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Preparation of nanospherical amorphous zircon powders by a microemulsion-mediated process

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A modified reverse micelle process has been developed for the synthesis of nanospherical amorphous zircon precursor powders. It has been found that the hydrolysis of a mixture of zirconium and silicon alkoxides within the water phase of a microemulsion can produce amorphous, nanospherical particles with a stoichiometric $ZrSiO_4$ composition. Microemulsions were obtained by using cyclohexane as the oil phase, ammonium solutions as the aqueous phase, and Igepal Co520 as surfactant. Precise control of the stoichiometry of the powders was achieved after the starting silicon and zirconium alkoxides were appropriately modified. In particular, silicon alkoxide was pre-hydrolyzed under acidic conditions while zirconium alkoxide was reacted with chelating agents. The as-prepared powders consisted of amorphous nanospherical particles with compositional homogeneity. Heating of powders led first to incipient tetragonal zirconia crystallization at a temperature of 900 °C. The onset of crystalline zircon formation was detected at 1200 °C, while the conversion was complete after heating the amorphous precursor powders at 1300 °C for 2 hours.

1. Introduction

Zircon ($ZrSiO_4$) is an important ceramic material due to its high resistance to thermal shock, its low thermal expansion coefficient and its high chemical stability. All of these properties make zircon a material widely used in the ceramic industry, for example as an opacifier in ceramic glazes and enamels.[1] Recently a new application of zircon has been proposed[2,3] as a potential host for ^{239}Pu waste resulting from the dismantling of nuclear weapons.

The preparation of ceramic powders with a particle size in the nanometric range (<100 nm), so-called nanocrystalline or nanophase powders,[4] has received attention not only because of their often unusual physical properties but also because such powders may significantly enhance sintering rates or dramatically lower sintering temperatures.[5,6] As such, nanophase powders may allow for the synthesis of novel bulk materials that cannot be produced by the sintering of their more commonly used, micron-sized counterparts. Another example of their application is in ceramic matrix composites where dispersed nanoparticles reportedly have improved mechanical properties such as strength and high temperature creep resistance.[7] Nanophase powders can also be useful in precursor form, leading to chemically homogeneous powders with a narrow particle size distribution.

Zircon powders have been synthesized by the sol–gel route,[8–11] which yielded heterogeneously shaped particles and agglomerated solids, while aerosol techniques,[12,13] spray pyrolysis and aerosol hydrolysis produced larger composite particles that were either hollow or had a broad size distribution.

Water-in-oil (W/O) microemulsions (*i.e.*, reverse micelle solutions) are transparent, isotropic, thermodynamically stable liquid media. In these systems, fine microdrops of the aqueous phase are trapped within assemblies of surfactant molecules dispersed in a continuous oil phase. The surfactant-stabilized microcavities provide a confinement effect that limits particle nucleation, growth, and agglomeration.[14] Recently, the use of these methods for the preparation of non-aggregated nanospherical oxide particles has been successfully demonstrated.[15,16] However, when applied to a binary system such as $BaTiO_3$, problems with the control of the stoichiometry have been reported.[17] The methodology used here for the preparation of non-agglomerated nanospherical precursor particles with a zircon composition, a binary oxide, may extend microemulsion-based methods for the preparation of nanospherical particles of other multicomponent ceramic powders and precursors.

This paper reports the preparation of nanospherical amorphous precursor particles with a stoichiometric zircon composition, by hydrolysis of mixtures of tetraethylorthosilicate and zirconium n-propoxide within the water droplets of water-in-oil microemulsions. These powders were characterized in terms of phase composition, morphology (size and shape) and bulk and surface chemical composition. The thermal evolution of the nanophase precursor powders, up to zircon crystallization, is also reported.

2. Experimental procedure

2.1. Materials and methods

Water-in-oil microemulsions (reverse micelles) were prepared using Igepal Co520 (Aldrich) as surfactant. Cyclohexane (Aldrich, 99.5% anhydrous) dehydrated with molecular sieves, was used as a continuous oil phase. Zirconium n-propoxide (TPOZ, Aldrich, 70% in 1-propanol), tetraethylorthosilicate (TEOS, Aldrich, 99%), ammonium hydroxide (EM, 29%), acetylacetone (Aldrich, 99+%), 1-butanol (Aldrich, 99.8% anhydrous), ethanol (Aldrich, 99.5% anhydrous) and HCl (EM, 37%) were used as received.

