Synthesis of Nanoporous SiO$_2$-TiO$_2$-ZrO$_2$ Ceramics Using Sol-gel Technology

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Abstract – **The aim of research is to develop an area of nanoporous ceramics of ternary systems. Nanoporous ceramic system SiO$_2$-TiO$_2$-ZrO$_2$ has been synthesized via sol-gel technology by hydrolysis of tetraethylorthosilicate (TEOS), zirconia and titanium alcoxides solutions. The sols have been polymerized at room temperature to obtain gels and dried at 100 ºC, then milled for 1 or 6 hours for particle homogenization, pressed into samples, and then sintered at 800 ºC or 1000 ºC in air. The samples have been characterized by XRD, particle size distribution, crystallite size distribution, compressive strength. Porosity of ceramic samples has been determined by nitrogen adsorption-desorption isotherms.**

Keywords – **Nanoporous ceramics, SiO$_2$-TiO$_2$-ZrO$_2$, sol-gel technology.**

I. INTRODUCTION

There are few studies of ternary nanoporous ceramic systems, for example, SiO$_2$-TiO$_2$-ZrO$_2$. Pure ZrO$_2$ and TiO$_2$ have a very small specific surface area, high hardness and high price, but ZrO$_2$ has an excellent thermal and chemical stability. The homogeneous incorporation of Ti and Zr into a SiO$_2$ matrix is important to obtain materials that exhibit chemical, thermal and mechanical stability [1]. There are comparatively many studies on SiO$_2$ that can be regarded as a kind of base in similar studies, and there are many publications on oxide systems consisting of 2 components.

It is difficult to produce a ternary system such as SiO$_2$-TiO$_2$-ZrO$_2$ by the traditional melting technology because the melting temperature of TiO$_2$ and ZrO$_2$ is very high; thus, higher energy consumption is needed. Ceramic materials synthesized by sol-gel technology are very pure at room temperature. In similar studies, the synthesising of TiZrO$_4$ ceramics was performed using the sol-gel technology, sintering was carried at temperature from 700 °C to 1400 °C for 8 hours [2]. Sol-gel technology is based on the hydrolysis of metal alcoxide precursors and allows mixing of elements into an atomic level without the need for very high processing temperatures, with a high degree of porosity. Although there is a lot of research on the sol-gel process, there are comparatively few studies on the details of the structure and how that evolves with temperature [3]. The homogeneous incorporation of metal (titanium und zirconium) into a silicon matrix is important to obtain materials that are characterized by an excellent chemical, thermal and mechanical stability. These properties are very essential in the application of nanoporous ceramic materials.

Mixed titanium-silica-zirconium nanoporous ceramic is potentially useful for a number of technological applications in various fields of science, for example, from catalysis to biology [4].

The control of nanoporous structures, volume and distribution of ceramic are very important from the viewpoint of their application in the field of separation and catalysis techniques. The usual route for nanoporous ceramic preparation is the sol-gel technique. The sol-gel process allows an excellent control of the nanoporous ceramic from the earliest stages of synthesis procedure. The structure of ceramic materials can be mostly tailored by solution chemistry of the sol-gel technique. Researchers have published numerous variations of the synthesis conditions (e.g., the type of precursor, using traditional synthesis technologies, solvent, sintering temperature) which cause modification in the structure. This review focuses on a summary of the reported chemical and mechanical (different milling time of powder) influence on the nanoporous structure of SiO$_2$-TiO$_2$-ZrO$_2$ ceramic. From the literature it is known that the presence of zirconia in titanium powder causes a remarkable increase of the surface area [5]. With more than 30 mol % ZrO$_2$ in the structure, the surface roughness (increases materially), and the mechanical strength increases [6]. The effects of catalyst (molarity of HCl acid), ratio of molar percentage of silica, zirconia and titanium alcoxides solutions, solvent, modifying agents are considered in detail in this paper. In this research, attention is devoted to the effect of nanosize pores and particle size distribution, mechanical properties of nanoporous SiO$_2$-TiO$_2$-ZrO$_2$ ceramics synthesised using the sol-gel technology. Controlled pore size distribution, density, compressive strength and other unique characteristics are important properties of nanoporous ceramic materials and determine new and improved properties and application.

The aims of the research are to prepare nanoporous SiO$_2$-TiO$_2$-ZrO$_2$ system ceramics via the sol-gel technology and to determine structural, mechanical properties and porosity of ceramics.

II. EXPERIMENTAL PROCEDURE

In the synthesis procedure of nanoporous ternary SiO$_2$-TiO$_2$-ZrO$_2$ ceramic, the sol was synthesized using tetraethylorthosilicate (TEOS, Aldrich, 99.9 %) as the SiO$_2$ source, zirconia propoxide (70 wt% solution in propan-1-ol, Aldrich) and titanium isopropoxide (Aldrich) alcoxides solution as ZrO$_2$ and TiO$_2$ source, propanol-2 (Sigma – Aldrich) was used as a reciprocal solvent. Acetic acid (Sigma – Aldrich), 0.1 M or 1 M hydrochloric acid (P.P.H. "Stanlab") and oxalic acid (Penta) were used as a catalyst to advance the hydrolysis and condensation reactions. Schmidt says that the Brunauer, Emmett and Teller (BET) surface area from SiO$_2$ gel can be

