The formation of phases with low or negative linear thermal expansion coefficient in porous mullite ceramics

Alacsony vagy negatív lineáris hőtágulási együtthatóval rendelkező fázisok kialakulása porózus mullit kerámiákban

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Abstract

Mullite ceramic has a low linear thermal expansion coefficient compared to other ceramics, such as alumina or zirconia ceramics. Applying porous mullite ceramics as modern refractory materials requires an extra reduction of linear thermal expansion. The main purposes of the investigation are the modification of porous mullite ceramic with WO_3 and differently stabilized ZrO_2 as well as in situ formation of crystalline phases with low or negative linear thermal expansion in such ceramic. Modified porous mullite ceramics were formed by slip casting the concentrated slurry of raw materials and were sintered at 1600 °C for 1 hour. Porosity of mullite ceramics obtained due to hydrogen gas evolution as a result of the reaction between the used aluminium paste and water. Using yttria stabilized zirconia (YSZ, 8 mol% Y_2O_3), magnesia stabilized zirconia (MSZ, 2.8 mol% MgO), WO_3 , α - and γ - Al_2O_3 , amorphous SiO_2 and kaolin allowed sintering the mullite ceramics with additional in situ formed crystalline phase of ZrSiO_4 and $\text{Al}_2(\text{WO}_4)_3$, which decreased the linear thermal expansion of certain porous mullite ceramics' samples. Used synthesis conditions allow to achieve stability of ZrSiO_4 and $\text{Al}_2(\text{WO}_4)_3$ phases. The differently stabilized zirconia additive had influence on the formation of ZrSiO_4 . Doubling the WO_3 content in the mixture of components increased the formation of $\text{Al}_2(\text{WO}_4)_3$ with a negative linear thermal expansion coefficient.

Keywords: powders, solid-state reaction, thermal expansion, mullite, $\text{Al}_2(\text{WO}_4)_3$

Kulcsszavak: porok, szilárd állapotbeli reakciók, hőtágulás, mullit, $\text{Al}_2(\text{WO}_4)_3$

1. Introduction

Mullite-based ceramic is an important type of refractory ceramic. Relatively low linear thermal expansion is very important for mullite ceramic application in conditions of rapidly changing temperatures [1]. The literature reports linear thermal expansion coefficient (LTEC) values for porous mullite ceramics ranging from 4.0 to $5.9 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$ (average between 30 °C and 1000 °C) [2]. The average LTEC of mullite ceramics can be decreased by adding materials with a low or negative linear thermal expansion coefficient or the in situ formation of additional crystalline phases with low LTEC during the ceramic sintering time. Previous research investigated whether the thermal expansion of mullite ceramics can be effectively decreased by modification with cordierite ($\alpha_{\text{cord}} \approx 0.5 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [3], aluminium titanate ($\alpha_{\text{alum. tit}} \approx 1 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [4, 5] and zircon ($\alpha_{\text{zircon}} \approx 4.1 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [6] due to low linear thermal expansion coefficient of these phases. The influence of phases with negative LTEC on the properties of mullite ceramics has not been well studied. Research on materials with a negative LTEC has been of high interest since the mid-20th century and continues to now [7-9]. Crystalline phases such as aluminium tungstate ($\text{Al}_2(\text{WO}_4)_3$) and zirconium tungstate ($\text{Zr}(\text{WO}_4)_2$) have an average negative linear thermal expansion coefficient. The LTEC of aluminium tungstate is $-1.5 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$ in the temperature

range from 25 to 850 °C [8], and the LTEC of zirconium tungstate is $-8.6 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$ from 0 to 777 °C [9]. According to the literature data, $\text{Al}_2(\text{WO}_4)_3$ formation can be observed by the co-precipitation reaction method, by the sol-gel method and from solid-state synthesis. The $\text{Al}_2(\text{WO}_4)_3$ formation temperature is in the 620–1050 °C range, and depends on the sintering method. The holding time at the formation temperature varies from 5 hours to much longer, about 30–40 hours [10, 11]. The particle size and the morphology of $\text{Al}_2(\text{WO}_4)_3$ depends on the treatment temperature and holding time. In the case of the co-precipitation reaction method, crystalline $\text{Al}_2(\text{WO}_4)_3$ formation occurred after firing the Al-W-precipitated composition at temperatures of 430 °C [12], 630 °C, 700 °C [13], 800 °C [11] and 830 °C [12] for 5 hours. The particle size of synthesized $\text{Al}_2(\text{WO}_4)_3$ powder was increased from 20 to 300 nm [12] or from 50 to 150 nm [13, 14] with increasing temperature. Koseva and Nikolov had concluded that in the case of the sol-gel modified Pechini method, the particle size of pure phase $\text{Al}_2(\text{WO}_4)_3$ was between 50 nm (at 620 °C for 12 hours) and 200 nm (at 830 °C for 36 hours) [10, 14]. Achary et al. [8] synthesized $\text{Al}_2(\text{WO}_4)_3$ by the solid-state reaction from Al_2O_3 and WO_3 at 900 °C for 42 hours followed by 1000 °C for 30 hours with

