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Sintering of zirconia composites obtained by slip casting

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Abstract

Composites containing a matrix of nanometric Ce-stabilized zirconia with an addition of micrometric monoclinic zirconia were processed by slip casting and sintered at a relatively low temperature. The ratio between nanometric and micrometric particles was determined according to the viscosity of the suspensions and the final density of the pellets. An optimum amount of micrometric particles was necessary to achieve improved suspension dispersion and higher pellet density. The amount of deflocculant in the suspensions containing the mixture of micrometric and nanometric particles was optimized by viscosity measurements. The pellets were characterized by dilatometry, Hg porosimetry, density measurement (the Archimedes method) and scanning electron microscopy. Despite the low green density obtained (35–38% of the theoretical density), densities as high as 97.5% were achieved after sintering.

Keywords: A. Slip casting; A. Sintering; D. ZrO_2; Nanometric particles

1. Introduction

Nanometric particle synthesis has received special attention in recent years owing to its properties [1,2]. Nanophase ceramics have mechanical, electrical and optical properties that are not present in systems containing coarse grains [3,4].

Although it is more difficult to produce dense bodies using nanometric particles than it is using micrometric particles, nanometric particle processing is not as widely studied. Several articles published in the literature [3,5,6] determine the properties of nanometric particles conformed by hot pressing. With regard to colloidal route processing, Zhang studied slip casting [7,8] and plastic extrusion [9] in the formation of nanometric particles, demonstrating that it is possible to obtain high density ceramic bodies.

It is well known that colloidal processing must be carefully controlled, particularly in relation to the development of appropriate repulsive forces among particles to allow them to slide over each other, forming a uniform structure before becoming rigid [10]. This condition is more difficult to attain with nanometric particles since their high surface areas are highly reactive and they tend to become tightly agglomerated.

This paper reports on a study of composites containing a matrix of nanometric Ce-stabilized zirconia with added micrometric monoclinic zirconia obtained by slip casting. Particle size distribution, the amount of deflocculant and the solid content of the suspension were optimized. The pellets were characterized prior to and following thermal treatment under optimized sintering conditions, resulting in high densities.

2. Experimental procedure

Ceria-stabilized zirconia (tetragonal phase with a small concentration of monoclinic zirconia) and fused monoclinic zirconia (Elfusa, Brazil) were used as raw material. Distilled water was used as solvent and ammonium polyacrylate–PAA (IQAPAC C, IQA, Brazil) was used as deflocculant. According to results found in the literature [11], the pH of the suspensions was adjusted to 9.5 by adding ammonium hydroxide (Merck).

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All the viscosity measurements were taken after attritor milling for 30 min at 500 rpm. Two millimeter diameter alumina balls were used as the milling media.

In order to attain a better particle packing, an optimization of zirconia particle size distribution through the addition of different amounts of a zirconia with a low surface area to a fine zirconia (0–30 mass%) was done. The solid content in the suspension was kept at 50% of the mass. The viscosity of the suspensions was measured after milling. The pellets were molded by slip casting in a plaster of Paris mold, dried at 110°C/12 h and sintered at 1300°C/2 h. The sintered pellets were characterized by density measurements using the Archimedes method.

After determining the optimum amount of micrometric particles, the optimum amount of deflocculant was defined by adding deflocculant a drop at a time to the suspension and taking viscosity measurements.

Suspensions with different solid concentrations and optimized amounts of deflocculant were milled in an attritor under the same conditions described earlier herein.

The pellets were then conformed again by slip casting in plaster of Paris molds. After casting, the pellets were dried at 100°C for 12 h. Calcining was carried out at 500°C for 1.5 h, after which the pellets were characterized by Hg porosimetry (9310, Micromeritics). The green pellets were sintered using a dilatometer (402EF, Netzsch) at a heating rate of 10°C/min up to 1500°C. The sintered samples were characterized by apparent density measurements, using Archimedes method in distilled water, and by scanning electron microscopy (SEM, DSM 940, Zeiss). The samples for SEM were cut transversally, polished and the grain boundary was revealed by thermal etching.

