sZrO$_2$-CeO$_2$ ceramic powders obtained from a sol-gel process using acetylacetone as a chelating agent for potential application in prosthetic dentistry

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**Purpose:** The main objective of this study was to obtain single-phase $\beta$-ZrO$_2$ powders with so-called soft agglomerates reproducible morphology with acetyl-acetone as a chelating-agent. To the best of our knowledge there is no available data which determine the effect of acetyl acetone on the phase composition and morphology of ceria-doped ZrO$_2$ powders for biomedical applications.

**Methods:** Twenty variants of powders with different water to zirconia precursor and acetylacetone to zirconia precursor molar ratios were prepared. 0.9ZrO$_2$:0.1CeO$_2$ powders were obtained by a hydrolysis and condensation and further calcination of zirconium n-propoxide in a simple one-step sol-gel process. Influence of acetyloacetone to zirconia precursor on the phase composition ratio and water to zirconia precursor was investigated. Samples have been characterized by X-ray diffraction (XRD), Raman spectroscopy (RS), thermal analysis (TGA/DTA) and scanning electron microscopy (SEM) measurements.

**Results:** Ceramic powders prepared by sol-gel process, according to the various concentration of chelating agent and water show different morphology and phase composition. With higher molar ratios of water to zirconium-n-propoxide so-called soft agglomerates and one phase powders are obtained.

**Conclusions:** Higher molar ratios of AcAc in range with smaller amounts of water cause hard agglomerates, obtained powders are characterized by highly thermally stable behaviour and various phase composition. With higher molar ratios of water to zirconium-n-propoxide so-called soft agglomerates and one phase powders are obtained.

**Key words:** sol-gel process, X-ray METHODS, thermal analysis, ZrO$_2$, prosthetic dentistry

1. Introduction

Zirconia is a type of advanced ceramic used as a thermal barrier coating in plane industry, anti-abrasive coating for cutting tools and as a functional ceramic in biomedical applications [5], [11]. Due to its mechanical strength and white color, it has been applied to dental restorations made by CAD/CAM [13], [19]. However, use of zirconia in dentistry raises a lot of reservations and is associated with reports of uncontrolled phase transformation from tetragonal ($\beta$) to monoclinic ($\alpha$), which occurs in oral environments [3], [16]. Such a transformation results in an increase of zirconia volume and possible cracking of prostheses. This is so-called low-temperature degradation, which especially accelerates in humid environments and with elevated temperature [2], [3], [14]. It has been proved that in order to prevent the unfavorable transformation of $\beta$-ZrO$_2$ is doping zirconia with metal oxides, which stabilizes the tetragonal phase in a crystal lattice and ensures the nanoscale grain size [9], [10]. Currently, the most commonly used dopant is Y$_2$O$_3$, which, however, does not fully ensure stability of $\beta$ phase for degradation processes in human body environment [5], [11]. Based on some research results, it can be assumed that CeO$_2$, as a dopant, provides complete stability of the $\beta$ phase and uniform grain size [5], [18], [23]. Stabilization of $\beta$-ZrO$_2$ structure of cerium oxide is possible thanks to the...
oxygen vacancies, which further stiffen the lattice network, preventing the unfavorable phase transformation [10], [15]. Another factor that makes CeO$_2$ a good stabilizer of the β phase is that Ce$^{4+}$ ion has a similar atomic radius to the Zr$^{4+}$ ion, which additionally stiffens the zirconia crystal lattice [4].

The method of preparing ceramic powders is also very important for stabilization. One of the best preparation methods available is the sol-gel process because it allows for strict control of the chemical composition and obtaining a homogeneous grain size distribution [6], [20], [23]. Therefore, the objective of this study is to prepare, using the sol-gel method, single-phase β-ZrO$_2$ powders doped with CeO$_2$ with so-called soft agglomerates reproducible morphology effect. The phase composition of ceramic powders is an important factor for ceramic implant resistance to low-thermal-degradation in the body fluids environment. Only homogeneous β-ZrO$_2$ ceramics is suitable for medical applications [9]. It is therefore essential that the phase composition was homogeneous as throughout all the production stages of biomedical ceramic from powders technology, green bodies preparations, compactions and solid ceramics. To the best of our knowledge, there is no information in the literature regarding the determination of the effect of acetylacetone on the phase composition and morphology of ceria-doped ZrO$_2$ ceramic powders. We believe that the investigation being undertaken is useful and worth further development of zirconia ceramics for CAD/CAM systems.

