

Characterization of magnesia-doped yttria-stabilized zirconia powders for dental technology applications

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Purpose: This paper is focused on the works concerning preparation of zirconium oxide ceramic blocks recommended for CAD/CAM systems used in prosthetic dentistry for manufacturing fixed prosthetic restorations.

Methods: Zirconium-yttrium-magnesium mixed ceramic oxides were prepared by sol-gel method via hydrolysis and condensation of zirconium alkoxide precursor (zirconium (IV) propoxide) with yttrium and magnesium nitrates diluted in 2-propanol. The aim of this work was to obtain 2% mol yttria-stabilized zirconia ceramic powders with magnesium as an additional tetragonal ZrO₂ phase stabilizer in amount between 2-6% mol (with 2% variable). Prepared gels were dried (24 h at 65 °C). Obtained powders were mixed with binder (carboxymethyl cellulose) and uniaxial pressed into specimens with a dimensions 38 × 22 × 6 mm. Afterwards green bodies were sintered in range of temperature between 1350–1550 °C. Powders and blocks were characterized by Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, Specific Area Measurement.

Results: Highly homogeneous powders with a low open porosity were obtained. Prepared blocks after sintering showed numerous cracks. Nevertheless blocks were fine grained and showed quite reproducible chemical composition.

Conclusion: A sol gel wet chemical route of powder synthesis allow us to obtain high homogenous ceramic materials with inconsiderable amount of pores with low variation in dimensions. In spite of a reproducible synthesis methods of a ceramic powders, applied to prepare green bodies procedure and sintering manner do not allowed to obtain zirconia ceramic blocks free from cracks.

Key words: full ceramic restorations, prosthetic dentistry, sol-gel method, zirconium oxide

1. Introduction

The last two decades of the twentieth century in fixed dentures prosthetic treatment belong to metal-ceramic dentures. Since the full-ceramic restoration (FCR) was developed porcelain-fused-to-metal (PFM) restorations represent the “gold standard” in prosthetic dentistry. Clinical success of PFM type of dentures is due to satisfactory esthetic results, predictability in mouth and acceptable quality of their marginal and in-

ternal adaptation [25]. Nevertheless there are some validated proofs which show fairly important shortcomings of PFM. Gray metal framework of PFM dentures makes it difficult to imitate natural tooth aesthetics, moreover metal core can cause the surrounding gum bluish shade [19]. Another drawback of PFM is complicated laboratory procedures including wax pattern preparation, metal casting procedures and veneering ceramics firing cycles. The large number of operative steps make PFM quality very sensitive to any oversights [25], [19]. Introduction of CAD/CAM In spite of a reproducible synthesis meth-

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ods of a ceramic powders, applied to prepare green bodies procedure and sintering manner do not allowed to obtain zirconia ceramic blocks free from cracks [2], [8], [10], [17], [19], [25]. Except high esthetic appearance use of ceramics in dentistry has been successful because of the advantages: biocompatibility, low thermal conductivity, low plaque retention and fluid absorption and chemical inertness [8], [17], [25]. Early dentistry ceramics had some drawbacks which made clinical problems: brittleness, low tensile strength and ease to crack propagation [25]. At present most frequently used ceramic for FCR manufacturing is natural and colored yttrium stabilized zirconium oxide (YSZ) [2], [5], [8], [10], [13], [17], [19], [25].

