RIGA TECHNICAL UNIVERSITY Faculty of Material Science and Applied Chemistry Institute of Silicate Materials

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INFLUENCE OF THE SYNTHESIS CONDITIONS AND ADDITIVES ON THE PROPERTIES AND STRUCTURE OF POROUS HIGH TEMPERATURE CERAMICS

Summary of Doctoral thesis

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DOCTORAL THESIS NOMINATED TO OBTAIN THE DOCTORAL DEGREE OF ENGINEERING SCIENCES IN RIGA TECHNICAL UNIVERSITY

The doctoral thesis for the Doctoral degree of engineering sciences will be defended in public at 14:30 o'clock on May 27 2015 at Riga Technical University, Faculty of Material Science and Applied Chemistry, Riga Paula Valdena Street 3/7, Room Nr. 272.

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CONFIRMATION

I confirm that I worked out this doctoral thesis, which is submitted for consideration of obtaining of Doctoral degree of engineering sciences in Riga Technical University. The doctoral thesis is not submitted in any other university for obtaining of doctoral degree.

Ludmila Mahnicka-Goremikina(Signature)

Date:

The doctoral thesis is written in Latvian and consists of general description, three chapters: review of literature, methodological part, experimental part with assessment of results and conclusions, references. The volume of the work is 136 p., 76 figures, 6 tables and 176 references.

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Riga, year 2015

L. Mahnicka-Goremikina

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GENERAL WORK DESCRIPTION

Relevance of the topic

Limited raw materials and energy resources are actual problems in the world economy. Increasing of the efficiency of the raw materials usage in production processes, reduction of the consumption of energy resources and reduction of negative impacts to the environment and human health are the possible solutions of these problems. Therefore, the scientific and practical attention of the thesis focuses on the high-temperature heat-insulating ceramics, which help to reduce heat loss, withstand the rapid temperature fluctuations and at the same time will be used as a load-bearing structural material.

The improvement of the high-temperature heat-insulating ceramics could be achieved by the reduction of the materials bulk density, improving of material thermal properties and increase longevity. These properties of the ceramics could be improved by increasing the apparent porosity of the ceramic and by doping of a mullite refractory ceramics with metal oxides. The doping with metal oxides affects the thermal properties of these ceramics. The CO₂ emitting materials are not used for the production of porous ceramics.

The refractoriness of the mullite-corundum thermal insulating ceramics is up to 1650°C temperature. The low thermal shock durability, destruction due to the rapid temperature fluctuations and formation of large thermal stresses are typical for this ceramics. The improvement of the thermal shock resistance of ceramics is possible by decreasing of the difference of expansion coefficients of crystalline phases in the ceramics or by creating of additive crystalline phase with significantly lower thermal expansion coefficient than the expansion coefficient of the existing crystalline phases in the current ceramic. Sometimes, this way of coordinating of thermal expansion coefficients may causes the increase of the ceramics thermal conductivity due to the increase of the bulk density. The creating of additive phases could also causes the increase of the sintering shrinkage of the ceramic materials.

It is necessary to obtain porous mullite ceramics with increased thermal shock resistance. Porosity and pore size distribution of the material help to ensure low thermal conductivity. The reduced crystals size and arrangement of phases play an important role in the ensuring of the low thermal conductivity. Usage of WO₃, MgO and ZrO₂ as doping additive allows obtaining the additional refractory crystalline phase in the ceramics or changing of crystalline structure. Doping of the ceramics with MgO and ZrO_2 is widely used in the case of dense mullite ceramics production. The influence of metal oxides on the properties of the porous mullite ceramics is not enough investigated. Advantages and disadvantages of doping of the porous mullite ceramics with WO₃ are not discovered.

Aim of the work

The aim of the work is with the suspension's slip casting method, in which pores are formed by chemical reaction, develop the heat-insulating thermal shock resistant highly porous mullite ceramic material; and using doping additives, reduce sintering temperature of mullite ceramic and ensure the improvement of the properties.

Tasks of the work

- 1. To assess the influence of the kaolin amount on the properties of suspension and formation of mullite phase in the ceramic material during sintering.
- 2. To determine the dependence of the some dopants such as MgO, ZrO_2 and WO₃ on synthesis and properties of porous mullite ceramics
- 3. To evaluate an influence of phases composition and microstructure on the properties of such ceramics.
- 4. To assess the influence of doping additive on formation's temperature and intensity of mullite phase.
- 5. To determine the influence of doping additive on utility of porous mullite ceramics' modification.

Scientific novelty

The new highly porous mullite ceramic material with low thermal conductivity and increased thermal shock durability is obtained. The sintering temperature of obtained material is about 250°C lower to sintering temperature of pure mullite ceramic.

The doping of highly porous mullite ceramic with tungsten oxide WO_3 by method of casting of concentrated suspension and pore formation in way of chemical reaction are developed. The influence of WO_3 on the formation of crystalline phases and structure as well as porosity is determined. The influence of aluminum tungstate crystalline phase on the thermomechanical properties – thermal conductivity and thermal shock durability is established.

Practical use of the work

The new results about doping of porous mullite ceramic with WO_3 are analysed and summarised. These results could be suitable for the further research. The obtained porous thermal insulating thermal shock resistant mullite ceramic could be useful as lining material in the furnaces.

APPROBATION AND PUBLICATION OF THE THESIS

The results presented in thesis paper are approbated in 3 full text articles, 1 full-text publication of international conference proceeding, 11 abstracts in abstracts book of the international conferences.

The results of thesis paper are presented in international conferences with 8 oral presentations and 5 posters.

The list of participation in conference:

- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Influence of WO₃ additive on the properties of porous mullite ceramics. The 22nd International Baltic Conference of Engineering Materials&Tribology – BALTMATTRIB 2013. November 14-15, **2013**, Riga, Latvia (oral presentation);
- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Influence of doping agent on the mullitisation process in alumosilicate ceramics. Conference for Young Scientists in Ceramics – the tenth Student's Meeting SM 2013. November 06-09, **2013**, Novi Sad, Serbia (**oral** presentations);
- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Influence of metal oxides additives on the porous mullite ceramics. Riga Technical University 54th International Scientific Conference. October 14-16, 2013, Riga, Latvia (oral presentation);
- <u>Mahnicka L.</u>, Svinka R., Svinka V. Porous mullite ceramics doped with metal oxides. Riga Technical University 53rd International Scientific Conference (Dedicated to the 150th Anniversary and The 1st Congress of World Engineers and Riga Polytechnical Institute / RTU Alumni. October 11-12, **2012**, Riga, Latvia (**oral** presentations);
- <u>Mahnicka L.</u>, Svinka R., Svinka V. Influence of metal oxides on porosity of mullite ceramics. The 14th International Conference-School "Advanced Materials and Technologies". August 27-31, **2012**, Palanga, Lithuania (**poster**);
- 6. <u>Mahnicka L.</u>, Svinka R., Svinka V. Properties of porous mullite ceramics doped with MgO and produced by slip casting method. VII.

