

# Tetragonal-to-Monoclinic Transformation Influence on the Mechanical Properties of CeO<sub>2</sub>- ZrO<sub>2</sub> Ceramics

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CeO<sub>2</sub>- ZrO<sub>2</sub> ceramics are considered a candidate material for applications as structural high performance ceramics. In this work are presented and discussed the tetragonal-to-monoclinic stress-induced transformation influence on the mechanical properties in these ceramics. Sintered ceramics were fabricated from powders mixtures containing ZrO<sub>2</sub> and 8 to 14 CeO<sub>2</sub> % mol. SEM observations were used to study de ceramic microstructures and X-rays diffraction to identification and determination of tetragonal and monoclinic phases. It was adopted the 4-point bending tests, Vickers surface hardness and fracture toughness technique to the determination of the mechanical parameters. The results showed that the mechanical properties were strongly dependent of the CeO<sub>2</sub> content, the microstructure and the fraction of tetragonal-to-monoclinic stress-induced transformation.

Keywords: CeO<sub>2</sub>-ZrO<sub>2</sub> ceramics, Ce-TZP ceramics mechanical properties, tetragonal-to-monoclinic stress-induced transformation

## Introduction

The reliability of structural ceramics is limited by their brittleness, since they show a tendency to fail catastrophically by growth of a single crack that originates from a very small structural defect. The defects are introduced during either fabrication or surface preparation or exposure to aggressive environments. These defects (e.g. pores, bulk and surface cracks) influence the reproducibility of mechanical properties, specially parameters such as the strength, hardness and toughness in ceramics materials [1], [2]. Garvie et al [3] indicated the possibility of attaining remarkable increases in strength and toughness of ceramic materials. Pure ZrO<sub>2</sub> presents phase transformations: monoclinic (m)  $\xrightarrow{1170^{\circ}\text{C}}$  tetragonal (t)  $\xrightarrow{2370^{\circ}\text{C}}$  cubic (c), where m and c are stable phases, and t is a metastable phase. The phenomenon of transformation toughened in ceramics relies on the volume expansion, 3-5%, and shear strain  $\cong$  7%, developed when tetragonal zirconia transforms to monoclinic phase.

Toughening of zirconia and zirconia-based ceramics is attained by retention of the tetragonal zirconia in a metastable state. This phase changes to monoclinic form being initiated by the tensile stress field of an advanced crack. Any metastable tetragonal zirconia will transform if to exist a elastic stress field in the vicinity of the crack tip. As a result of this, the volume expansion due t $\rightarrow$ m transformation and accommodating shear strains exerts a back stress on the crack. This mechanism introduces the concept of a process zone around a crack tip. A number of other mechanisms associated with the second phase zirconia phase particles have been used to explain the enchanted mechanical properties in these kinds of ceramics. Phenomenon of great technological importance is the crack branching (Fig.1a) and the development of a grinding-induced surface transformation which develops a compressive surface stress (Fig.1b) [1-7].

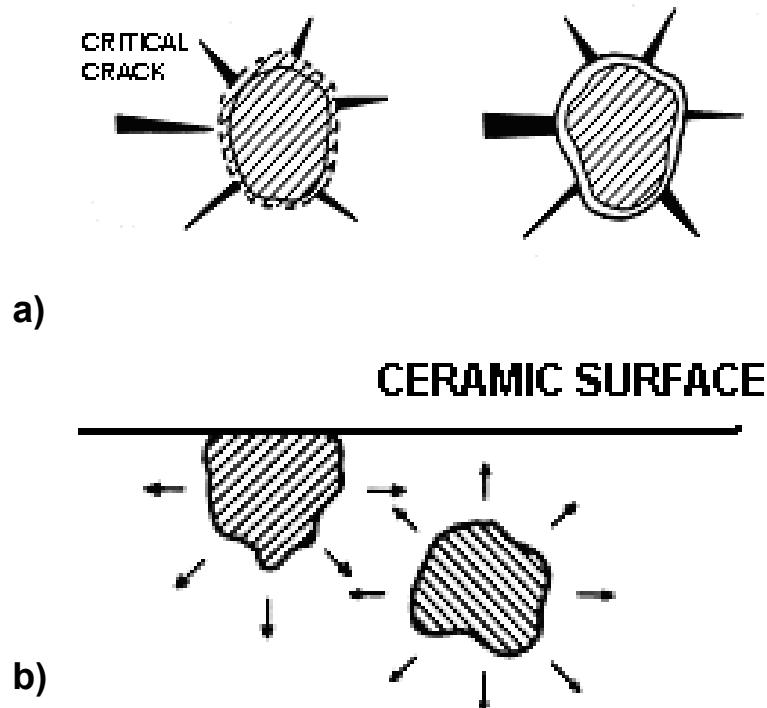


Figure 1. Schematic representation of: (a) the more common crack particle interaction (crack branching) and (b) the development of compressive surface layer by  $t \rightarrow m$  transformation via martensitic shear process (grinding-induced transformation in a compressive surface layer).