### 2. Materials and methods

#### 2.1. Sample preparation

Zirconium $n$-propoxide (ZNP) (Acros Organics), 2-propanol (PrOH) (analytical grade, Avantor), acetylacetone (AcAc) (Aldrich), cerium nitrate hexahydrate (CNH) (Sigma Aldrich) and ultrapure water were used as starting materials. All reagents were used without further purification. The whole sol-gel synthesis and reagent dosing were carried out in nitrogen in a humid-free environment. Stabilization of the zirconia precursor was achieved by the addition of acetylacetone (chelating agent). Based on previous empirical data, the molar ratio of AcAc and ZNP was fixed between 0.19 and 0.75, thus obtaining full-homogeneous sols and gelation times below 24 hours. The molar ratio of water and ZNP was varied between 2 and 10 with the ratio changing every second step. The molar ratio of PrOH and ZNP was held constant at 2:1. The molar ratios of 20 variants of colloidal systems are presented in Table 1. Composition of the final powder has been calculated at 0.9 mol% ZrO$_2$ and 0.1 mol% CeO$_2$. CNH was introduced into the sealed three neck round flask as a 1 M solution in PrOH. Due to its high reactivity, water was mixed at half volume with calculated propanol and carefully added drop-by-drop as the last reagent to the sol. Obtained gels were dried at 80 °C for 24 h and later ground with mortar and pestle. Ground powders were calcined in a 2.5 h pre-heating step and at 750 °C. Subsequently, powders were again ground in a hand mortar. The block diagram in Fig. 1 shows the stages of laboratory procedure.

#### 2.2. Characterization

X-ray diffraction measurements were performed on a Seifers XRD7 diffractometer equipped with Co Kα radiation ($\lambda = 0.179021$ nm). The Raman spectra were taken with N-TEGRA Spectra (NT-MDT); wavelength equalled 633 nm. The TGA/DTA studies were carried out on a Q 1500D (MOM) in static air with a heating rate of 10° min$^{-1}$ in the range from 24 to 1000 °C. The morphology and level of the agglomeration was evaluated by SEM analysis. Microphotographs were taken with FEI INSPECT S50 microscope.
3. Results

3.1. Synthesis

Powders obtained according to the molar ratios of AcAc and water showed differences in the structure, agglomeration and, in a few cases, in phase composition. Powders where the molar ratio of water was higher than that expected from the stoichiometry were characterized by a very high degree of agglomeration. This dependence is observed for all samples in the examined range from 2 to 10, as analyzed against water:ZNP. In the systems where the water ratio was significant (from 6 to 10), the solids obtained were represented as very large “cauliflower-shaped” particles, which were very easy to grind in the mortar, resulting in smaller particles. However, a greater content of AcAc with a smaller amount of water obtained large, monolithic, crystal-like agglomerates which were hard to disintegrate with a hand mortar. This situation particularly favors molar ratios of AcAc between 0.38 and 0.58 and the water from 2 to 4. Obtained powders based on their morphology were classified into two groups: soft agglomerates and hard agglomerates [17]. Comparative macroscopic images of soft and hard agglomerates powders after drying are shown in Fig. 2.

3.2. Characterization

3.2.1. Thermal studies

Figures 3a–c show the samples of thermograms for extreme molar ratios of AcAc and water; for comparison, an example of intermediate ratios is also given. From the TG curve it is clear that increasing concentration of AcAc leads to greater shrinkage after calcination. For samples with a molar ratio of AcAc:ZNP (0.75:0.38) and the ratio of water:ZNP (2:4), it was found that weight loss of the powders after calcination is in the range of 41.5 to 72% and corresponds to the sample shown in figure (Fig. 3a). For low molar ratios of AcAc: ZNP (0.19) and water from 6 to 10, weight loss was 30–35%, thermograms being similar as shown in Fig. 3c. Powders with an intermediate relationship of ZNP:H₂O (4 to 6) and the ZNP:AcAc (0.38:0.58) similarly were characterized by various weight loss in the range from 37 to 48% (Fig. 3b). Depending on the molar ratios of ZNP:H₂O and ZNP:AcAc, it is possible to identify the characteristic peaks. On this basis, from the samples with significant differences in thermal behaviour, 3 powder samples A₁, A₃, and A₁₄ were chosen for phase composition and morphology testing by SEM. The curves from the other samples were rejected due to the lack of repro-

![Fig. 1. Preparation procedure of 0.9ZrO₂0.1CeO₂ powders via controlled hydrolysis and condensation](image)

![Fig. 2. Comparative photos of: (a) “hard agglomerates”, (b) “soft agglomerates”](image)
ducibility and will not be taken into account in future research.