varied from $0\ m^2/g$ to $600\ m^2/g$ simply by changing the concentration of added hydrochloric acid [7] that exerts the fundamental influence on mechanical and structural properties of final bulk nanoporous material that also contains SiO_2. Molar percentage ratio of elements $SiO_2/TiO_2/ZrO_2$ was 25/25/50 and 15/35/50, but 0.1 or 1 – molarity of added hydrochloric acid, 1h or 6h – milling time of powder heat-treated at 500°C and the heating rate was fixed at 5 °C/min. In both ceramic systems, preparation of sols was a considerate ratio of chemical solutions: alcoxide/propanol-2 = 1/8, alcoxide/acetic acid = 1/3 and hydrochloric acid (0.1M or 1M)/alcoxide = 1/5, oxalic acid 4.5 g /100 ml of sol, Fig. 1.
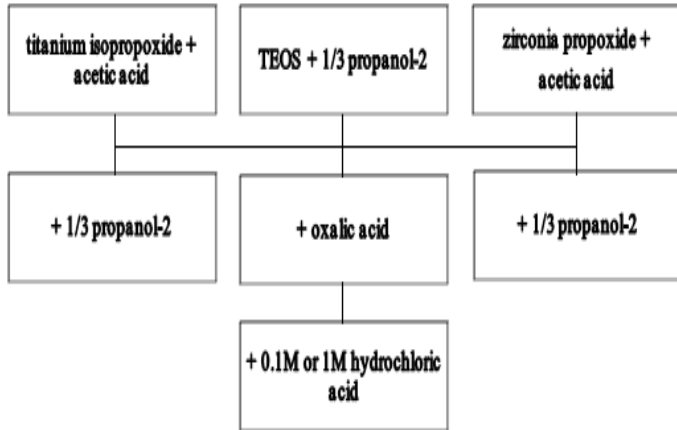

Fig. 1. Preparation of sol.

When the gel was formed, it was dried at 100 °C for 72 h. The xerogel was calcined at 500 °C for 1 hour and the heating rate was fixed at 5 °C/min. Obtained powder was milled (planetary ball mill, "Retsch PM 400") for 1 or 6 hours for particle homogenization. Size distribution of powder particles was determined by "MAS ZetaPALS Brookhaven Instr." using ethyl lactate as surfactant and ethyl alcohol. Ceramic samples were axially pressed by manual press (SPRUT 10/185, Latvia), pressure 220 bars, time 20 seconds. For the compressive strength ("Compression Test Plant Toni Norm, Toni Technik by Zwick", ultimate 300 kN, program "Setsoft 2000") tests, the nanoporous ceramic samples were sintered at 800 °C or 1000 °C for 1 hour and the heating rate was fixed at 5 °C/min. Ceramic samples – cylinders, whose diameter was 1.2 cm and height was more than 1.2 cm. All the samples were prepared by a scheme shown in Fig. 2.

The quality of samples was characterized by X-rays (XRD) diffraction data collected using a Rigaku Ultima+ (Japan) diffractometer. (Cu) K_α wavelength was used, the scan conditions were 2°, but 2 θ mode – for the range over which the diffraction patterns were recorded. The crystallite size was evaluated using the Debaj–Schreder equation (1):

$$D = \frac{\lambda}{B*cos\theta} \qquad (1)$$

where D – is the crystallite size, nm;
λ – the length of x-radiation wave, nm;
B – the full width at half maximum of the diffraction peak;
θ –the Wulf–Breg angle.
Apparent density of nanoporous ceramic samples was evaluated using equation (2):

$$\rho_{ap} = \frac{g_o \times \rho_{H_2O}}{(g_1 - g_2)} \qquad (2)$$

where ρ_{ap}– apparent density, g/cm^3;
g_o– mass of dry ceramic sample, g;
g_1– mass of watered ceramic sample into air, g;
g_2– mass of watered ceramic sample into water, g;
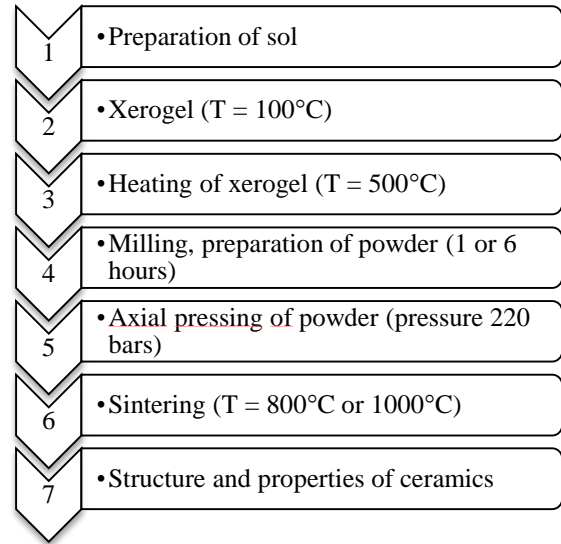ρ_{H_2O}– water density, g/cm^3.

Fig. 2. Preparation of nanoporous ceramic samples.

The BET specific surface areas of all ceramic samples were determined by BET nitrogen adsorption-desorption isotherms and were recorded by using "Nova 1200 E-Series, Quantachrome Instruments" (for pore size of 0.35 nm – 200 nm). Field emission low vacuum scanning electron (SEM) microscope FEI Nova NanoSEM 650 was used for the analysis of morphology.