Tetragonal zirconia polycrystals (TZP ceramics) show the metastable tetragonal phase at room temperature. In  $\text{CeO}_2\text{-ZrO}_2$  system exists an extensive solid solution region with tetragonal phase which is stable at near room temperature (Fig.4), that is must possible fabricate ceramics composed of the tetragonal phase containing widely different amount of  $\text{CeO}_2$  content [4].  $\text{Y}_2\text{O}_3$ -stabilized tetragonal  $\text{ZrO}_2$  polycrystals (Y-TZP...

The commercial application of  $\text{ZrO}_2$ -based ceramics is well under way: i) cutting tool tips of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$ , ii) wear resistant as tappet heads, valve guides, valves seating, piston crowns, scissors an scalpels and iii) internal combustion engine and turbine parts( in experimental development programmers).

In the present study we are reporting the Ce-TZP mechanical properties dependence on  $\text{CeO}_2$  content, microstructure and fraction of tetragonal-to-monoclinic stress-induced transformation.

## Experimental Procedure

Several  $\text{CeO}_2\text{-ZrO}_2$  mixture containing different amounts of  $\text{CeO}_2$  were prepared by conventional mechanical mixtures of these powders. Commercial grade  $\text{ZrO}_2$  (ZS2 from Von Mel, England) and  $\text{CeO}_2$  (from Nuclemon, Brazil) were used. In the Fig.2 is shown the experimental procedure adopted in this work.

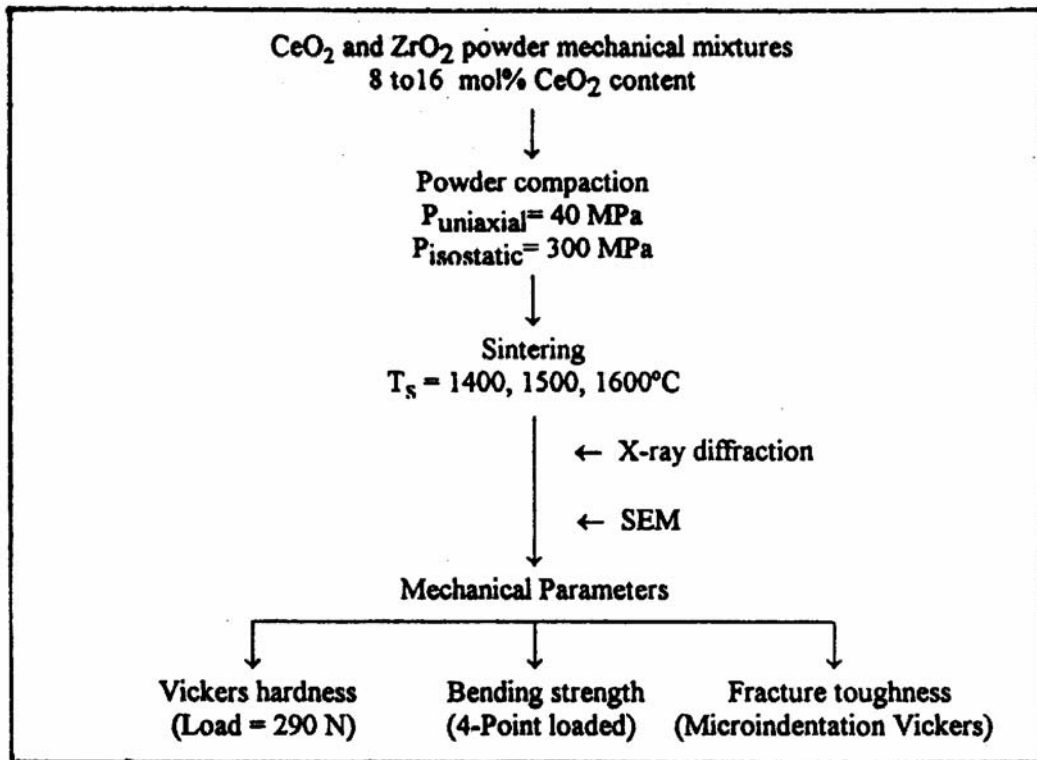


Figure 2 Schematic flowchart for Ce-TZP preparation and its mechanical parameter characterization.