The sintering conditions were optimized by varying the sintering temperature from 1310 to 1410°C and the sintering time from 2 to 8 h.

3. Results and discussion

3.1. Rheologic properties

Due to the use of a zirconia with nanometric particles (29.2 nm), optimization of the particle size distribution was necessary to prevent particle agglomeration. This was done by adding a fused monoclinic zirconia (NSZ) with a mean particle size of 0.33 μm. This allows for higher particle packing, which in turn leads to a higher green density and hence, to better sintering.

Fig. 1 shows the relation between suspension viscosity and the amount of NSZ added. A minimum viscosity can be observed between 10 and 20 mass% of NSZ, as shown in the plot. The higher viscosity observed when no NSZ was added is ascribed to the higher interaction among nanometric particles, which made dispersion more difficult. Another important point is the reaction between hydroxylated particles of zirconia, which causes it to polymerize in an aqueous medium and, consequently, to form aggregates. This polymerization is characterized by the formation of a chain zirconium–oxygen, with adsorbed hydroxyls bonded to it. Adding NSZ not only favors particle packing but also makes it more difficult for this polymerization to occur. This is due to the low reactivity of electromelted particle surfaces, making hydroxylation and consequently polymerization more difficult. The problem of this lower reactivity is the difficulty in polymer adsorption, leading to a higher viscosity when a larger amount of NSZ is added, as presented in Fig. 1.

Fig. 2 illustrates the samples' density results after sintering at 1300°C/2 h. The results indicate that higher densities were obtained for pellets molded from suspensions containing 10 mass% of NSZ. This is in agreement with the results of viscosity, since less viscous suspensions are more easily dispersed and, therefore, particle packing during casting is enhanced. Another point worth mentioning is that, when no NSZ is added, the formation of

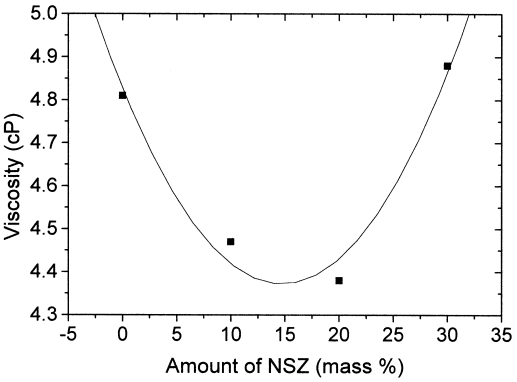

Fig. 1. Variation of viscosity as a function of the amount of NSZ added.

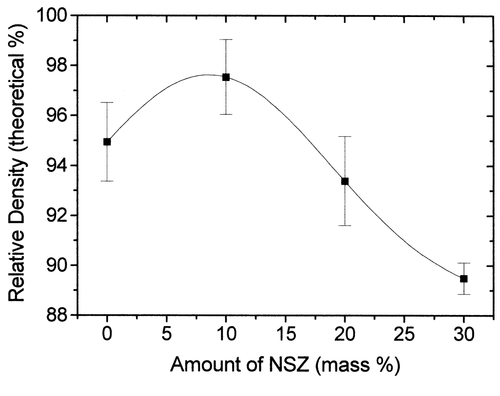

Fig. 2. Variation of density after sintering as a function of the amount of NSZ.

agglomerates among nanometric particles causes the density to decrease.

After optimizing the particle size distribution, the amount of NSZ was fixed at 10 mass%, after which the amount of deflocculant in different solid contents (13.9–23.0 vol.%) was optimized. Fig. 3 presents the deflocculant optimization curves for suspensions containing different solid concentrations. Suspensions containing a smaller solid content (13.9–19.4 vol.%) present similar behavior, with a well-defined value of minimum viscosity. These suspensions also have the same viscosity range.