Chemical pure zirconium oxide (zirconia) in standard conditions is monoclinic ($m\text{-ZrO}_2$). With increasing temperature it becomes metastable: tetragonal ($t\text{-ZrO}_2$) approximately at 1170 °C and cubic ($c\text{-ZrO}_2$) from 2370 °C to 2716 °C (melting point) [5], [11], [13]. Lattice transformation are martensitic characterized by: diffusionless, occurring athermally, causing volume increase and shape deformation [5], [11], [13]. For such reasons zirconium is also known as transformation ceramics [11]. Pure zirconia is vulnerable to uncontrolled transformation occurring under cooling. Volume changes on cooling are approx. 2.31% mol $c\text{-ZrO}_2 \rightarrow t\text{-ZrO}_2$, and approx. 4–5% mol $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$. As a result of transformation zirconia becomes more fragile and grains may tend to fall out [5], [11], [13], [24]. Martensitic transformation can also occur as a result of: uncontrolled grain growth during sintering, external stress interaction with moisture [11], [13]. The consequence of transformation in moisture environment at low range of temperatures (0–500 °C) is uncontrolled degradation of zirconia also known as Low Thermal Degradation (LTD) [5], [11], [16], [24]. LTD was one of the reasons of fatal clinical accidents with St. Gobain-Desmarques zirconium HIP ball prostheses [5], [6]. Based on these facts, it can be concluded that the oral environment is strongly predisposing factor for uncontrolled martensitic transformation. Solution of this negative phenomenon is stabilization of metastable phases (especially $t\text{-ZrO}_2$) at room conditions. Alloying ZrO_2 with lower valence oxides like CaO , MgO , Y_2O_3 , La_2O_3 , Gd_2O_3 and CeO , disfavored stress-induced phase transformation. Dopant make $c\text{-ZrO}_2$ and $t\text{-ZrO}_2$ phases lattice more desirable [13]–[15]. Metastable phases are analogous to pure zirconia phases but have dopant ions substituted on Zr^{4+} sites and have a fraction of oxygen sites vacant to retain charge neutrality [13]. The type and concentration of the dopant affect to the zirconia stability and suscepti-

bility to LTD. At present, the most commonly used stabilizer is yttrium oxide [16]. Only YSZ reached the actual status of having a dedicated ISO standard for surgical implants application [16].

A wide range of chemical synthesis methods are used to prepare ceramic powders. Among them coprecipitation, electrophoretic deposition (EPD), aerosol-derived powders, chemical vapor deposition (CVD), spray pyrolysis and sol-gel method are used [9], [21], [23]. Obtaining a high homogeneity and dispersion of the powders is possible by using wet chemistry methods of synthesis, inter alia sol-gel processing of colloids and metal-organic compounds [20], [21]. In this kind of synthesis liquid precursors undergo hydrolysis and condensation. Resultant gel is continuous oxide network formed through polymerization at room temperature. Sol-gel post-processing treatment allows obtaining ceramic powders with recurrent properties [20].

The first objective of this study was to produce stable sols of 2% mol MgO , 2% mol Y_2O_3 YSZ, rather than with the same procedure 4% mol and 6% mol MgO doped YSZ without any precipitates. There are some reports about troubles with sol-gel processing with zirconium alkoxides precursors which may subsequently have negative impact on technological treatment of ceramic powders [20]. The second aim of investigation was to determine the impact of the chemical composition and thermal treatment on the structure, porosity and distribution of the pores in the blocks prepared from powders.

2. Materials and methods

2.1. Powders and block preparation

Magnesium doped yttria-stabilized zirconia powders have been prepared with the procedure shown in Fig. 1. Table 1 contains chemical composition of the powders. At room temperature zirconium (IV) propoxide 70% solution in 1-propanol (ZNP) (Sigma-Aldrich) was stirred for a period of 5 min with nitric acid (HNO_3) (AVANTOR) as a catalyst. Starting solution was mixed with a 2-propanol (PrOH) (AVANTOR) and 0.5 mol solutions of metal oxides precursors diluted in 2-propanol: yttrium nitrate hexahydrate (YPr) (Sigma-Aldrich) and magnesium nitrate hexahydrate (MgPr) (Sigma-Aldrich). After 20 min distilled water was added with continuous stirring of mixture to obtain white-transparent homogenous gel without any precipitates. The $\text{ZNP}:\text{HNO}_3:\text{PrOH}:\text{H}_2\text{O}$