III. RESULTS AND DISCUSSION

High-energy ball milling or mechanical-chemical processing, which was initially invented for ceramic strengthened alloys, has been successfully used to synthesize a wide range of nano-sized ceramic powders, including ZrO_2 [8]. Figure 3 summarizes the powder size distribution of both ceramic series after 1- or 6-hour milling process. After 6 hours, milling samples exhibited wider particle size distribution (shown as dispersion), but their average particle size (shown as a column) decreased. Only sample S25T25Z50-0.1 after 6h exhibited a higher average particle size distribution after longer milling time. Taking into account the classical concepts of colloid chemistry, a colloid is a suspension in which the dispersed phase is so small (1 nm – 1000 nm) that the gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges [9]. It enables for agglomeration of smaller particles into lager. The increase in average particle size distribution was in the range of 15.5 %, but the decrease in an average particle size was in the range of 7.1 % – 24.5 %. It was noticed that the grain size of the as-milled (3 h) powders had already been reduced to tens of nanometers [8].
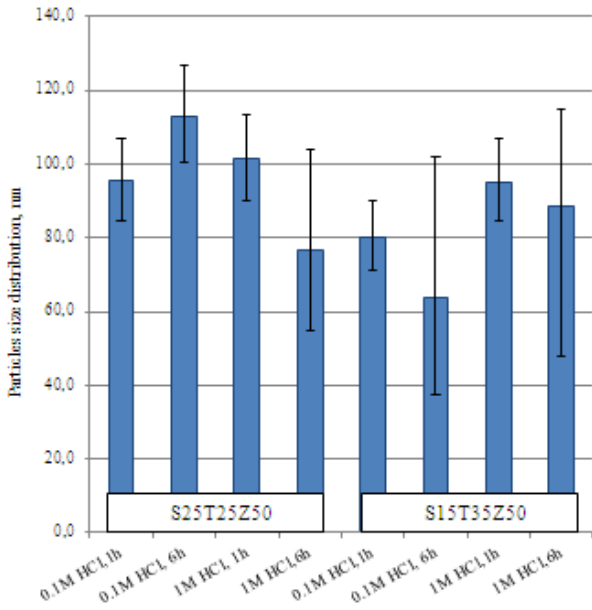
Fig. 3. Particle size distribution of powders after 1- or 6-hour milling time.

In the solid-state process, the mixture of ZrO_2 and TiO_2 powders was usually sintered at temperature as high as 1100 °C to ensure the phase formation. Sintering of such high temperature-derived powders would be at very high temperatures ranging from 1400 °C to 1600 °C [10].

Tables 1 and 2 show the results of X-ray diffraction (XRD) patterns for both series of powder samples (S25/T25/Z50 and S15/T35/Z50) of the ternary SiO_2-TiO_2-ZrO_2 system heat-treated for 1 hour at 1000 °C. 1M hydrochloric acid was added to both samples, but homogenization time of both samples was the same – 1 hour or 6 hours into high-energy ball mill. Table 1 shows that XRD patterns exhibit the peaks of the monoclinic zirconia phase, but their intensity is different. The sample that exhibited smaller intensity contained greater volume of metal (titanium) alcoxide of the primary sol. Silica and titanium were also present in the sintered sample, but these phases were not detected by XRD. The analytical results are based on identification using Rigaku Ultima+ (Japan), and the database results are summarized in Table 2.

TABLE 1

XRD PATTERNS OF TERNARY SiO_2-TiO_2-ZrO_2 SYSTEM SINTERED AT 1000 ^{O}C

Mol % Ratio / Milling time of powder, h	$SiO_2/TiO_2/ZrO_2$ 25/25/50	$SiO_2/TiO_2/ZrO_2$ 15/35/50
1		
6		

TABLE 2

XRD PATTERNS OF THE SAMPLES AFTER SINTERING AT 1000°C

Molarity of added HCl	Powder milling time, hours	Molar ratio of SiO_2-TiO_2-ZrO_2	Reference code	Chemical formula	Compound name	Mineral name	Crystal system
0.1 M	1	25/25/50	04-005-4478	ZrO_2	Zirconium oxide		Orthorombic
		15/35/50	04-005-4478	ZrO_2	Zirconium oxide		Orthorombic
	6	25/25/50	01-074-1504	$ZrTiO_4$	Zirconium titanate	Shrilankite	Orthorombic
		15/35/50	01-074-1504	$ZrTiO_4$	Zirconium titanate	Shrilankite	Orthorombic
1 M	1	25/25/50	04-005-4478	ZrO_2	Zirconium oxide		Orthorombic
		15/35/50	04-005-4478	ZrO_2	Zirconium oxide		Orthorombic
	6	25/25/50	01-074-1504	$ZrTiO_4$	Zirconium titanate	Shrilankite	Orthorombic
		15/35/50	01-074-1504	$ZrTiO_4$	Zirconium titanate	Shrilankite	Orthorombic

The formation of ZrO_2 is possible because volume of zirconia propoxide is greater (50 mol% of primary sol). The reaction time of alcoxides solutions is not similar. The hydrolysis and condensation reactions of Zr or Ti precursors are fast. The silicon atoms carry substantially less positive charge; thus, the hydrolysis and condensation reactions of silicon alcoxides occur at a much lower rate. The ionic character is increasing as follows: SiO_2<TiO_2<ZrO_2. The bonds of SiO_2 can be characterized by about 50 % covalent feature. This order corresponds to the reactivity sequence of tetravalent alcoxides in hydrolysis reactions: $Si(OiPr)_4$<<$Ti(OiPr)_4$<$Zr(OiPr)_4$ [11]. Zirconium titanate is an intermediate compound in the binary system ZrO_2–TiO_2.