The suspension containing 23.0 vol.% of solids showed a much higher viscosity, which is due to increased particle interaction when the solid content is higher. This effect is more important in this case, since nanometric particles have a higher surface area available for reaction and, thus, a stronger tendency to form agglomerates. Another factor that causes agglomerates to form is the tendency of this material to polymerize.

The suspension containing 23.0 vol.% showed increased viscosity at the beginning of optimization (Fig. 3). Hashiba [12] observed that a certain amount of PAA is initially consumed to neutralize the positive charge of zirconia particles, which causes the viscosity to increase. Adding more PAA leads to a negative zeta potential that causes particle dispersion. After the point at which minimum viscosity is reached, the particles are saturated and the extra polymer added remains in solution, leading to an increase of ionic forces in the suspension and, hence, to increased viscosity.

Another point worth mentioning was the low solid content obtained in relation to the suspensions containing micrometric particles. Shan and Zhang [7] state that the average distance between nanometric particles is much smaller than that between micrometric particles in suspensions that have the same solid content. Consequently, the attractive forces among nanometric particles are higher and the flow decreases. Furthermore, there is a greater adsorption of water film on the particle surface.

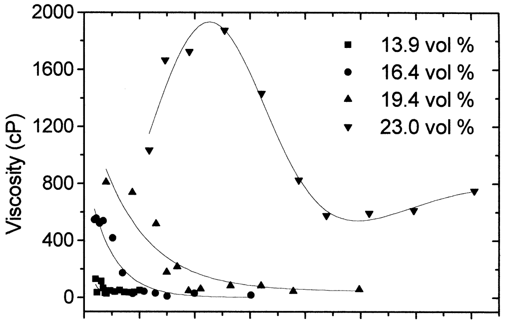

Fig. 3. Optimization of deflocculant in suspensions with different solid contents.

3.2. Bulk properties of the pellets

The results of Hg porosimetry are shown in Figs. 4 and 5. The results for green density (Fig. 4) indicate a small increase in density values as the solid content of the suspension increases. All the samples presented a low green density (35–38% of the theoretical value) compared to samples molded from suspensions containing micrometric particles [7] (40–60% of the theoretical value).

Shan and Zhang [6] point out the difficulty of removing the water layer strongly adsorbed on the particle surface using only the capillary force of a plaster of Paris mold. This mold contains micrometric and submicrometric pores, while the pores of pellets constituted of nanometric particles are nanometric sized. Capillary forces are inversely proportional to pore diameter; thus, the capillary forces in the mold are far inferior to those in molded pellets. Therefore, the water layer strongly adsorbed on the particle surface is not taken in by the mold and remains on the samples until the drying process is reached, which leads to the formation of pores. A relatively low green density is one of characteristics of nanometric particles molded by slip casting.

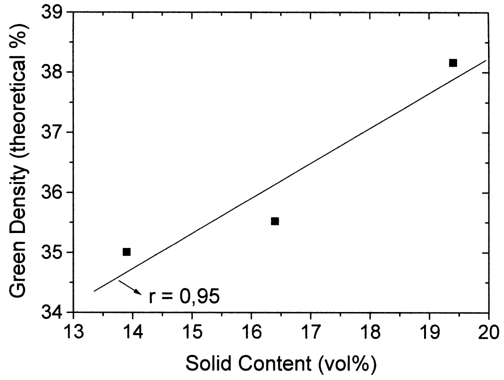

Fig. 4. Green density of the samples.

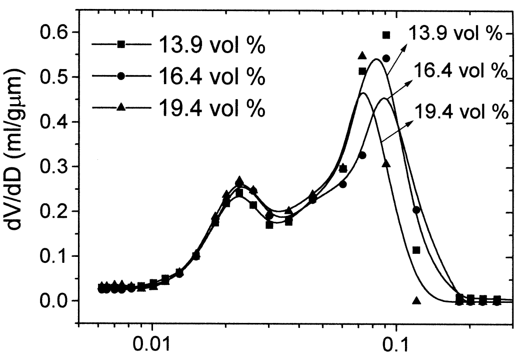

Fig. 5. Pore structure of the samples.

