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Synthesis and sintering of ZrO_2-CeO_2 powder by use of polymeric precursor based on Pechini process

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Nanocrystalline ZrO_2-12 mol % CeO_2 powders were synthesized using a polymeric precursor method based on the Pechini process. X-ray diffraction (XRD) patterns showed that the method was effective to synthesize tetragonal zirconia single-phase. The mean crystallite size attained ranges from 6 to 15 nm. The BET surface areas were relatively high reaching 97 m^2/g. Studies by nitrogen adsorption/desorption on powders, dilatometry of the compacts, and transmission electron microscopy (TEM) of the powders, were also developed to verify the particles agglomeration state. Both citric acid : ethylene glycol ratio and calcination temperature affected the powder morphology, which influenced the sinterability and microstructure of the sintered material, as showed by scanning electron microscopy (SEM). © *2001 Kluwer Academic Publishers*

1. Introduction

Ceria doped tetragonal zirconia polycrystal (Ce-TZP) represents a very interesting ceramic material attributed to its remarkable high fracture toughness and thermal stability, considered to be caused by stress-induced transformation from the tetragonal to the monoclinic phase [1–3]. These properties are strongly dependent on CeO_2 content and the grain size of the sintered bodies, due to its effects on the transformability of the tetragonal phase. Decreased CeO_2 content lead to the reduction of stability of the retained tetragonal phase, as described in the phase relations in ZrO_2-CeO_2 system [4, 5]. The stability is also reduced by increase of the grain size [3, 6–8]. Reducing stability, the tetragonal phase is easily transformed to the monoclinic phase by applied stress. The transformation renders effective the toughening mechanism. However, spontaneous tetragonal-to-monoclinic transformation during cooling from the fabrication or service temperature must be avoided.

The microstructural parameters of sintered material such as grain size and density depend mainly on the characteristics of the starting powder, which differs depending on the synthesis methods and conditions used. Characteristics include purity, homogeneity, particle shape and size, particle size distribution, presence of agglomerates, etc. The control of physical and chemical homogeneity during powder synthesis, powder preparation, powder consolidation, and sintering are required for densification of stabilized zirconia ceramics at relatively low temperatures. Fine powders sinter better, i.e., faster and/or at lower temperatures than coarse ones. However, powders of very fine particles, usually synthesized by wet-chemical routes, do not always show good sinterability, because of the formation of agglomerates [9, 10]. Thus uncontrolled agglomeration or the presence of high-strength agglomerates (aggregates) can be detrimental to the properties of final products.

Wet-chemical method using polymeric precursor based on the Pechini process [11], has been investigated to prepare a wide variety of ceramic oxides [12–19]. The process offers several advantages for processing ceramic powders such as, direct and precise control of stoichiometry, uniform mixing of multicomponents on a molecular scale, and homogeneity. In this process an alpha hydroxycarboxylic acid, preferentially citric acid, is used to chelate various cations by forming a polybasic acid. In the presence of a polyhydroxy alcohol, normally ethylene glycol, these chelates react with the alcohol to form ester and water by-products. When the mixture is heated, polyesterification occurs in the liquid solution and results in a homogeneous sol, in which metal ions are uniformly distributed throughout the organic polymeric matrix. When excess solvents are removed, an intermediate resin is formed. Oxide powders are obtained by burning the resin to

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remove all organic substances. The powder morphology made by the Pechini-type process is affected mainly by the composition of the polymeric precursor (Citric Acid : Ethylene glycol ratio) [20, 21]. The method was applied to synthesize zirconia-ceria [22] showing to be effective to prepare zirconia with a tetragonal structure. In the present study a polymeric precursor method based on the Pechini process is used to synthesize ZrO_2-12 mol % CeO_2 powders. The objective of this study is to evaluate the influence of variables such as citric acid : ethylene glycol ratio and calcination temperature in the phase formation and powder morphology. The sinterability and microstructure of sintered material are also considered.

