ELABORATION AND CHARACTERIZATION OF MULLITE-ZIRCONIA COMPOSITES FROM GIBBSITE, BOEHMITE AND ZIRCON

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In this study we prepared mullite-zirconia composites by reactive sintering of gibbsite and boehmite as alumina sources and zircon powder. All raw materials have been ball milled and isostatically pressed followed by sintering in the temperature range of 1400-1600°C during 2 h of soaking. Then the sintered samples have been characterized by X-ray diffraction, ATD/TG analysis and microstructural observation. X-ray diffraction peaks showed the formation of mullite-zirconia composites in both mixtures. The microstructure of all composites was composed of irregularly shaped mullite grains and round-shaped zirconia grains, which are distributed intragranularly and intergranularly. These microstructures had microcracks in the samples prepared from gibbsite and zircon, contrary to the samples prepared from boehmite and zircon where no microcracks were present. These microcracks are caused by evaporation of structure water at 300°C. So the preparation of mullite-zirconia composites with the substitution of the α-alumina by the boehmite is feasible.

INTRODUCTION

Mullite is considered a promising candidate for high temperature structural applications because of its relatively low thermal expansion, good high temperature strength, excellent creep resistance and chemical stability [1-2]. However, as structural materials, mullite ceramics show poor mechanical properties. Dispersed zirconia particles, added as a second phase to mullite materials, enhance their thermomechanical properties mainly by transformation toughening [3-7] and also by other mechanisms such as microcracking or crack deflection. Reactive sintering of zircon and α-alumina mixed powders is an easy and inexpensive route to obtain homogeneous mullite-zirconia composites with enhanced mechanical properties [8-9].

The purpose of the present work is to prepare mullite-zirconia composites starting from raw materials without chemical added. These composites were reaction-sintered from gibbsite-zircon and boehmite-zircon mixtures. The gibbsite and boehmite powders (for α-alumina replacement) were used to decrease processing cost.

EXPERIMENTAL

The following powders were used as starting materials:

1) gibbsite $Al(OH)_3$ and boehmite AlOOH (supplied by Diprochim, Algeria) were used as the alumina sources. The average particle size of these powders is 75 μm.
2) Fine zircon ($ZrSiO_4$) powder (supplied by Moulin des près, France) with 1.5 μm average grain size (given by the producer).

The chemical composition of starting materials is listed in Table 1. The gibbsite and boehmite powders were milled by attrition with alumina balls in aqueous media for 3 h to reduce d_{50} to 1.5 μm. The stoichiometry

Table 1. Chemical composition of raw materials.

Elements	Gibbsite (wt.%)	Boehmite (wt.%)	Zircon (wt.%)
LOI*	33.00	6.00	-
Al_2O_3	62.97	88.34	-
ZrO_2	-	-	63.05
SiO_2	2.75	3.86	35.25
F	0.64	0.90	-
Na_2O	0.24	0.34	-
CaO_2	0.13	0.18	-
Fe_2O_3	0.07	0.10	0.08
Ti_2O	0.06	0.08	0.10
HfO_2	-	-	1.50
K_2O	0.05	0.07	-

* *LOI: Loss of Ignition*

of the powders mixtures used for the synthesis of mullite-zirconia was calculated using the total reaction of the Al_2O_3 with SiO_2, according to the equation and the following molar proportions:

$$2\ ZrSiO_4 + 3\ Al_2O_3 \rightarrow 3Al_2O_3.2SiO_2 + 2\ ZrO_2$$

The samples compositions are expressed by the weight ratios of gibbsite to zircon and boehmite to zircon of 59.87/40.12 and 51.54/48.45 respectively. Homogenization of the mixtures of alumina and zircon was achieved by ball-milling for 20 h in distilled water using alumina balls with a diameter of 1.5-2 mm and a plastic container.

After milling, the mixtures were dried at 110°C and 1% PVA + 0.5% PEG was added as binder by mortar and they were granulated through a 45 µm sieve. The samples were uniaxially pressed at 7 MPa followed by cold isostatic pressing at 250 MPa as disks (diameter: 15 mm) and heated up to 600°C at a rate of 1°C/min to avoid cracking the samples. They were sintered at a rate of 5°C/min up to different temperatures (1400-1600°C) with 2 h soaking and cooled down inside the furnace.