The pore structures of the samples are bimodally distributed (Fig. 5), which is characteristic of the presence of agglomerates [13]. Smaller diameter pores (around 0.025 μm) are formed inside agglomerates and larger diameter pores (from 0.072 to 0.091 μm) are formed among agglomerates.

The results of the most frequent pore diameter and pore size distribution obtained (FWHM, full width to half maximum) are shown in Table 1. A small reduction was observed in the most frequent pore diameter for samples molded from suspensions containing 19.4 vol.%, which is ascribed to the smaller amount of water in the suspension. The pore size distribution values, represented by the half width to half maximum (FWHM) of the curves did not present significative differences.

With regard to dilatometry, all the samples showed a high linear shrinkage (around 28%). Shan and Zhang [7] observed a relative linear shrinkage up to 34.3% for nanometric zirconia particles. This high linear shrinkage has not been reported in the literature for micrometric zirconia particles obtained by slip casting. Thus, besides low green density, high linear shrinkage is also a characteristic of samples molded from suspensions containing nanometric particles.

The derivative of the linear shrinkage curve as a function of temperature (Fig. 6) presents two peaks, the first at 1200°C and the second between 1300°C and 1310°C. The two peaks indicate the presence of agglomerates. The first peak originates from the sintering inside agglomerates, while the second one is due to the sintering among agglomerates. A small increase of 10°C in the maximum linear shrinkage temperature of the two samples molded from the most concentrated suspensions is also observed.

Table 1
Results of pore size distribution

Solid content (vol.%)	Most frequent peak (μm)	FWHM (μm)
13.9	0.084±0.001	0.045±0.002
16.4	0.088±0.002	0.058±0.005
19.4	0.073±0.002	0.041±0.004

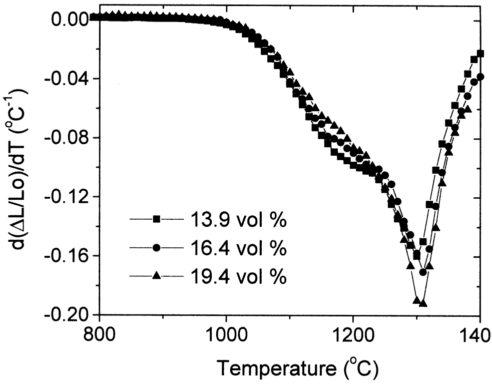

Fig. 6. Derived curve of the linear shrinkage curve as a function of temperature.

An important point is the low temperature of maximum shrinkage compared to the results of micrometric particle sintering.

Fig. 7 illustrates the sintering model obtained from Eqs. (1) and (2):

$$D = \frac{D_0}{[1 + (\Delta L/L_0)]^3}, \tag{1}$$

$$\frac{dD}{dt} = \frac{-3D_0}{[1 + (\Delta L/L_0)]^4} \times \frac{d(\Delta L/L_0)}{dt}, \tag{2}$$

where D is the relative density, D_0 is the green density, $\Delta L/L_0$ is the relative linear shrinkage, and t is the time.

Samples cast from suspensions containing 13.9 and 16.4 vol.% of solids present almost the same sintering behavior. Since the most frequent pore diameter in these samples is the same, this indicates that sintering is influenced by pore structure.

Fig. 8 shows the results of density after sintering at 1340°C/2 h. Samples molded from less concentrated suspension present a small decrease in density. The major point to highlight is the decrease in dispersion

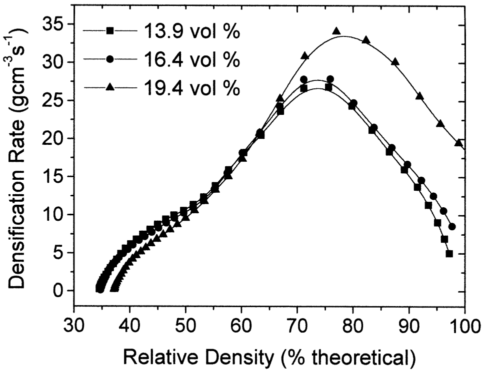

Fig. 7. Model illustrating behavior during sintering.