Several authors have studied this system to establish the equilibrium phases. McHale and Roth heated samples of $ZrTiO_4$ at $T \approx 1273$ K around 4 months and they concluded that a more stable compound of the binary system ZrO_2–TiO_2 at room temperature was $ZrTi_2O_6$. The synthesis of $ZrTiO_4$ has been reported in literature, including several methods such as sol-gel, co-precipitation, mechanochemical processing and solid state reaction. These methods have been used to make powders or small pieces of $ZrTiO_4$. However, a structural application requires bulk materials, so it is necessary to combine synthesis and processing methods which allow the preparation of zirconium titanate 3D-shaped materials [12]. It is supposed that a phase transition in this case is caused by the solid state reactions taking place during the milling process, but it does not depend on the molarity of the added hydrochloric acid.

For the samples milled for 6 hours, XRD patterns have shown a phase transition from ZrO_2 to zirconium titanate oxide ($ZrTiO_4$). This may have resulted in an incomplete solid-state reaction, yielding nonstoich isometric zirconia titanate. According to literature [13], at a high speed (3200 rpm), only an amorphous phase was formed. We consider milling process to be a very important parameter of nanoporous SiO_2-TiO_2-ZrO_2 ceramic synthesis. The rotation speed determines the kinetic energy and the momentum transfer to the sample inducing the milling effects mentioned above. Milling is a stochastic process, and the number of variables involved is very large [13], and that could be the main reason for phase transitions.

Figure 4 summarizes the crystallite size distribution of nanoporous ceramic samples. For all nanoporous ceramic samples, only one crystalline phase was detected within the whole range of composition. Average crystallite size was determined from broadening of the XRD maxima by Scherrer equation, using ZrO_2 and $ZrTiO_4$ samples crystallized at 800 °C and 1000 °C for 1- and 6-hour milling time. The peak intensity of X-ray diffraction (XRD) patterns for powder samples for ZrO_2 and $ZrTiO_4$ increases with the sintering temperatures indicating the crystal growth of both phases. The diagram shows that milling time and sintering temperature exert an effect on crystallite size distribution. The increase in the crystallite size testifies that monoclinic ZrO_2 transforms into the tetragonal form at ≈ 1000 °C [10]. In multicomponent systems, basically the addition of one component to the others increases the crystallization temperatures compared to pure oxides. The crystallite size at 1000 °C is from 103.7 nm to 137.0 nm and testifies the formation of a more arranged structure. This higher physical agglomeration of crystallites originates from higher surface energy of smaller crystallites. Increase in sintering temperature promotes crystallite growth, which is apparent from decreased width and increased intensity of XRD maxima.

According to literature [2], high-energy milling of ZrO_2 and TiO_2 reduces crystallite size and gives almost amorphous powders and decreases the transition temperature as low as 1100 °C.

Figure 5 summarizes the results of samples according to compressing strength tests. The diagram shows that the higher compressive strength is characteristic of samples of both series sintered at 1000 °C. At higher temperatures, particles of ceramic were sintered and air inclusions became smaller and, thus, the compressive strength was affected. Increased temperature of sintering also increases the mechanical strength of tablets: while tablets sintered at 800 °C crumble easily, those sintered at 1000 °C are much more resilient in spite of their porosity. Compressive strength after sintering at 800 °C is from 33.7 MPa to 62.2 MPa, but after sintering at 1000 °C from 37.4 MPa to 69.2 MPa. Another effect shows powder milling

time. In case of a longer period of milling time, ceramic samples exhibit lower compressive strength in comparison with the ones milled only for one hour, Fig. 3. Particle size distribution of powders after 1 or 6 hours of milling time shows wider particle size distribution of powders milled for a longer period of time. Compressive strength increased by 0.2 % to 29.1 %. Wider particle size distribution decreases the compressive strength of nanoporous ceramic samples. It is supposed that the strength is determined basically by the presence of principal component ZrO_2.
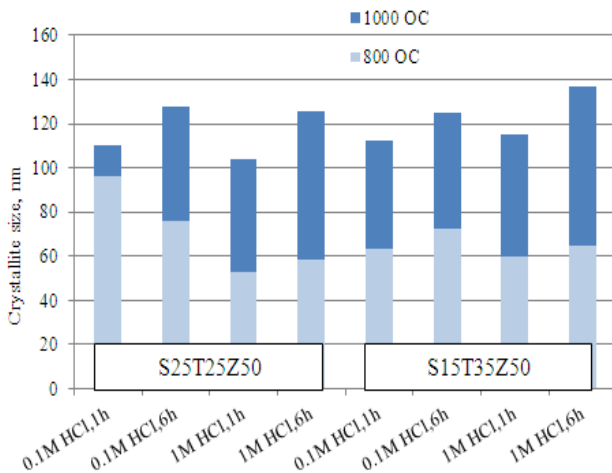