Powders were subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using SETARAM TGA 92 with α-alumina as the reference material at a heating rate of 5°C/min in air. Phases of sintered composites were identified by X-ray diffraction using a RIGAKU diffractometer [using Ni-filtered CuK_α radiation (40kV-25mA) with a scanning speed of 2° (2θ) per minute and 0.05° of step]. The fraction of monoclinic zirconia (m-ZrO_2) (F_t) present in the composites was estimated using the equation [10]:

$$F_t = \frac{I_m(111) + I_m(11\bar{1})}{I_t(111) + I_m(111) + I_m(11\bar{1})}$$

where I_t (111), I_m (111), and I_m ($11\bar{1}$), refer to the intensity of (111) reflection of tetragonal, monoclinic, and ($11\bar{1}$) reflection of monoclinic zirconia, respectively. The samples were polished and thermally etched to observe the micro-structure by a JEOL 840 A scanning electron microscope (SEM). The final density and porosity of the sintered were determined by the Archimedes method using distilled water. Flexural strength (σ_F) tests were carried out on Instron 8502 machine at room temperature by using four points bending with a 10 mm span between the inner rods and 35 mm span between the outer rods. The samples used were machined in order to obtain bars with parallel surfaces of dimensions 50 × 6 × 4 mm^3. The tensile surface was polished using slurry containing 1 µm diamond grains. A standard Vickers Testwell FV-700 tester was used to obtain the Vickers hardness values, using a load of 10 kg.

RESULTS AND DISCUSSION

The chemical composition of the starting materials used in this study is presented in Table 1. It clearly shows that the content of impurity is high in all powders. The gibbsite has a high loss during ignition due to the presence of structural water (≈ 33%); While, the boehmite has a small loss during ignition (≈ 06%).

The reaction sintering of α-Al_2O_3/$ZrSiO_4$ mixtures involves two reactions, i.e., zircon dissociation and mullite formation. The preparation of mullite-zirconia composites using this method leads to a relatively homogenous distribution of zirconia dispersed. Therefore the sinterability of gibbsite/zircon mixed powders is it possible to obtain a good dispersion of the zirconia particles in mullite.

The results of thermogravimetric and differential thermal analysis of gibbsite-zircon mixture are given in Figure 1. The TGA result shows that the total water loss is very high (≈ 20%). The DTA curve shows one endothermic peak around 310°C due to the loss of structural water from gibbsite. A much smaller endothermic peak is found around 1500°C due to decomposition of zircon to zirconia and silica.

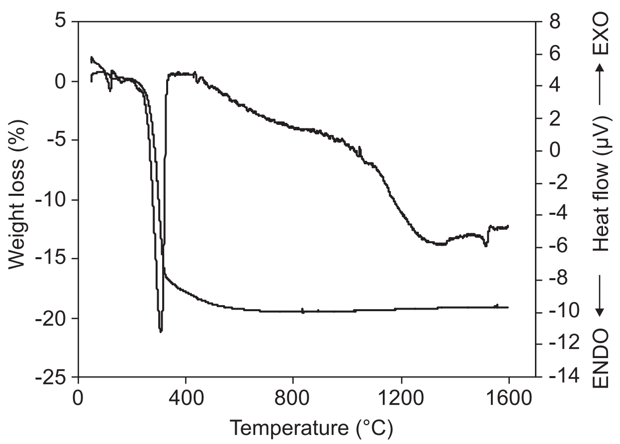


Figure 1. DTA/GTA curves of gibbsite-zircon mixture.

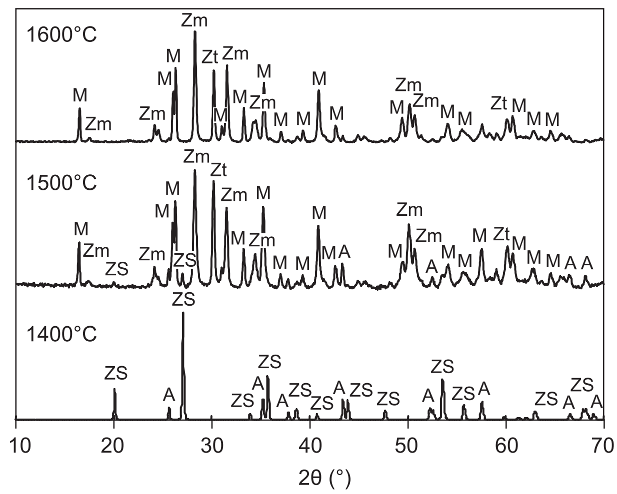
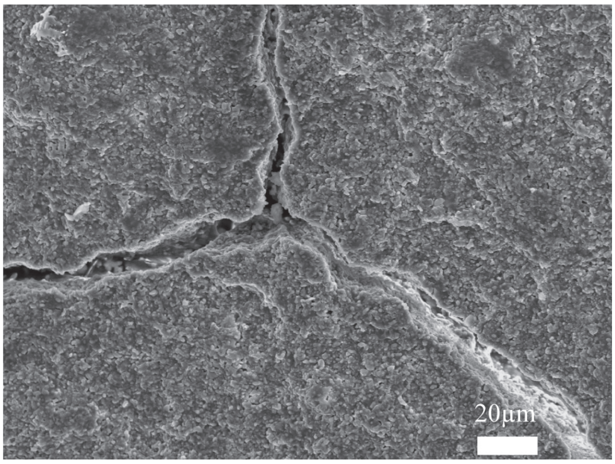