International Scientific Conference - Refractories, furnaces and thermal insulations. April 17-19, **2012**, Novy Smokovec, Slovakia (**oral** presentations);

- Mahnicka L., Svinka R., Svinka V. ICFMTE 2012 Influence of raw materials ratio and sintering temperature on the properties of the refractory mullite-corundum ceramics. International Conference on Fluid Mechanics and Thermal Engineering. March 28-30, 2012, Madrid, Spain (oral presentations);
- Mahnicka L., Svinka R., Svinka V. Influence of ratio of raw materials on porosity and pore size distribution in porous mullite-corundum materials. Riga Technical University 52nd International Scientific Conference. October 13-15, 2012, Riga, Latvia (oral presentations);
- <u>Mahnicka L.</u>, Svinka R., Svinka V. Porous mullite ceramics formation by slip casting of suspension of raw materials. The 13th International Conference-School "Advanced Materials and Technologies" August 27-31, **2011**, Palanga, Lithuania (**poster**);
- <u>Mahnicka L.</u>, Svinka R., Svinka V. Influence of kaolin and firing temperature on the mullite formation in porous mullite-corundum materials. BaltSilica 2011 – 5th Baltic Conference on Silicate Materials. May 23-25, **2011**, Riga, Latvia (**poster**);
- 11. <u>Mahnicka L.</u>, Svinka R., Svinka V. Effect of SiO₂ on the properties of porous corundum-mullite ceramic. Joint International Summer School-Conference. The 12th International Conference "Advanced Materials and Technologies" and Summer School "European Doctorate in Physics and Chemistry of Advanced Materials". August 27-31, **2010**, Palanga, Lithuania (**poster**);
- Svinka R., Svinka V., Zake I., <u>Mahnicka L</u>., Mozolevskis G. Highly porous ceramic by slip casting of concentrated clay and oxides suspension. ICCPS-11th International Conference on ceramic processing science. 29th August – 1st September 2010, Zurich, Switzerland (poster);
- 13. Svinka R., Svinka V., Zake I., Butlers A., <u>Mahnicka L.</u>, Mozolevskis G. Porous alumina-mullite ceramics, structure and properties. The 9th International Conference on Global Research and Education, Inter-Academia. August 9-12, **2010**, Riga, Latvia (**oral** presentation);

List of published papers:

Articles in journals:

- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Influence of metal oxides additives on the porous mullite ceramics // Key Engineering Materials. – 2014. – Vol. 604. – pp. 293-296 (Scopus);
- <u>Mahnicka L.</u> Influence of Raw Materials Ratio and Sintering Temperature on the Properties of the Refractory Mullite-Corundum Ceramics // World Academy of Science, International Journal of Engineering and Technology. – 2012. – Vol.6. – pp. 51-56;
- <u>Mahnicka L.</u>, Svinka R., Svinka V. Influence of kaolin and firing temperature on the mullite formation in porous mullite-corundum materials // IOP Conference Series: Materials Science and Engineering. 5th Baltic Conference on Silicate Materials, BaltSilica 2011; Riga; Latvia; 23 May 2011 through 25 May 2011; Code 88028. Article number 012008–2011. Vol. 25. Issue 1. pp. 1-9 (Scopus and Ebsco);

Articles in proceedings:

 <u>Mahnicka L.</u>, Svinka R., Svinka V. Properties of Porous Mullite Ceramics Doped with MgO and Produced by Slip Casting Method // Proceedings of The International Scientific Conference Refractories, Furnaces and Thermal Insulations, Novy Smokoves - High Tatras, Slovakia, April 17-19, **2012**, pp. 130-135 (Academia.edu)

Conference theses:

- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Influence of WO₃ additive on the properties mullite ceramics // Abstracts of the 22nd International Baltic Conference of Engineering Materials&Tribology – BALTMATTRIB 2013. Riga, Latvia, November 14-15, **2013**, p. 38;
- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Influence of doping agent on the mullitisation process in alumosilicate ceramics // Abstracts of Conference for Young Scientists in Ceramics – the tenth Student's Meeting SM 2013. Novi Sad, Serbia, November 06-09, 2013, p. 95;
- <u>Mahnicka-Goremikina L.</u>, Svinka R., Svinka V. Porous Mullite Ceramics Doped with ZrO₂ // Abstracts of the Riga Technical University 54th International Scientific Conference. Riga, Latvia, October 14-16, **2013**, p. 59;

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- <u>Mahnicka L.</u>, Svinka R., Svinka V. Influence of Metal Oxides on Porosity of Mullite Ceramics // Abstracts of the 14th International Conference-School "Advanced Materials and Technologies". Palanga, Lithuania, August 27-31, **2012**, p. 108;
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- Mahnicka L., Svinka R., Svinka V. Porous Mullite Ceramics Formation by Slip Casting of Suspension of Raw Materials // Abstracts of the 13th International Conference-School "Advanced Materials and Technologies", Palanga, Lithuania, August 27-31, 2011, p. 107;
- Mahnicka L., Svinka R., Svinka V. Porous mullite ceramics formation and modification with some additives // Abstracts of the Students' Meeting Processing and Application of Ceramics. Novi Sad, Serbia, November 16-18, 2011, p. 47;
- <u>Mahnicka L.</u>, Svinka R., Svinka V. Influence of kaolin and firing temperature on the mullite formation in porous mullite-corundum materials // Abstracts of BaltSilica **2011** – 5th Baltic Conference on Silicate Materials. Riga, Latvia, May 23-25, p. 89-90;
- <u>Mahnicka L.</u>, Svinka R. Effect of SiO₂ on the Properties of Porous Corundum-Mullite Ceramic // Abstracts of the Joint International Summer School-Conference The 12th International Conference "Advanced Materials and Technologies" and Summer School "European Doctorate in Physics and Chemistry of Advanced Materials". Palanga, Lithuania, August 27-31, **2010**, p.83;
- Svinka V., Svinka R., Zake I., Butlers A., <u>Mahnicka L.</u>, Mozolevskis G. Porous Alumina-Mullite Ceramics, Structure and Properties // Abstract of the 9th International Conference on Global Research and Education, Inter-Academia Riga, Latvia, August 9-12, **2010**, p. 106-107.