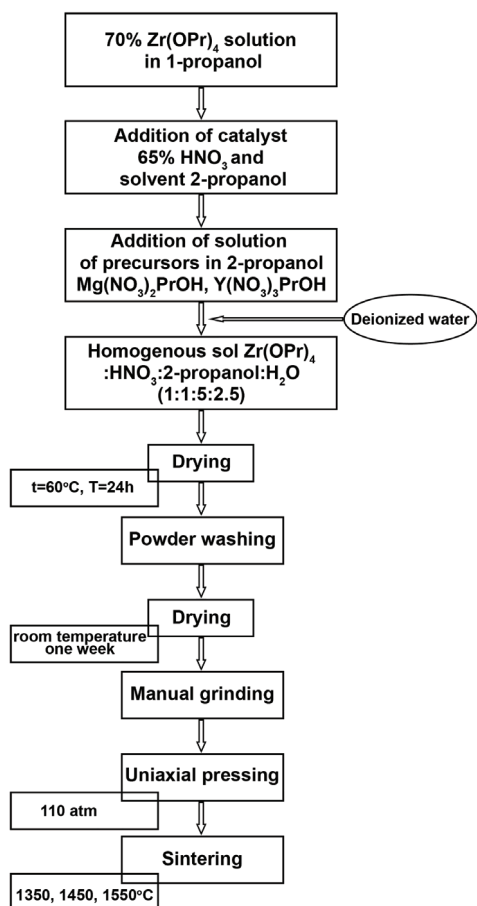


Fig. 1. Experimental procedure scheme of MgO-doped YSZ powders and sintered blocks

molar ratio of the final solution was 1:1:5:2.5. Gel was dried at 65 °C for 24 h (Binder FED dryer) and later ground in a porcelain mortar. The obtained powder was filtered under low pressure to rid out the rest of nitric acid. The resultant materials were left to dry at room temperature for 1 week. Green bodies were prepared from dried powders mixed with carboxymethyl

cellulose as a binder. The mixture was pressed at uniaxial hydraulic press (PHM 63) at 110 atm. The obtained 9 blocks (dimensions 38 × 21.3 × 5.7 mm, 3 for each concentration of magnesium oxide) were sintered (Robocam P1 Plus furnace) at temperatures 1350, 1450, 1550 °C (heating rate 300 h⁻¹, sintering time 1 h, isothermal hold in 900 °C for 1 h, cooling rate 600 h⁻¹) for each of magnesium oxide sample concentration.

Table 1. Chemical composition of powders

Powder (-)	1	2	3	
Chemical composition (% mol)	ZrO ₂	96	94	92
	MgO	2	4	6
	Y ₂ O ₃	2	2	2

2.2. Methods

Scanning Electron Microscopy (SEM). Morphology of the sintered blocks was investigated under scanning electron microscope Hitachi TM 3000.

Fourier transform infrared spectroscopy (FTIR). The functional groups expected in the materials developed were examined using FT-IR spectroscopy (FTIR Bruker IFS 66v/S spectrometer) in range 4000–500 cm⁻¹. Powdered samples were mixed with potassium bromide in weight ratio of 1:20, and placed in a measuring flask, which was passed by the beam of infrared light.

Low-temperature nitrogen adsorption. The nitrogen adsorption/desorption isotherms were measured using Quantachrome Instruments iQ₂ Autosorb. Before analysis, all samples were degassed for 3,6 h at 300 °C. Specific surface area was calculated using BET method (Brunauer–Emmett–Teller). Porosity and pore size distribution was specified by BJH method

Table 2. Gel preparation – empirical data

Pre-proper Reaction (-)	Stirring time (min)	Gelation point (min)	Stirring speed (rpm)	Heating (50 °C)	Molar ratio (ZNP:H ₂ O)	Gel structure
1	28	28	200–350	no	1:5	inhomogeneous/precipitates
2	36	25	200–300	no	1:5	inhomogeneous/precipitates
3	20	15	200–500	no	1:5	inhomogeneous/precipitates
4	35	30	200–600	no	1:5	inhomogeneous/precipitates
5	32	29	200–500	no	1:1.25	inhomogeneous/precipitates
6	30	25	200–500	no	1:1.25	inhomogeneous/precipitates
7	30	26	200–400	no	1:1.25	inhomogeneous/precipitates
8	43	30	200–500	no	1:1.25	inhomogeneous/precipitates
9	28	25	200–450	no	1:2.5	homogeneous/clear
10	25	23	200–450	yes	1:2.5	homogeneous/clear
11	24	21	200–400	yes	1:2.5	homogeneous/clear
12	25	23	200–400	yes	1:2.5	homogeneous/clear

(Barrett–Joyner–Halenda) using apparatus producer software. Approximate pore shape was specified via de Boer adsorption hysteresis classification.