## Results

### Grain Size in Sintered Ce-TZP Ceramics

Scanning electron micrographics of Ce-TZP analyses indicated that the average grain size increased with the sintering temperature (Fig.3). Results of SEM observation for these samples containing about 8 to 16 mol% CeO<sub>2</sub> revealed that shape and size of grains were invariable with changing of CeO<sub>2</sub> content.

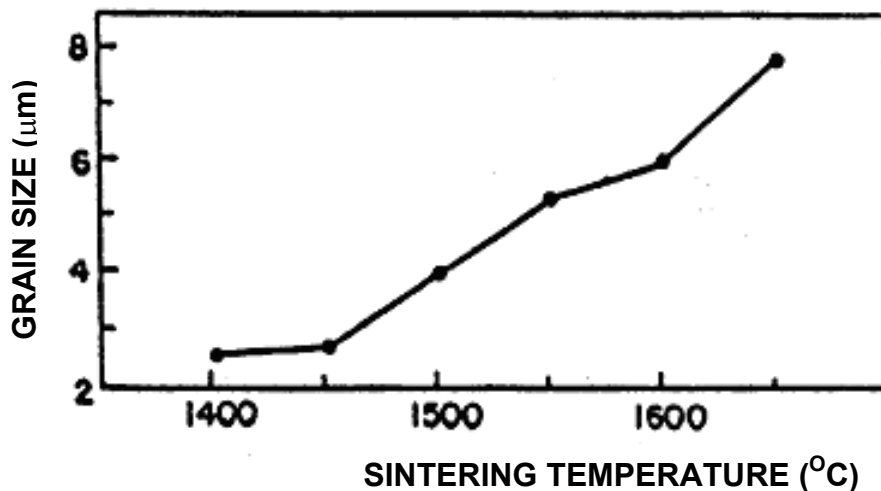


Figure 3. Behavior of temperature-grain size curve.

### Dependence of Stress-induced Transformation on CeO<sub>2</sub> Content and Grain Size

The fraction of tetragonal-to-monoclinic stress-induced transformation that occurred during the surface grinding and the fracture is shown in Fig.4. These curve behavior indicate that amount of monoclinic phase formed under applied stress depends strongly on CeO<sub>2</sub> content and grain size. These results suggest that amount of energy due to stress applied influences the amount of t→m transformation.