2. Experimental procedure

2.1. Powder synthesis

Zirconium (IV) oxide chloride, $ZrOCl_2{\cdot}8H_2O$ (Merck, Darmstadt, Germany), purity of 99.5+%, was first dissolved in distilled water. Zirconium hydroxide was precipitated from this solution by ammonium hydroxide addition until pH = 8.0. The solution thus obtained was then filtered. The zirconium hydroxide precipitated was washed with distilled water until complete elimination of chlorine ions in the liquid phase. The zirconium hydroxide was then dissolved with nitric acid (65% w/w). Distilled water was added to obtain zirconium nitrate solution containing 35 g ZrO_2/l. Cerium hydroxide (Nuclemon, São Paulo, Brazil), purity of 99+%, was dissolved in nitric acid (65% w/w) at 80° C, after that

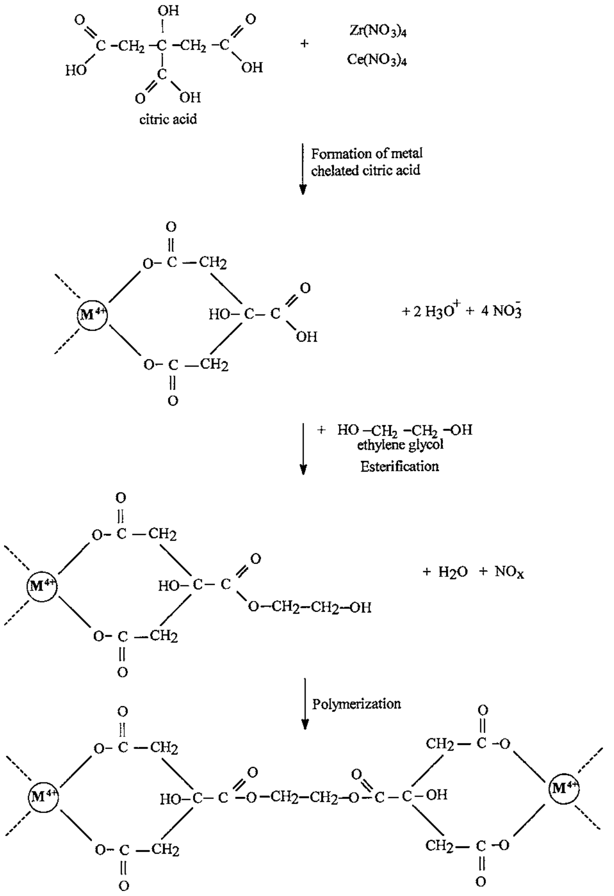

Figure 1 Chemical reactions of polymeric precursor synthesis.

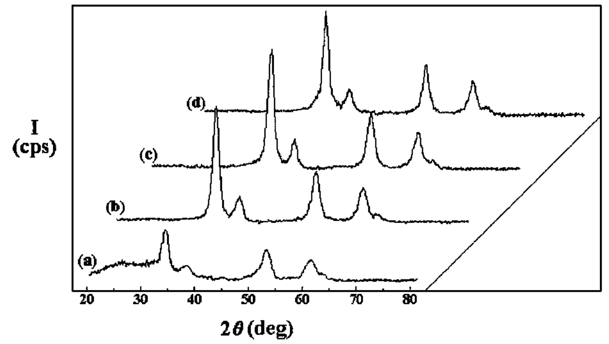

Figure 2 X-ray diffraction patterns of the ZrO_2-CeO_2 powders, synthesized at different CA : EG ratios, and calcination temperatures. (a) CA : EG = 1 : 1, T = 400° C; (b) CA : EG = 1 : 5, T = 600°C; (c) CA : EG = 1 : 1, T = 600°C; (d) CA : EG = 2 : 1, T = 600° C.