CONTENT OF THE THESIS

Review of literature

The review of literature includes analysis of available published reports related to the thesis topics. The synthesis methods, specific properties, raw materials and improvement ability used to make porous mullite ceramics (3Al₂O₃·2SiO₂) are considered.

The first chapter describes the methods of synthesis of porous mullite ceramics, which allow using slip casting of the raw materials concentrated suspension in the moulds. The advantages and disadvantages of each method, economic efficiency, the influence of porosity on the ceramics' mechanical and thermal properties, as well as application possibilities are analysed.

The second chapter of the literature review starts with the history of mullite ceramics production. The analysis of mullite orthorombic structure is also performed in this part of the work. This chapter summarizes the information about the reaction processes in the solid state, properties of the mullite ceramics obtained from kaolinite clay with high kaolinite content, as well as the usage of Al₂O₃ and SiO₂ powders with a purity of around 99% as raw materials (mainly mixing of α -Al₂O₃ and quartz, α -Al₂O₃ and cristobalite, α -Al₂O₃ and amorphous SiO₂) [8]. An analysis of the influence of sintering temperature and the holding time is also presented in this chapter.

In the third chapter of the literature review the mullite ceramic doping with different type of metal oxides is described. The influence of metal oxides amount and properties of corresponding MeO–Al₂O₃–SiO₂ phase equilibrium diagram on the mullitisation velocity, initial temperature, phase composition, microstructure, porosity and other properties is analysed in this chapter. The usage of alkali oxides for preparation of porous mullite ceramic is not desirable due to appearance of strong fluxes together with mullite formation temperature reduction, large shrinkage and reduction of porosity [7]. Doping with the alkaline earth metals oxides causes an increase of mullitisation temperature, shrinkage of ceramics and bulk density depending on the oxide type in the following order: MgO<CaO<SrO<BaO [3]. Doping with such transition metal oxides as TiO₂, V₂O₃, Cr₂O₃ and Fe₂O₃ causes the Al³⁺ (0.53 Å) ion replacement in the AlO₆ by cations Ti⁴⁺, V³⁺, Cr³⁺ and Fe³⁺ with similar ionic radius (0.54-

0.62Å) in the AlO₆. This process changes the mullite crystalline lattice properties. The ion substitution or solubility degree depends on the cations radius, oxidation stages, method of sample preparation and sintering temperature. The substitution of the ion doesn't occur, if the size of the metal cations is higher to size of Al^{3+} , but corresponding metal and Al_2O_3 form spinel, and influence on mullite formation. The mullite ceramics doping with Y₂O₃, La₂O₃, CeO₂, ZrO₂ and WO₃ affects the mullite crystal growth and structural homogeneity or heterogeneity [5].

The review of literature sources allowed to select appropriate synthesis mode, type and quantity of metal oxide additives for doping of porous mullite ceramics, as well as to compare obtained results with the results of other researches.

Methods

In the first chapter of the methodical part such commercial raw materials as α -Al₂O₃ and γ -Al₂O₃, kaolin, ZrO₂ partially stabilized by 10% of MgO (below in the text marked as ZrO₂), WO₃, MgO and Al paste are described in details. These raw materials are used for preparation and doping of porous ceramic. Specification of the raw materials is shown in Table 1.

specification of faw materials							
Raw material	Brand	Characteristics					
		The average					
		μm					
α-Al ₂ O ₃ , (NO 725)	NABALOX [®] ,	2					
γ-Al ₂ O ₃ , (NO 201)	Nabaltec, Germany	80					
Kaolin,	MEKA, Amberger						
(mineral kaolinite -	Kaolinwerke,	1.5					
$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$	Germany						
SiO ₂ , fused		6.9					
WO ₃	Peaхим, Russia	7					
MgO		0.9					
7rΩ.	Raushert,	0.9					
2102	Germany						
Al naste	"Aquapor-9008",	12					
in puste	Schlenk, Germany	12					

Specification of raw materials

Designation, compositions and sintering temperatures of the synthesized and analysed samples are shown in Table 2. The choice of sintering temperature depends on the individual characteristics of the used metal oxides and location of the corresponding composition in the phase equilibrium diagram of ternary system MeO-Al₂O₃-SiO₂. The amount of doping additives is optimized using experimental results and literature information.

Table 2

	1 series of samples			2 series of samples			
	Symbol of samples						
	Undoped samples			Doped samples			
Quantity of raw materials, wt%	10K	20K	30K	with ZrO ₂	with WO3	with MgO	
	Ratio of Kaolin/Al ₂ O ₃ +SiO ₂ parts by weight						
	1/9	2/8	3/7	3/7	3/7	3/7	
Kaolin	10	20	30	30	30	30	
a-Al ₂ O ₃	16.2	14.4	12.6	12.6	12.6	12.6	
γ-Al ₂ O ₃	48.6	43.2	37.8	37.8	37.8	37.8	
SiO ₂	25.2	22.4	19.6	19.6	19.6	19.6	
ZrO ₂	-	-	-	5	-	-	
WO ₃	-	-	-	-	5	-	
MgO	-	-	-	-	-	5	
Al paste	0.18	0.18	0.18	0.18	0.18	0.18	
Water content	40	40	40	40	38	115	
Sintering temperature, °C	1650°C, 1700°C, 1750°C	1650°C, 1700°C, 1750°C	1500°C, 1650°C, 1700°C, 1750°C	1650°C, 1500°C	1200°C, 1300°C, 1400°C, 1500°C	1200°C, 1300°C, 1400°C, 1500°C	

Compositions of the synthesized samples

In the second chapter of the methodical part the information about the preparation method of samples is provided (Figure 1). Porous mullite ceramics were obtained by slip casting of concentrated slurry of raw materials. During the first stage the raw materials (kaolin, α - and γ -alumina, SiO₂ as well as the corresponding doping additive) were mixed in the dry state. Then, in the second stage, the suspension of raw materials was created. In the third stage of samples preparation process the suspension of aluminium paste was created and mixed about 5 minutes with the main

suspension. The suspension should be homogenous and easy castable into polyurethane mould with dimensions of 162x110x70 mm.