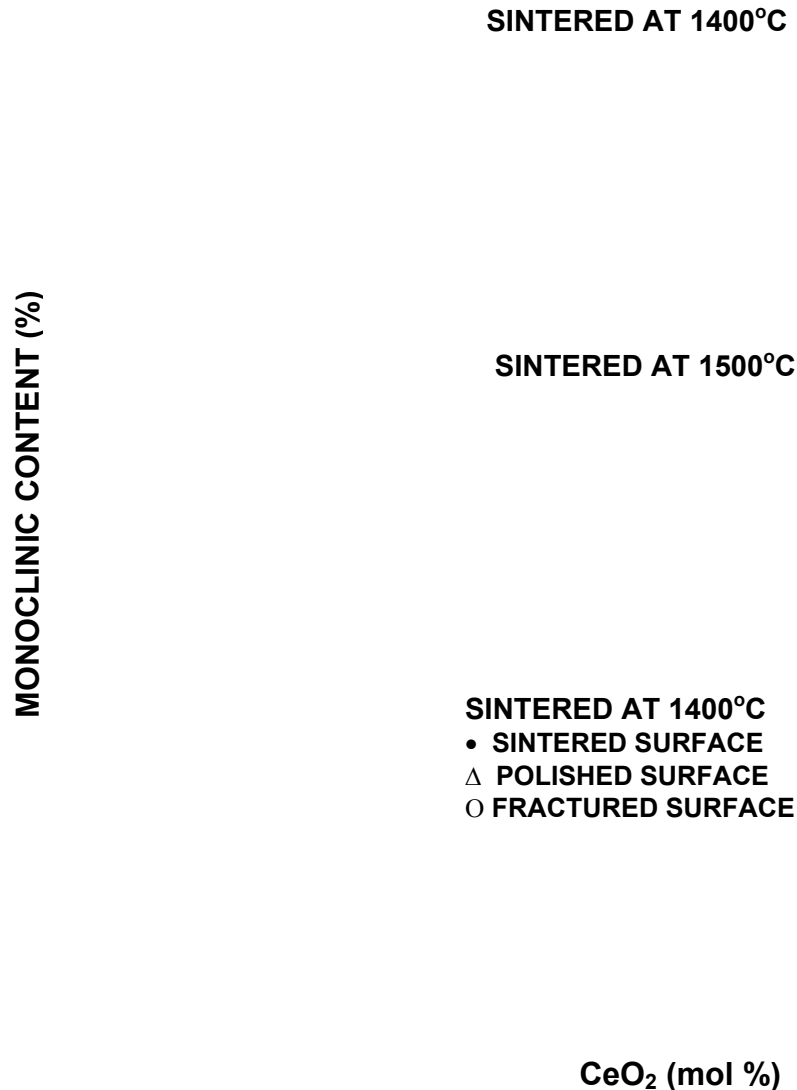


Figure 5. Dependence of stress-induced transformation on CeO<sub>2</sub> content.

### Bending Strength

The results shown in Fig.5 indicate higher fracture strength values for ceramics composed by 12 to 14 mol% CeO<sub>2</sub> content and sintered at 1600°C. Tsukuma and Shimada [4] reported that fracture strength depends on grain size and when it was smaller than 1 μm the values of this parameters can be about 800 MPa. They obtained stress-strain curves from 3-point bending strength measurement that showed a non-elastic region which was due to significant plastic deformation prior to failure (in a non-linear stress-strain relationship under a higher stress field). They suggested that this plastic deformation was due to decreasing CeO<sub>2</sub> content and increasing grain size.

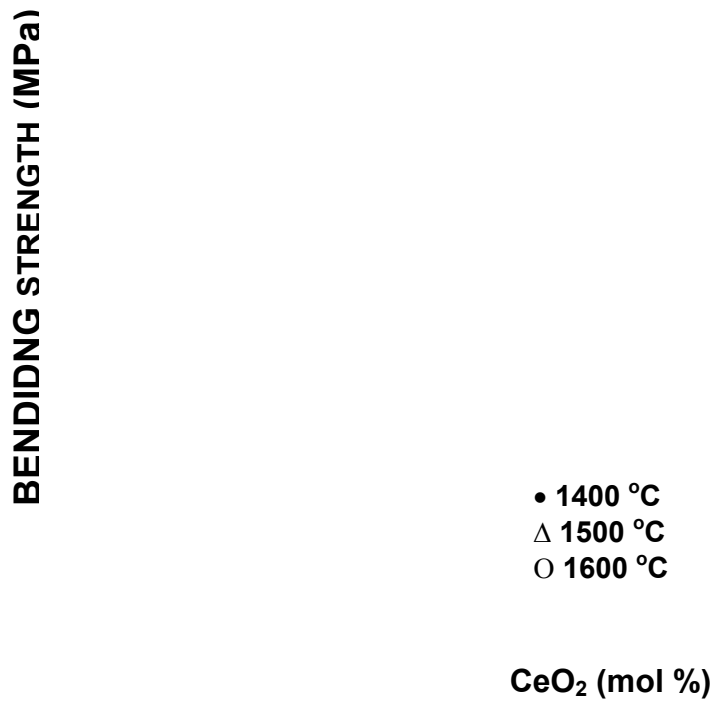


Figure5. Bending strength of Ce-TZP ceramics containing different amount of CeO<sub>2</sub> and sintered at several temperatures.

### Vickers Hardness

Vickers hardness of Ce-TZP ceramics decreased extensive with decreasing CeO<sub>2</sub> content and grain size (Fig.6).