3. Results

The approach we used for the preparation of mixed zirconia-yttria-magnesia oxide solution was a sol-gel method with nitric acid as a hydrolysis catalyst. All reagents were analytical grade purity and were dispersed by drop-by-drop addition. The result showed that the blocks prepared from mixed oxides clear sols are highly uniform. Correlation between zirconium (IV) propoxide and distilled water molar ratio and the impact for gel structure and gelation point are shown in Table 2. All of the investigations were made on sintered blocks. Sintered blocks had an 31.8% average shrinkage level (measuring the thickness of the block before and after sintering) and a lot of cracks. Specimen characteristics are shown in Table 3.

Table 3. Sintered blocks naming

Block/powder composition (-)	Sintering temperature (°C)
1/1	1350
1/2	
1/3	
2/1	1450
2/2	
2/3	
3/1	1550
3/2	
3/3	

3.1. Electron microscopy

Examples of SEM microphotographs for blocks with 2% mol MgO sintered at each temperature from the range are shown in Fig. 2. In general, the morphology of all sintered blocks shows relatively small differences. Occurring porosity is related to the temperature of sintering (Fig. 2). With the rise of sintering temperature there is observed a tendency to associate

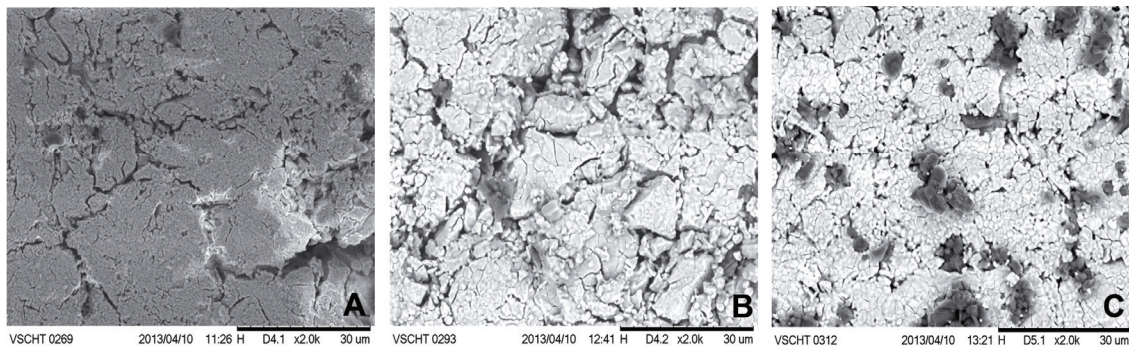


Fig. 2. Scanning electron microphotographs of 2% mol MgO blocks sintered at: A) 1350 °C, B) 1450 °C, C) 1550 °C

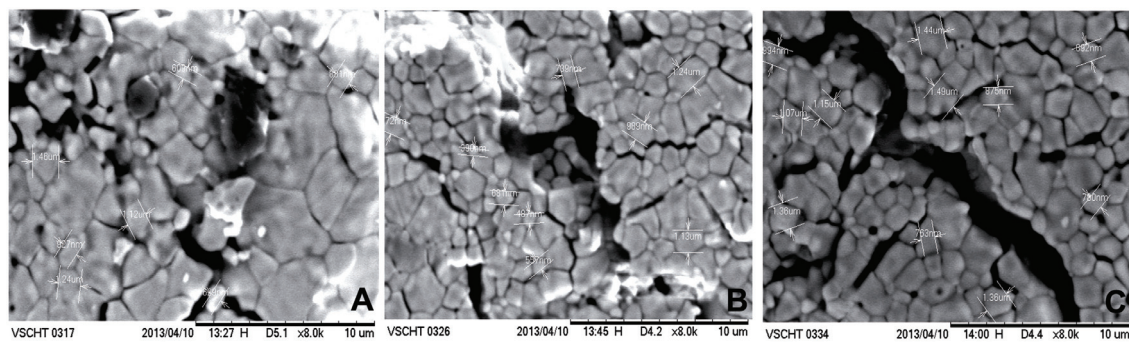


Fig. 3. Scanning electron microphotographs of blocks sintered at 1550 °C. Magnesium oxide concentration: A) 2% mol, B) 4% mol, C) 6% mol

the pores in clusters. Nevertheless share of the pores is so negligible that it does not have a significant effect on the structure of the sintered blocks. The observed aggregates are quite uniform. Differences appear at blocks sintered at 1550 °C. The observed heterogeneity shows many places with large grain agglomeration. Examples are shown in Fig. 3. All of the sintered blocks have numerous cracks without evidence of exfoliation. Table 4 shows the results of estimated average grain size.