Fig. 1. Scheme of samples' preparation process

The formation of pores occurs after 5-15 min due to the reaction of aluminium and water at the room temperature:

$$2AI + 6H_2O \rightarrow 2AI(OH)_3 + 3H_2\uparrow.$$
(1)

The volume of suspension increases by 100–150% during the hydrogen elimination process. The solidification of samples was performed firstly at the air temperature (20–25°C). Then, porous samples were dried within 24–78 hours at the temperature of 50°C and then sintered at the required temperature. Temperature raising speed 250°C/h was applied and holding time was 1 hour. Obtained materials were cut into bars (150x20x20 mm). The kaolin was used as a binder to stabilize a suspension of Al₂O₃ and SiO₂ raw materials. The total amount of water in the suspension is 38–40%.

The testing equipment and methods for determination of the properties of synthesized ceramics and to analyse the results are described in the third chapter of the methodical part.

The pH of raw materials suspension was analysed by *Mettler Toledo SevenMulti* pH-meter, electrode *InLab*® 413. The processes during sintering in the temperature range 25–1300°C were analysed by differential thermal analysis (DTA) and thermogravimetry (TG) using thermal analysis equipment *SETSYS Evolution TGA-DTA/TMA SETARAM (1750°C)*. The mineralogical composition of sintered samples was analysed using X-ray diffractometer *RIGAKU ULTIMA*+ (*Rigaku Company, Japan*). This diffractometer uses copper cathode CuKa₁ radiation with goniometer scanning speed 2°/min. Three types of scanning electron microscopes (SEM) were used to analyse microstructures of samples (*Hitachi TM3000*, *Hitachi S4800* and high resolution *FEI Nova NanoSEM 650*). The elemental and phase analyse for some samples was performed using Energydispersive X-ray spectroscopy. For this purpose the X-ray fluorescence spectrometer *Apollo X SDD* created by *TEAMTM Integrated EDS* was used.

Determination of bulk density, apparent porosity and water uptake is based on the Archimedes principle according to the European standard EN 623-2. Mercury porosimeter *Pore Master 33 (Quantachrome Instruments, USA)* was used to determine pore size distribution and total pore volume. This machine allows to measure pores in the range of 0.0064–950 micrometres.

Mechanical properties of the samples were determined by three point bending test using the universal deformation machine *Zwick ProLine BDO-FB020TN*. The thermal shock resistance of ceramics was determined during 10 cycles of thermal shocks. The temperature in the tests was rapidly changed by scheme $1000^{\circ}C \rightarrow 20^{\circ}C \rightarrow 1000^{\circ}C$ with one hour exposure at temperature. Modulus of elasticity was determined by non-destructive method using the impulse excitation equipment *Buzz-O-Sonic 5.0 (BuzzMac International, LLC, USA)*. Contrary to the destructive method, nondestructive method provides an opportunity to examine the same sample after each thermal shock cycle. This procedure reduces the dissipation of the results. Thermal expansion coefficients of samples were determined by the horizontal dilatometer *L76/1600D* in the temperature range from 20 to $1300^{\circ}C$. The thermal conductivity and specific heat capacity of the mullite ceramics were determined by the laser flash contactless method using the universal equipment *NETZSCH LFA 457 MicroFlash*.

Results and assessments of their impacts

The synthesis process of alumosilicate ceramic and doping with MgO, ZrO_2 and WO_3 were analysed in the experimental part of the thesis. Interaction of metal oxides with the basic raw materials was established. The doping metal oxides influence on the ceramic formation process and sintering temperatures, on such properties as phase composition and structure, bulk density and porosity, mechanical and thermal properties was assessed. The effectiveness of the doping for the obtaining of highly porous mullite ceramic at lower sintering temperature was estimated and defined.

Influence of the samples' compositions on the phase formation and structure

Influence of samples compositions and doping metal oxidex on the processes during sintering was analysed by differential thermal analysis (Figure 2). In the case of stoichiometric composition with Al_2O_3 and SiO_2 ratio 2.57:1 the beginning of mullite formation observed at $\approx 1220^{\circ}C$. Primary mullite crystals rich with Al (2/1 mullite) formed at this temperature. The kaolinite dehydroxylation and formation of metakaolin occurs at $\approx 550^{\circ}C$ and Al-Si spinel-type phase formation occurs at temperatures $\geq 980^{\circ}C$ for all the compositions with 30 wt% of kaolin.

Doping with ZrO_2 doesn't affect the temperature reduction of spinel type phase formation. Doping with WO₃ and MgO relatively slightly reduces the formation temperature of the spinel type phase. Doping with ZrO_2 increases the temperature of mullite formation beginning.



Doping with WO₃ and MgO has a positive influence on decreasing of mullite formation beginning temperature.

Fig. 2. Results of differential thermal analysis

The XRD patterns of the undoped samples with all quantities of kaolin show that corundum phase dominates over mullite phase after sintering at the temperature of 1650°C (Figure 3). Mullite phase becomes dominant over the corundum by increasing of the kaolin quantity from 10 to 30 wt% and sintering at the temperature above 1650°C. The mullite is the single crystalline phase that was formed in these compositions after sintering at the maximum temperature 1750°C. It is important to note, that not reacted cristobalite does not remain after sintering of samples with the increased amount of the kaolin at temperature of 1650-1750°C. This result is observed due to the increase of kaolin amount leads to decrease the amount of commercial Al_2O_3 and SiO_2 , but quantity of the amorphous SiO_2 is complemented after kaolinite transformation. As a result, the number of grains contact points increases and provides the reaction of SiO₂ with large aggregates of α -Al₂O₃, which are formed by modifications change from γ to α -alumina. This process promotes the mullite nucleation, but higher temperatures provide and improve the Si⁴⁺ and Al³⁺ ion diffusion and further mullite crystal growth.





a - with 10 wt% of kaolin; b - with 20 wt% of kaolin; c - with 30 wt% of kaolin

The composition with 30 wt% of kaolin is selected as an optimal solution after analyse of the kaolin quantity influence on increase of the mullite phase in ceramic. This composition is used to analyse the influence of 5 wt% metal oxide additives MgO, ZrO_2 and WO_3 on the mullite phase formation, structure, porosity, mechanical and thermal properties.