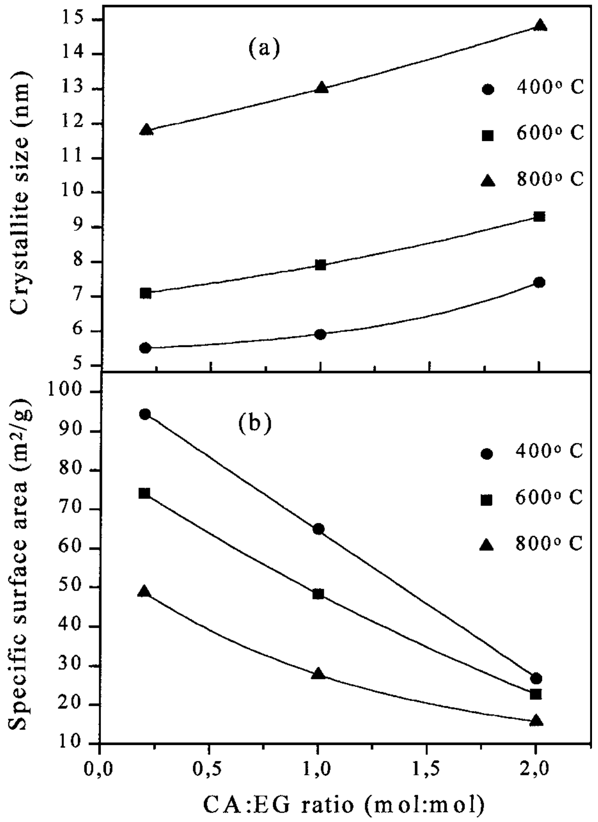

Figure 3 (a) Crystallite size, and (b) surface area of the powders as a function of the CA : EG ratio at different calcination temperatures.

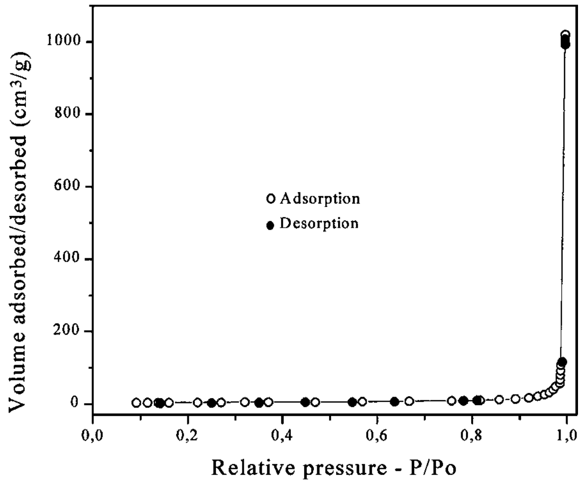

Figure 4 Nitrogen adsorption/desorption isotherms for the ZrO_2-CeO_2 powder synthesized at CA : EG = 2 : 1, and calcined at 600° C.

distilled water was added to obtain cerium nitrate solution containing 20 g CeO_2/1. The nitrate solutions were mixed, considering the stoichiometry ZrO_2-12 mol % CeO_2. On stirring, the mixture was heated at 100° C. Citric acid (CA) was added at CA : total oxides molar ratio (CA : TO) of 4 : 1. Total oxides denote the sum of ZrO_2 plus CeO_2 in the final ceramic powder. After 15 min. ethylene glycol (EG) was added into solution at different CA : EG molar ratios, i.e., 1 : 5, 1 : 1, and 2 : 1. The solution was then heated up to 140° C, to promote the polyesterification reaction. After 40 min. when nitrous oxides and water were eliminated, a clear resin was obtained. Fig. 1 illustrates the chemical reactions involved in this process presenting one feasible structure of the polymer. The polymeric resin was heated at 250° C to remove organic substances. Char flakes were obtained, which were dry ball milled to obtain particle size below 150 μm. The black powder thus produced was calcined for 2 h in crucible at different temperatures, i.e., 400, 600, and 800° C, to obtain the ZrO_2-CeO_2 ceramic powder.

2.2. Sintering

ZrO_2-CeO_2 powders calcined at 600° C for 2 h, were compacted using direct uniaxial pressing to obtain cylindrical samples, having a diameter of 9 mm and green density of 37% of the theoretical value of 6250 kg/m^3. The theoretical density was calculated from lattice parameters measurements by XRD. These samples were sintered in a dilatometer furnace (Nestzch model 402 E), with a constant heating rate of 10° C/min. and in an electrical furnace up to 1500° C and soaking time of 4 h at this temperature in atmospheric air. The densities after sintering were determined by measuring the mass and volume by the Archimedes method.