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intermittent grinding. Later Nikolov et al. [14] also synthesized pure $\text{Al}_2(\text{WO}_4)_3$ by this method at similar temperatures, but with a shorter holding time, respectively at 930 °C for 16 hours, at 990 °C and 1050 °C for 8 hours. Romao et al. prepared $\text{ZrW}_2\text{O}_8/\text{Al}_2\text{W}_3\text{O}_{12}$ ceramics composites by the solid-state reaction from yttria stabilized zirconia, monoclinic ZrO_2 , Al_2O_3 and WO_3 during sintering at 1200 °C, with holding times varying from 6 to 21 hours [15]. A ZrW_2O_8 phase, in turn, can be synthesized by the combustion method [16], by hydrothermal synthesis of raw compounds at 160 °C for 36 hours with further sintering at 570 °C for 1 hour [17, 18], by the co-precipitation reaction with drying at 60–80 °C and firing at 1150 °C for 10 hours, and by the sol-gel method with firing at 600 °C for 10 hours [18]. From the literature, ZrW_2O_8 is stable in a narrow temperature range from 1105 to 1257 °C, but this phase decomposes to ZrO_2 and WO_3 at about 700–850 °C, respectively. The melting temperature of this phase is above 1257 °C [15–18].

The aim and novelty of this work is to investigate the use of ZrO_2 and WO_3 additives for the in situ formation of phases with negative LTEC, ($\text{Al}_2(\text{WO}_4)_3$ and ZrW_2O_8), in porous mullite ceramics sintered from powder raw materials by a solid-state reaction method.

2. Materials and methods

2.1 Raw materials and sample preparation

Materials	Average particle size, d_{50} (μm)	Name, Manufacturer
$\alpha\text{-Al}_2\text{O}_3$	2.0	Nabalox NO 725, Nabaltec AG, Germany
$\gamma\text{-Al}_2\text{O}_3$	80.0	Nabalox NO 201, Nabaltec AG, Germany
SiO_2 amorphous	3.0–5.0	GetNanoMaterials, France
Kaolin (SiO_2 – 56.5 wt%, Al_2O_3 – 31.0 wt%)	1.5	MEKA, Amberger Kaolinwerke, Germany
ZrO_2 stabilized by 8 mol% Y_2O_3	0.5	GetNanoMaterials, France
ZrO_2 stabilized by 2.8 mol% MgO	0.8	Goodfellow, United Kingdom
WO_3	5.0	GetNanoMaterials, France
Aluminium paste (solid content of 70 ± 2%)	12.0	Aquapor-9008, Schlenk Metallic Pigments GmbH, Germany

Table 1 Raw material specifications

1. táblázat A felhasznált alapanyagok pontos megnevezése

Commercially available raw powders, such as $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, amorphous SiO_2 , kaolin, two types of ZrO_2 and WO_3 were used for ceramics materials samples preparation. Table 1 summarises the raw materials specifications. In all compositions, the amount of kaolin was 30 wt%, the ratio of Al_2O_3 to SiO_2 was 2.57:1 and the ratio of $\alpha\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$ was 1:3. The ratio of Al_2O_3 to SiO_2 corresponded to the mullite stoichiometric composition, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The ratio of $\alpha\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$ was determined as effective in previous studies [19]. Yttria stabilized zirconia (YSZ, 8 mol% Y_2O_3), magnesia

stabilized zirconia (MSZ, 2.8 mol % MgO) and WO_3 were used as modification additives. 5 wt% of each type of zirconia was used, both separately as well as in a mixture with WO_3 in a 1:1 and 1:2 ratio. Aluminium paste (0.18 wt%) was used as a pore-forming agent to prepare porous mullite ceramic.