The microemulsions were prepared at room temperature by addition of the aqueous phase (ammonium hydroxide) to a

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solution containing the surfactant and cyclohexane. To obtain the microemulsion the solution was thoroughly shaken. A mixture containing the zirconium and silicon alkoxides in the desired proportion (Si/Zr molar ratio of 1) and an aliquot of cyclohexane (10% of the total) was mixed at RT under magnetic stirring. This solution was added to the microemulsion also under constant stirring, and hydrolyzed for different periods of time. This powder was washed with acetone and dried under vacuum.

To obtain nanospherical amorphous particles with a stoichiometric zircon composition, values of the water/surfactant molar ratio, *R*, the water/alkoxide molar ratio, *h*, and the alkoxide concentration, hydrolysis time, and composition of the initial alkoxide mixture were appropriately modified.

In some experiments, the zirconium alkoxide was added to the microemulsion 2, 4, 8 or 24 hours after the silicon alkoxide. In other experiments, the starting alkoxide mixture was partially hydrolyzed before its addition to the microemulsion. To this end, the mixture was placed in a beaker (100 cm^3) with a resulting liquid surface/volume ratio of 0.65 cm^{-1}, and kept under magnetic stirring, at room temperature, in an atmosphere of 60% of relative humidity, for different periods of time.

In addition, experiments were carried out with alkoxide mixtures in which the zirconium alkoxide was modified, previous to its addition to the TEOS/cyclohexane solution, by mixing with two reactants, acetylacetone and 1-butanol (Zr/acetylacetone/butanol = 1/0.5/3), for 20 hours. In some of these experiments TEOS was also modified. In particular, TEOS was hydrolyzed with water set at a pH of 1.6 by the addition of HCl, in the presence of ethanol (TEOS/water/ethanol = 1/1/4) for 4 hours, and then mixed with the zirconium alkoxide, acetylacetone and 1-butanol for 3 hours.

2.2. Characterization techniques

The particle size and shape of the powders was examined by transmission (TEM) and scanning electron microscopy (SEM). The size distribution was determined from the electron micrographs by measuring several hundred particles. Elemental analysis of samples (Si/Zr molar ratio) was done with an energy dispersive spectrometry analyzer (EDS, Oxford Link 5118) integrated into a scanning electron microscope (SEM, Zeiss DSM 960).

The different phases present in the solids were assessed by X-Ray diffraction (XRD, PW1710, Philips, Eindhoven, The Netherlands) and infrared spectroscopy (IR, 20SXC, Nicolet, Madison, WI). To record the infrared spectra, the powders were diluted in a KBr matrix. Thermogravimetric (TG) and differential thermal (DTA) analyses (STA 781, Stanton, London, UK) were conducted in air, at a heating rate of 10 °C min^{-1}.

The isoelectric point (i.e.p.) of the powders was determined (Delsa 440, Coulter, Hialeah, FL) by measuring electrophoretic mobilities of aqueous dispersions as a function of pH. NaCl was used to keep the ionic strength constant, and the pH was varied with NaOH and HCl. Particle velocities were determined at several positions across the cell and the electrophoretic mobility in the stationary layer was calculated by the procedure of Pelton *et al.*[18]

3. Results and discussion

3.1. Powder preparation

Values of *R*, *h*, hydrolysis time and alkoxide concentration were systematically changed to obtain the nanospherical powders. It was found that at alkoxide concentrations lower than 7.5×10^{-3} M, the hydrolysis of a freshly prepared mixture of zirconium n-propoxide and TEOS produced nanoparticulate $ZrO_2 \cdot SiO_2$ powders. However, the Si/Zr molar ratio of this powder was 0.50, lower than that corresponding to the starting liquid mixture (Si/Zr = 1.00). This result may be attributed to the lower hydrolysis rate of TEOS compared to that of the zirconium alkoxide.[19] To achieve a Si/Zr molar ratio of 1.0 in the powder, the silicon and zirconium alkoxides were subjected to different treatments.

Given that zirconium alkoxide has a higher hydrolysis rate than TEOS it was first decided to prehydrolyze the TEOS within the microemulsion. For this, zirconium propoxide was added to the microemulsion 2, 4, 8 and 24 hours later than TEOS. However, the Si/Zr molar ratio obtained after these treatments was still lower than 1.0 (0.81 for prehydrolysis times longer than 8 hours).