Fig. 4. Crystallite size distribution of ternary SiO_2-TiO_2-ZrO_2 system sintered at 800°C and 1000°C.
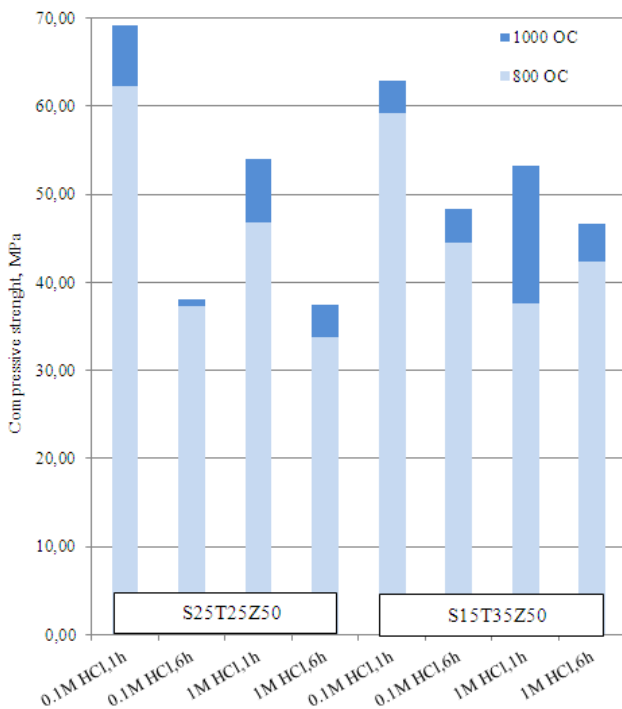

Fig. 5. Compressive strength of ternary SiO_2-TiO_2-ZrO_2 system sintered at 800 °C and 1000 °C.

Figure 6 summarizes the results of apparent density of nanoporous ceramics after sintering at 800 °C and 1000 °C. After

sintering at 800 °C, the apparent density of the nanoporous material samples ranged from 2.31 g/m^3 – 2.72 g/m^3, but after sintering at 1000 °C it increased to 2.44 g/m^3 – 2.78 g/m^3. After sintering at 1000 °C, the compressive strength of the samples increased; moreover, changes in volume of nanosize pores and pore size distribution were observed.
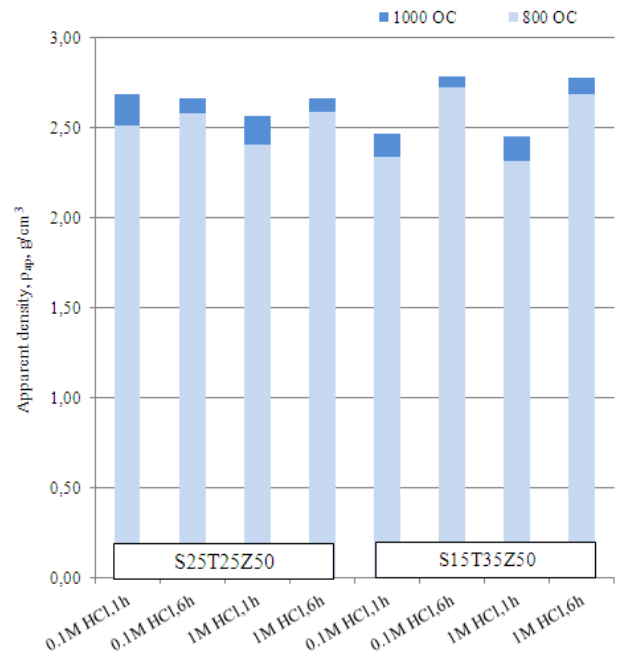

Fig. 6. Apparent density of ceramic samples after sintering at 800 °C and 1000 °C.

The pore size distribution was determined using nitrogen adsorption-desorption measurements. The detection of micropores using the nitrogen adsorption-desorption method is difficult. Unreacted alcoxides could remain without the heat treatment in case of samples sintered at lower temperatures. This could influence the formation of microstructure. Figure 7 (a, b) and Table 3 summarize the results of surface area histogram of nanoporous ceramic sample S25T25Z50 after sintering at 800 °C or 1000 °C, but different molarity of added hydrochloric acid: a) 0.1M HCl, b) 1M HCl. BET results show that a lager surface area is characteristic of a sample after sintering at 800 °C, but it decreases after sintering at 1000 °C if powder milling time is 1 hour. A lager surface area was observed in cases, when half pore width was in the range from 0.82 nm to 0.92 nm. As the sintering temperature increases, the pores are closed, and smaller grains grow together to form larger ones, Fig. 7a. However, if 1 M hydrochloric acid was added to the same sample, a lager surface area was observed, and half pore width was in the range of 0.82 nm – 1.1 nm. Longer milling time of powder contributed to the formation of a lager surface area ($\approx$ 88 m^2/g) depending on sintering temperature, Table 3. The observed pore size values depend on the sintering temperature and the different molarity of added hydrochloric acid of the samples. The mean pore diameter of the ternary oxide nanoporous SiO_2-TiO_2-ZrO_2 ceramics decreases with decreasing molarity of added hydrochloric acid. Figure 7 indicates this correlation.