Doping with metal oxide influences the phase composition of ceramics. Pure mullite phase was not observed after sintering at temperature $1500-1650^{\circ}$ C. Mullite phase of samples doped with MgO was observed after sintering only at only 1400° C (Figure 4, *a*). In case of MgO-doped samples the mullite becomes dominant over corundum phase after sintering at temperature 1500° C. This might happen due to increase of the amount of glassy phase as the result of MgO addition and cordierite decomposition to the mullite and glassy phase at 1465° C temperature [9]. XRD patterns of the samples that were doped with ZrO_2 and sintered at 1500°C show that the corundum, cristobalite and zircon are dominant phases (Figure 4, *b*). Mullite is the major crystalline phase in samples that are sintered at 1650°C. A small amount of monoclinic-ZrO₂ was detected. In case of ZrO₂-doped (1650°C) compositions, the intensity of XRD peaks of mullite was larger than the intensity of mullite lines in the undoped composition with 30 wt% of kaolin and sintered at the temperature of 1750°C. This could happen due to the mullite formation in presence of ZrO₂ by two parallel reaction processes. The direct reaction of SiO₂ and Al₂O₃ is the first process. The second process is the formation of zircon - ZrSiO₄ (2) phase and its subsequent reaction with Al₂O₃ (3) at the temperature range \approx 1600°C. Mullite nucleation activation energy in presence of zirconia decreases since the beginning of zircon formation [6].

$$ZrO_2 + SiO_2 \leftrightarrow ZrSiO_4$$
 (2)

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 3Al_2O_3 \\ 2SiO_2 + 2ZrO_2$$
(3)

In case of the WO₃-doped compositions, the mullite phase becomes dominant over other crystalline phases already after sintering at 1300°C. This temperature is the lowest sintering temperature in comparison with others compositions. In case of sintering of WO3-doped samples at temperature 1500°C the intensity of XRD peaks of mullite is relatively the same as in case of sintering of undoped compositions with 30 wt% of kaolin at higher temperature 1750° C (Figure 4, c and d). Due to the doping of samples with WO₃, the XRD patterns show the peaks at 2θ =23.3°, 23.8° and 24.6° that indicates to the presence of aluminum tungstate 2Al₂O₃·6WO₃. The intensity of the aluminum tungstate increases with the increase of sintering temperature. It is important to note that some diffraction peaks of Al₂(WO₄)₃ corresponding to cristobalite, mullite and WO₃ phases or insignificantly differ from peak of other phase, therefore detection of aluminum tungstate is complicated. Consequently, it is possible that some part of WO₃ remains unreacted. From literature is known that $Al_2(WO_4)_3$ is obtained by the reaction of Al₂O₃ and WO₃ in result of solid state reaction. Depending on the particle size of Al₂O₃ and WO₃ in the raw powders, Al₂(WO₄)₃ can be formed at temperatures from 800 to 1175°C with long holding time up to 30 hours [1, 11]. In our case the possible formation of $Al_2(WO_4)_3$ occurs during the heating of samples, when the alumina and

tungsten oxide reaction may be accompanied by an alumina modification changes from γ - to α -Al₂O₃. The formation of Al₂(WO₄)₃ and $\gamma \rightarrow \alpha$ modifications change occur at the same temperature $\geq 850^{\circ}$ C, and during the sintering the reaction activity of WO₃ and γ -Al₂O₃ is going at the lower temperature [2].



Fig. 5. Scanning electron microscopy micrographs of samples:
a - with 10 wt% of kaolin (1650°C); b - with 10 wt% of kaolin (1750°C);
a' - with 20 wt% of kaolin (1650°C); b' - with 20 wt% of kaolin (1750°C);
a'' - with 30 wt% of kaolin (1650°C); b'' - with 30 wt% of kaolin (1750°C);
c - doped with MgO (1300°C); c' - doped with MgO (1500°C);
d - doped with ZrO₂ (1650°C) samples

The SEM micrographs (Figure 5, a-a'') show that the structure of undoped samples with 10, 20 and 30 wt% of kaolin and sintered at 1650°C is quite similar and its mullite crystals are in form of short prisms. The increase of kaolin quantity in the composition and sintering temperature up to 1750°C causes the growth of elongated mullite crystal with closely interlinked borders. (Figure 5, b-b''). The doping with metal oxides influences the structure of samples. The structure of the MgO-doped

composition sintered at 1300° C (Figure 5, *c*) is grainy and relatively homogeneous, weakly sintered, but after sintering at 1500° C (Figure 5, *c'*) structure becomes more denser and formed from elongated thick mullite crystals with rounded edges, it is due to the formation of a low melting point liquid phase at peritectic temperature (1425° C) according to the MgO– Al₂O₃–SiO₂ ternary phase diagram [9].

The structure of ZrO₂-doped (1650°C) samples (Figure 5, *d*) consists of non-oriented prismatic mullite crystals and isometric ZrO_2 crystals. The length and thickness of mullite crystals in these samples are relatively lower than in undoped samples (with 30 wt% of kaolin, T=1750°C), because the usage of ZrO_2 prevents the growth of mullite crystals [6].

The doping with WO₃ has the important influence on the formation of ceramic structure. The crystalline clusters with diameter about 50-80 µm were formed in structure of WO₃-doped samples and sintered from 1200°C to 1500°C. The middle part (M) and peripheral (P) part of these clusters are formed from various crystals. After XRD results of phase composition, SEM microstructures, EDS point and mapping analysis with associated distribution of chemical elements and EDS spectrums' analysis (Figure 6) concluded, that middle (M) part of clusters is composed from corundum phase - α -Al₂O₃ crystals, that form porous agglomerates, but peripheral (P) part is composed from different sizes elongated prismatic mullite crystals, some of which are much larger in the results of its growing and recrystallization. Between themselves mullite-corundum clusters are connected by bridges that after EDS and XRD results consist the $Al_2(WO_4)_3$ and mullite phases. The clusters located in matrix that contains cristobalite, mullite and Al₂(WO₄)₃ phase. The mullite-corundum clusters formation is due to during preparation of samples, the WO₃ particles relative evenly were distributed in samples. During the sintering WO₃ inhibits the modification change of big γ -Al₂O₃ (d₅₀=80 µm) particles to the α -Al₂O₃, stabilizes the γ -Al₂O₃ surface, promotes γ -Al₂O₃ and SiO₂ reaction on the alumina's surface and formation of mullite at $\approx 1200^{\circ}$ C, because the ion diffusion energy is less in γ -Al₂O₃ case [3, 11]. When $\gamma \rightarrow \alpha$ modification change occurs, the α -Al₂O₃ reacts with already crystallized cristobalite at the samples' sintering from 1200°C to 1500°C, therefore continues mullite formation. It is known that WO₃ sublimation takes place about at 800°C, but in our results it doesn't characterize. This may be due to the formation of metakaolin from kaolinite at 550°C temperature, as well as due to the formation of Al₂(WO₄)₃ phase as the result of γ -Al₂O₃ reaction with WO₃.



