



# Fast-low temperature microwave sintering of $\text{ZrSiO}_4\text{-ZrO}_2$ composites

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## ABSTRACT

Today, many industrial applications require components that work under extreme conditions, especially at very high temperatures ( $>1200\text{ }^\circ\text{C}$ ) for a long time. An excellent combination of properties such as low thermal conductivity, low coefficient of thermal expansion and high chemical resistance are required for such applications. Advanced ceramic materials based on zircon-zirconia composites ( $\text{ZrSiO}_4\text{-ZrO}_2$ ) possess these properties, thus making them attractive for, i.e., high-level radioactive waste immobilisation. The main drawback of these materials are the high temperatures and long residence times required to sinter them and obtain high densities, which entails high energy consumption and costs. Therefore, non-conventional microwave sintering is a very powerful and efficient technique capable of reducing sintering temperatures and holding times. The objective of this study is to evaluate the microwave sinterability of zircon-zirconia powders obtained by colloidal methods (80–20 vol% and 20–80 vol%  $\text{ZrSiO}_4\text{-ZrO}_2$ ). A stability study of the phases present was carried out by X-ray diffraction and the mechanical and microstructural properties were evaluated in order to obtain the best materials with outstanding final properties.

## 1. Introduction

The urgent problem of managing the radioactive waste generated by nuclear reactors and decommissioned nuclear weapons affects the future development of the nuclear industry. The immobilisation of this radioactive waste in solid waste forms has attracted numerous materials, geochemical and environmental scientists. The key challenge, i.e. to safely remove these hazardous elements, is a difficult issue for environmental protection and advanced fuel cycles [1–6]. After many decades of efforts by scientists, zircon ( $\text{ZrSiO}_4$ ) has been recognized as a key material for the immobilisation of these elements, as it has excellent chemical stability, a low coefficient of thermal expansion and high thermodynamic resistance [7–10]. Zircon is a readily available raw material with attractive physical and chemical properties for technological use. Its main properties are: relatively low linear thermal expansion ( $4.10\text{-}6\text{ }^\circ\text{C}^{-1}$ ) and inertness [11]. It is therefore used in applications at high temperatures (1300–1500  $^\circ\text{C}$ ) with low chemical attack, such as in the steel or glass manufacturing industry.

Due to the difficulty of achieving high densities and reducing porosity, zircon can be combined with other phases, such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,

clays, etc. However, these additions can be detrimental for mechanical properties, such as hardness or fracture toughness, especially in the case of silica and silicates that can form glassy phases at the high temperatures required for zircon densification. To improve the mechanical properties of zircon, the incorporation of a secondary phase such as TiC, SiC,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and mullite has been proposed [12–14] due to their superior mechanical properties.

Rendtorff et al. obtained high-density  $\text{ZrSiO}_4\text{-ZrO}_2$  composites by spark plasma sintering (SPS) [15]. The results showed that the zirconia can effectively improve the mechanical properties of the samples, and high density at low temperatures (1300–1400  $^\circ\text{C}$ ) and short holding time were achieved with SPS. But due to the high cost of SPS and the geometrical constraint associated with uniaxial pressing, its accessibility is limited and difficult to scale up to industrial production. Other authors successfully prepared  $\text{ZrSiO}_4\text{-ZrO}_2$  materials by hydrothermal and sol-gel processes, but these two methods lead to a large amount of waste water and exhaust gases, leading to a second contamination which is totally contrary to the purpose of nuclear waste disposal [16].

In the last decade, microwave sintering technology has been widely used in the production of materials due to its advantages of high

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efficiency and environmental sustainability [17,18]. However, to our knowledge, very few studies on microwave sintering of zircon/zirconia ceramics have been published. Yang et al. [19] sintered high density zirconia/zircon ceramics by microwave sintering at 1500 °C with 1 h, 8 h and 12 h of holding time, reaching the best density values with 12 h. These authors only studied the phase structure and density of the samples.

In summary, this work explores the microwave sintering process as a promising route for the rapid low-temperature preparation of zircon-zirconia ceramic composites. The properties of the ceramic composites optimised by colloidal processing and sintered with microwaves were analysed in terms of phase evolution, microstructure and mechanical properties and compared with those obtained by conventional sintering to demonstrate the advantages of the fast-sintering route. In addition, the dielectric properties and energy absorption during microwave heating cycle of ZrSiO<sub>4</sub>-ZrO<sub>2</sub> with 20 vol% of zircon composites were studied. This composition was selected due to its higher efficiency in absorbing microwave radiation over the entire temperature range.