a)

Half pore width, nm
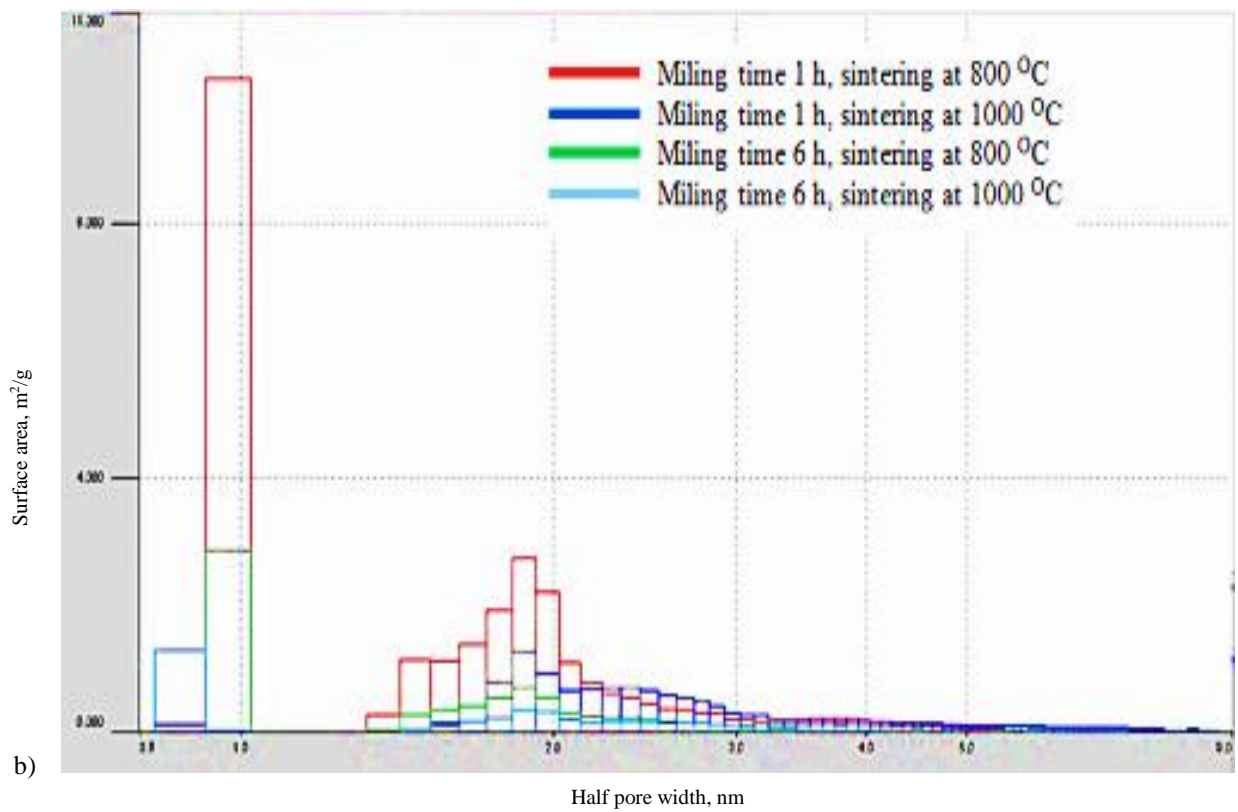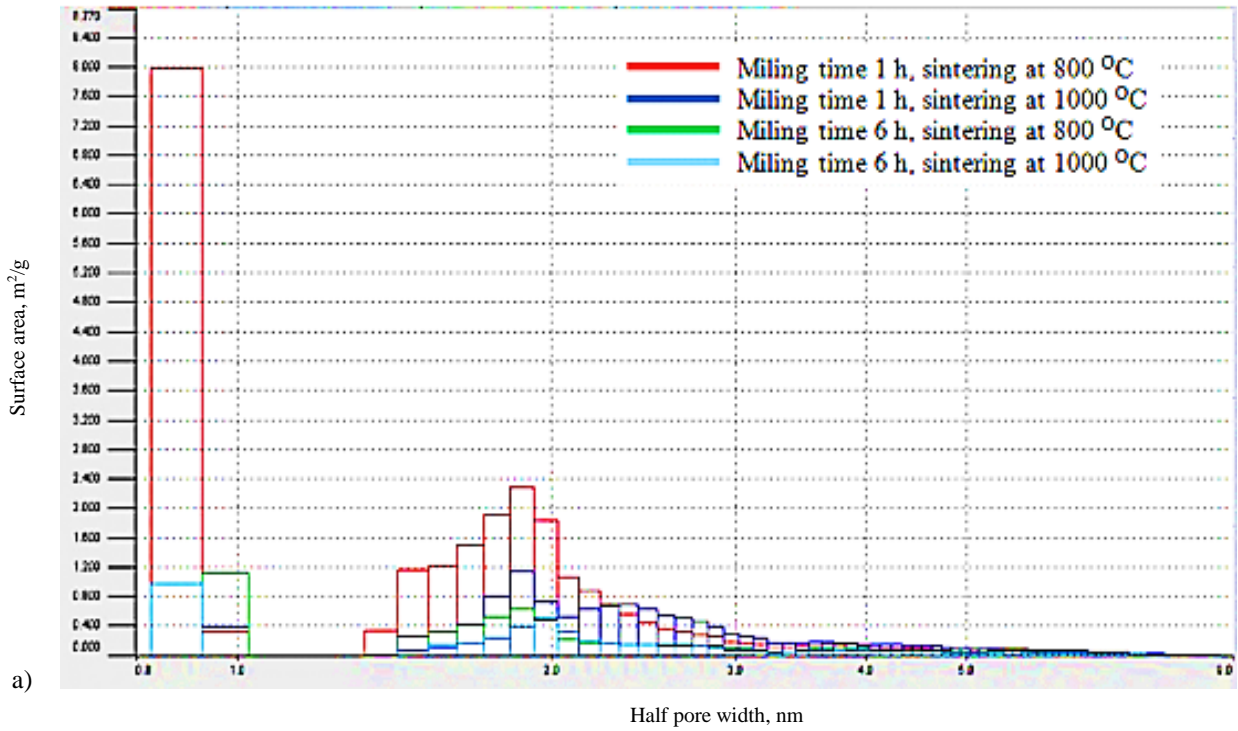