3.2.2. X-ray diffraction

The composition and the structure of $A_1$, $A_3$, and $A_{14}$ were confirmed by XRD analysis. Figure 4a and b exhibit the examples of diffraction plots of the two most differentiated powder samples: $A_3$ and $A_{14}$. The XRD pattern of $A_1$ was similar to $A_{14}$ with a slightly less intensity peaks. For $A_1$ we found a pure monoclinic phase, the peaks at $2\theta = 28.49^\circ$, $32.88^\circ$, $36.70^\circ$, $40.21^\circ$, $47.71^\circ$, $52.53^\circ$, $59.53^\circ$, $65.31^\circ$, $78.04^\circ$. For the pure regular phase, the peaks at $2\theta = 35.55^\circ$, $59.60^\circ$, $71.56^\circ$. Sample (b) is full tetragonal as is $A_1$. For the pure tetragonal phase, peaks were $2\theta = 34.99^\circ$, $40.27^\circ$, $40.80^\circ$, $58.64^\circ$, $59.07^\circ$, $69.80^\circ$, $70.54^\circ$, $73.92^\circ$. A full description of the XRD-peaks is given in Table 2.

Table 2. Full description of X-ray patterns from Fig. 4

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*cubic phase
3.2.3. Raman spectroscopy

The obtained phase compositions were additionally confirmed by Raman spectroscopy. Figure 5 a–b displays the Raman spectra for samples A₁ and A₁₄. Five bands at 147, 268, 313, 460, and 600 cm⁻¹ correspond to the Raman-active modes, which correspond to the β-ZrO₂ phase (1A_g+2B_g+3E_g; Fig. 5a.) [22].

Fig. 5. Raman spectra for: (a) A₁₄ – full tetragonal ceria-doped zirconia, (b) A₁ – monoclinic-tetragonal ceria-doped zirconia

Fig. 6. SEM images of the as-obtained powders: (a) A₁, (b) A₁₁, (c) A₁₇
Monoclinic zirconia is seen in spectrum bands at 190, 306, 333, 475, and 638 cm\(^{-1}\) (Fig. 5b) [7]. In addition, there was observed the presence of cubic fluorite CeO\(_2\) band at 465 cm\(^{-1}\), which is a clear sign of inhomogeneity in this powder variant.

### 3.2.4. Morphology studies

Figure 6a–c shows SEM microphotographs of samples A\(_1\), A\(_{11}\) and A\(_{17}\). Based on the SEM images, the difference between prepared powders with changing molar ratios of the ZNP:AcAc:H\(_2\)O can be clearly seen. In Fig. 6a, big, solid sharp-edged grains in the size range 250–500 μm are clearly seen. Additionally, there is a very low degree of grain agglomeration. Figure 6c shows sample A\(_{17}\) with radically different morphology. The A\(_{17}\) grains are significantly smaller, characterized by a considerable degree of agglomeration. From the appearance of breakthrough at the edge it can be stated that they are much softer than those from sample A\(_1\). An intermediate situation is observed for sample A\(_{11}\) (Fig. 6b).

### 4. Discussion

#### 4.1. Synthesis

The well-known parameters of the sol-gel process strongly influenced the properties of the gel and final powders and especially the subsequent thermal evolution [17]. Caruso et al. [17] reported the occurrence of so-called soft and hard-agglomerates, whose shape corresponds with those obtained in our work. The binding mechanism of soft-agglomerates corresponds to the formation of weak bonds of close-range van der Waals forces, and, therefore, the resulting powders can be easily disintegrated. On the other hand, hard agglomerates are held together by strong binding forces (chemical bonds in solid bridges) [17]. The shape and morphology of the powders obtained are very important for the preparation of green bodies and subsequent sintering of the CAD/CAM blocks. Powders from hard agglomerates require a higher pressing pressure; their structure favors inhomogeneity and the appearance of pores in green bodies. This requires raising the temperature and time of sintering, which leads to adverse changes in the phase composition of zirconia. The powders from soft-agglomerates improve sinterability, high packing density and good flowability [17].