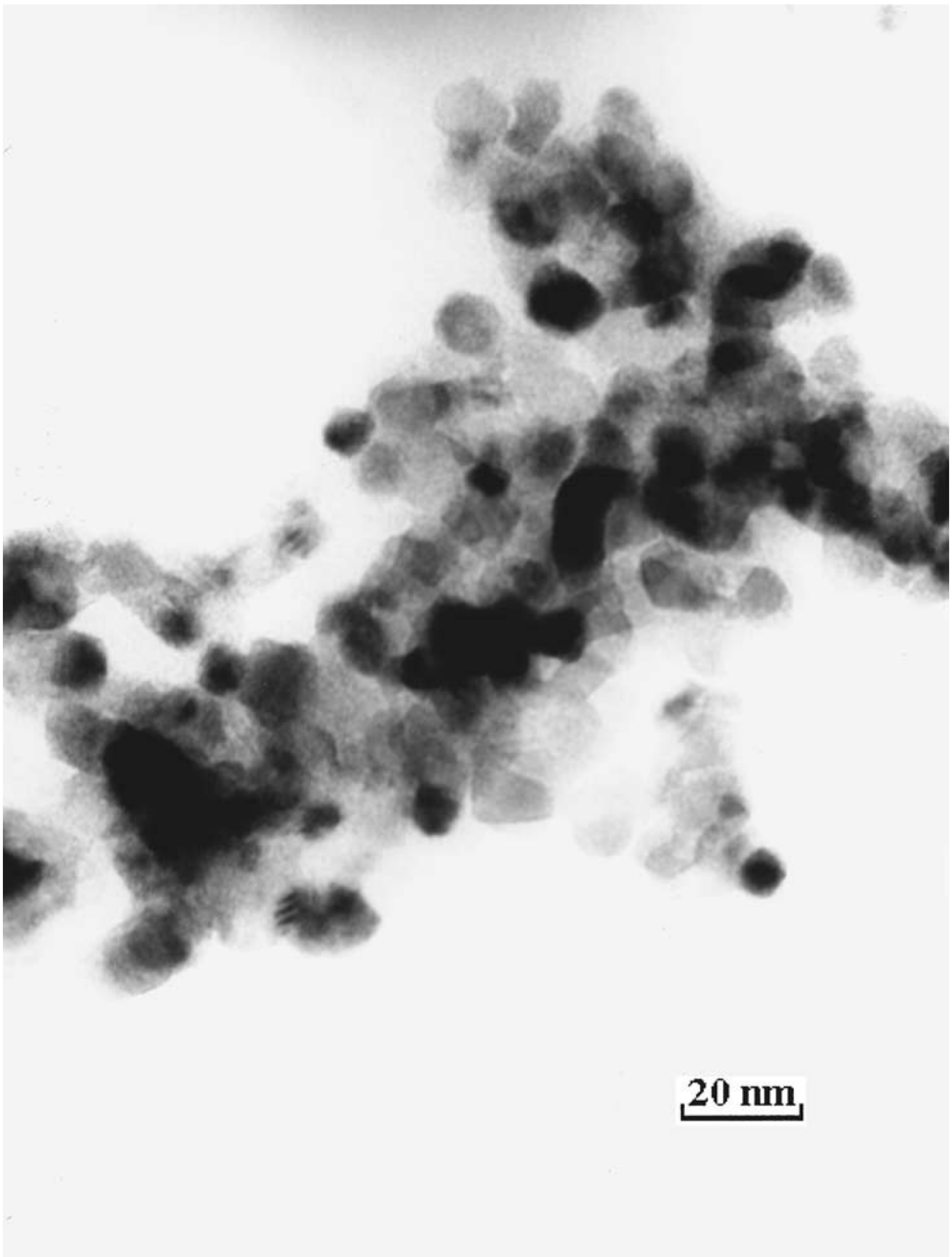

Figure 5 TEM micrograph of ZrO_2-CeO_2 powder synthesized at CA : EG = 1 : 5, and calcined at 600° C.