Figure 2. XRD patterns of the gibbsite-zircon mixture heated at different temperature.

The XRD analysis shows (Figure 2) the formation of mullite-zirconia composites at 1500°C, complete mullitization was achieved at 1600°C. Interestingly, ZrO_2 formed existed in both tetragonal and monoclinic phases. Figure 3 shows the microstructures of gibbsite/zircon samples sintered at 1600°C for 2 h. As it can be seen, the ZrO_2 grain (white grains) surrounded by the mullite matrix (dark grains). Also, we note the presence of a residual porosity in these samples. The pores are well distributed in the grains boundary of mullite.



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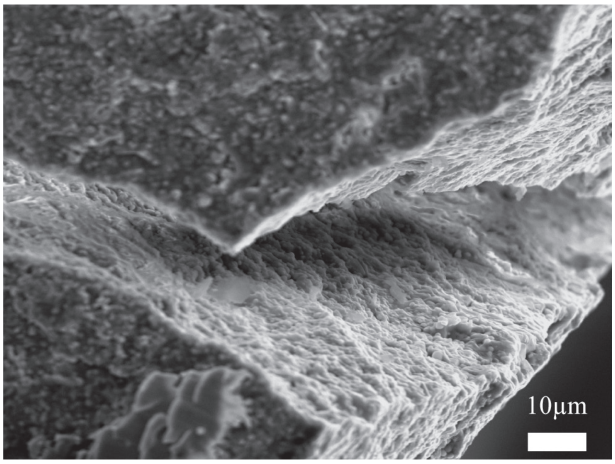

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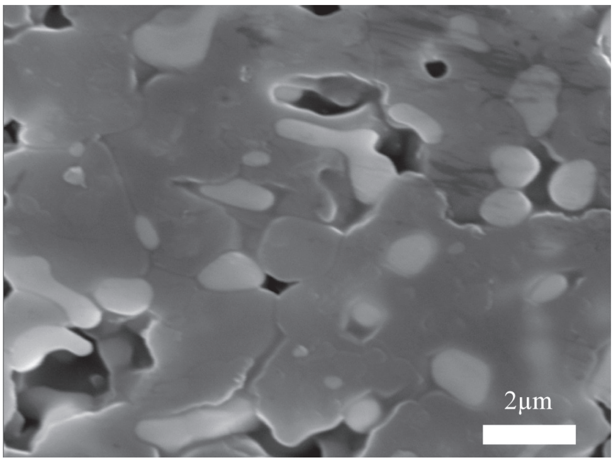


c)

Figure 3. SEM micrographs of mullite-zirconia composite sintered at 1600°C, 2 h (prepared by gibbsite/zircon mixture).

Figure 3 shows the presence of fractures in all samples prepared by gibbsite/zircon mixtures powders. This problem of cracking is related directly to the brutal loss of structural water. It is pointed out that one found the same phenomenon in the case of the gibbsite only [11]. Then we substituted the powder of gibbsite by a partially dehydrated gibbsite (boehmite: AlOOH), to remedy this problem. We prepared the zirconia dispersed mullite composites by reaction sintering of boehmite and zircon.

XRD patterns for samples of boehmite-zircon are given in Figure 4. In these figures, the ZrO_2 peaks can be observed at lower temperatures (~ 1400°C); while, at the same temperature no ZrO_2 peaks appear in the gibbsite-zircon sample. As it is well-known that pure zircon usually dissociates at a temperature higher than 1665°C [12]. With increasing temperature to 1450°C, mullite peaks are observed. Complete dissociation of zircon is achieved at 1500°C.

