
# Submicronic Yttria-Stabilized $ZrO_2$ ceramics densified by Spark Plasma Sintering: fracture strength and fracture toughness

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***Highlights***

- Full densification
- Controlled microstructure
- High levels of fracture strength and fracture toughness

## 1. Introduction

For many years, Zirconia (*$ZrO_2$*) has been one of the most studied ceramic due to its high mechanical properties such as high fracture strength and fracture toughness compared to others ceramics. This ceramic also known as "ceramic steel" is now used in a wide range of fields, from aeronautics to medical. This particularity is obtained by stabilizing the metastable tetragonal (*t*) phase at room temperature instead of the stable monoclinic (*m*) phase alloying $ZrO_2$ with specific oxides, in particular $Y_2O_3$. It is well-known that strong correlation exists between microstructure and mechanical properties of ceramics [1]. Further, according to Gupta *et al* [2] for $ZrO_2$ containing 3% mol $Y_2O_3$ (*3Y-$ZrO_2$*), there is a critical grain size around 300 nm above which a drop of strength can be observed. Densification by Spark Plasma Sintering (SPS) permits to prepare highly densified ceramics (*nearby 100%*) with nanoscale microstructures. The aim of this work is to prepare fully dense 3Y-$ZrO_2$ ceramics with grains around 300 nm in size, to characterize their microstructure and to measure their mechanical properties (*microhardness, fracture strength and fracture toughness, the latter measured by the single-edged notched beam (SENB) method*).

## 2. Methods

Commercial 3Y-$ZrO_2$ powder (TZ-3Y-E, Tosoh, purity > 99.99%) of crystallite size 50 ± 10 nm was consolidated by SPS (*Dr Sinter 2080, SPS Syntex Inc., Japan located at the Plateforme Nationale de Frittage located at the Université Toulouse III Paul Sabatier*). Samples were loaded into a 20 mm inner-diameter graphite die. A sheet of graphitic paper (*Papyex®Mersen*) was previously placed between the die and the powder as well as between the punches and the powder for easy removal. The powders were sintered under vacuum. Conditions are reported in Table 1. An optical pyrometer, focused on a little hole at the surface of the die, was used to monitor the temperature. A pressure of 100 MPa was applied et the dwell temperature and maintained during the dwell. The produced pellets denoted A1, A2… A5 hereafter were 20 mm in diameter and about 2.5 mm thick. Partial reduction of zirconia (*characterized by the grey color of the pellets*) was observed due to the low oxygen partial pressure during the sintering cycle. As a consequence, the pellets were annealed 4 h at 900 °C in air in order to remove the graphitic surface contamination layer and to re-oxidize zirconia. Starting powder and sintered samples were characterized by X-Ray Diffraction (XRD) using a Bruker D4 Endeavor diffractometer equipped with a Cu $K_\alpha$ radiation tube. After a polishing down to 1 µm (*using diamond slurries*), densities were determined by the Archimedes method. The powder and fracture surfaces of the sintered specimens were observed by field emission-gun scanning electron microscopy (*FESEM, JEOL JSM 7800F*). Then pellets were cut into parallelepiped shape test bars of dimensions about 2 x 2 x 18 mm. Microhardness was determined on polished surface of the specimens by loading a Vickers indenter at 200g during 10s (*Shimadzu HMV 2000*), the corresponding diagonals of the indentation were measured using an optical microscope attached to the indenter. The calculated microhardness values correspond to the average of twelve measurements. Transverse fracture strength ($\sigma_f$) was measured by the 3 points bending method (*MTS 1/M machine*). Fracture toughness was measured by the


SENB method on specimens notched with a 0.17 mm diameter diamond wire. Notch depth and width were measured by an optical microscope on both sides of samples. The fracture toughness ($K_{Ic}$) was calculated using the calibration factor proposed by Brown and Strawley [3].

## 3. Results and discussion

SEM observations of the starting powder confirm that the average grain size is around 50 ± 10 nm. XRD pattern reveals that powder is composed of 77 and 23% of tetragonal and monoclinic $ZrO_2$ phases, respectively. XRD patterns of all the sintered pellets show that only tetragonal phase is present. The relative densities of all the sintered pellets, with the conditions reported in Table 1, are around 99%. The average grain sizes are in the desired range (*ie at the vicinity of the predicted threshold of 300nm, see above*). The average Vickers microhardness is equal to 14.2 GPa, a value comparable with those reported for fully tetragonal stabilized 3Y-$ZrO_2$ ceramics of similar submicronic average grain size [4]. Sample A2 presents the lowest fracture strength (*588 MPa*) which is associated to a particularly wide distribution of 238 MPa. A5, which have the highest one, also presents a wide distribution of 200 MPa, this could reflect a lack of microstructural homogeneity, despite this was not detected by FESEM observations. The average fracture strength (*655 MPa*) is similar or higher to most of those reported for 3Y-$ZrO_2$ of equivalent microstructures [5]. XRD analyses performed on fracture surfaces after mechanical tests did not reveal a t → m transformation for all of the samples, in agreement with the tetragonal phase retention below the critical grain size of 300 nm determined for 3Y-$ZrO_2$. The higher fracture toughness is obtained for A2 (14.4 MPa.$m^{1/2}$).

| Specimen | T( °C) | t (min) | v (°C.$min^{-1}$) | RD (%) | G (nm) | HV0.2 (GPa) | $\sigma_f$ (MPa) | $K_{Ic}$ (MPa.$m^{1/2}$) |
|---|---|---|---|---|---|---|---|---|
| A1 | 1200 | 2 | 100 | 99 | 230 ± 62 | 13.8 ± 0.3 | 678 ± 53 | 14.1 ± 3.6 |
| A2 | 1200 | 10 | 100 | ~100 | 267 ± 79 | 13.9 ± 0.4 | 588 ± 238 | 14.4 ± 2.7 |
| A3 | 1200 | 60 | 100 | ~100 | 285 ± 67 | 14.1 ± 0.2 | 631 ± 120 | 11.3 ± 1.5 |
| A4 | 1200 | 10 | 300 | 99 | 298 ± 58 | 14.1 ± 0.6 | 676 ± 78 | 12.5 ± 1.7 |
| A5 | 1150 | 10 | 100 | 99 | 223 ± 70 | 15.1 ± 0.3 | 704 ± 200 | 13.1 ± 2.6 |

**Table 1.** SPS parameters (T: dwell temperature, t: time, v: heating rate) and characteristics and properties (RD : Relative Density (± 1%), G: Grain size, HV0.2: Vickers microhardness, $\sigma_f$: fracture strength, $K_{Ic}$: fracture toughness) of the specimens, Standard deviations are indicated for average grain size and mechanical properties.

## 4. Conclusions

Samples were sintered by SPS at 1150 °C and 1200°C for 10 to 60 min under uniaxial pressure of 100 MPa. The product pellets are fully densified (*up to 100% of relative density*). Whether monoclinic and tetragonal phases are present in the starting powder only the latter is present in the sintered samples before and after mechanical characterization. By optimizing the SPS parameters the microstructure of the ceramics can be controlled and the grain size does not exceed 300nm. Vickers microhardness and fracture strength values are in agreement with those reported in other works. Interestingly, fracture toughness values ranging from 11.3 to 14.4 MPa.$m^{1/2}$ are the highest reported up to know for such a fine microstructure. SEVNB method will be used in further works to determine the intrinsic values of fracture toughness.

## References

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***Keywords***
Yttria Stabilized Zirconia, Spark Plasma Sintering, Fracture Toughness