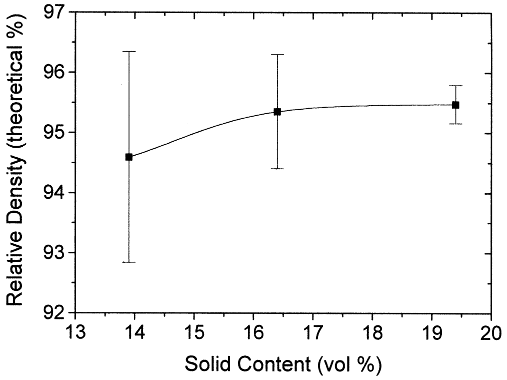

Fig. 8. Density of samples after sintering at 1340°C/2 h.

around the density values as solid content of suspensions increase. The high dispersion in density values of samples molded from less concentrated suspensions may be due to homogeneity problems during the slip casting forming process.

Fig. 9 illustrates the comparison between the density after sintering and the green microstructure using parameters such as green density [Fig. 9(a)] and pore structure [Fig. 9(b)]. The highest sintered density is obtained when the microstructure has the smallest most frequent pore diameter and the smallest pore size distribution (FWHM).

According to Reed [14], sintering of ceramic materials depends, to a great extent, on pore size distribution and the homogeneity of pellet porosity. In the sintering of homogeneous pellets of uniform particles, the uniform interstices that are smaller than the grains retract quite rapidly and evenly.

An analysis of density in relation to sintering temperature (Fig. 10) indicates that thermal treatment at the temperature of maximum linear shrinkage (1310°C) favors densification. Final density showed weak dependence with sintering time.

It may also be observed that the microstructure in Fig. 11 is homogeneous, with low porosity and greatly varying grain sizes. This variation originates from the use of a mixture between nanometric and micrometric particles during pellet processing. The medium grain size obtained by the intercept method varied from 0.84 µm for samples sintered at 1310°C/2 h to 1.36 µm for samples sintered at 1410°C/2 h.

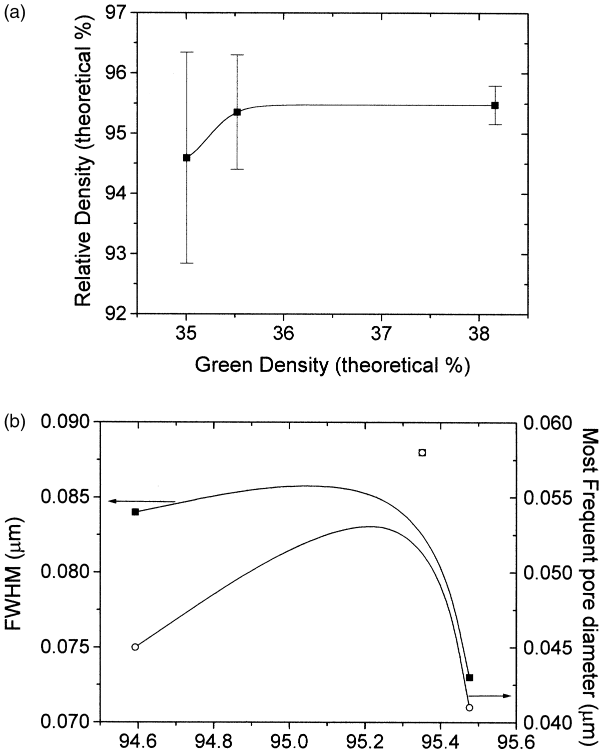

Fig. 9. Comparison between green microstructure and density after sintering. (a) In relation to green density; (b) in relation to pore structure.