Slip casting the concentrated slurry of raw materials was used for samples preparation. The water content of the concentrated slurry was 38–40 wt%. The method and process of samples preparation were described in more detail in previous articles [19–21]. The dried samples were sintered at 1600 °C with a 250 °C/h (4.2 °C/min) heating rate and the holding time at maximum temperature was 1 hour. The fired samples cooling process was as slow as the heating process.

2.2 Characterisation

Appropriate equipment was used to analyse the crystallographic phases, different phase transformations and reactions in the samples at the heating treatment time and the sintered sample microstructure. X-ray powder diffraction (XRD) was carried out with a Rigaku Ultima+ (Japan) using Cu K_α radiation and operating at 30 kV and 20 mA. XRD patterns were scanned in the 5–60 2 θ° measurement angle range with a 0.02° step and a 2°/min goniometer scanning rate. Differential thermal analysis was done using „SETSYS Evolution TGA-DTA/TMA SETARAM”. The heating for DTA was 12 °C per minute at a temperature range from 0 to 1300 °C with air as the carrier gas. The samples microstructures were analysed using two scanning electron microscopes (SEM), -Hitachi TableTop Microscope TM3000 and high-resolution field emission low vacuum scanning electron microscope (FEI Nova NanoSEM 650). The samples were observed in low vacuum mode eliminating the need for metal coating sputtering. The sample elemental composition was determined using energy-dispersive X-ray spectroscopy (EDX) with an X-ray fluorescence spectrometer (Apollo X SDD) created by TEAMTM Integrated EDX. The shrinkage after ceramics' sintering and bulk density of the samples was calculated mathematically. The determination of apparent porosity and water uptake was based on the Archimedes principle according to the European standard EN 623-2. The temperature dependence of the linear thermal expansion coefficient for sintered samples was determined by high temperature horizontal dilatometer L76/1600 D (Linseis, Selb, Germany).

3. Results and discussion

3.1 X-ray diffraction

The X-ray diffraction patterns in Fig. 1 represent the phase compositions of samples with yttria stabilized zirconia and magnesia stabilized zirconia additives. The mullite phase was the dominant phase of the samples for both raw material compositions, which were sintered at 1600 °C. The ZrO_2 phase was mainly expressed in monoclinic modification in both samples. Cubic ZrO_2 was detectable in samples with yttria stabilized zirconia, but tetragonal ZrO_2 modification observed in samples with magnesia stabilized zirconia. The corundum phase was found in the samples with YSZ additive (Fig. 1 (a)) as opposed to samples with MSZ (Fig. 1 (b)).

Fig. 1 XRD patterns of the samples with ZrO_2 additives: (a) with YSZ, (b) with MSZ
1. ábra ZrO_2 -t tartalmazó minták röntgen diffrakciós analízisének eredménye: (a) YSZ-t tartalmazó, (b) MSZ-t tartalmazó

Fig. 2 XRD patterns of the samples with ZrO_2 and WO_3 additives in the ratio of 1:1: (a) with YSZ and WO_3 , (b) with MSZ and WO_3
2. ábra ZrO_2 -t és WO_3 -t 1:1 arányban tartalmazó minták röntgen diffrakciós analízisének eredménye: (a) YSZ-t és WO_3 -t tartalmazó, (b) MSZ-t és WO_3 -t tartalmazó

Fig. 2 shows the XRD patterns of the samples with YSZ or MSZ addition in a 1:1 ratio in the mixture with WO_3 , sintered at 1600 °C. The mullite and monoclinic ZrO_2 were the main phases of these samples. Tetragonal ZrO_2 and corundum phases were not detectable. The intensity peaks of WO_3 were less definite for samples with YSZ and WO_3 (1:1) than for samples with MSZ and WO_3 (1:1). The XRD pattern in Fig. 2 (b) shows that zircon was formed as an additional phase after firing in samples with MSZ and WO_3 (1:1). In the samples with the addition of only YSZ or MSZ (Fig. 1 (a) and (b)) and with the YSZ: WO_3 =1:1 (Fig. 2 (a)), the zircon phase was not observed. This is because the presence of stabilizers such as Y_2O_3 and MgO, respectively from YSZ and MSZ, led to the forming a liquid phase in the Y_2O_3 - Al_2O_3 - SiO_2 system at 1550 °C and MgO- Al_2O_3 - SiO_2 at 1450–1550 °C that promoted zircon dissociation with subsequent mullite phase formation [22]. In the case using YSZ, this influence was much more pronounced due to the higher amount of Y_2O_3 as a stabilization additive rather than MgO, respectively 8 mol% and 2.8 mol%. Using the WO_3 prevented liquid formation in the MgO- Al_2O_3 - SiO_2 system, and zircon was retained in the phase composition of synthesized mullite ceramics with MSZ and WO_3 (1:1), unlike the samples with YSZ and WO_3 (1:1).

