were characterized by gas adsorption (BET), laser diffraction and scanning electron microscopy. The characterization of as-sintered samples was carried out by apparent density measurements (Archimedes method). Quantitative phase analysis and determination of theoretical density were performed by Rietveld refinement of X-ray diffraction patterns of the polished surfaces prepared by a standard ceramographic procedure. Hardness ( $H_v$ ) and fracture toughness ( $K_{IC}$ ) were measured by Vickers indentation technique. It was used an indentation load of 60 N.

$H_v$  values were calculated by the following Eq. 1 [13]:

$$H_v = 1.8544 \times \frac{P}{d^2} \quad (\text{Eq. 1})$$

where  $H_v$  is the Vickers hardness ( GPa );  
 P is the indentation load ( N ); and  
 d is the indent diagonal length ( m ).

To calculate fracture toughness it was employed the equation developed by Shetty, Wright, Mincer and Clauer [14] for Palmqvist cracks:

$$K_{IC} = 0.0319 \times \frac{P}{a \times l^{1/2}} \quad (\text{Eq. 2})$$

where  $K_{IC}$  is the fracture toughness (MPa.m<sup>1/2</sup>);  
 P is the indentation load (N);  
 a is the indent half-diagonal length (m); and  
 l is the crack length (m).

The microstructure of polished and thermally etched samples was observed by scanning electron microscopy. Grain size was estimated by Quantikov image analysis [15].

### Results and discussion

A great similarity of physical properties was observed in synthesized powders. Agglomerate mean size, determined by laser diffraction, is around 2 μm. The surface area values are in the range of 50-80 m<sup>2</sup>.g<sup>-1</sup>. A typical SEM micrograph of these samples, showed in Fig. 1, indicates that particles are in the nanometer scale.

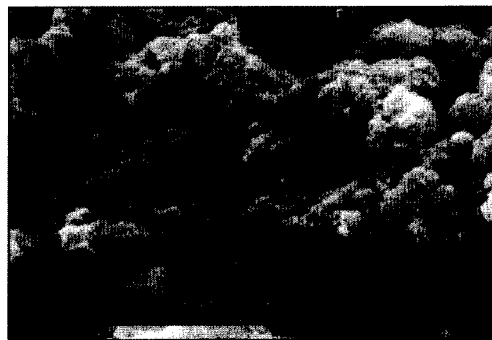


Fig. 1: Typical SEM micrograph of coprecipitated TZP powders submitted to ball milling.

The results of the Rietveld refinement of X-ray diffraction patterns and the apparent density of as-sintered pellets are shown in Table 3. It can be observed the predominance of the tetragonal phase in all samples. In these ceramics the occurrence of monoclinic phase may be a consequence of the transformation – toughening phenomena during cooling and/or polishing procedures. Apparent densities higher than 95% of the theoretical values were achieved for all samples.

Fig. 2a exemplifies the feature of Vickers indentations and cracks obtained for the investigated samples. The observation of this surface after polishing (Fig. 2b) shows that cracks are shallow at the indentation corner rather than connecting at a large depth below the surface. This is an evidence of Palmqvist morphology [14, 16].

According to the Table 4, hardness and fracture toughness values of prepared TZP ceramics are very similar. The slight decrease of these properties for 3M4Tb pellet may be a consequence of the lower yttria content in this sample (74 wt%). It is also important to notice that the results obtained in this work are in agreement with those reported in the literature for Y-TZP commercial ceramics [16, 17].

Table 3: Phase analysis and density values of TZP ceramics.

Sample code	Phase composition (wt%)		$\rho_{\text{theoretical}}$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\rho_{\text{aparent}}$	
	tetragonal	monoclinic		( $\text{g}\cdot\text{cm}^{-3}$ )	% $\rho_{\text{theoretical}}$
3P	96	4	6.07	$5.92 \pm 0.03$	$95.5 \pm 0.5$
3M1	96	4	6.11	$5.96 \pm 0.03$	$97.6 \pm 0.5$
3M2	97	3	6.09	$5.87 \pm 0.01$	$96.4 \pm 0.2$
3M3Dy	98	2	6.10	$5.91 \pm 0.03$	$96.9 \pm 0.5$
3M3Er	96	4	6.09	$5.91 \pm 0.06$	$97.0 \pm 1.0$
3M3Ho	97	3	6.09	$5.89 \pm 0.05$	$96.7 \pm 0.8$
3M3Yb	96	4	6.10	$5.94 \pm 0.05$	$97.4 \pm 0.8$
3M3Tb	96	4	6.08	$5.79 \pm 0.06$	$95.2 \pm 1.0$
3M4Tb	96	4	6.09	$5.90 \pm 0.09$	$96.8 \pm 1.5$