Table 4. Sintered blocks average grain size

Chemical composition	1	2	3
Sintering temperature (°C)	Average grain size (nm)		
1350	769	906	669
1450	938	757	595
1550	930	761	779

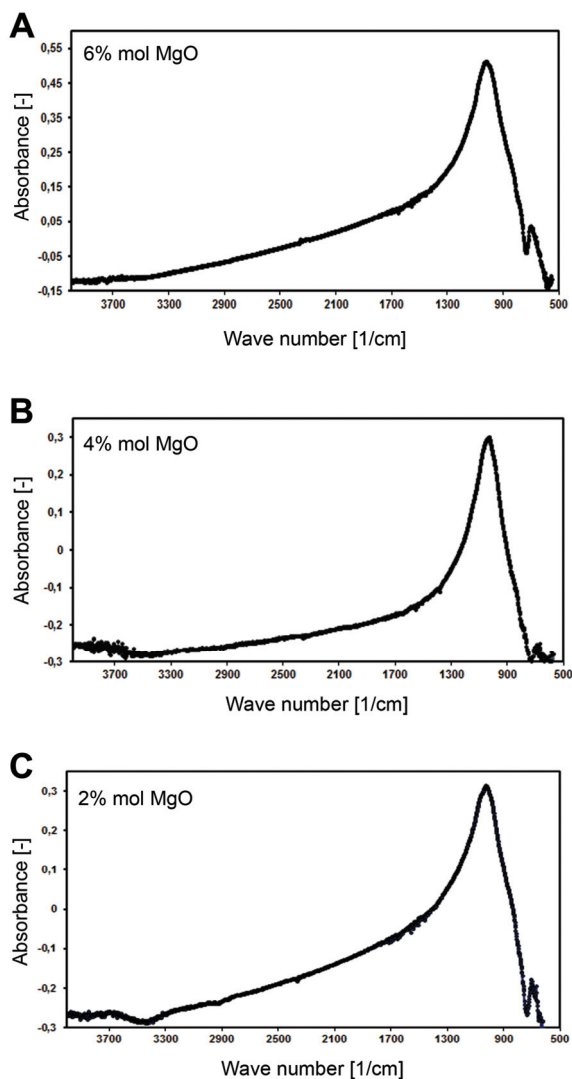


Fig. 4. FTIR spectra of samples. Magnesium oxide concentration: A) 2% mol, B) 4% mol, C) 6% mol

3.2. FTIR spectra

Fourier transform infrared spectroscopy (FTIR) was applied to determine the presence of specific groups. Figure 4 shows the FTIR spectra of 1/1, 1/2, 1/3 blocks. All samples have similar waveforms. Narrow band from 500 to 750 cm^{-1} is attributed to vibrations of Zr-O bond. The broad band from 900 to 1600 cm^{-1} is attributed to vibrations of C-C, C-N, C-O, C=C, C=O and C=N bonds. Only in one case, there was found a weak but visible peak from 3400 to 3600 cm^{-1} probably attributed to the O-H bonding vibrations (1/1). Recent case could suggest undesirable occurrence of zirconium hydroxide in the sample. The presence of hydroxyl groups is one of the reasons of annihilation of the oxygen vacancies in ZrO_2 structure and is the source of uncontrolled phase transition which in an electrolyte environment can lead to LTD [5]. The