The XRD patterns in the $2\theta^\circ$ range from 20° to 24° (Fig. 2 (a) and (b)) show the mixture of crystalline and amorphous phases for both samples with ZrO_2 and WO_3 (1:1). The presence of separate peaks on the XRD patterns of these compositions in the $2\theta^\circ$ range from 20° to 24°, at 32°, 35° and 43° corresponded to the aluminium tungstate phase.

Doubling the WO_3 amount contributed to the zircon and aluminium tungstate formation in both sample compositions with two types of stabilized ZrO_2 (Fig. 3 (a) and (b)). In the case of these samples, the number of intensity peaks ZrO_2 phase decreased due to ZrO_2 participation in forming $ZrSiO_4$. The location of t- ZrO_2 in the neighbourhood of amorphous SiO_2 promoted zircon formation at a lower temperature by a diffusion reaction. Zircon formation in the corresponding ceramic samples was proposed to occur via several successive reactions. First, $ZrSiO_4$ began forming by reacting t- ZrO_2 with amorphous SiO_2 at about 1200 °C. Then, zircon formation continued by the reaction of t- ZrO_2 with cristobalite at 1400–1470 °C owing to the crystallization and corresponding modification of SiO_2 . Complete formation of this phase occurred by the reaction of m- ZrO_2 with cristobalite after ~1580 °C due to t- ZrO_2 gradually transforming into m- ZrO_2 with an increase in temperature because of the decrease in excess surface energy [23–26]. In turn, increasing the WO_3 amount also prevented liquid formation and zircon dissipation in the case of samples with YSZ and WO_3 (1:2). 1600 °C was not high enough for decomposing $ZrSiO_4$ to ZrO_2 and SiO_2 according to the literature [23]. The mullite phase also remained dominant in these samples, but the intensity of this phase's diffraction maximums decreased (Fig. 3) because the Al_2O_3 and SiO_2 mullite components were used forming phases such as aluminium tungstate and zircon. The intensity of aluminium tungstate phase diffraction maximums increased in samples with ZrO_2 and WO_3 additives (1:2) due to the increasing WO_3 amount. The ZrW_2O_8 phase was not observed in sintered samples compositions. The XRD pattern of the ceramic material with YSZ: WO_3 (1:2) shows the significant presence of WO_3 phase than in samples with MSZ: WO_3 (1:2).

Fig. 3 XRD patterns of the samples with ZrO_2 and WO_3 additives in the ratio of 1:2: (a) with YSZ and WO_3 , (b) with MSZ and WO_3

3. ábra ZrO_2 -t és WO_3 -t 1:2 arányban tartalmazó minták röntgen diffrakciós analízisének eredménye: (a) YSZ-t és WO_3 -t tartalmazó, (b) MSZ-t és WO_3 -t tartalmazó

3.2 Differential thermal analysis

The DTA curves for heating and cooling the MEKA kaolin and the non-sintered sample compositions are shown, respectively, in Fig. 4 and Fig. 5. In the DTA plots (Fig. 4) for all samples, the first endothermic peak at about 180 °C represented the elimination of free water absorbed between the particles. In the case of kaolin (Fig. 4 (a)), the second strong endothermic peak at 530 °C corresponded to the dehydroxylation of kaolinite and the formation of metakaolinite [27]. The dehydroxylation

process should be considered a crystal-chemical process of the kaolinite's bilayer lattice changing with the absorption of a significant amount of heat [28-31]. The exothermic effect in the 647 to 660 °C temperature range defined the crystallization of some amorphous phase [32]. The sharp exothermic peak within 1000 °C was due to the formation of new crystalline phases such as a Si-containing γ - Al_2O_3 with spinel structure plus amorphous SiO_2 or a 2:1 mullite plus amorphous SiO_2 [30, 31]. Then, the mullite phase ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formation and cristobalite were followed at about 1235–1245 °C, which is represented as a gently sloping exothermic peak [30, 31].