## 2. Materials and methods

### 2.1. Starting powders and mixtures

High-purity 3 mol% Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> powder (TZ3YS, Tosoh, Japan), whose composition is 95.00 ZrO<sub>2</sub>, 4.98 Y<sub>2</sub>O<sub>3</sub>, 0.005 Al<sub>2</sub>O<sub>3</sub>, 0.004 Fe<sub>2</sub>O<sub>3</sub>, 0.003 Na<sub>2</sub>O, 0.002 SiO<sub>2</sub> (oxide wt%), and ZrSiO<sub>4</sub> powder (Zircobit®, Industrie Bitossi S. p.a. Italy), whose composition is 63.00 ZrO<sub>2</sub>, 32.50 SiO<sub>2</sub>, <2.00 Al<sub>2</sub>O<sub>3</sub>, <1.30 HfO<sub>2</sub>, <0.15 TiO<sub>2</sub>, 0.07 Fe<sub>2</sub>O<sub>3</sub> (oxide wt %), were used in this study. Their average particle diameters are 0.4 and 1.6 μm and the specific surface areas are 6.7 and 7.9 m<sup>2</sup>/g, respectively. These powders were mixed to obtain the composites ZrSiO<sub>4</sub>-ZrO<sub>2</sub> with 20 and 80 vol% relative content of zircon, labelled as ZS20 and ZS80, respectively. In addition to the mixtures, the starting zircon powder was studied also.

For the preparation of the composite materials, aqueous suspensions with a total solids content of 30 vol% were prepared using both commercial powders, with the reported volumetric ratio of 80:20 and 20:80. For this, a commercial ammonium salt of polyacrylic acid (PAA; Duramax TM D-3005, Rohm & Haas, USA, with 35 wt% active matter) was employed as a deflocculant, adding 0.1 wt% with respect to zircon powder and 0.2 wt% with respect to zirconia one, according to previous studies [20,21]. The pH of the suspensions was not furtherly adjusted, presenting a natural pH of around 5.5 for the zircon-based suspensions and around 6 for the zirconia-based ones. In addition, 1 min of ultrasound was applied using a sonication probe (dr. Hielscher, UP400S, Germany) for a better dispersion of the particles and homogenisation of the mixtures. Once the suspensions were optimised, they were frozen in a rotary evaporator (RV10 basic, IKA, Germany) immersed in a bath of liquid N<sub>2</sub> and subsequently lyophilised in a freeze dryer (Cryodos-50, Telstar, Spain) at -50 °C and 0.3 mPa for 24 h.

### 2.2. Sintering processes

The freeze-dried powders were sintered by conventional sintering in an electric furnace and by microwave sintering. The following sintering temperatures have been selected for conventional sintering: 1500, 1550, and 1600 °C. The heating rate used was 10 °C/min with 2-h dwell time. Under these conditions, it can be assumed that the total time required is approximately 7 h.

Microwave sintering was carried out in an experimental furnace which consisted of a single-mode cylindrical cavity operating in the TE<sub>111</sub> mode, with a tunable system to keep the resonance frequency of 2.45 GHz, with maximum *E*-field in the center of the cavity. Details of the sample mounting is reported in Ref. [22]. The consolidation temperatures were 1200 and 1300 °C in air with dwell time of only 10 min. Sintering temperatures were measured on the sample surface with the

aid of an optical pyrometer (OPTRIS GmbH, Berlin, Germany) previously calibrated (emissivity) for the selected temperatures. The heating rates achieved in this technique are 75 °C/min; therefore, the total duration of this process is 46 and 50 min for temperatures of 1200 and 1300 °C, respectively. It should be noted that a SiC susceptor was used to stabilize the temperature at the beginning of the cycle to avoid the runaway heating.