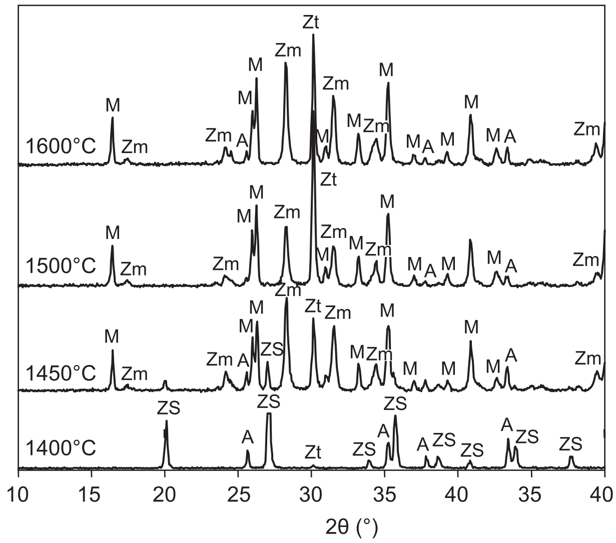


Figure 4. XRD patterns of the boehmite-zircon mixture heated at different temperature.

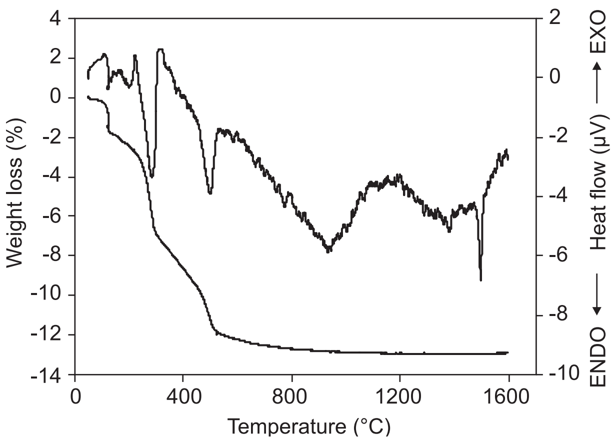
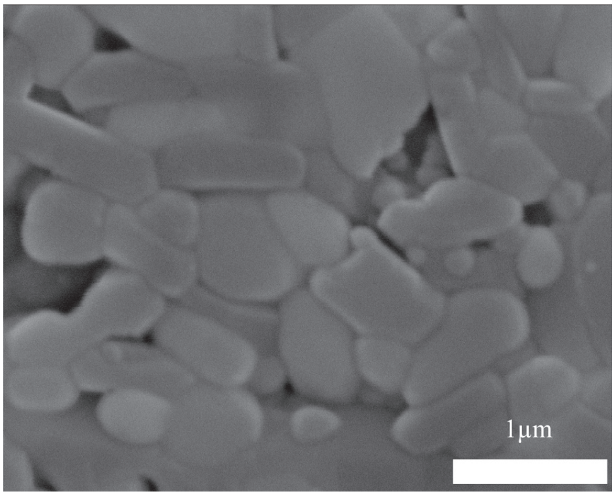


Figure 5. DTA/GTA curves of boehmite-zircon mixture.



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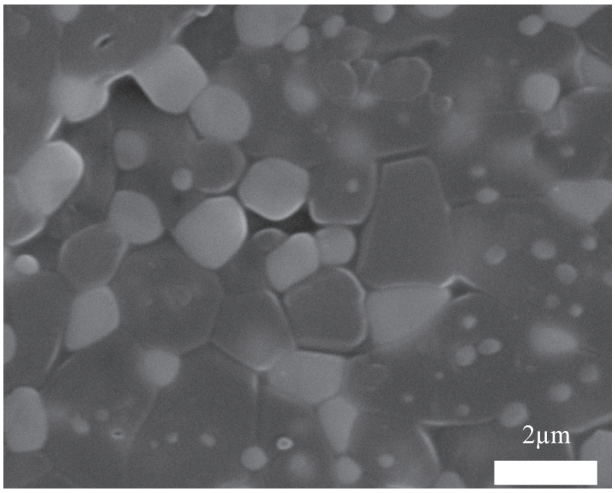