X-ray maps (Fig. 12) obtained by EDS analysis show a homogeneous distribution of all the components (zirconia, ceria and oxygen) throughout the microstructure

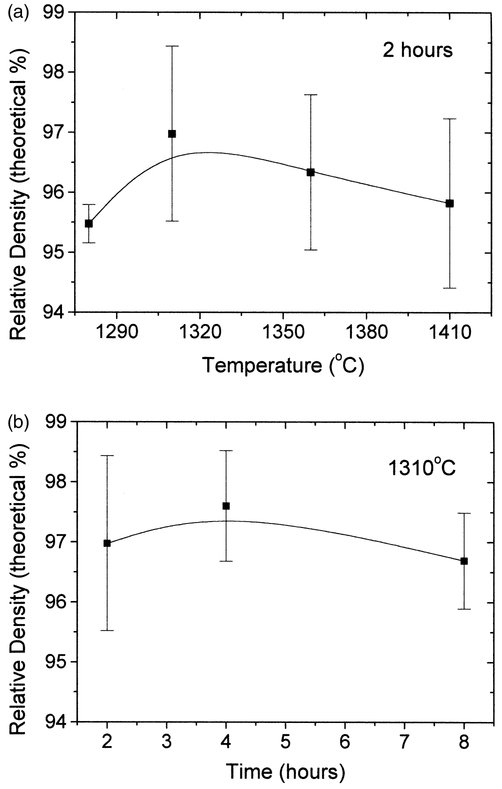

Fig. 10. Comparison between density after sintering in relation to: (a) temperature; (b) time.

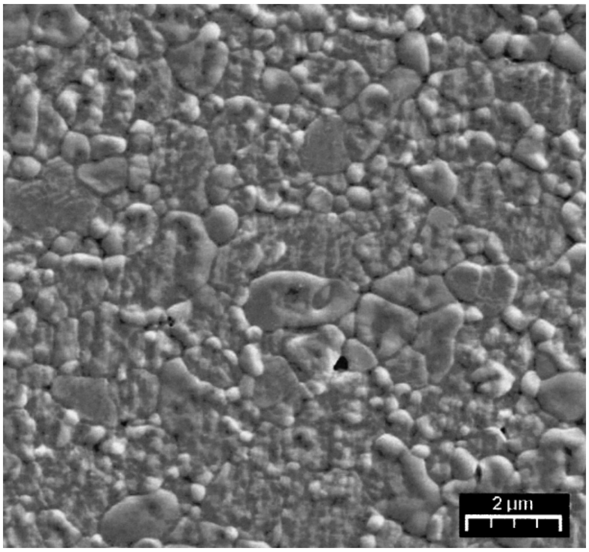

Fig. 11. Micrographies of the sample sintered at 1310°C/4 h.