### 2.3. Characterization methods

#### 2.3.1. Measurements of dielectric properties

To determine the dielectric properties of the composites, cylindrical samples with 15 mm in height and 10 mm in diameter were prepared and placed on a quartz support in the center of the circular microwave cavity [23,24]. Heating was carried out at a rate of 15 °C/min up to a maximum temperature of 1200 °C and with a homogeneous distribution of the electric field. The temperature was measured with the help of an IR pyrometer (OPTRIS GmbH, Germany) and the dielectric properties with the cavity perturbation method. Dielectric measurements were only performed for the composite ZS20, since zircon-based materials required the use of a SiC susceptor that interacts with the radiation and alters the dielectric properties.

#### 2.3.2. X-ray diffraction and relative density

The crystalline phases of the sintered materials were determined by X-ray diffraction (XRD) with a D8 Advance diffractometer (Bruker, Germany) using Cu K $\alpha$  radiation. Measurements were performed in the range 10°-80°, and the step size and the reading time were 0.02° and 0.2 s, respectively. The relative density of the sintered materials was measured by Archimedes' principle by immersing the samples in water (ASTM C373-14) [25]. A value of 4.56 g/cm<sup>3</sup> was used as the theoretical density of ZrSiO<sub>4</sub> and 6.05 g/cm<sup>3</sup> for TZ3YS to estimate the relative density, according to the X-ray diffraction files of the PDF database PDF#06-0226 and PDF#37-1484, PDF#50-1089, PDF#49-1642, respectively.

#### 2.3.3. Microstructure characterization and mechanical properties

The microstructures of the specimens were analysed by field emission scanning electron microscopy (FESEM, S4800 Hitachi, Japan). All samples were polished with 1 μm diamond paste for a mirror shine finish. The thermal etching was performed for 30 min at 100 °C below the maximum sintering temperature to reveal the grain boundaries. The average grain size of at least 500 grains was measured from the FESEM images using Image software according to the linear intercept method [26]. Images of two different samples from each sintering condition were analysed.

Mechanical properties were evaluated via micro-indentation technique. Vickers hardness (*Hv*) values were obtained with a Shimadzu HMV-20 micro-indenter applying a load of 9.80 N for 10 s, and 20 measurements were taken for each specimen. Fracture toughness (*K<sub>IC</sub>*) values were studied by the cracks induced by applying loads of 49.0 N for 10 s and an image analysis program and calculated by using the formula proposed by Evans et al. [27]. 6 measurements were taken in each sample.

## 3. Results

The temperature evolution with the dielectric parameters of the ZS20 composite can be seen in Fig. 1, which shows that both the dielectric constant and the loss factor increase with temperature, until stabilization is reached at around 1100 °C. The microwave heating of a ceramic material depends on its dielectric properties. At room temperature, most ceramic materials are almost transparent to microwave radiation due to their low dielectric loss factor, such as 3Y-TZP material, which exhibits at 25 °C a  $\tan\delta = 0.0011$ . However, the dielectric loss factor of 3Y-TZP increases fast above 600 °C ( $\tan\delta = 0.15$ ) and 1200 °C

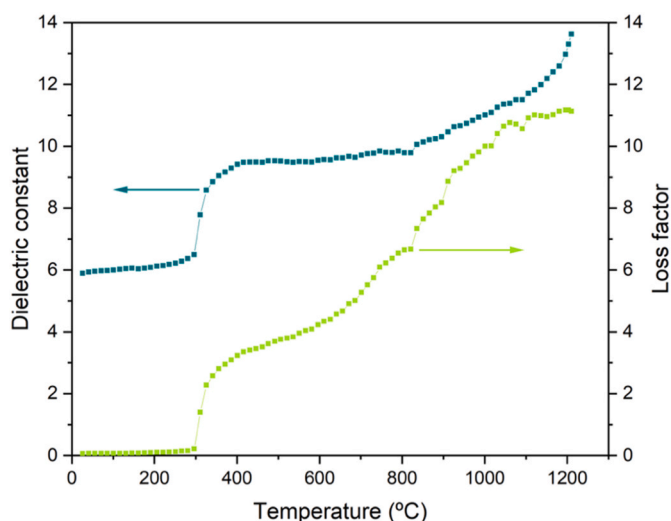


Fig. 1. Evolution of dielectric properties with the temperature of ZS20 composite.

( $\tan\delta = 1.86$ ), leading to an effective high-temperature heating [28].

