

Porous Cordierite Ceramics from Natural Clays

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Abstract — In this report the obtaining and properties of high-temperature porous ceramic materials using local carbonate clays and quartz sand resources was studied. Materials with two different porosities were obtained by using different synthesis temperatures. The test results show that these materials contain cordierite as their main crystalline phase. The porosity directly influences the compressive strength and it is greatly reduced when overall porosity increases. The CTE of obtained materials is low – about $3\text{--}10^{-6}$ 1/°C.

Keywords — Clay, cordierite, pore ceramic, solid-state synthesis.

I. INTRODUCTION

Ceramic materials containing cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) as the main crystalline phase are well known for their outstanding thermal properties. Such materials are usually characterized by their low coefficient of thermal expansion (about $1.5\text{--}4.0\cdot 10^{-6}$ 1/°C) and high resilience towards thermal shocks [1]. Since natural cordierite is a rare substance, in most cases this material is produced by synthesis using either solid-state, sol-gel or glass recrystallization methods [2]. The artificial production is the result of the wide varieties of possible applications of cordierite that include, but are not limited to, substrate materials for catalytic converters and electronic circuitry boards for microelectronics, electronic packing, and insulation material for furnaces and crucible materials – all of which are mainly to replace alumina products [3]. In order for cordierite materials to be able to successfully compete with alumina not only cordierite materials must have similar or better properties, but also lower production costs; production costs are mainly influenced by the raw materials used and final synthesis temperature [4].

Although some of the cordierite properties like flexural and compressive strength pale in comparison to properties of alumina, they are of lesser importance in case of a porous ceramic material; whereas thermal properties, especially the coefficient of thermal expansion, have higher importance. In some cases CTE of cordierite substrate must be tailored to that of silica (about $4\cdot 10^{-6}$ 1/°C) in order to avoid delamination and cracking that is the result of local thermal gradient [5]. In order to achieve this state, several cordierite composites with mullite [6], SiC [7], ZrO_2 [8] and others have been proposed, all of which use solid-state synthesis.

Current production temperature of pure cordierite ceramics using solid-state synthesis is close to its melting point that is about 1400 °C, if a mixture of magnesia, silica and alumina is used. Since the melting point of pure cordierite (about 1440 °C) is very close to the synthesis temperature that is usually employed, it is rather difficult to produce the desired products

that are not deformed [2]. Required temperature can be lowered, if various other raw materials like kaolin and talk are used instead. In some cases artificial fluxes like B_2O_3 are introduced in to the mix. However, this leads to deterioration of final product properties, namely, its thermal expansion coefficient and other related properties [9].

Other commonly employed cordierite preparation methods are sol-gel method and recrystallization from melts. Both are very advantageous methods, if compared to conventional solid-state synthesis. Sol-gel method, for example, allows the synthesis of cordierite at temperatures that are below 1000 °C. The obtained materials also are highly pure and their stoichiometric composition can be fine-tuned precisely. This is accomplished due to liquid-state (either aqueous or non-aqueous) chemical reactions that already take place at room temperature. Further increase of synthesis temperature is mainly for grain growth; the grains are usually nano-level at the start of synthesis and therefore highly reactive. This is the main reason for exceptionally low sintering temperatures [10]. The main disadvantage of this method (which is common for synthesis of any related material) is the high cost of raw materials, which, in turn, is due to the high purity required from these materials. Also, toxicity (Al and Mg organic compounds and TEOS is usually used) and cost are the main reason why this particular method is not applicable to a large scale production; if anything, sol-gel method is therefore more favorable for small-scale production of coatings, powders, single crystals, etc.

Glass melt recrystallization, on the other hand, is a similar method in terms of purity requirements. It also employs the use of high temperatures that exceed even those of solid-state synthesis. It is due to the need to completely melt the mixture of raw ingredients and, therefore, this temperature is no less than 1600 °C. The following steps definitely include repeated heating of obtained glass frit in order to induce cordierite crystallization in the final material [10]. The main advantage of this method is that the natural raw minerals can also be employed, provided that they are previously purified (which is required in order to precisely control crystallization product). The obtained material is glass-ceramic with varying crystal phase content; it usually does not exceed 80 %.