b)

Half pore width, nm

Fig. 7. (a, b) BET surface area of nanoporous ceramic sample S25T25Z50 after sintering at 800 °C or 1000 °C, molarity of hydrochloric acid : a) 0.1M or b) 1M.

TABLE 3

BJH Surface Area of Nanoporous Ceramic Sample S25T25Z50 after Sintering at 800 °C or 1000 °C

Molarity of added HCl	Powder milling time, hours	Sintering temperature, °C	BJH cumulative adsorption surface area, m²/g
0.1 M	1	800	24.98
		1000	17.44
	6	800	8.95
		1000	76.77
1 M	1	800	26.33
		1000	19.05
	6	800	9.22
		1000	80.33

Figure. 8 (a, b) summarizes the results of morphology of nanoporous ceramics (S25T25Z50) after sintering at 800 °C and 1000 °C.
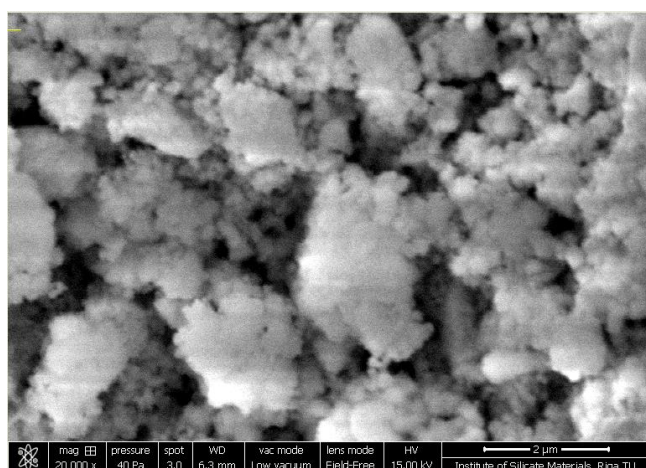
a)
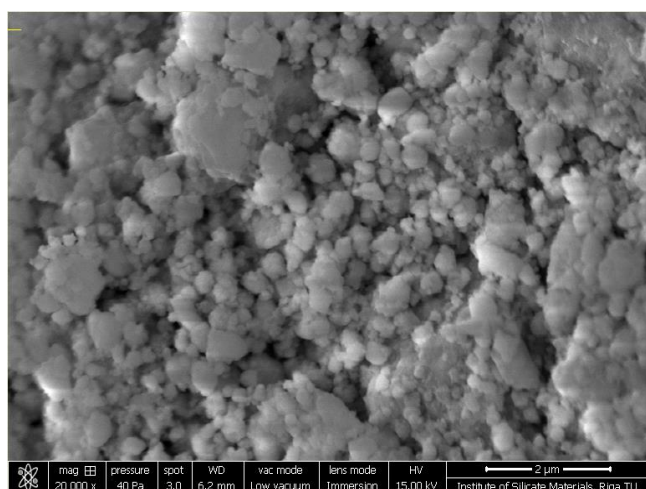
b)

Fig. 8. SEM images of nanoporous ceramics S25T25Z50 after sintering at 1000 °C and adding 0.1 M HCl into primary sol. Samples were pressed from powder milled for different period of time: a) 1 hour, b) 6 hours.

As it can be seen from the photos, nanoporous ceramic samples pressed powder milled for 1 h have comparatively homogeneous particle size. In photos taken from ceramic samples pressed from powder milled for 6 h, the distribution of particle size is less homogenous, pores have become comparatively smaller, and individual denser areas can be observed that could be formed by sintering particles.

IV. Conclusions

Nanoporous ceramic materials in the system SiO_2-TiO_2-ZrO_2 were prepared from silicon, titanium and zirconium alcoxides by the sol-gel technology. Different molarities of hydrochloric acid were assessed and influence of powder milling time on the structural and mechanical properties was determined.

The nanoporous ceramic samples were prepared by sintering high-energy ball milled powders. The average particle size after 1 hour-long milling time was in the range of 80.3 nm – 101.3 nm, but after 6 hour-long milling time it was from 63.9 nm – 112.8 nm. It is observed that with an increase in powder milling time, particle size distribution becomes wider.