Fig. 4 DTA for samples, heating curves: (a) kaolin, (b) with YSZ, (c) with MSZ, (d) with YSZ:WO₃ (1:1), (e) with MSZ:WO₃ (1:1), (f) with YSZ:WO₃ (1:2), (g) with MSZ:WO₃ (1:2)

4. ábra Differenciális termoanalízisből származó fűtési görbék egyes mintákra: (a) kaolin, (b) YSZ-t tartalmazó, (c) MSZ-t tartalmazó, (d) YSZ:WO₃ (1:1) arányban tartalmazó, (e) with MSZ:WO₃ (1:1) arányban tartalmazó, (f) with YSZ:WO₃ (1:2) arányban tartalmazó, (g) with MSZ:WO₃ (1:2) arányban tartalmazó

Fig. 5 DTA for samples, cooling curves: (a) kaolin, (b) with YSZ, (c) with MSZ, (d) with YSZ:WO₃ (1:1), (e) with MSZ:WO₃ (1:1), (f) with YSZ:WO₃ (1:2), (g) with MSZ:WO₃ (1:2)

5. ábra Differenciális termoanalízisből származó hűtési görbék egyes mintákra: (a) kaolin, (b) YSZ-t tartalmazó, (c) MSZ-t tartalmazó, (d) YSZ:WO₃ (1:1) arányban tartalmazó, (e) with MSZ:WO₃ (1:1) arányban tartalmazó, (f) with YSZ:WO₃ (1:2) arányban tartalmazó, (g) with MSZ:WO₃ (1:2) arányban tartalmazó

The DTA thermal behaviour of the samples compositions with YSZ and MSZ demonstrated processes similar to those seen in heating pure kaolin: the dehydroxylation of kaolinite at about 514 °C, spinel structure or primary mullite formation with amorphous SiO_2 at 1000 °C and secondary mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formation at about 1200 °C. The DTA curves of the samples with a mixture of ZrO_2 and WO_3 in a 1:1 and 1:2 ratio showed an endothermic peak at about 400–460 °C (Fig. 4 (d–g)), which indicated the WO_3 phase transformation from the monoclinic modification to the orthorhombic [33–35]. The exothermic peak within 1000 °C for all samples with a ZrO_2 and WO_3 mixture was smaller than for kaolin and samples without WO_3 . It is important to note that after this small exothermic peak at 1000 °C, an endothermic peak immediately followed at 1015–1090 °C, which was also characteristic of all samples with a mixture of ZrO_2 and WO_3 . This can be explained by the combination of two processes that came at relatively the same time in the 950–1090 °C range. Therefore, the exothermic peak at 1000 °C corresponded to one of the stages of the thermal conversion of kaolin, which was described above, and the subsequent endothermic peak was associated with the formation of zirconium tungstate from ZrO_2 and WO_3 [16, 17, 36]. This was also confirmed by the behaviour of the cooling curves (Fig. 5 (d–g)). The elongated endothermic peak of the cooling curves at the 1185–1200 °C region was due to the formation of zirconium tungstate at the samples cooling as verified by the ZrO_2 and WO_3 system phase diagram [37] and the works of Dedova and Lommens [17, 36], and is not typical behaviour of an unmodified mullite ceramic DTA cooling curve. The ZrW_2O_8 phase intensity peaks were not observed in the XRD patterns after sample sintering because ZrW_2O_8 melting occurs above 1257 °C [17, 33], which is lower than the sample sintering temperature. ZrW_2O_8 was not present after slowly cooling the samples due to the decomposition of this phase into ZrO_2 and WO_3 within the narrow 770–825 °C temperature range [16, 36, 37]. ZrW_2O_8 decomposing into oxides caused a smooth rise in the DTA cooling curves from 825 °C to lower temperatures (Fig. 5 (d–g)).