Fig. 6. SEM-EDS analysis of samples doped with WO₃:

SEM micrographs of samples: a, a', a"- sintered at 1400°C; b, b', b" - sintered at 1500°C;
M - medium part of clusters, P - periphery part of clusters, S - space between clusters;
EDS point analysis of area marked with 1, 2, 3 numbers and coloured circles; c-f - chemical elements' distribution maps of samples doped with WO₃ and sintered 1500°C; g - EDS mapping analysis of samples doped with WO₃ (1500°C); g' - EDX spectrums of analysed areas;
h - percentage of scanned area with definite EDX spectrum marked by correspond colour

Influence of the samples' compositions on the porosity and pore size distributions

In case of mullite ceramic the low bulk density is possible to attain when the porosity is higher than 40%. The apparent porosity and water uptake of undoped samples that were sintered at the temperatures of 1650° C, 1700° C and 1750° C in proportion decrease by increasing of kaolin quantity. The samples with 10 wt% of kaolin after sintering at $1650-1750^{\circ}$ C have the higher apparent porosity 50-58%. Samples with 30 wt% of kaolin and sintered at 1750° C have only mullite phases but its apparent porosity (14%) is lower than for another undoped samples. Water uptake for all undoped samples is less than the apparent porosity about $10\pm2\%$ (Figure 7).



Fig. 7. Apparent porosity and water uptake of undoped samples with different quantity of kaolin (*a*) and of samples doped with 5 wt% of metal oxide (*b*)

The apparent porosity of WO₃ doped samples is higher than 40% and it relatively low decreases about $5\pm1\%$ by increasing of sintering temperature from 1200°C to 1500°C. In case of MgO-doped compositions sintered at 1200°C and 1300°C the usage of alkaline earth metal oxide increases the apparent porosity of samples (62–67%) and it is higher than of all synthesised samples. The apparent porosity of MgO-doped samples rapidly decreases by increase of sintering temperature to 1400°C and 1500°C due to the formation of liquid phase in MgO–Al₂O₃–SiO₂ ternary phase system. The apparent porosity of samples doped with ZrO₂ (1650°C) is slightly higher than for samples with 30 wt% of kaolin and sintered at 1750°C. The apparent porosity and water uptake decrease with the increase of firing temperature due to the increase of samples' sintering degree.

The pH value of suspension that must be equal to pH=8-10 plays an important role in the reaction of aluminum with water at room temperature. This reaction leads to elimination of H_2 and pore formation by thickening and drying of the suspension. The suspension pH of stoichiometric composition (Al₂O₃:SiO₂=2.57:1) is equal about 8.8 (Figure 8). The pH of kaolin suspension is 6.9 or slightly acidic. pH of suspension decreases with

the increase of kaolin quantity, and as result the Al and H₂O reaction rate reduces and intensity of H₂ gas also. elimination decreases The pН of suspension becomes higher by doping wih 5 wt% of WO₃, MgO or ZrO₂ of the composition with 30 wt% of kaolin.



Fig. 8. pH of suspensions

The increase of pH corresponds to sequence of used dopants WO₃>ZrO₂>MgO, respectively pH is 8.4, 8.5 and 10.4. The usage of these metal oxides has positive effect on the pore formation in result of chemical reactions in the suspension.

Figure 9 shows the pore size distributions of undoped samples with 10 and 30 wt% of kaolin, as well as of doped samples.



Fig. 9. Pore size distributions of samples with 10 wt% of kaolin (a), with 30 wt% of kaolin (b), of samples doped with metal oxides (c)

The pore volume as for both pores of small size (D \leq 0.5µm) and of large sizes (D \geq 100µm) decreases, by increasing of the sintering temperature for samples with 10 wt% of kaolin sintered at 1700°C and 1750°C (Figure 9, *a*). The pore size becomes larger, and pore diameter increases from 80 to 200 µm after samples with 10 wt% of kaolin were sintered at 1750°C. The samples with the largest amount of kaolin (20 and 30 wt %) have pores with diameter \approx 10–20 µm. Such a pore size distribution is associated with the suspension pH \approx 8.1 that provides the similar conditions for Al and H₂O reaction and hydrogen elimination. The volume occupied by pores of 20 µm decreases in samples with 30 wt% of kaolin after sintering at 1750°C.

The pore size distribution of doped samples is very different. The pores with a size range from 0.5 to 5 μ m and from 10 to 1000 μ m occupy the larger volume of MgO-doped samples (1300°C). Samples doped with MgO (1400°C and 1500°C) have low porosity and pore size distribution is not been fixed by mercury porosimetry. Samples doped with ZrO₂ (1650°C) mainly have pores with a diameter of 15–20 μ m and 150 μ m. The pores with diameter of 0.2–5 μ m occupy the larger volume of WO₃-doped samples sintered at 1500°C.

Influence of the samples' compositions on the shrinkage and bulk density

During the analysis of properties of synthesized ceramic materials it was concluded, that shrinkage of undoped samples increases by increasing both quantity of kaolin and sintering temperature (Figure 10). The increasing of shrinkage correlates closely with kaolinite dehydroxylation at 550°C, further reaction of metakaolin at 920°C and with an increase of suspension polydispersity due to the small size of kaolin particles (1.5 µm). The usage of kaolin with small size of particles influences the more closed packing of samples after slip casting of suspension as well as after the sintering above $\geq 1200^{\circ}$ C temperature. The mullite intensive nucleation and growth significantly contribute to increase of shrinkage.



Doping with 5 wt% of the metal oxides WO_3 , ZrO_2 or MgO brings to the significant impact to the shrinkage of samples. Doping with WO_3 decreases the shrinkage of samples due to the formation of mullite-corundum crystalline clusters, which impede the shrinkage of samples. The shrinkage is higher than 18% in case of MgO- and ZrO_2 -doped samples due to the smaller size of these raw materials particles and additionally due to the formation of the liquid phase.



The bulk density comparably decreases by increasing of sintering temperature in case of samples with correspond amount of kaolin (10, 20 and 30 wt%) (Figure 11). This is due to the mullite phase with the smaller theoretical density (\approx 3 g/cm³) becomes dominant over corundum phase with higher theoretical density (4 g/cm³). The bulk density of samples becomes higher by increasing of kaolin quantity after sintering at the each given temperatures due to the decrease of samples porosity and increase of sintering degree as well as due to the increase of the amount of mullite phase that relative indicates after intensity of mullite phase XRD peaks.