To bring the hydrolysis rates of both alkoxides into agreement to form Si–O–Zr bonds in the starting liquid, the TEOS and TPOZ mixture was prehydrolyzed at RT in an atmosphere of 60% relative humidity for different periods of time. This approach was already shown to be successful for controlling the stoichiometry of amorphous zircon particles produced by methods based on aerosol hydrolysis,[13] even though NMR studies revealed that only 55% of TEOS had reacted to produce species containing Si–O–Zr bonds. Chemical analyses carried out on the as-prepared powders showed that the maximum Si/Zr molar ratio obtained was 0.83 for pre-hydrolysis times of 24 hours and hydrolysis times in the microemulsion of 120 hours. The reason for not achieving in this particular system a Si/Zr ratio in the powder equal to the one in the starting liquid mixture may be associated with the presence of unreacted TEOS and with the different mechanisms involved in the powder synthesis methods. In aerosol systems, differences in hydrolysis rate and vapor pressure of alkoxides produce differences between the stoichiometry of powders and that of the starting liquid mixture.[20] In microemulsion systems, differences in partitioning coefficients (differences in transference of alkoxides from the oil phase to the reverse micellar pseudophase) and differences in hydrolysis rate of alkoxides determine the stoichiometry.[15,17,21,22] Also, the increase of viscosity of TEOS and TPOZ mixtures, *i.e.* beginning of gelation, makes longer pre-hydrolysis times ineffective.

Chelating ligands such as acetylacetone are often used to slow the hydrolysis rate of zirconium alkoxides.[23,24] The intent is to replace the reactive alkoxide ligands by less hydrolyzable ones, and to increase the zirconium-ion coordination. Therefore, TPOZ was reacted with acetylacetone in the presence of 1-butanol in the molar ratio given in the experimental procedure. It is important to mention that microemulsions were still produced even though the presence of both acetylacetone and 1-butanol must affect their detailed structure. In particular, the alcohol can penetrate into the layer making the surfactant layer more rigid as the alcohol chain expands.[15,25] Under conditions in which nanoparticulate powders were produced (alkoxide concentration $\leqslant 7.5 \times 10^{-3}$ M), an increase in the Si/Zr molar ratio in the powder was observed from 0.50 (mixture without treatment) to 0.65 which, however, was still much lower than the one of the starting liquid.

Finally, nanoparticles with zircon composition (Table 1, Fig. 1) were generated by using precursors obtained after following a method similar to that described by Delattre *et al.*[26] The goal of this method was both to produce precursors with a higher number of Si–O–Zr bonds and to minimize the differences in hydrolysis rate of the silicon and zirconium precursors. Using this treatment it was reported[26] that the starting alkoxide mixture contains a largest percentage of Si–O–Zr bonds (70%), in contrast to the lower percentage conversion (55%) obtained for the case of the pre-hydrolyzed mixture at room temperature in an atmosphere of 60% of relative humidity.[13]

As seen in Table 1, to obtain a Si/Zr molar ratio in the final

Table 1 Chemical composition of the zirconia–silica powders obtained by hydrolysis in reverse micelles of a mixture of TPOZ and TEOS previously reacted with chelating agents and water in acidic medium, respectively

t/h	$(Si/Zr)_{molar\ ratio}$
4	0.81
8	0.87
24	0.96
48	1.00
72	1.01
120	1.00

powder equal to the one of the starting liquid (Si/Zr = 1) is necessary to employ hydrolysis times in microemulsions longer than 48 hours. This result suggests that the surface layers of the initial particles are enriched with SiO_2.

3.2. Powder characterization

A TEM micrograph of the powder with the zircon composition (under the conditions specified) is shown in Fig. 2. The particle size distribution analyses gave a mean diameter of 65 nm with a coefficient of variation less than 10%, which is considered within the limit for a monodisperse material. Microanalyses carried out by TEM on a number of single particles indicated that the Si/Zr molar ratio was the same as that of the average of the powder (1.0), revealing the good compositional homogeneity of the powder, at least at particle level.