The $\text{Al}_2(\text{WO}_4)_3$ formation is shown in the sample heating DTA curves (Fig. 4 (d–g)) as an exothermic effect at 1075–1100 °C. The mullite phase formed at temperatures higher than 1200 °C in the case of a mixture of differently stabilized zirconia and WO_3 in a 1:1 and 1:2 ratios. The wide exothermic peak of the cooling curves (Fig. 5 (d–g)) for samples with YSZ and WO_3 (1:1) at 1055 °C was due to the formation of aluminium tungstate while cooling, as verified by the Al_2O_3 – WO_3 system phase diagram [38, 39]. For samples with the addition of $\text{MSZ:WO}_3=1:1$, $\text{YSZ:WO}_3=1:2$ and $\text{MSZ:WO}_3=1:2$, the $\text{Al}_2(\text{WO}_4)_3$ formation also occurred while cooling but at lower temperatures, respectively at ~905 °C, ~878 °C and ~875 °C. The $\text{Al}_2(\text{WO}_4)_3$ formation temperature was lower in case of mullite ceramics with MSZ and WO_3 mixture of both ratios.

3.3 Scanning electron microscopy

SEM micrographs showing the microstructure of samples with the YSZ additive are presented in Fig. 6. The structure of these samples was composed of densely packed, elongated mullite crystals, which are located in a glassy phase (Fig. 6 (a))

and (b)). The glassy phase was formed with the participation of yttrium oxide and increased the sintering of the samples. Sample fracture occurred in the glassy phase at the time of sample preparation for the SEM (samples were broken in half), which is visible in Fig. 6 (c). The SEM micrograph from the TableTop SEM Microscope TM3000 (Fig. 6 (a)) shows large and small white inclusions, which confirm the presence of ZrO_2 .

Fig. 6 SEM micrographs of the microstructure of sintered samples with YSZ
6. ábra Az YSZ-t tartalmazó szinterelt mintákról mikroszerkezetéről pásztázó elektronmikroszkóppal készített felvételek

The structure of ceramics samples with the MSZ additive was similar to the structure of the samples with YSZ (Fig. 7 (a) and (b)). The white particles in the SEM micrographs (Fig. 7 (a)) for samples with MSZ showed that m- ZrO_2 particles have a smaller size and are more uniformly distributed in the sample structure after sintering.

Fig. 7 SEM micrographs of the microstructure of sintered samples with MSZ
7. ábra Az MSZ-t tartalmazó szinterelt mintákról mikroszerkezetéről pásztázó elektronmikroszkóppal készített felvételek

Fig. 8 SEM micrographs of the microstructure of sintered samples with YSZ and WO_3 additive in a 1:1 ratio
8. ábra Az YSZ-t és WO_3 -at 1:1 arányban tartalmazó szinterelt mintákról mikroszerkezetéről pásztázó elektronmikroszkóppal készített felvételek

The sample structure changed with the use of a ZrO_2 and WO_3 mixture in the case of both ratios of these oxides. The structure of samples with $YSZ:WO_3=(1:1)$ was formed from needle-like mullite crystals. Parts of the mullite crystals were covered by a continuous glassy phase that was white in the SEM micrograph from the TableTop SEM (Fig. 8 (a)). The structure of these samples also contained granular inclusions.

Table 2 presents the elemental compositions of samples' certain areas after EDX point analysis. EDX analysis results showing that some grains were ZrO_2 , other grains were aluminium tungstate, respectively EDX points 1 and 2 in Fig. 8 (b) and in Table 2. The mullite crystals were distinguishable at the larger magnification (Fig. 8 (b-e)) after using the high-resolution SEM (FEI Nova NanoSEM 650). The EDX results (EDX point 3) in Fig. 8 (c) and data in Table 2 show that the existing amorphous phase contained a higher weight per cent of elements such as O, Al, Si, W and a lower weight per cent of Zr and Y, which can correspond to the alumina-silica glassy phase [40] and alumina-tungstate glassy phase with dissolved ZrO_2 and Y_2O_3 . This amorphous part of the samples contained crystalline grains (Fig. 8 (c), EDX point 2), which were identified as aluminium tungsten crystalline grains after the EDX analysis. Some mullite crystals contained relatively small white points (Fig. 8 (a)), which were another phase. The SEM micrographs at the higher magnification (Fig. 8 (d) and (e)) demonstrated small crystals on the surface of the mullite crystals. These crystals were identified as aluminium tungstate crystals by the results of the EDX point analysis (point 2) in Table 2.

Fig. 9 shows the structure of the samples with MSZ and WO_3 in a 1:1 ratio. Relatively fine particles (marked in light grey in Fig. 9. (a)) were distributed in the sample structure. These faceted crystals were zircon, by the EDX analysis (EDX point 4 and 5) (Fig. 9. (a-c) and Table 2). The prismatic mullite crystals in these samples are relatively thinner and longer than mullite crystals of the $YSZ:WO_3=(1:1)$ samples.