The porosity decreases and bulk density increases by rising of sintering temperature also in case of doped samples. The ceramic materials with relatively low bulk density are obtained after usage of WO₃ as doping additive. The bulk density of WO₃-doped samples sintered at 1500° C is less about by 24% than the bulk density of undoped samples from initial composition with 30 wt% of kaolin sintered at 1750° C.

Doping with MgO oxide strongly influences on the bulk density of samples, because it is less than 1 g/cm³ after sintering at 1300°C due to the weakly sintering and high porosity. At the same time the increase of sintering temperature above 1400°C of MgO-doped samples causes the high sintering, porosity decreasing and increase of bulk density as the result of liquid phase formation. Doping with ZrO_2 increases the bulk density of the

samples due to the lower porosity and high theoretical density of m-ZrO₂ (5.8 g/cm³) and t-ZrO₂ (6.1 g/cm³) that are included in the phase composition of these samples, as well as due a presence of large amount of mullite phase.

Influence of the samples' compositions on the mechanical and thermal properties

In both cases of undoped and doped samples the bending strength decreases with decreasing of bulk density, increasing of porosity and difference of pore size distributions diapasons (Figure 12). This is explained by lower strength of the strut then the strength of monolithic material. The pores are acting as the stress concentrators. The stronger local stresses occur around pores after application of external forces in the material with greatly different sizes of pores. The destruction of the sample occurs after exceeding the maximum stresses in the material. After analysis of the structure and phase influence on the mechanical properties, was concluded, that the bending strength increases by increasing of mullite phase dominance and its intensity, as well as by increasing of the size of the mullite crystals. This is observed for samples with 20 and 30 wt% of kaolin that were sintered at 1700–1750°C, for samples doped with WO₃ and ZrO₂ that were sintered at 1500°C and 1650°C, respectively. In contrast the bending strength decreases in case of samples with 10 wt% of kaolin sintered at 1650-1750°C and of samples doped with MgO (1200°C and 1300°C) due its granular structure.



Fig. 12. Influence of samples' compositions, porosity and pore size on the bending strength

The application of dilatometry methods determines that temperature dependence of the relative change in length for all undoped samples sintered at the different temperatures is linear and comparably similar between themselves (Figure 13) that correspond to evenly change of its linear thermal expansion coefficients. Linear thermal expansion coefficients of undoped samples exceed $6.10 \cdot 10^{-6} \cdot ^{\circ} C^{-1}$ at the 900-1000°C (Figure 14).





The increase of the amount of kaolin and sintering temperature accordingly increase of the mullite phase dominance over the corundum phase causes the reduction of the linear thermal expansion coefficient in range of the corresponded temperatures and as result the decreasing of the relative change in length of undoped samples. This is due to the smaller expansion of mullite phase and the lowest average coefficient of linear thermal expansion of mullite in the temperature range from 20°C to 1000°C ($\alpha_{\text{mullite}}=5.3\cdot10^{-6}\cdot^{\circ}\text{C}^{-1}$) than for the corundum ($\alpha_{\text{corundum}} = 8-8.8\cdot10^{-6}\cdot^{\circ}\text{C}^{-1}$) in the same range of temperatures [1].

The separate samples were selected to determine the influence of doping metal oxides on the thermal properties of the ceramics (Figure 15). The temperature dependence of relative change in length of the samples doped with ZrO_2 (1650°C) is regular and the same as in the case of the samples with 30 wt% of kaolin (1750°C). The average coefficient of linear thermal expansion of these samples in the temperature range from 60 to 1300°C is lower than for other doped samples.



Fig. 15. Temperature dependence of the relative change in length (*a*) and of the linear thermal expansion coefficient (*b*) for doped samples

The relative change in length of samples doped with WO₃ and sintered at the three temperatures (1300°C, 1400°C and 1500°C) as well as of samples doped with MgO (1300°C) occurs with rapid change at \approx 220°C. The rapid increase of linear thermal expansion coefficients of these samples are observed also at range of this temperature. This is due to the presence of the cristobalite low temperature modification (α -cristobalite) in these samples. When samples are heated, the α -cristobalite converts to the high temperature modification (β -cristobalite) at 220°C that leads to volume increase based on the literature date by 2.8% or 4.9% [10]. The presence of phases with smaller thermal expansion (mullite phase $\alpha_{mullite}=5.3 \cdot 10^{-6} \cdot ^{\circ}C^{-1}$ and aluminum tungstate phase ($\alpha_{alum.tungt.}=-1.5 \cdot 10^{-6} \cdot ^{\circ}C^{-1}$ [1]) reduces the $\alpha \rightarrow \beta$ cristobalite transition effect for WO₃-doped samples in contrast of MgO-doped samples. The dependence of synthesized ceramic thermal conductivity coefficient (λ) on temperature was determined for samples with the highest content of mullite (Figure 16, *a*). The thermal conductivity of samples in the temperature range from 25°C to 1000°C decreases in the following order: $\lambda_{undoped, 1750°C} > \lambda_{ZrO_2, 1650°C} > \lambda_{WO_3, 1500°C}$, which also corresponds to the increase of these samples porosity Pundoped, 1750°C=14%, PzrO_2=16% and PwO_3=42% and the increase of structural heterogeneity.

The thermal conductivity coefficients of WO₃-doped samples at the corresponded temperatures are $\lambda_{25^\circ C}=0.93$ W/m·K, $\lambda_{900^\circ C}=0.86$ W/m·K and $\lambda_{1000^\circ C}=1.02$ W/m·K. The thermal conductivity of WO₃-doped samples is lower by 58% at 25°C and by 49% at the temperature of 900°C in comparison with undoped samples (Figure 16, *b*). The lower thermal conductivity of WO₃-doped samples can be described firstly, with higher porosity and small pore size from 1 to 5 µm in which located air has the very small thermal conductivity (T=25°C, $\lambda_{air}=0.026$ W/m·K) and secondly, with the different structure due to presence of mullite-corundum porous clusters. These mullite-corundum clusters are composed of small size crystal and obstacle to the conduction of the heat.