The as-prepared nanospherical particles were amorphous to XRD. The infrared spectrum (Fig. 3) displayed absorption bands at 960, 650 and 450 cm^{-1}, which can be attributed to Si–O and Zr–O vibrational modes. The shift of the Si–O asymmetric stretching vibrations to lower frequencies (960 cm^{-1}) in comparison with amorphous silica (1200–1065 cm^{-1}),[27] and the absence of the network Si–O–Si symmetric bond stretching vibration at 800 cm^{-1} may manifest the incorporation of the Zr^{4+} cations within the silica network forming either very small ZrO_2-rich clusters or Si–O–Zr bridging bonds or both.[13,28–30] In addition, the spectrum displayed bands at 3400 (not shown) and 1630 cm^{-1} due to the OH vibrational modes. Other bands at 3150 (not shown) and 1390 cm^{-1} due to the N–H vibrational modes and bands at 1705, 1560, 1510, 1460 and 1250 cm^{-1} due to the presence of organic C=O and C–H groups were also detected.

The thermal evolution of the initial particles was studied by TGA and DTA (Fig. 4). In the temperature range between 25 and 700 °C, TGA showed a weight loss of 40%, which can be associated with the release of adsorbed water, alcohols, ammonium hydroxide and the decomposition of organic species. Accordingly, DTA (Fig. 4) showed an endothermic peak centered at 100 °C associated with the elimination of adsorbed water and alcohols, and an exothermic peak (320 °C) mainly due to surfactant and acetate elimination. This assignment was further confirmed after recording the IR spectrum of a sample heated at 700 °C (Fig. 3), in which absorption bands due to this type of species were not detected. An additional exothermic peak was observed in the DTA at a temperature of 890 °C, which according to the X-ray diffraction data corresponds to either the crystallization of metastable cubic or tetragonal zirconia. The fact that on heating at high temperatures, the XRD pattern (Fig. 5) clearly showed diffraction peaks associated wih the latter, suggests that the exothermic peak is associated with the crystallization of the tetragonal phase. The temperatures of crystallization of t-ZrO_2 reported for $ZrO_2 \cdot SiO_2$ samples vary between 500 °C and 900 °C.[12,13,30–33] The retardation effect in t-ZrO_2 crystallization has been related to the initial homogeneity of amorphous powders,[13] as is the case here for the amorphous precursor powders prepared by the microemulsion-mediated processes. However, the ZrO_2 phase separating from SiO_2 suggests that small zirconia rich clusters exist within the silica network, which can be the precursors for the nucleation of ZrO_2 crystalline phases on heating. It is important to mention that the tetragonal phase crystallization was not associated with a loss of residual carbonaceous species, as was reported for the heating of an amorphous powder prepared by aerosol hydrolysis.[34] The retardation effect that organic impurities have on the zircon crystallization rate lead one to anticipate that the zircon formation rate in powders prepared by microemulsion-based methods could be accelerated compared to the aerosol hydrolysis method. The IR spectra of the sample (Fig. 3) heated at increasing temperatures showed a progressive shift of the Si–O stretching mode (960 cm^{-1}) towards high frequencies, indicating that the exsolution of ZrO_2 from the silica network was gradual. Finally, the appearance at 900 °C of bands at 1180, 1070, 810 and 470 cm^{-1} characteristic of

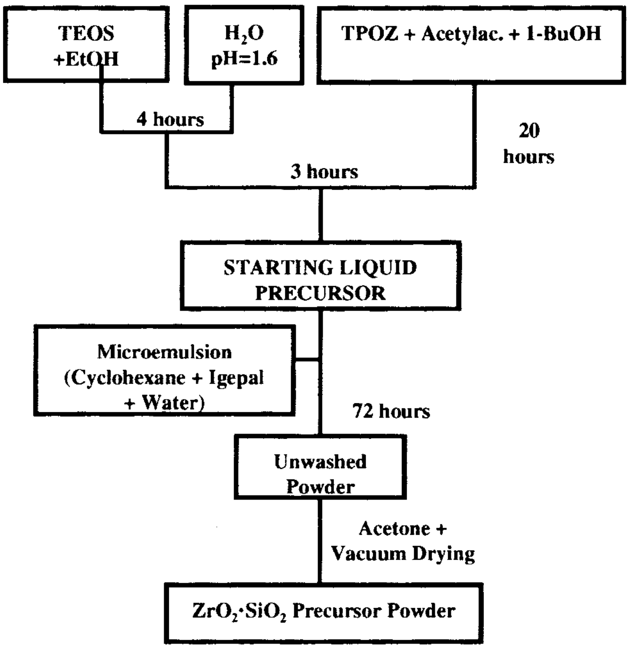

Fig. 1 Processing route for the preparation of the nanospherical amorphous precursor powders with zircon composition. The molar ratio was 1 : 1 : 4 for the TEOS/H_2O/EtOH mixture and 1 : 0.5 : 3 for TPOZ/acetylacetone/1-BuOH.