When sintering a material by microwaves, the radiation promotes the motion of the ions and dipoles according to the direction of the electromagnetic field and the material must be able to absorb this energy. The microwave heat absorption capacity depends on the dielectric properties of the material, especially on the imaginary part, also called the loss factor. Therefore, microwaves are a versatile way to decrease the sintering temperature required in the conventional technique [22,23]. It is due to the molecular vibrations triggered by the electromagnetic field. According to Fig. 1, both dielectric properties, the real part and the loss factor, increase with temperature. At low temperatures there are no significant changes in these variables due to the evaporation of the water retained in the starting powders. Then, at around 300 °C, there is a considerable increase in dielectric properties, followed by a stage of stability of the dielectric constant up to 800 °C. From this temperature up to 1200 °C it increases again. The loss factor has a linear increase until it stabilises at around 1100 °C.

Fig. 2 shows the evolution of the power absorbed during the heating of the material as a function of time. A variation in any of the dielectric parameters is reflected in the power absorbed by the sample. Therefore, Fig. 1 is directly related to Fig. 2, which indicates a jump in power absorption of 300 °C, from 300 °C to 600 °C after 12–13 min of heating,

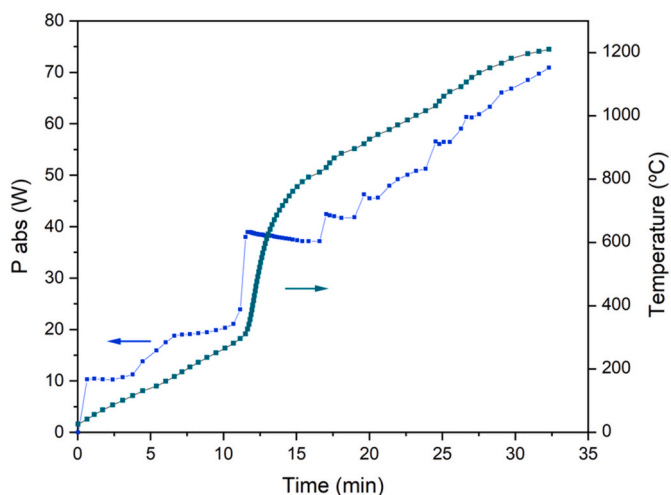


Fig. 2. Microwave absorbed power vs. sintering temperature of ZS20 composite.

followed by a stabilization at 40 W for 5 min reaching 800 °C in approximately 2 min. Subsequently, both power and temperature behave homogeneously until the end of the cycle where an increase is observed until the maximum absorbed power of 75 W. Consequently, an important result to obtain these materials in a sustainable and economically profitable way is the low energy consumption of only 75 W to reach 1200 °C with a single cycle of 35 min.

The results of apparent and relative densities obtained after sintering are shown below (Table 1). In this way, it is possible to compare the degree of densification for the same material at different temperatures and sintering methods, conventional sintering (CS) and microwave sintering (MW).

A first conclusion can be drawn from Table 1, which indicates that the degree of compaction is very high in all cases. A noticeable effect observed in Table 1 is that density always increases with the zirconia content for any temperature and sintering method. This is to be expected since the sintering temperature of zirconia is lower than that of zircon. This allows the diffusion mechanisms to be favoured, even at lower temperatures when the proportion of  $Y_2O_3$ -stabilized zirconia is higher in the composite. It can also be observed that, for the microwave sintering process, as the sintering temperature increases, there is a significant increase in the degree of densification. However, in the conventional sintering process, the same does not occur. At 1550 °C and 1600 °C, both composites present very similar relative density values, and only changes are observed at 1500 °C, where the density is lower. Interesting results were obtained for samples heated by microwaves. At relatively low temperatures, 1200 °C and 10 min of dwell time, densities of the order of the materials obtained at 1500 °C by conventional heating have been obtained. The energy absorbed by microwaves can cause changes in sintering mechanisms which accelerate the densification process. At 1300 °C, values close to those obtained by conventional sintering at 1550 °C have been obtained, which means that the same level of densification is reached using microwave technology at a temperature 250–300 °C lower than that needed in a conventional furnace. A second point is that to achieve a high density for zircon (above 96% TD) conventional sintering requires at least 1550 °C-2h whereas this density level is reached with microwave sintering at 1300 °C-10min.