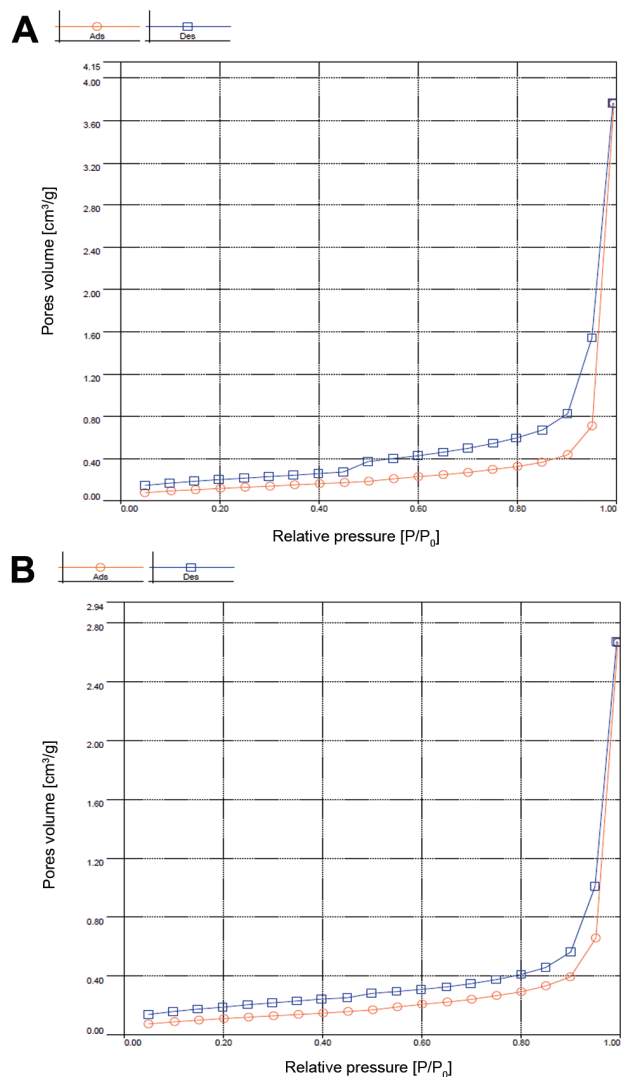


Fig. 5. N_2 adsorption/desorption isotherms for blocks: A) 1/3 and B) 2/3

absence of O-H bending vibrations in other cases demonstrates the successful use of the sol gel technique and adopted thermal treatment.

3.3. Low-temperature nitrogen adsorption

In order to know the porous structure of prepared zirconium oxide bioceramics, the low-temperature nitrogen adsorption was done. Examples of adsorption/desorption isotherms for samples 1/3 and 2/3 are shown in Fig. 5. According to IUPAC classification [12], all isotherms are similar to type II and type IV corresponding to mesoporous materials (2–50 nm) [22]. Table 5 shows the type of material (IUPAC porous material classification), mean pore volumes and size calculated via BJH method, approximate pore shape via de Boer classification and specific surface areas calculated by BET.

($\delta = 0,65$) results that the reactions of hydrolysis and condensation occurs spontaneously and uncontrolled which may results in inhomogeneous products [12]. Therefore, it is important to choose the molar ratio of the precursor to solvent (distilled water). The optimal molar ratio between ZNP and distilled water was 1:2.5. In other cases molar ratios result as inhomogeneous sols of significant quantities of agglomerates. Another important factor under the synthesis is a method of dispensing water and control of the viscosity of the sol. Fast addition of water resulted in a rapid hydrolysis and the precipitation of a large amount of agglomerates and consequently a rise of viscosity of sol. Therefore, in the present study, was very carefully water added with “drop-by-drop” method while increasing the speed of the magnetic stirrer. Our observations coincide with the experimental results obtained by Bansal [3].

The obtained morphology of materials is quite uniform. Average grain size varies in the range from

Table 5. Results of low-temperature nitrogen adsorption

Block/powder composition (-)	Type of material (IUPAC)	Pores distribution	Approximate pores shape	Pores diameter (nm)	Pores volume (cm^3g^{-1})	Specific surface area (m^2g^{-1})
1/1	mesoporous	homogeneous	spherical	3.063	0.007	0.667
1/2	mesoporous	homogeneous	spherical	3.066	0.005	0.420
1/3	mesoporous	homogeneous	spherical	3.066	0.005	0.525
2/1	mesoporous	homogeneous	spherical	3.066	0.005	0.425
2/2	mesoporous	bimodal	spherical	3.425	0.004	0.382
2/3	mesoporous	bimodal	spherical	3.426	0.004	0.411
3/1	mesoporous	homogeneous	spherical	4.326	0.006	0.402
3/2	mesoporous	homogeneous	spherical	4.328	0.004	0.349
3/3	mesoporous	bimodal	spherical	3.066	0.003	0.349