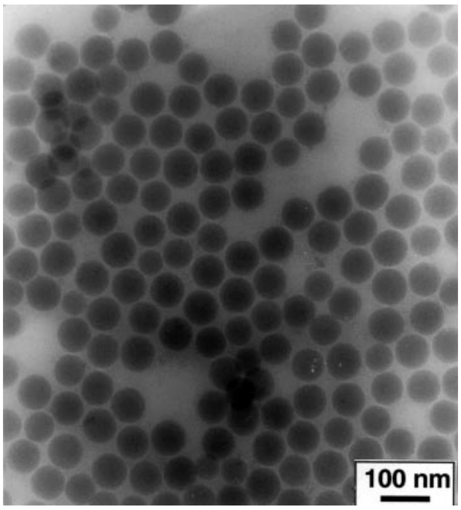

Fig. 2 TEM micrograph of a $ZrO_2 \cdot SiO_2$ sample prepared by the hydrolysis of an alkoxide mixture previously modified according to the treatments showed in Fig. 1. The alkoxide concentration was kept at 7.5×10^{-3} M, $R = 0.8$, $h = 10$ and the hydrolysis time was 72 hours.

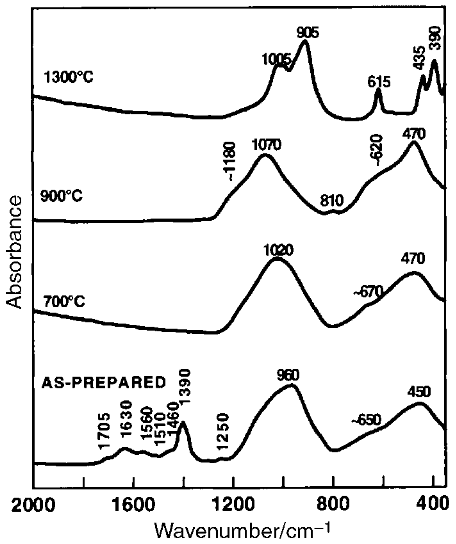

Fig. 3 IR spectra of the sample shown in Fig. 2 in the as-prepared (initial) state and after heating at different temperatures for 2 hours.

amorphous silica[27] indicated that the segregation had ceased at this temperature.

Following these results, and to gain additional information on particle homogeneity, the electrophoretic mobility as a function of pH was measured for powders heated at 900 °C for 2 hours (Fig. 6). At this temperature, as mentioned above, organic impurities are no longer present, the ZrO_2 crystalline phase is the tetragonal one, and traces of zircon are not yet detected. Therefore, qualitative information about the chemical composition may be inferred. The i.e.p. value of 2.8 is very close to the one reported for silica (3),[35] and much lower than those of t-ZrO_2 (10)[36] and zircon (5.7).[37] This result is consistent with an enrichment of SiO_2 on the particle surface layers, and supports the conclusion suggested by the chemical analyses of samples hydrolyzed for different periods of time (Table 1).

XRD of a sample heated at 1200 °C for 2 hours (Fig. 5) displayed diffraction peaks corresponding to the partial transformation of tetragonal to monoclinic zirconia. The latter most likely formed on cooling to room temperature where tetragonal zirconia is the thermodynamic stable phase.[38] The presence of silica, which keeps the zirconia crystallite size below its critical value, has been suggested to be responsible for the retardation of the tetragonal–monoclinic transformation[39,40] compared to pure zirconia.[41] For this heat treatment the X-ray diffraction pattern also showed the crystallization of α-cristobalite, formed after transformation of the β-cristobalite during cooling,[42] and the beginning of zircon crystallization.

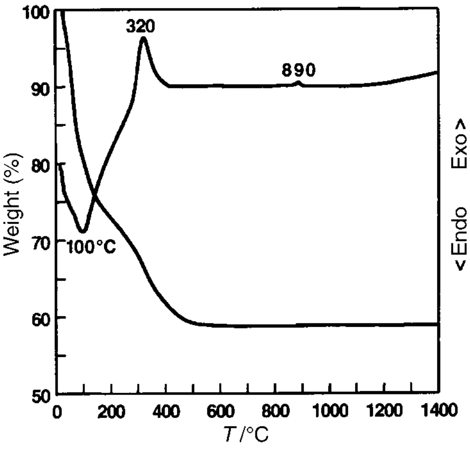

Fig. 4 DTA/TG analyses of the sample shown in Fig. 2.