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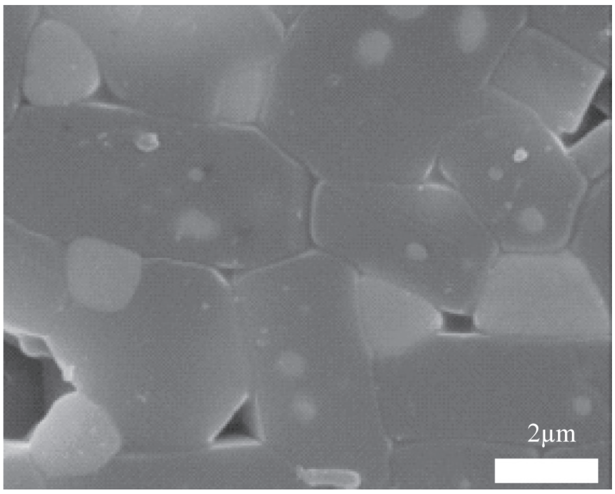

c)

Figure 6. SEM micrographs of mullite-zirconia composites prepared by boehmite/zircon mixtures and sintered at: a) 1400°C, 2 h; b) 1500°C, 2 h; c) 1600°C, 2 h.

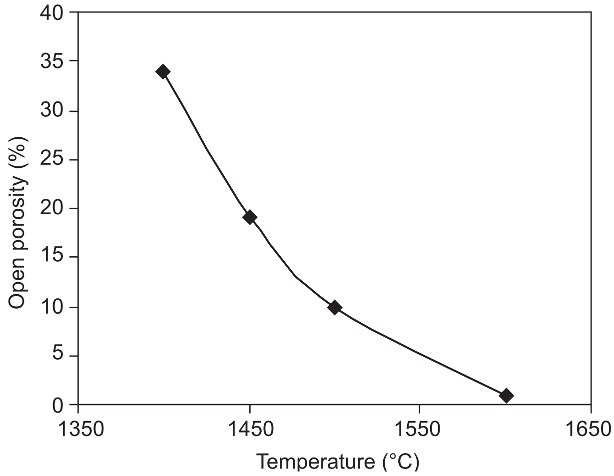

Figure 7. Open porosity changes of the samples as a function of sintering temperature after 2 h.

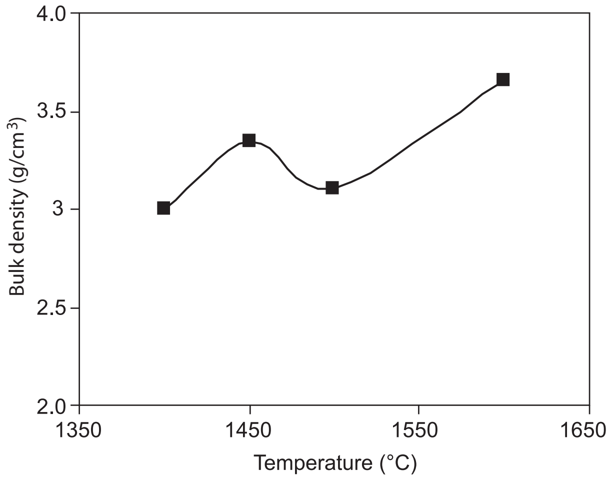

Figure 8. Bulk density of composites as a function of sintering temperature.

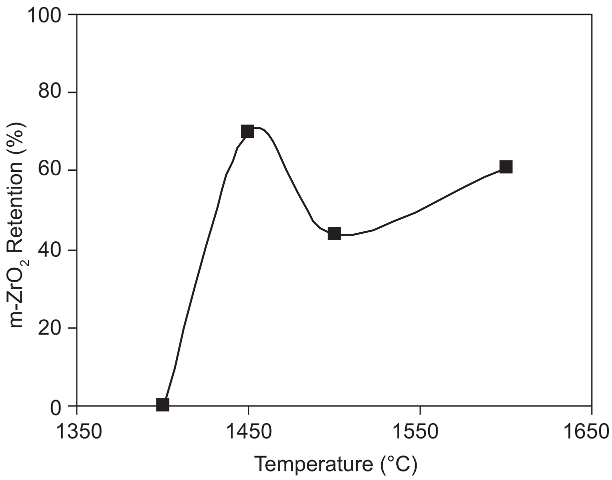

Figure 9. Monoclinic zirconia fraction in reaction-sintered samples as a function of sintering temperature after 2 h.