Natural raw minerals have a great potential to substitute either synthetic components, such as alumina, or traditionally used raw materials, such as talc. Natural clays which, among other components, usually consist of no less than 50 % of SiO_2 are suitable candidates, if required cordierite stoichiometry is maintained by a proper amount of additives, mainly in the form of a magnesia source. Moreover, carbonate containing clays are even more beneficial raw material due to additional amount of MgO, thus requiring lesser amount of synthetic source material.

II. MATERIALS AND METHODS

Illite clays containing carbonates from Apriki and Nicgale deposits were used in preparation of pre-ceramic powder as the mineral raw materials of Latvian origin. Oxide compositions of these clays are given in Table I.

TABLE I

OXIDE COMPOSITION OF USED CLAYS IN WT%

Clay	SiO ₂	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃ + TiO ₂	Na ₂ O + K ₂ O	LOI*
Apriki	53.0	15.8	2.8	6.4	6.3	3.9	11.8
Nicgale	51.0	16.5	2.4	6.8	6.3	5.0	11.4

* — Loss of ignition

Ground quartz sand (> 98 % purity) from Bale quarry was used as a SiO₂ source. Required stoichiometry was adjusted with the help of MgCO₃ and Al(OH)₃ (99.99 % purity, *Sigma Aldrich*) so that the theoretical composition of cordierite was achieved. The compositions are summarized in Table II.

Raw mixtures were ground in water medium with 1:1,5 ratio for 2 h in planetary ball mill (agate container and grinding bodies). All mixtures were dried in a laboratory oven at 60 °C for 24 h. Dry samples were crushed in a mortar into powders and pressed into cylindrical samples with height:diameter ratio 1:1 for compression tests and 1:5 for testing of CTE.

Compaction was done with uniaxial hydraulic press using 15 MPa pressure.

TABLE II

COMPOSITIONS OF PREPARED SAMPLES IN WT%.

Sample	Clay	Amount of clay	Sand	MgCO ₃	Al(OH) ₃
A5	Apriki	33.6	22.5	16.0	27.2
N5	Nicgale	33.2	24.2	17.0	26.2

Prepared samples were fired in a muffle furnace with heating rate of 6 °C/min and residence in maximum temperatures (1250 °C and 1300 °C) was 3 h.

Crystalline phase composition of the powdered samples was determined using powder X-ray diffraction (*Rigaku Ultima* apparatus, Cu K α radiation; scanning rate — 4 °/min, 2 θ range — 5–50°). Bulk density and apparent porosity were determined using Archimedes' water immersion method. Compressive strength was determined using *ToniNorm* compression test plant (*Zwick*, Germany). CTE of samples was determined using a horizontal dilatometer (*Linseis L76 Platinum Series*, Germany) with temperature range of 20–1000 °C and heating rate of 10 °C/min. SEM images of sample surface were taken using *Hitachi Tabletop 3000* apparatus.

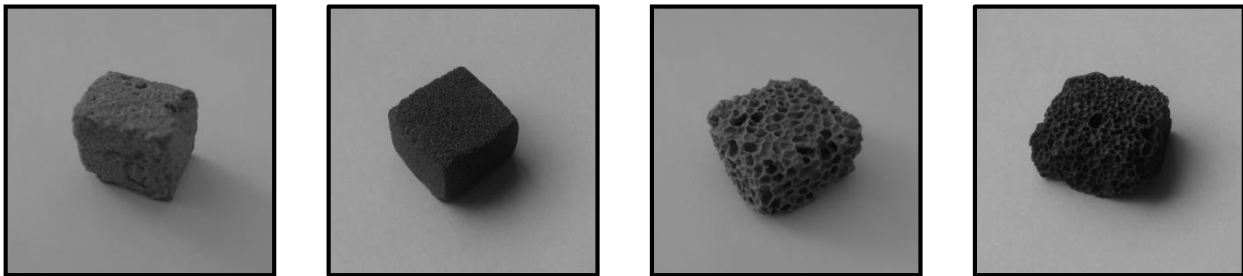


Fig. 1. Photo images of samples N5 (a and c) and A5 (b and d) synthesized at 1250 °C (a and b) and 1300 °C (c and d).