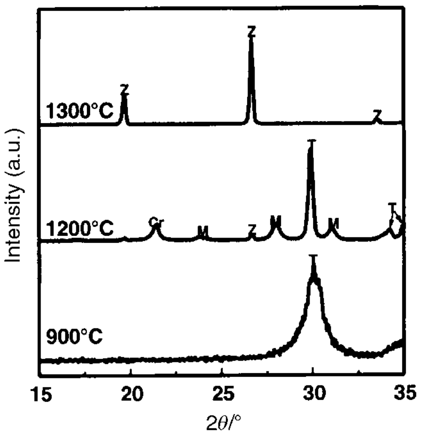

Fig. 5 XRD patterns of the sample shown in Fig. 2 heated at different temperatures for 2 hours. The symbols represent: (T) tetragonal zirconia, (M) monoclinic zirconia, (Cr) cristobalite and (Z) zircon.

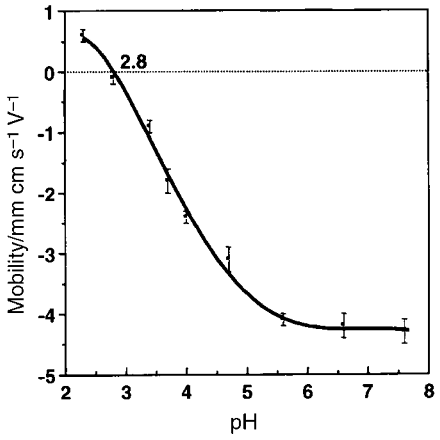

Fig. 6 Electrophoretic mobilities as a function of pH of the sample shown in Fig. 2 heated at 900 °C for 2 hours.

Complete zircon formation was achieved after heating the powder at 1300 °C for 2 hours, as revealed by XRD (Fig. 5) and IR spectroscopy[43] (Fig. 3). It must be mentioned that this temperature is lower than those reported by other authors who have studied zircon crystallization starting from amorphous powders prepared by different chemical routes.[10–13,30–33] For example, the temperature of complete zircon crystallization in the case of powders obtained by a microemulsion mediated process (1300 °C) was lower than that obtained for powders prepared by aerosol hydrolysis[13] (1500 °C). Given that zircon crystallization is controlled by diffusionally limited nuclea-

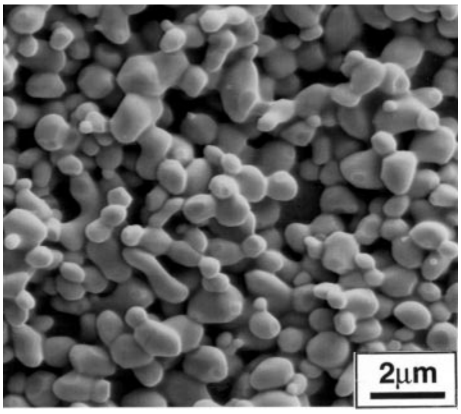

Fig. 7 SEM micrograph of the sample shown in Fig. 2 after heating at 1300 °C for 2 hours.

tion,[34,44] the increase in the zircon crystallization rate could be due to both differences in particle size and, as suggested above, the absence of residual carbonaceous species which, if located in the grain boundaries, could slow down the diffusion process.[34] Finally, it must be mentioned that SEM micrographs (Fig. 7) revealed evidence of significant coarsening of sintering after the 1300 °C conversion treatment. The sintering behavior of the amorphous precursor powders and the converted powders remains for future study.

4. Conclusions

It has been shown that nanospherical stoichiometric $ZrO_2 \cdot SiO_2$ amorphous precursor particles can be prepared by the hydrolysis of zirconium and silicon alkoxides within the aqueous water phase in water-in-oil microemulsions prepared using Igepal Co-520 as surfactant and cyclohexane as the oil phase. To control the stoichiometry of powders the hydrolysis rate of the zirconium propoxide must be slowed using a chelating agent (acetylacetone) while the silicon alkoxide must be prehydrolyzed in an acidic medium. The resulting powder transforms into zircon upon heating to 1300 °C, a relatively low temperature. Compared to other methods, the lower conversion temperature for this amorphous powder can be attributed to the initial compositional homogeneity, the absence of carbonaceous residual species on heating, and the small particle size obtained by the modified reverse micelle microemulsion method.

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