In order to understand the benefit of the microwave sintering, the phase composition of the obtained  $ZrSiO_4$ - $ZrO_2$  composites was analysed by XRD. Fig. 3 shows the XRD diffraction patterns of the ZS80 sintered at 1200 °C and 1300 °C by microwave (MW), and conventional sintering process (CS) at 1600 °C.

The main crystalline phases, as expected, are zircon and *t*-zirconia. The main reflections of *m*-zirconia (−111 and 111) in the composites obtained by microwave were not detected. The *c*-zirconia content was in

Table 1  
Relative density of  $ZrSiO_4$  and  $ZrSiO_4$ - $ZrO_2$  composites at different sintering conditions.

Nomenclature	Sintering parameters	Relative density (% T.D)
ZS	CS 1500°C-2h	93.8 ± 0.5
ZS80		95.4 ± 0.5
ZS20		96.2 ± 0.5
ZS	CS 1550°C-2h	96.6 ± 0.5
ZS80		97.7 ± 0.5
ZS20		98.4 ± 0.5
ZS	CS 1600°C-2h	96.4 ± 0.5
ZS80		98.1 ± 0.5
ZS20		98.6 ± 0.5
ZS	MW 1200°C-10min	92.1 ± 1.0
ZS80		93.5 ± 1.0
ZS20		94.5 ± 1.0
ZS	MW 1300°C-10min	96.2 ± 0.5
ZS80		97.9 ± 0.5
ZS20		98.9 ± 0.5

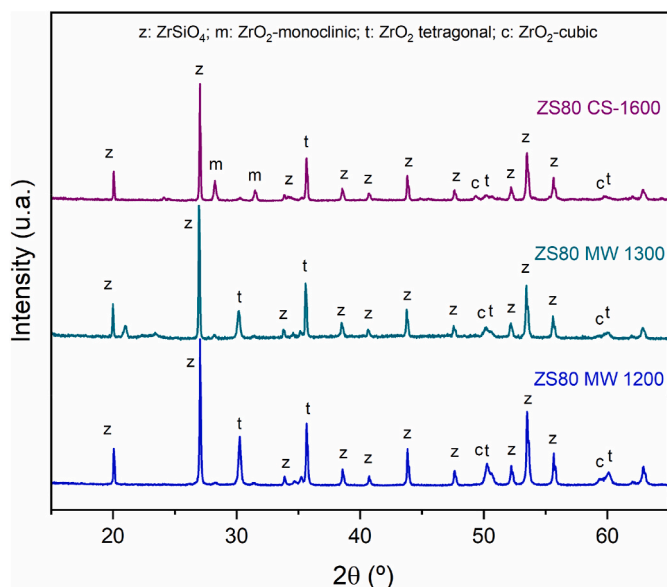


Fig. 3. XRD patterns of zircon-zirconia composites.

all cases less than 10% of the total zirconia [29]. The formation efficiency of  $ZrSiO_4$  prepared at low sintering temperature (1200 °C) and short time (10 min) by the microwave sintering is much higher than that of conventional sintering at 1600 °C. The results revealed that the microwave sintering can be used to obtain ceramic composites at low-temperature and shorter time.

FE-SEM micrographs of the composites and pure zircon obtained under different sintering conditions and processes are shown in Fig. 4. Fig. 4a, b and 4c show FE-SEM images of the samples ZS, ZS80 and ZS20 prepared at 1600 °C-2h by conventional process, respectively. Fig. 4d, e and 4f represent the samples ZS, ZS80 and ZS20 prepared by microwave sintering at 1300 °C-10min, respectively.

In Fig. 4, the porosity is more remarkable in the  $ZrSiO_4$  samples, which is in agreement with the density data obtained. With respect to the composites ZS20, it can be observed that the grain size of zirconia is lower than that of the composite with ZS80. In the samples obtained by conventional route, the grain size of zircon increases as the percentage of zirconia decreases. Therefore, it can be inferred that zirconia inhibits the growth of zircon. Using microwaves, where the heating transfer is

completely different from the conventional furnace, zircon maintains a very similar grain size regardless of the zirconia percentage. It can also be observed in Fig. 4a and d, that at 1600 °C the zircon grains (2–3 μm) have a larger size than those obtained by microwaves at 1300 °C (1–1.5 μm). These results are consistent with the high temperatures reached in conventional. Regarding the materials obtained by microwaves, in Fig. 4f, zircon grains (1–1.5 μm) have had an exaggerated growth with comparison to zirconia grains (approximately 0.4–0.5 μm). This fact is similar to the microstructure ZS80, where the homogeneous distribution of zircon with respect to zirconia can also be observed. These characteristics are reflected in the mechanical properties described below.