2.3. Characterization

The existing phases in the ceramic powders and sintered bodies were investigated by X-ray diffraction-XRD (Siemens diffractometer, model D-5000, with Cu K_α radiation and a graphite monochromator). Powder crystallite size was determined using the X-ray line broadening method, by Scherrer equation [23, 24]. Nitrogen adsorption/desorption on the powder surface at 77 K (Micromeritics, ASAP 2000) was used to verify the hysteresis occurrence and to measure specific surface area by applying the BET method [23]. The powder morphology was observed using transmission electron microscopy (Philips-CM200 microscope). The microstructure of the surface of as-sintered samples was analyzed using scanning electron microscopy (TOPCOM-300 microscope). The average grain size was determined by the linear intercept method.

3. Results and discussion

3.1. Powder synthesis

In Fig. 2 the XRD pattern of the powder synthesized at CA : EG ratio of 1 : 1, and calcined at 400° C showed the presence of an amorphous region, indicating that at this temperature not all organic substances were burned during calcination. At the same temperature and for the another CA : EG ratios used the behavior was similar. For powders calcined at 600° C a well crystallized tetragonal zirconia single-phase, for all CA : EG molar ratios, was attained. This behavior was also observed for samples calcined at 800° C. Thus, the method was successfully used to synthesize ceria-doped tetragonal zirconia single-phase.

As observed in Fig. 3a, both CA : EG ratio and calcination temperature affected the crystallite size. The decrease of the CA : EG ratio (increase of ethylene glycol amount) and decrease of calcination temperature favored the decrease in crystallite size. Increasing ethylene glycol amount an increase in the polymeric chain length occurs, increasing the distance between chelated cations. This suggests that weaker interactions among primary particles occur during crystallization, leads to smaller particle sizes. The mean crystallite size ranges from 6 to 15 nm, showing that the method is effective for the synthesis of nanosized powders.

As shown in Fig. 3b, surface areas decreased with increase of the CA : EG ratio and with rising calcination temperature, because of particles coarsening. Surface areas were relatively high due to presence of very fine particles, reaching 95 m^2/g.

The nitrogen adsorption/desorption isotherms for the powder synthesized at CA : EG = 2 : 1 and calcined at 600° C are illustrated in Fig. 4. As observed, no hysteresis was observed, indicating no capillary condensation in mesopore structures [25]. This suggests the absence of high-strength agglomerates (aggregates). The behavior of powders synthesized using the other CA : EG ratios was similar. This observation was confirmed by TEM micrograph in Fig. 5. As observed in this micrograph the primary particles, with average size of 7 nm, are uniform and weakly agglomerated. This agrees with the mean crystallite size value determined on basis of Scherrer equation. However, assuming spherical particles (as done in the XRD line broadening calculations) and using the crystallite sizes calculated by Scherrer equation, the BET surface areas should be higher than the values showed in Fig. 3b. This indicate that inaccessible surface are present, denoting particles aggregation.

3.2. Sintering

The linear shrinkage rate of powder compacts, sintered in a dilatometer furnace with a constant heating rate of 10° C/min. are illustrated in the curves of Fig. 6. The three curves (CA : EG = 1 : 5, 1 : 1 and 2 : 1) are similar in shape, showing only one peak for the maximum linear shrinkage rate. The absence of another lower-temperature peak suggests the absence of intraaggregated pores [26]. The powders synthesized at CA : EG = 1 : 5, 1 : 1 and 2 : 1 had a maximum rate at about 1180, 1250, and 1480° C respectively. Thus, the increase of ethylene glycol amount favored the decrease of the temperature of maximum shrinkage rate. As