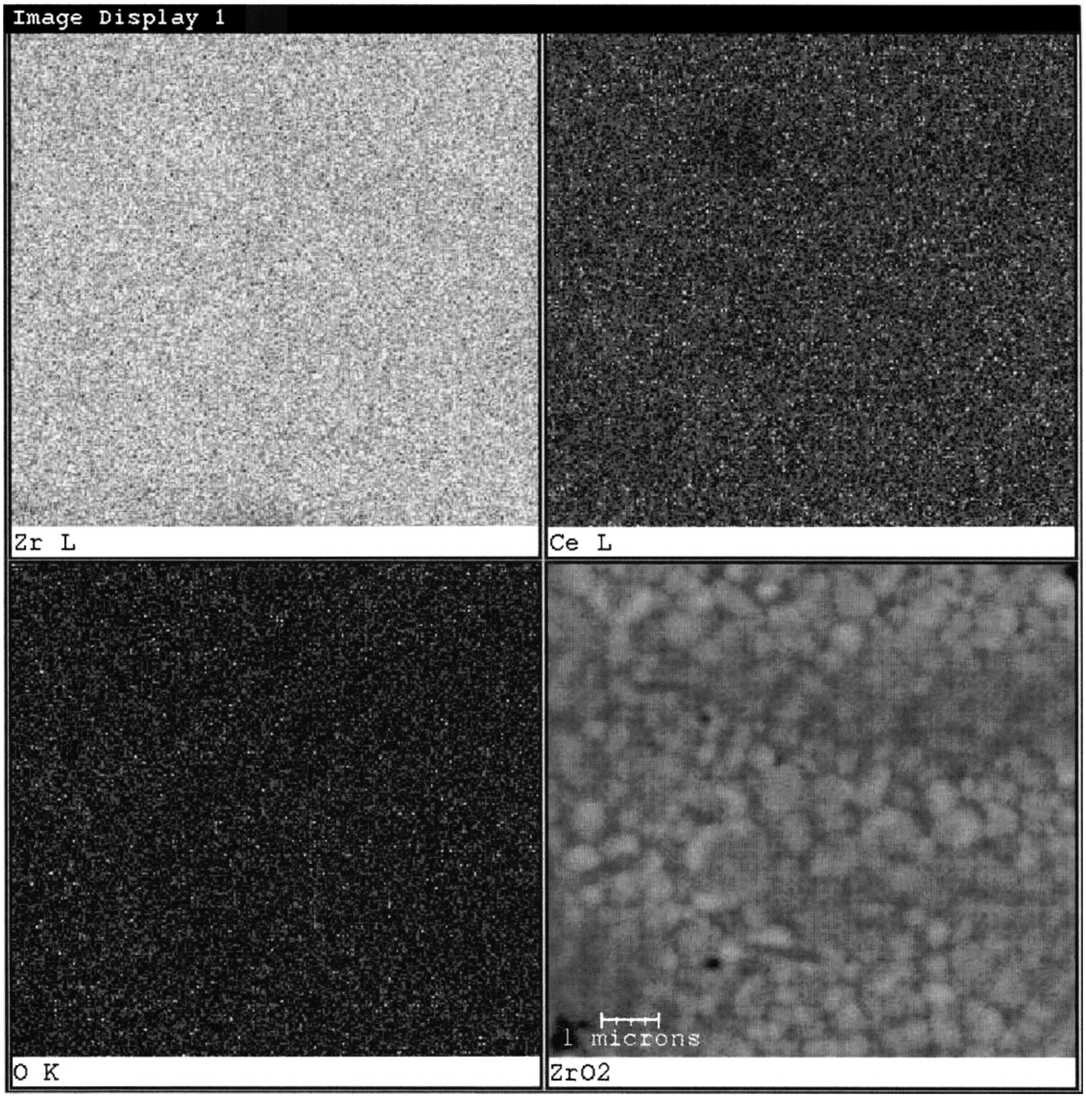

Fig. 12. Map obtained by EDS analysis after sintering at 1310°C/2 h.

indicating that ceria, initially present only in the nanometric stabilized particles, diffuses throughout the largest grains, which originate from micrometric monoclinic particles. This may lead to higher stabilization of the final sintered body.

4. Conclusion

The use of nanometric particles causes behavior that differs from that reported in the literature for micrometric particles. Optimizing particle size distribution demonstrated that a certain amount of larger particle size NSZ is needed to achieve good dispersion and, thus, higher density of the slip cast samples. Optimizing the deflocculant showed that suspensions with a smaller solid content (13.9–19.4 vol.%) had a well defined value of minimum viscosity, while suspensions with a higher solid content (23.0 vol.%) presented a higher viscosity due to increased particle interaction and the tendency of this material to polymerize.

Pellet density after casting was low due to the formation of a layer of water on the particle surface that was not removed by the mold during the casting process. On the other hand, the high linear shrinkage of the samples during sintering, favored by small particle diameters, led to a final density of around 95% of the theoretical density. Higher densities were attained by optimizing the sintering. Another aspect to point out is that in these systems, as in the systems constituted of micrometric particles, final density depends on the green microstructure, mainly on the pore structure.

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