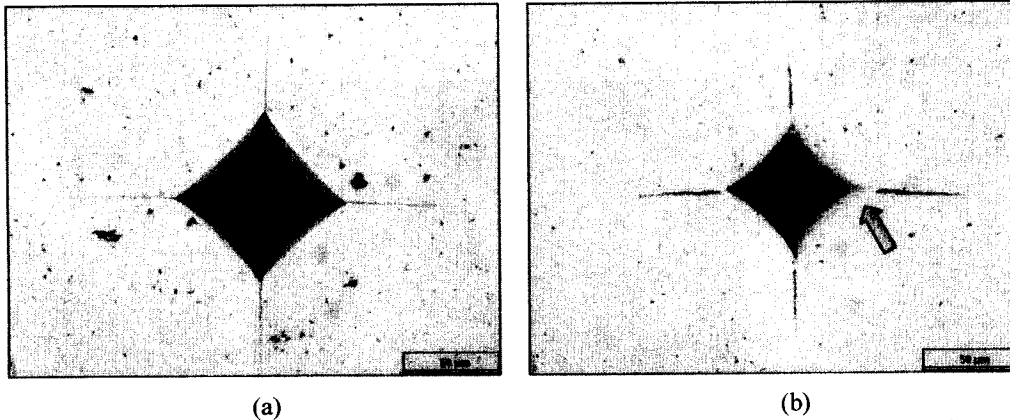


Fig. 2: Optical micrographs of 3P sample showing the formation of Palmqvist cracks after Vickers indentation test: (a) as-indented sample and (b) polished sample.

Table 4: Vickers hardness, fracture toughness and mean grain size values of TZP ceramics.

Sample code	$H_v$ (GPa)	$K_{IC}$ ( $\text{MPa}\cdot\text{m}^{1/2}$ )	Mean grain size ( $\mu\text{m}$ )
3P	$13.5 \pm 0.3$	$6.0 \pm 0.2$	$0.34 \pm 0.13$
3M1	$13.4 \pm 0.1$	$6.1 \pm 0.2$	$0.34 \pm 0.12$
3M2	$12.6 \pm 0.4$	$6.0 \pm 0.1$	$0.35 \pm 0.12$
3M3Dy	$13.1 \pm 0.2$	$6.1 \pm 0.2$	$0.36 \pm 0.12$
3M3Er	$13.2 \pm 0.4$	$6.2 \pm 0.2$	$0.42 \pm 0.15$
3M3Ho	$13.0 \pm 0.2$	$6.0 \pm 0.1$	$0.34 \pm 0.12$
3M3Yb	$13.3 \pm 0.3$	$6.4 \pm 0.2$	$0.35 \pm 0.12$
3M3Tb	$12.2 \pm 0.2$	$6.0 \pm 0.2$	$0.33 \pm 0.11$
3M4Tb	$9.5 \pm 0.4$	$5.8 \pm 0.2$	$0.33 \pm 0.11$

Mean grain size values (Table 4) are also similar, although erbium addition seems to increase this parameter. This tendency is confirmed by SEM micrographs of polished and thermally etched samples showed in Fig. 3. The presence of coarser grains in the microstructure of TZP ceramics is an indication of the existence of monoclinic phase. Probably, these grains transformed during cooling due to the greater grain size. The transformation of some grains from the tetragonal to monoclinic symmetry is also evidenced by typical twinning features indicated in Fig. 3 [1, 17].