The weight loss occurred in boehmite-zircon mixture at three temperature levels (Figure 5). The first one located around 110°C is due to adsorbed water, the second (around 250°C) is correlated to the losses of structural water from gibbsite. A part of boehmite rehydrates and crystallizes to form the gibbsite (Al $(OH)_3$) during milling [13]. The third one around 460°C is due to removal of structural water in boehmite. The TGA results of boehmite-zircon mixture shows that the total water loss is very high (≈ 11%).

The DTA curve of boehmite-zircon mixture shows two successive endothermic peaks. The first one around 290°C is due to the loss of structural water from gibbsite formed during milling and the second endothermic peak is due to transformation of boehmite into γ-alumina [14]. A sharp endothermic peak is found at 1500°C due to decomposition of zircon.

The microstructure (Figure 6) of boehmite-zircon mixture showed the formation of mullite-zirconia composites after sintering at 1500°C. We note a more homogeneous structure with a uniformly distributed porosity. All samples were composed of irregularely shaped large mullite grains and round shaped zirconia grains, which were distributed both intergranularly and intragranularly. We see the growth of the grains of mullite in the sample sintered at 1600°C.

After confirming the possibility of preparing the composite mullite-zirconia by zircon and boehmite, the properties of theirs mixtures were investigated.

As shown in Figure 7, in the temperature range lower than 1500°C, the porosity of the samples decreased more rapidly. Furthermore, at this temperature (lower than 1500°C) the α-Al_2O_3 reacts with SiO_2 and forms the mullite. The porosity continued these decreased into the temperature reached 1600°C.

Figure 8 shows the change in bulk density of the samples with temperature. Here, bulk density of the samples decreased with increase in temperature. The formation of mullite is responsible of the density decease between 1450 and 1500°C, as confirmed by the enhancement of the mullite peaks intensity in the X-ray diffraction patterns. Thereafter, between 1500 and 1600°C the density increases and the maximum has been observed at 1600°C (3.65 $g.cm^{-3}$).

The Figure 9 reveals that at 1450°C the zirconia formed from dissociation of zircon. The decomposition of zircon is achieved at 1500°C. The more retention of monoclinic zirconia phase is found at 1450°C which can be attributed to the formation of zirconia phase at lower temperature. Presumably, the formation of m-ZrO_2 at lower temperature implies the existence of some particles below the critical size for transformation. This result is consistent with reducing of the tetragonal phase concentration by increasing sintering temperature. At 1600°C the retention of m-ZrO_2 is lowest than 60%. It has been found [1, 4, 7, 15-19] that an amount of 70% of m-ZrO_2 affects positively the mechanical properties by microcraking.

Table 2 exhibits the flexural strength and Vickers hardness values of the samples sintered at different temperatures for 2 h. As observed, the samples obtain the progressive strength with increase in temperature. This increase in strength is believed due to the decrease of porosity and the presence of dispersed zirconia particles in mullite matrix. It has been found [20] that the fracture energy of a ceramic can be increased by a second phase dispersion. The samples showing a decreasing in hardness (H) as the sintering temperature increases, this is may be due to the presence of different phases ($H_{alumina}$ = = 18 GPa > $H_{mullite} \approx H_{zirconia}$ = 10-15 GPa > H_{zircon} = 8 GPa [20-22]). The lowest hardness (5.8 ± 0.3) was obtained for samples sintered at 1450°C and it may be attributed to their high porosity. A slight hardness reduction in the samples sintered at 1500°C which may be associated with the alumina content decrease.

Table 2. Flexural strength and hardness of the samples prepared by boehmite/zircon mixtures and sintered at different temperature.

Temperature (°C)	Flexural strength (MPa)	Hardness (GPa)
1400	112 ± 18	5.8 ± 0.3
1450	225 ± 23	8.2 ± 0.4
1500	230 ± 34	7.4 ± 0.3
1600	308 ± 28	12.1 ± 0.2

CONCLUSIONS

In this work, we substituted the α-alumina by the gibbsite $Al(OH)_3$ to elaborate mullite-zirconia dispersed composite. We encountered a problem of fracture of samples in the case of gibbsite-zircon mixture. This problem is related directly to the brutal loss of structural water. Then we substituted the powder of gibbsite by a partially dehydrated gibbsite (boehmite: AlOOH), to remedy to this problem. We prepared the zirconia-dispesed mullite composites by reaction sintering of boehmite and zircon. Through these results, we lighted the possibility of preparing the composite mullite-zirconia by zircon ($ZrSiO_4$) and boehmite (for α-alumina replacement). This composite presents extremely interesting mechanical properties.

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