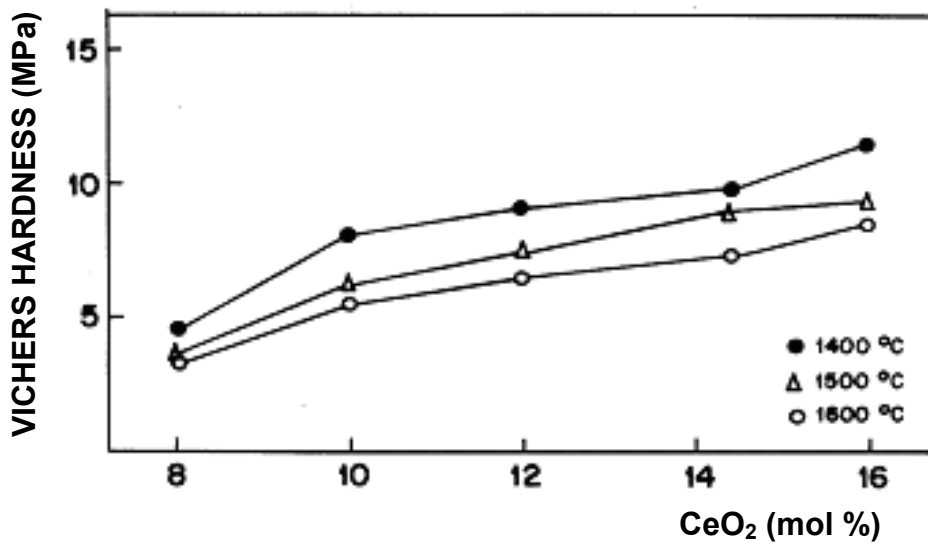


Figure 6. Relation between Vickers hardness, CeO<sub>2</sub> content and grain size.

In Fig.7 is shown that Vickers hardness decreased linearly with the amount of monoclinic phase formed by stress-induced transformation. Hannink and Swain [8] reported that the hardness decreased with an increasing of amount of stress-induced transformation due to the plastic deformation zone formed around the indent. In this case, the result suggests that the plastic deformation, which is introduced by stress-induced transformation, is responsible for the decrease of surface hardness. However, on the surface of zirconia ceramic exists a compressive stress due to the volume expansion that occurs during  $t \rightarrow m$  transformation.

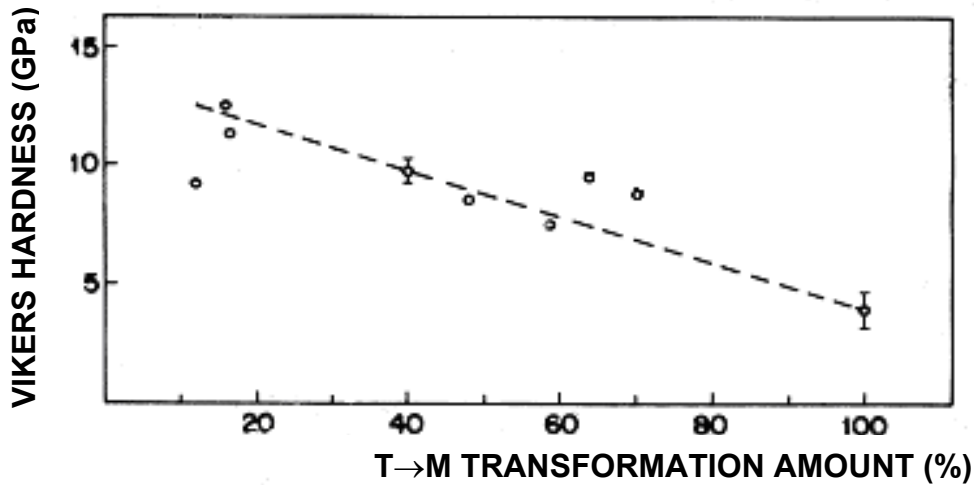


Figure 7. Dependence of Vickers hardness on the amount of monoclinic phase formed by stress-induced transformation.

### Fracture Toughness ( $K_{1C}$ )

The results of fracture toughness indicate that there is a composition range (about 10 to 12 mol%  $CeO_2$  content) with the better  $K_{1C}$  values (about 16 to 17  $MPa \cdot m$ ) (Fig.8).