Fig. 16. Temperature dependence of the thermal conductivity (a) and coefficient of the thermal conductivity (b) on porosity and pore size at 900°C



Fig. 17. Dependence of relative change of Elastic modulus on the cycles' number of thermal shock

The figure 17 shows the dependence of elastic modulus relative change on the cycles' number of thermal shock, the sample porosity and pore size distribution. Samples doped with WO₃ and sintered at 1500°C, together with the thermal insulating ability show the best thermal shock resistance. The comparable high porosity and the presence of the small pores with relatively equal size (0.1-0.5 μ m and 1-5 μ m) do not cause the localization of stress at the moment of the thermal shock due to of rapidly change of temperatures. Otherwise the such samples as undoped with 30 wt% of kaolin (1750°C) and doped with MgO (1300°C) and ZrO₂ (1650°C) which are with larger pores and big difference of pore size have lower resistance of the thermal shock due to the localization of stress around the pores, formation and propagation of crack in the result of thermal stress impact on samples at the time of the thermal shock. The structure and difference of thermal expansion of crystalline phase of WO₃-doped samples have the important influence on the thermal shock resistance. The middle part of characteristic clusters of WO₃ samples formed from corundum that has the higher thermal expansion $(\alpha_{corundum} = 8.8 \cdot 10^{-6} \cdot C^{-1})$ than mullite $(\alpha_{mullits} = 5.3 \cdot 10^{-6} \cdot C^{-1})$ and aluminum tungstate ($\alpha_{alumin,tungst.=}$ -1.5·10^{-6.o}C⁻¹) that are deposited at the periphery of clusters and between clusters. The middle part of the cluster is porous and corundum crystals have place for expansion, but aluminum tungstate with its negative α shrinks, that compensates the expansion of corundum and mullite. The cracks of WO₃-doped samples that specially were sintered at 1500°C do not propagated and elastic modulus does not change in the result of rapid temperature change due to compensation of stresses.

CONCLUSIONS

- 1. The highly porous mullite ceramics by method of slip casting of concentrated suspension and pores formation in result of chemical reaction is obtained. The aluminum paste is used as pore forming agent that after reaction with water in alkaline medium forms hydrogen gas. The influence of kaolin's quantity, sintering temperature and doping with 5 wt% of additives on properties of porous mullite ceramic was analysed. MgO partially stabilized ZrO₂, MgO and WO₃ as doping additives were used.
- 2. The decrease of kaolin content reduces the pH of suspension, because the kaolin suspension in water has pH=6.9. ZrO₂, MgO and WO₃ additives increase the pH value of the suspension and it becomes the alkaline (pH≥8.4), which accelerate chemical reaction of the aluminum and water, and the intensity of hydrogen gas elimination increases.
- 3. In the case of usage of WO₃ as additive and after sintering at the four different temperatures from 1200°C to 1500°C, the porosity of samples exceeds 40%. The samples doped with WO₃ and sintered at temperature of 1500°C have relatively low bulk density 1.29 g/cm³ and low shrinkage \approx 5%.
- 4. The sintering of samples doped with MgO and ZrO₂ at the temperatures 1300°C or 1500°C, respectively, sharply reduces the porosity (P \leq 16%) and increases the bulk density of the sample (\geq 1.70 g/cm³) which is associated with the formation of a liquid phase.
- 5. The results of thermal analysis show that in comparison with the output composition (30 wt% of kaolin) the MgO and WO₃ additives reduce the beginning temperature of mullite formation from 1234°C to \approx 1211°C. The MgO additive decreases the liquid phase formation temperature which accelerates the formation of mullite. The presence of WO₃ inhibits modification change of γ -Al₂O₃ to α -Al₂O₃, therefore the reaction of γ -Al₂O₃ with amorphous SiO₂ accelerates the formation of mullite. In the samples doped with ZrO₂ and sintered at temperature of 1650°C common content of mullite increases due to mullite formation by two parallel reactions.
- 6. In the samples doped with WO₃, the mullite phase becomes dominant already after sintering at the temperature of 1300°C that is lower than 200°C, by doping with MgO lower then 350°C and by doping with ZrO₂ lower than 400°C in comparison with undoped samples with 30wt% of kaolin.

- 7. The structure of undoped and with MgO and ZrO₂ doped samples contain prismatic mullite crystals with different size. The use γ -Al₂O₃ as raw material with large size particles (\approx 80 µm) and doping of compositions with WO₃ change the structure of samples and form crystalline mullite-corundum clusters.
- 8. The mechanical properties, thermal conductivity and thermal shock resistance of the samples depend on the porosity, pore size distribution, phase composition and structure of the material.
- 9. A similar pores size in the samples provides increased bending strength and thermal shock resistance because the mechanical or thermal stresses don't localize around individual pores which could lead to break of samples.
- 10. Ceramic materials with higher porosity, relatively small pores and similar pore size distribution and a different structure have low thermal conductivity. The additives reduce the thermal conductivity of ceramic in the following order: WO₃>ZrO₂. Additive of tungsten oxide (WO₃) changes the phase composition and structure of the material, which prevents heat transfer and reduces the thermal conductivity of samples: $\lambda_{25^{\circ}}C = 0.93 \text{ W} / \text{m.K}$ and $\lambda_{900^{\circ}}C = 0.86 \text{ W} / \text{m.K}$
- 11. Ceramic materials with multiple crystalline phase composition, high porosity, relatively small pores and similar pore size distribution have increased thermal shock resistance. With WO₃ doped mullite ceramics sintered at 1500° C have good thermal shock resistance. This is due to the presence of the aluminum tungstate crystalline phase with a negative coefficient of linear thermal expansion in the samples. Mullite and corundum phases have a positive coefficient of linear thermal expansion and during the rapid change of temperature the thermal stresses in a material are mutually compensated and the modulus of elasticity remains unchanged.
- 12. Doping with WO₃ can change the properties of mullite ceramics: the porosity of the sample increases, the bulk density and thermal conductivity reduces while thermal shock resistance increases. The sintering temperature reduces by 250° C (from 1750 to 1500° C) in comparison with undoped ceramics. Thanks to low thermal conductivity and good thermal shock resistance this mullite ceramic can be used as a high-temperature thermal insulation material in rapidly changing temperature conditions.

STATEMENTS TO DEFEND

- 1. The highly porous mullite ceramics that are formed by slip casting method of concentrated suspension; and pores formation as result of chemical reactions is possible to get by doping of mullite ceramics with WO_3 .
- 2. The temperature of mullite phase's formation is possible to decrease by doping of mullite ceramics with WO₃. The doping with WO₃ allows to lowering the sintering temperature and provides the necessary properties of materials.
- 3. The developed composition of ceramic and synthesis conditions allow obtaining highly porous mullite ceramics with low thermal conductivity and improved thermal shock resistance.

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