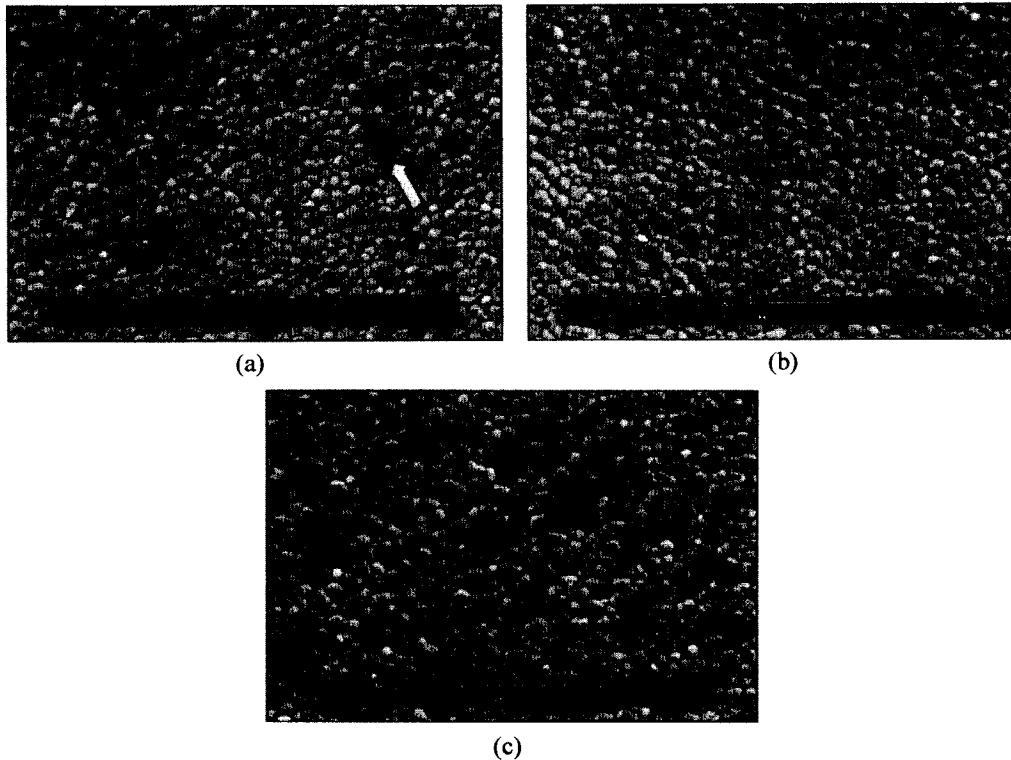


Fig. 3: SEM micrographs of TZP ceramics polished surfaces: (a) 3P , (b) 3M1 and (c) 3M3Er.

Similar mechanical properties and microstructure of the investigated TZP ceramics can be attributed to the close ionic radius of heavy rare earth trivalent ions: 1.019 Å for  $Y^{3+}$  and in the range of 0.98 to 1.04 Å for  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$  and  $Yb^{3+}$ . Besides that, the stabilization process provided by cations greater than  $Zr^{4+}$  (0.84 Å) is based on the same model. These dopants tend to form an 8-fold coordination with oxygen, leaving the oxygen vacancies near to the zirconium ions. For zirconia ceramics doped with a mixture of tri and tetravalent ions, such as  $Tb^{3+}$  (1.04 Å) and  $Tb^{4+}$  (0.88 Å), the 8-fold coordination is also observed, despite the decrease of oxygen vacancy number [18-20]. Considering these statements it is possible to explain the similar behaviour, verified in this paper, between yttria and heavy rare earths on zirconia stabilization.

### Conclusions

Coprecipitated zirconia powders doped with 3 mol% of an yttria concentrate allow the production of dense TZP ceramics. The tetragonal phase can be retained at room temperature though monoclinic phase is observed as a minor phase. An homogeneous microstructure composed by grains smaller than 0.5  $\mu\text{m}$  was verified for all samples. Mechanical properties such as Vickers hardness and fracture toughness values were as high as 13 GPa and 6  $\text{MPa}\cdot\text{m}^{1/2}$ , respectively. Similar properties were obtained for TZP ceramics stabilized with high purity yttria. This behaviour was attributed to the analogous ionic radius of heavy rare earth trivalent ions used as stabilizing agent.

Considering these results it can be concluded that a mixture of heavy rare earths containing more than 85 wt% of yttria is a suitable precursor for the production of zirconia structural ceramics. Cost reduction in yttria purification process could certainly enhance the industrial production of this material.

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## **Advanced Powder Technology III**

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## **Evaluation of Hardness and Fracture Toughness of TZP Ceramics Stabilized with Yttria Concentrates**

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