4. Discussion

The obtained results show that it is possible to obtain ceramic powders via sol-gel method for potential dental technology applications. Simple “drop-by-drop” sol-gel method allowed us to obtain high homogeneous gels without any precipitates. After 20 min distilled water was carefully added with continuous stirring to avoid uncontrolled rise of mixture viscosity. In consequence, white-transparent macroscopic homogeneous gel without any precipitates was obtained. The problem is particularly important in the case of transition metal alkoxides such as zirconium (IV) *n*-propoxide. High value of positive partial charge of zirconium

0.595 to 0.938 μm . The smallest values were obtained for sintering at 1550 $^{\circ}\text{C}$. It should also be noted that the smallest grain size is obtained for materials with 6% mol MgO concentration. However, it should be mentioned that zirconia grain size dedicated for biomedical applications, according to the possibility of transformation toughening and resistance to LTD occurrence, should be in the range from 0.2 to 0.4 μm [7], [13]. There were found only a few papers which comprehensively described the synthesis and heat treatment influence on the grain size of zirconia ceramics systems [4], [18]. Grain sizes obtained by those authors with coprecipitation and slurry powders methods are in the range from 2 to 8 μm . In practice, the stage which has a significant influence on the

grain size is the chemical synthesis of powders. As shown by the results obtained, the sol gel method allows a lower value of the grain size to be achieved than with the methods mentioned above. The use of other types of pressing different than single stage uni-axial, without the binder and more efficient thermal treatment should allow one to obtain zirconia solid ceramics with particle size in the range characterized for biomedical applications. It seems that the most sufficient technique suitable for use in pressing colloidal zirconia ceramics powders is a three-stage compression process which includes: forming green bodies made by uni-axial pressing, initial structure densifying made by cold isostatic pressing (CIP) and finally structure densifying coupled with presintering made by hot isostatic pressing (HIP) [4], [13].

The present results (FTIR) show that the sol gel method is useful for the manufacturing of zirconia ceramic powders. Only in one sample are likely to present hydroxyl groups which could be the explanation of blocks destruction during sintering. In the range of sintering temperatures of undertaken heat treatment zirconium hydroxide should be due to its thermolability decomposed at 550 °C, thereby leading to destruction of green bodies during sintering [1]. This explanation of the given fact seems unlikely because all of the sintered blocks were cracked. In future works, to have complete confidence about occurrence of hydroxyl groups, there should be performed additional nuclear magnetic resonance investigation (NMR). One should note the fact of organic contaminants occurrence which are associated with the use of carboxymethyl cellulose as a binder. In further studies, in fact of the biomedical applications of manufactured zirconia ceramics, use of the binders and lubricants which may be accumulated in biomaterials will be abandoned.

As a result of nitrogen adsorption (BET) it can be concluded that all of the sintered samples have almost similar properties. Some differences can be observed considering the influence of sintering temperature to pore volume and specific area. The largest pore volume and consequently most developed specific area are observed in specimens sintered at 1350 °C. Considering the pore distribution curve as a criterion for comparison, some differences can be observed for 2/2, 3/2 and 3/3 specimens, which have been characterized as bimodal. In addition to the dominant pore size, observed was also: for 2/2 pores with diameter 4.4 nm and specific surface area $0.0031 \text{ cm}^3 \text{ g}^{-1}$, 3/2 7.1 nm and $0.0032 \text{ cm}^3 \text{ g}^{-1}$ and for 3/3 3.8 nm and $0.0021 \text{ cm}^3 \text{ g}^{-1}$. The differences are probably the result of too low density of the structure (too low pressing pressure).

5. Conclusions

To obtain fine grain dispersed zirconia oxide bioceramics used in prosthetic dentistry the sol-gel method was used. Developed process has allowed to obtain homogeneous gel, from which were obtained solid ceramic materials with a very small surface area and low porosity. Nonetheless prepared by uniaxial pressing green bodies were destroyed during sintering in furnace. As a result, obtained ceramic blocks show many signs of cracks, but without any signs of the exfoliation. The use of combined uniaxial pressing with initial structure densifying and finally hot isostatic pressing should bring measurable results in the form of solid zirconia blocks machinable in CAD/CAM dental systems.

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