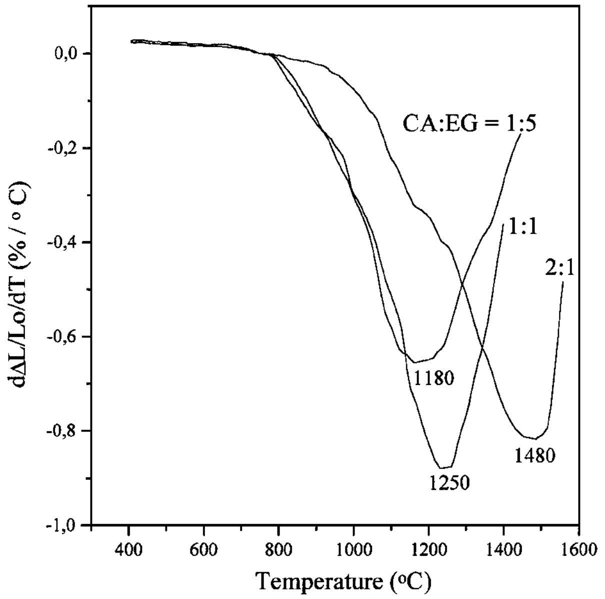

Figure 6 Linear shrinkage rate as a function of sintering temperature for ZrO_2-CeO_2 compacted powders.

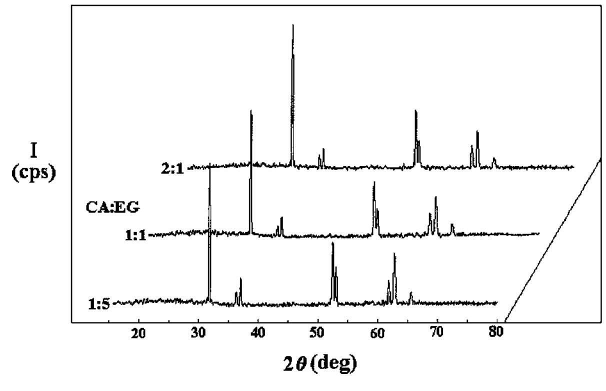

Figure 7 X-ray diffraction patterns of ZrO_2-CeO_2 compacts sintered at 1500° C for 4 h, obtained from powders synthesized at different CA : EG ratio.