#### 4.2. Characterization

##### 4.2.1. Thermal studies

For samples A\(_1\), A\(_2\), A\(_6\), and A\(_9\), TGA curves were similar (Fig. 3a.). Thermal decomposition was almost explosive, as can be seen from a high endothermic peak at about 233 °C, associated with the rapid decomposition of propanol, whose temperature of decomposition was shifted due to the formation of a very stable complex between zirconia propoxide and AcAc. The big exothermic broad bump occurring in the range 248–431 °C is associated with the thermal decomposition of AcAc [12], [21]. In contrast, a very small endothermic peak in the range from 82 to 134 °C is associated with the evaporation of water.

TGA curves presented in Fig. 3b correspond to the curves of samples A\(_3\), A\(_4\) and A\(_5\). The presence of four characteristic peaks can be identified on the curves: endothermic 60–110 °C, associated with the evaporation of water; exothermic at approximately 135 °C, associated with the disintegration of propanol; exothermic at 242 °C, associated with decomposition of AcAc; and a big broad exothermic bump between 267–490 °C, which we expected came from crystallization of a new phase.

The curves in Fig. 3c were characteristic of powders A\(_{11}\), A\(_{13}\), A\(_{14}\), A\(_{17}\), A\(_{19}\) and A\(_{20}\). We have identified four characteristic peaks: endothermic associated with the evaporation of water at 60–110 °C; exothermic at 140 °C, associated with the disintegration of propanol; exothermic at 265 °C, associated with the disintegration of AcAc; and a small sharp exothermic peak at 400 °C that probably came from crystallization of another new phase but different than it was in the case of curves shown in Fig. 3c.

##### 4.2.2. Phase composition (XRD and Raman spectra)

Based on the results of XRD, we verified the presence of characteristic “new-phase” peaks in the TGA of curves. The presence of a broad exothermic bump in the A\(_3\) sample between 267–490 °C corresponds to the monoclinic phase (α-ZrO\(_2\)) crystallization. For A\(_{14}\) there occurs a small sharp exothermic peak at 400 °C that corresponds with the crystallization of zirconia tetragonal phase (β-ZrO\(_2\)), which seems to confirm the result of XRD patterns. Referring this result to the ZNP:H\(_2\)O:AcAc molar ratios, we saw that the crystallization of the β-ZrO\(_2\) phase favors the ratios of ZNP:AcAc in the range of 0.19–0.38 and the ZNP:H\(_2\)O in
the range from 6 to 10. In contrast, crystallization of the α phase has a favorable ratio of ZNP:AcAc is equal to 0.75 and the ZNP:H2O from 6 to 10. Interestingly, sample A1 has a high molar ratio of AcAc (0.75) and thus increasing the thermal stability does not cause any crystallization of α-ZrO2 phase. Based on the data in Table 1, it can be stated that this situation is the result of a lower ratio of ZNP:H2O. Also, there are no TGA curves, even at the same formation as described by Caruso et al. [19], the so-called hard agglomerates. However, increasing the ratio of ZNP:H2O over 4 and decreasing the ratio of ZNP:AcAc below 0.38 resulted in the presence of soft agglomerates, which makes it possible to obtain full-value ceria-doped zirconia solid green bodies. [17].

4.2.3. Morphology studies

Comparing morphology of the powders to the molar ratios, it is clear that the high ratio of ZNP:AcAc (0.75) with low water contents promotes the same formation as described by Caruso et al. [19], the so-called hard agglomerates. However, increasing the ratio of ZNP:H2O over 4 and decreasing the ratio of ZNP:AcAc below 0.38 resulted in the presence of soft agglomerates, which makes it possible to obtain full-value ceria-doped zirconia solid green bodies. [17].

5. Conclusion

1. This work described the influence of molar ratios of chelating agent and water on a zirconia precursor as observed in phase composition and macroscopic morphology of 0.9ZrO2·0.1CeO2 powders. It was expected that a molar ratio of AcAc and water to ZNP plays an important role in agglomerate morphology, phase composition and thermal behavior during calcination.

2. According to the data obtained, it can be stated that higher molar ratios of AcAc in the range 0.58–0.75 with smaller amounts of water (2:4) cause hard agglomerates, highly thermally stable powders with various phase composition.

3. Water molar ratios higher than 6 and AcAc ratios that are reduced below 0.38 predispose obtaining so-called soft agglomerates and powders with full tetragonal structure. This is particularly desirable for CAD/CAM prothetic system blocks manufacturing.

4. We hope that the obtained results will allow us, in our future studies, to prepare zirconia-ceria green bodies and produce valuable blocks for CAD/CAM systems with suitable properties like poor porosity, very good compressibility and exceptionally stable mechanical properties in oral environments.

References