Fig. 9 SEM micrographs of the microstructure of sintered samples with MSZ and WO_3 additive in a 1:1 ratio
9. ábra Az MSZ-t és WO_3 -at 1:1 arányban tartalmazó szinterelt mintákról mikroszerkezetéről pásztázó elektronmikroszkóppal készített felvételek

Element	Point 1		Point 2		Point 3		Point 4		Point 5	
	Weight %	Atom %	Weight %	Atom %	Weight %	Atom %	Weight %	Atom %	Weight %	Atom %
O	37.1	72.7	39.3	61.7	39.1	66.6	34.9	66.5	46.4	69.1
Al	4.9	5.6	30.8	28.6	15.9	16.1	-	-	13.3	11.8
Si	2.3	2.6	7.1	6.3	11.3	11.0	16.7	18.5	14.6	12.4
W	-	-	22.9	3.4	26.9	4.0	-	-	-	-
Zr	55.7	19.1	-	-	2.8	1.1	48.4	15.0	25.7	6.7
Y	-	-	-	-	4.0	1.2	-	-	-	-

Table 2 The elemental compositions of samples' certain plots after EDX point analysis
2. táblázat Az EDX (energia diszperzív röntgensugár) analízis egyes pontjaiban a minták elemi összetételei

The structures of samples with YSZ:WO₃ and MSZ:WO₃ in a 1:2 ratio were formed from crystal agglomerates of mullite and aluminium tungstate crystals. The aluminium tungstate crystals were located on and between the mullite crystals (Fig. 10 and Fig. 11). Comparing the SEM micrographs of samples with YSZ:WO₃ mixtures in ratios of (1:1) and (1:2) in Fig. 8 and Fig. 10, the quantity of aluminium tungstate crystals increased with increasing WO₃ quantity. In turn, thinner mullite crystals were randomly located among the larger mullite crystals. The presence of aluminium tungstate crystals in samples with MSZ:WO₃ also became noticeable after increasing the WO₃ quantity (Fig. 11. (b) and (c)).

Fig. 10 SEM micrographs of the microstructure of the sintered samples with YSZ and WO₃ additive in a 1:2 ratio

10. ábra Az YSZ-t és WO₃-at 1:2 arányban tartalmazó sinterelt mintákról mikroszerkezetéről pásztázó elektronmikroszkóppal készített felvételek

Fig. 11 SEM micrographs of the microstructure of the sintered samples with MSZ and WO₃ additive in a 1:2 ratio

11. ábra Az MSZ-t és WO₃-at 1:2 arányban tartalmazó sinterelt mintákról mikroszerkezetéről pásztázó elektronmikroszkóppal készített felvételek

The possible growth of aluminium tungstate crystals on the mullite crystals occurred from the Al₂O₃ and WO₃ solid-state reaction during sintering and from the alumina-tungstate liquid phase during cooling. The nucleation and growth of aluminium tungstate crystals proceeded in possible defect sites on mullite crystals. Supersaturation of the alumina-tungstate liquid phase occurred with increasing WO₃ in samples with YSZ:WO₃ (1:2) and MSZ:WO₃ (1:2) mixtures and aluminium tungstate crystalline grains continued to grow.

3.4 Shrinkage, bulk density and apparent porosity of the sintered samples

The ceramics samples, modified only with YSZ or MSZ, have shrinkage higher than 35±1% and bulk density 1.55±0.05 g/cm³ (Fig. 12). Using the mixture of stabilized ZrO₂ and WO₃ additive decreases the shrinkage and bulk density of the samples. The results of the bulk density decrease with increasing of the samples apparent porosity (Fig. 13). The apparent porosity of all samples compositions is higher than 40% and maximum porosity is 66–73%. The samples with YSZ:WO₃ (1:1) and MSZ:WO₃ (1:2) have porosity about 63–66% and the bulk density of 1.24±0.05 g/cm³. Modifying of the porous mullite ceramics with mixture of magnesia stabilized zirconia and WO₃ has higher influence on the apparent porosity and water uptake of the samples than the yttria stabilized zirconia in mixture with WO₃. The mixture of MSZ and WO₃ in a 1:1 ratio caused increasing of the apparent porosity of ≈15%, but these

oxides mixture in a 1:2 ratio caused increasing of the apparent porosity of ≈11%, respectively in comparison with YSZ:WO₃ (1:1) and YSZ:WO₃ (1:2). Doubling the WO₃ amount slightly decreases the porosity.