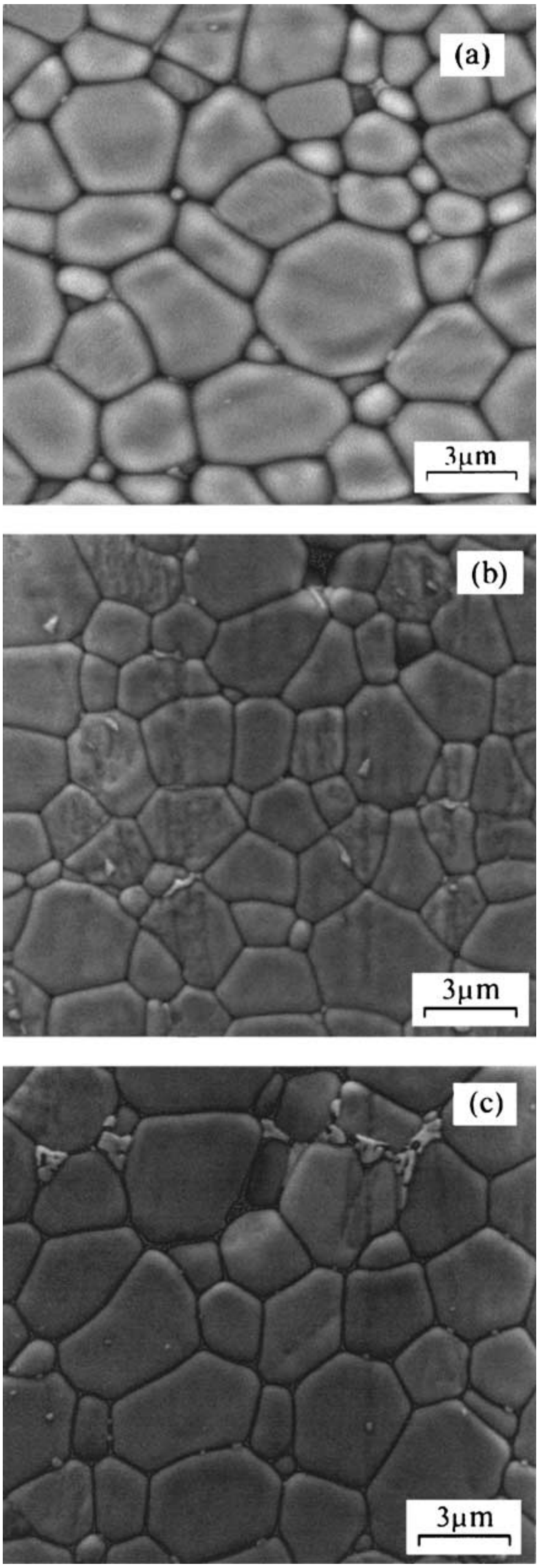

Figure 8 SEM micrographs of ZrO_2-CeO_2 compacts sintered at 1500° C for 4 h. Compacts were obtained with powders synthesized using the following conditions: (a) AC : EG = 1 : 5; (b) AC : EG = 1 : 1; (c) AC : EG = 2 : 1.

showed before, the increase of ethylene glycol amount favors the decrease of the crystallite size and an increase of the surface area. Finer powders sinter faster and/or at lower temperatures, because there is more surface area per unit volume, and the mass transport distances are shorter, leading to a decrease in the temperature of maximum shrinkage rate.

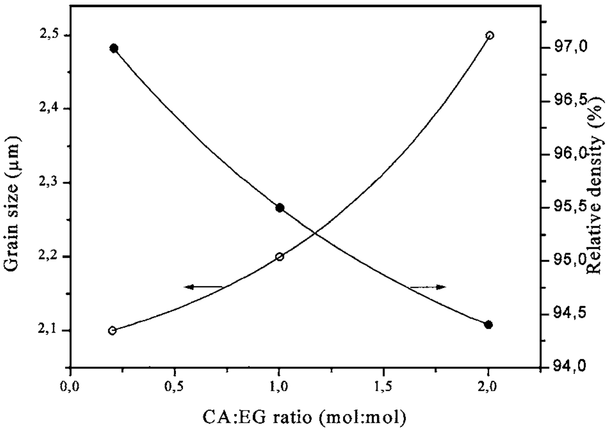

Figure 9 Grain size and relative density of the sintered material as a function of the CA : EG ratio used for powder synthesis.

The tetragonal single-phase was also observed in the sintered samples, for all CA : EG ratio used during powder synthesis, as showed in Fig. 7. The microstructure of the as-sintered surface is revealed by the SEM and is presented in Fig. 8. The average grain sizes after sintering are estimated to be 2.1, 2.2, and 2.5 μm for samples obtained using CA : EG ratio of 1 : 5, 1 : 1, and 2 : 1, respectively.

Both average grain size and relative density of the sintered samples were plotted as a function of the CA : EG ratio of powders synthesis, as showed in Fig. 9. With the increase of ethylene glycol amount an increase of the relative density and decrease of the grain size occured. These results indicated that the finer powders of higher areas, generated sintered bodies with higher densities and smaller grain sizes. Densities were relatively high reaching 97% of the theoretical value using CA : EG = 1 : 5. Moreover, higher densities could be obtained by improving the green compaction of the powders.

4. Conclusions

A polymeric precursor method based on Pechini process was successfully used to synthesize nanosized Ce-TZP powders. Both citric acid : ethylene glycol ratio and calcination temperature affected the powder characteristics regarding crystallite size and surface area. The increase of ethylene glycol amount and decrease of calcination temperature favored the decrease in crystallite size and increase of the surface area. Studies by nitrogen adsorption/desorption on powders, dilatometry of the compacts, and transmission electron microscopy (TEM) of the powders, seem to support the existence of non-aggregated particles, but results of BET surface areas indicated that aggregates are present. Thus, to determine the agglomeration state, several ways of powder characterization should be considered. The powder characteristics affected the sintering behavior and the grain size of sintered bodies. Powders composed by finer crystallites and higher surface area lead to lower temperatures for the maximum shrinkage rate and smaller grain sizes. Tetragonal zirconia single-phase, with grain sizes ranging from 2.1 to 2.5 μm, was obtained after sintering at 1500° C during 4 h. Thus, Ce-TZP with different microstructures were produced by using polymeric precursor through changing the CA : EG ratio of powder synthesis.

Acknowledgments

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