Toughening improvement can be obtained by incorporating  $ZrO_2$  particles in a ceramic matrix. Vickers hardness ( $H_v$ ) and fracture toughness ( $K_{IC}$ ) as a function of sintering process and final temperature were measured for the zircon and zircon-zirconia composites, as can be observed in Table 2 and Fig. 5.

Based on the results obtained in Table 2, it can be concluded that a higher proportion of zirconia in the material leads to higher hardness in both microwave and conventional sintering, as the material also exhibits a higher density. The best values obtained using the microwave technique are at the final temperature of 1300 °C (~14.0 GPa). These values are close to those obtained conventionally at high temperatures, 1600 °C. The smaller grain size obtained by microwave at 1300 °C leads to a slight increase in hardness compared to sintering at 1600 °C, with similar densities, but 300 °C below. Porosity also affects these properties.

Regarding the fracture toughness values represented in Fig. 5, by microwave sintering only representative values have been obtained for the sample at 1300 °C, due to the high porosity found and the differences in grain size of zirconia and zircon in the materials sintered at 1200 °C. Moreover, the error in the final value is very high in these samples. The

Table 2

Vickers hardness values of the ZS, ZS80 and ZS20 composites obtained by microwave (MW) and conventional (CS) sintering methods at different temperatures.

Sintering temperature	MW		CS		
	1200 °C	1300 °C	1500 °C	1550 °C	1600 °C
ZS	6.4 GPa	10.9 GPa	9.2 GPa	10.2 GPa	11.1 GPa
ZS80	7.3 GPa	11.7 GPa	10.5 GPa	10.9 GPa	11.8 GPa
ZS20	8.4 GPa	13.9 GPa	11.2 GPa	12.1 GPa	13.5 GPa

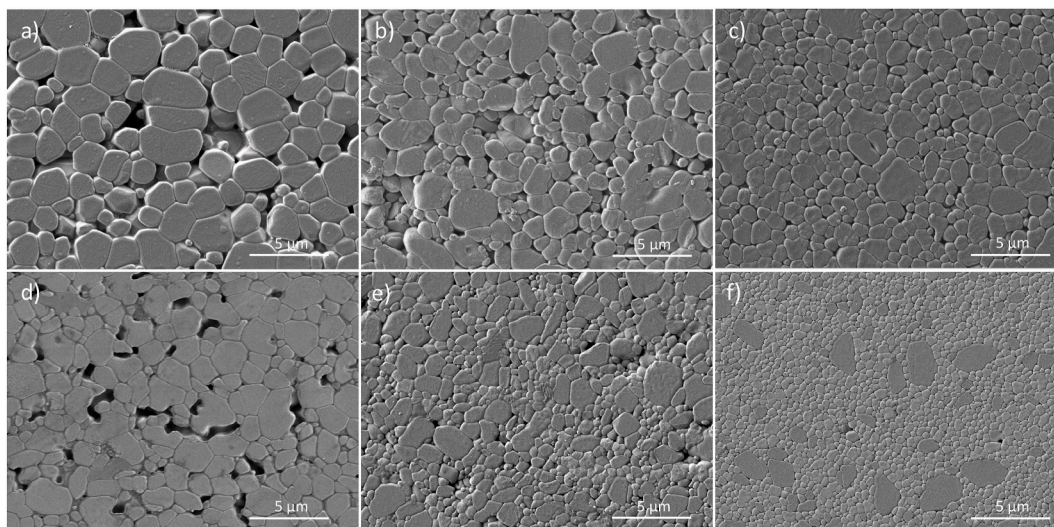


Fig. 4. FE-SEM micrographs of the ZS, ZS80 and ZS20 samples obtained at 1600 °C-2h by conventional (4a, 4b and 4c) and microwave sintering (4d, 4e and 4f) at 1300 °C-10min, respectively. All pictures have the same magnification.