Fig. 12 Shrinkage and bulk density of the sintered samples
12. ábra A sinterelt minták zsugorodása és testsűrűsége

Fig. 13 Apparent porosity and water uptake of the samples
13. ábra A minták látszólagos porozitása és vízfelvétele

3.5 Linear thermal expansion of the sintered samples

The analysis of the thermal property in Fig. 14 shows that samples only with YSZ or MSZ have the similar linear thermal expansion as the pure mullite ceramics due to the mullite phase dominance in these samples. The presence of such phases as zircon ($\alpha_{\text{zircon}} = 4.1 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [6] and aluminium tungstate ($\alpha_{\text{aluminium tungstate}} = -1.5 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [8] decreased the linear thermal expansion of samples with YSZ:WO₃ mixture in a 1:1 ratio and with MSZ:WO₃ in a 1:2 ratio. At the same time, samples with YSZ:WO₃ mixture in a 1:2 ratio and with MSZ:WO₃ in a 1:1 ratio, containing unreacted WO₃ (confirmed by XRD results), have higher expansion due to the high linear expansion coefficient of WO₃ ($\alpha_{\text{tungsten oxide}} = 13\text{--}15 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [8, 9]. The expansion of samples with the ZrO₂ and WO₃ mixture decreases in the temperature range approximately from

950 to 1020 °C due to the formation of zirconium tungstate ($\alpha_{\text{zirconium tungstate}} = -8.6 \cdot 10^{-6} \cdot ^\circ\text{C}^{-1}$) [9] from ZrO_2 and WO_3 during the heating and at these temperatures the ceramic materials have an effect of contracting.

Fig. 14 Temperature dependence of the linear thermal expansion coefficient for sintered samples: 1 - with YSZ, 2 - with MSZ, 3 - with YSZ:WO₃ (1:1), 4 - with MSZ:WO₃ (1:1), 5 - with YSZ:WO₃ (1:2), 6 - with MSZ:WO₃ (1:2)

14. ábra A szinterelt minták lineáris hőtágulási együtthatójának hőmérséklet függése: 1 - YSZ-t tartalmazó, 2 - MSZ-t tartalmazó, 3 - YSZ-t és WO₃-at 1:1 arányban tartalmazó, 4 - MSZ-t és WO₃-at 1:1 arányban tartalmazó, 5 - YSZ-t és WO₃-at 1:2 arányban tartalmazó, 6 - MSZ-t és WO₃-at 1:2 arányban tartalmazó

4. Conclusions

Modified porous mullite ceramics were fabricated by slip casting a concentrated slurry of raw materials and were sintered at 1600 °C for 1 h with a slow cooling process. It was established that the in situ formation of crystalline phases with low or negative LTEC in mullite ceramics can be found after adding YSZ (8 mol% Y₂O₃) or MSZ (2.8 mol% MgO with WO₃ mixture in a 1:1 and 1:2 ratio at the correspond sintering conditions. These synthesis conditions are much simpler than the applicable methods and long holding time considered above from literature date, which is an advantage for obtaining porous mullite ceramics. Only Al₂(WO₄)₃ or two crystalline phases, ZrSiO₄ and Al₂(WO₄)₃, were formed into the porous mullite ceramics after its modification with metal oxides such as differently stabilized zirconia and WO₃. The Zr(WO₄)₂ phase was not detectable due to the not appropriate firing-cooling process, which does not allow remaining this phase in phase composition of investigated mullite ceramics. The 8 mol% Y₂O₃ stabilized zirconia additive has higher influence on decreasing temperature of ZrSiO₄ dissociation than 2.8 mol% MgO stabilized zirconia. Using the certain amount of WO₃ prevent the ZrSiO₄ dissociation in mullite ceramic modified with ZrO₂ and WO₃. Addition of the 2.8 mol% MgO stabilized zirconia in mixture with WO₃ increases the porosity of mullite ceramic. Sintered porous mullite ceramics with YSZ:WO₃ mixture in a 1:1 ratio and with MSZ:WO₃ in a 1:2 ratio have the potential application in conditions of elevated temperatures ≥1200 °C as thermal insulator with lowered linear thermal expansion.

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