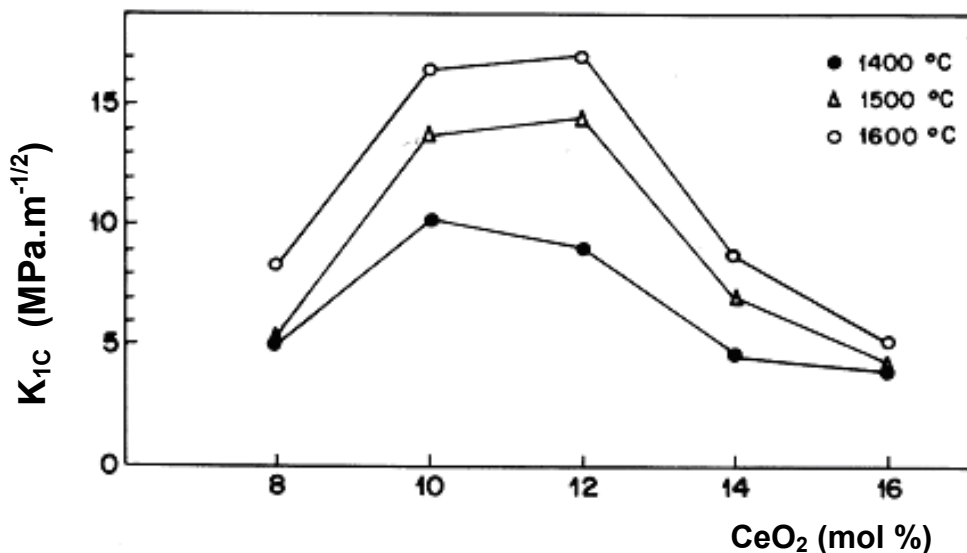


Figure 9. Dependence of fracture toughness on  $CeO_2$  content and grain size.

The curve behavior shows the influence of grain size on fracture toughness. Nevertheless, these Ce-TZP ceramics were exhibited a maximum strength at the intermediate value of fracture toughness (Fig.9). In previous study [3] was suggested that the strength of

transformation-toughened zirconia (such as Mg-PSZ, Y-TZP and Ce-TZP) is governed by two factors, i.e. flaw size and transformation limited stress. The curve region when exist a proportional relation between strength and toughness the strength is limited by the flaw size, and the region of inverse relation the strength is limited by the critical stress required for initiates the  $t \rightarrow m$  transformation.

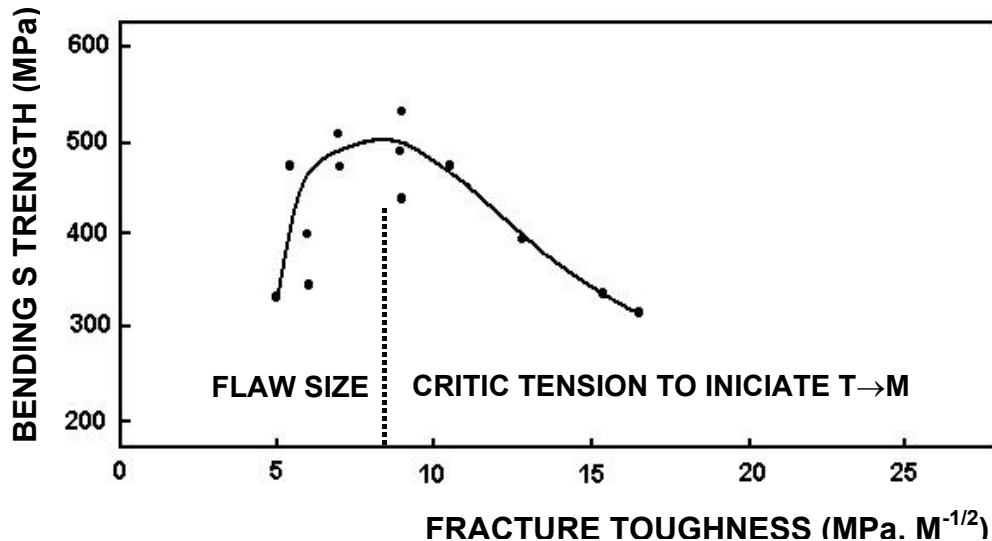


Figure 10. Relation between fracture toughness and the bending strength for Ce-TZP ceramics.

## Conclusions

The present study revealed that the mechanical properties were strongly dependents on the amount of monoclinic phase formed by stress-induced transformation and structural defects. Tetragonal monoclinic phase transformation in Ce-TZP ceramics was influenced by  $\text{CeO}_2$  content and grain size. The bending strength, fracture toughness and Vickers hardness parameters were analyzed on basis of the correlation with the amount of stress-induced transformation. The results showed that the mechanical properties were strongly dependent of the  $\text{CeO}_2$  content, the microstructure and the fraction of tetragonal-to-monoclinic stress-induced transformation.

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