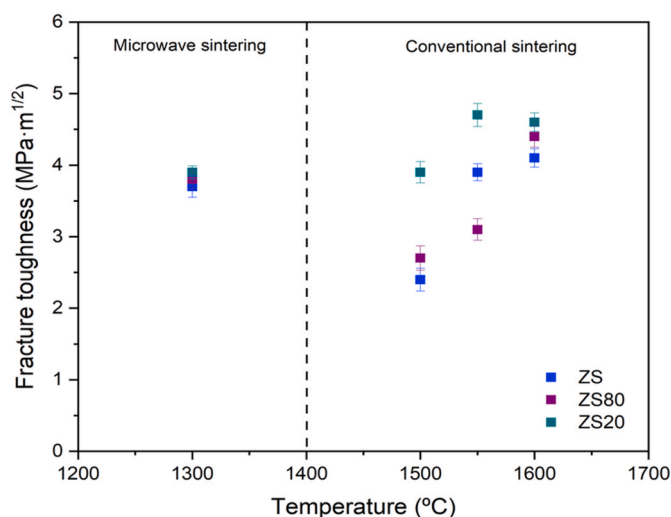


Fig. 5. Fracture toughness values of the ZS, ZS80 and ZS20 samples obtained by microwave and conventional sintering at different temperatures.

increase in fracture toughness observed in Fig. 5 is well documented in the literature. The highest value obtained corresponds to the ZS20 composite conventionally sintered at 1550 °C (4.7 MPa m<sup>1/2</sup>). Composites with high percentages of zirconia have the best fracture toughness. The values for all microwave sintered samples are around 3.8–4.0 MPa m<sup>1/2</sup>. These values are above those of samples sintered at 1500 °C by conventional sintering.

Compared to reported data on the zircon obtained from colloidal processing and sintered at 1600 °C-2h by conventional (8.5 GPa and 1.7 MPa m<sup>1/2</sup>) [30], the results obtained in this study by microwave sintering at 1300 °C-10min, the hardness value increases to 10.9 GPa (a relative enhancement of 28%), but the fracture toughness increases to 3.7 MPa m<sup>1/2</sup>, which corresponds to a relative enhancement of 118%.

With regard to reported data on the ZrSiO<sub>4</sub>-ZrO<sub>2</sub> (20 vol%) obtained from mechanically activated commercial powders and spark plasma sintering (SPS) at 1300 °C-10min (1304 kg/mm<sup>2</sup> and 3.02 MPa m<sup>1/2</sup>) [15], by microwave at 1300 °C-10min the hardness is slightly lower but the toughness values are above (20% higher), it should be noted that for SPS a pressure of 100 MPa was applied during the sintering cycle. These results suggest that it is possible to obtain dense zircon-zirconia materials with high mechanical properties at low temperatures with very low energy consumption using microwave radiation.

#### 4. Conclusions

- The energy factor is one of the most relevant issues for the use of microwave as a clean energy source for the manufacture of zircon-zirconia materials. The total processing cycle is reduced by 88%, which shows that microwave produce significant energy and production cost savings compared to conventional processing.
- For the same composition, but different sintering methods and temperatures, the same phases are identified by XRD. The presence of monoclinic phase in the zirconia is practically negligible.
- The composites obtained are highly dense, reaching values > 98% at 1550 °C and 1600 °C by the conventional method whereas similar high densities are obtained by microwave at only 1300 °C.
- Scanning electron microscopy shows a homogeneous distribution of the phases and particle size distribution, which becomes clearly bimodal in the mixtures sintered by microwave technology, with a smaller particle size for zirconia and higher uniformity for zircon. As the proportion of zirconia increases, the porosity decreases.
- As for the mechanical properties, the highest hardness value (~14.0 GPa) was obtained by microwave at 1300 °C-10min for ZS20

composite, while values of 13.5 GPa were reached for conventional heating at 1600 °C. The best fracture toughness values are found in composites with high percentages of zirconia. The samples obtained by microwave at 1300 °C are around 3.8–4.0 MPa m<sup>1/2</sup>. These values are above those of samples sintered at 1500 °C by conventional sintering, despite the fact that the final temperature reached is 200 °C lower.

In summary, microwave fast sintering is a pioneering and competitive technique with the conventional method with shorter dwell times, lower temperatures and reduced power used without affecting to its mechanical properties, which could be considered to be widely used in disposal of the long-lived nuclear wastes.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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