Regardless of molarity of the added hydrochloric acid, the phase transition of samples was dependent on the milling time – 1 hour of milling time leads to the formation of ZrO_2, while 6 hours – $ZrTiO_4$. The reason for these changes could be explained by the solid state reaction during the milling process. Essential influence of milling time and acid molarity on the apparent density was not observed.

The compressive strength decreased essentially if the sample was pressed from powder milled for 6 hours because an increase in particle size distribution was observed after the milling process.

As it was anticipated, there was essential influence of hydrochloric acid molarity on porosity – because it affected the hydrolysis and condensation reactions, and the time of gel formation. The porosity of ceramic samples was dependent on the molarity of added hydrochloric acid, milling time of powder and sintering temperature.

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Margarita Karpe, Gundars Mežinskis, Laimons Timma. Nanoporainas SiO_2-TiO_2-ZrO_2 keramikas sintēze ar sola – gēla tehnoloģiju

Paplašinoties pētījumu jomai, pēdējā laikā arvien vairāk tiek pētītas nanoporainas keramikas trīskomponentu sistēmas, lai iegūtu jaunus materiālus vidi piesārņojošo savienojumu adsorbcijai, katalīzei un membrānām. Darba mērķis bija iegūt mikro- un mezoporas saturošu trīskomponentu keramiku sistēmā SiO_2-TiO_2-ZrO_2, sintezējot ar sola-gēla tehnoloģiju. Uzsākot šo pētījumu, izvēlētā ZrO_2 saturs bija 50 mol% un tam tika pievienotas dažādas TiO_2 un SiO_2 mol % attiecības. Kā optimālais sastāvs turpmākiem sistēmas pētījumiem tika izvēlētas šādas oksīdu SiO_2/TiO_2/ZrO_2 mol% attiecības: 25/25/50 un 15/35/50. Veicot sintēzi ar sola-gēla tehnoloģiju, salīdzinājumā ar tradicionālajām sintēzes tehnoloģijām tai ir vairākas priekšrocības: nav nepieciešamas augstās sintēzes temperatūras, pastāv iespēja nodrošināt sajaukšanos atomu līmenī, kā arī sintezēt materiālus ar unikālām mehāniskajām un struktūras īpašībām. Darba gaitā abām paraugu sērijām pēc saķepināšanas 800 °C vai 1000 °C temperatūrā, atkarībā no pievienotās sālsskābes molaritātes (0,1 M vai 1 M), presējamā pulvera malšanas ilguma (1 vai 6 stundas), tika noteikta un izvērtēta ietekme uz nanoporainas keramikas produktu morfoloģiju, mikrostruktūru un mehāniskajām īpašībām. No iegūtajiem RTg fāžu difrakcijas rezultātiem konstatēts, ka malšanas procesā notiek fāžu pāreja abām paraugu sērijām – no ZrO_2 uz $TiZrO_4$ (šrilankīts), kā arī spiedes stiprības izturība ir labāka paraugiem, kas presēti no 1 stundu malta pulvera. Domājams, ka šiem nanoporainajiem keramikas paraugiem lielāko ietekmi uz poru struktūru un virsmas laukumu rada solam pievienotā sālsskābe un daļiņu izmēra sadalījuma izmaiņas malšanas procesa gaitā.

Маргарита Карпе, Гундарс Межинскис, Лаимонс Тимма. Синтез нанопористой SiO_2-TiO_2-ZrO_2 керамики с помощью золь-гель технологии

В последнее время все больше исследуется нанопористая керамика на основе трехкомпонентных систем, которую можно применять в роли материалов, способных адсорбировать вещества, загрязняющие окружающую среду, а также применяемых как катализаторы и мембраны. Целью работы было получение с помощью зол-гель технологии трехкомпонентной керамики из системы SiO_2-TiO_2-ZrO_2, содержащей микро- и макропоры. В начале исследования количество ZrO_2 было определено как 50-мольный, в свою очередь к нему были добавлены в разных молярных отношениях TiO_2 и SiO_2. Для дальнейшего исследования системы был выбран оптимальный состав с характерным молярным соотношением вышеупомянутых оксидов: SiO_2/TiO_2/ZrO_2 - 25/25/50 и 15/35/50. По сравнению с традиционными технологиями синтеза, у синтеза с помощью золь–гель есть определенные приемущества: нет необходимости применения высоких температур, возможность смешивания веществ на атомном уровне, а также синтез материалов с уникальными механическими и структурными свойствами. В ходе экспериментов обе серии образцов были обожены при температурах 800 ºC и 1000 ºC, а также была определена и оценена зависимость молярности присоединенной соляной кислоты (0.1M и 1M), а также влияние длительности измельчения прессуемого порошка (1 или 6 часов) на морфологию, микроструктуру и механические свойства нанопористой керамики. Из полученных результатов рентгенофазового анализа констатировано, что в ходе процесса измельчения для обоих серий образцов происходит фазовый переход - из ZrO_2 в $TiZrO_4$ (шриланкит), а также устойчивость на сжатие лучше для образцов, которые спрессованы из порошков, измельченных в течение одного часа. Предполагается, что на структуру образцов и площадь поверхности нанопористых керамических образцов влияет присоединенная к золю соляная кислота и изменение распределения по размеру частиц в ходе процесса измельчения.