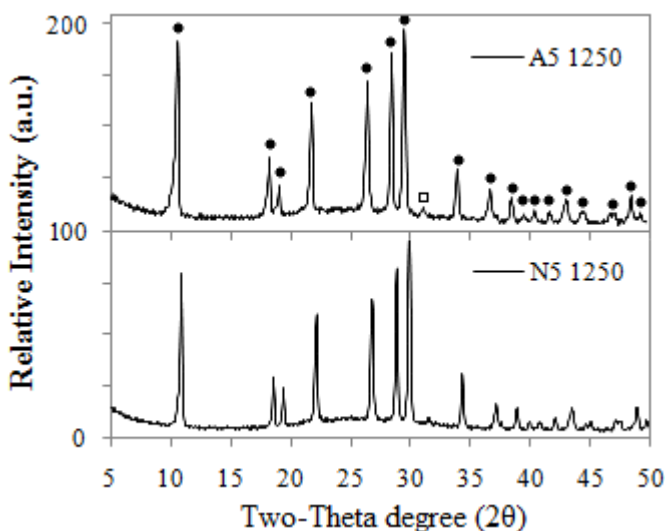


Fig. 2. X-ray diffraction patterns of samples A5 and N5 synthesized at 1250 °C. ● — cordierite, □ — spinel.

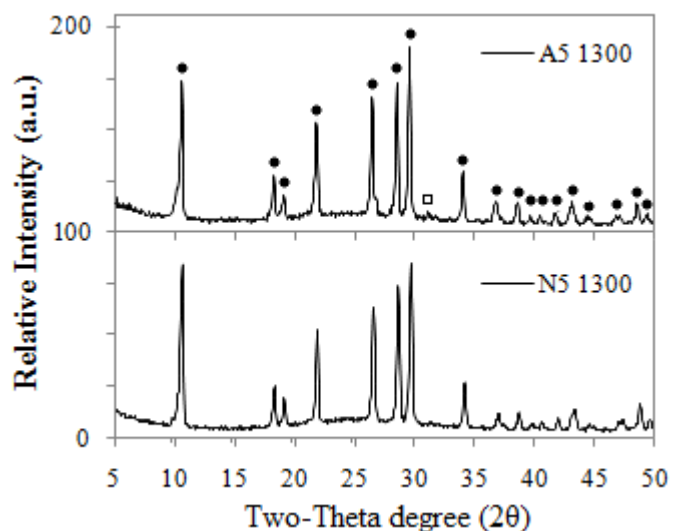


Fig. 3. X-ray diffraction of samples A5 and N5 synthesized at 1300 °C. ● — cordierite, □ — spinel.

III. RESULTS AND DISCUSSION

Obtained samples can be visually examined in Fig. 1. As it can be seen, all samples were porous, but with noticeable difference in pore sizes, which directly depended on synthesis temperature rather than on the source material used. However, it can be seen that sample color changed depending on the clay used; this could be explained by the presence of different amount/type of coloring ions (that are mainly iron).

A. X-ray Diffraction

The main crystalline phase revealed in X-ray diffraction in all samples is cordierite. The phase formation at 1200 °C in similar conditions was already proved in the previous research. Spinel was formed as a secondary phase in samples that are synthesized in 1250 °C (see Fig. 2).

According to the previous research [12], anorthite and crystalline quartz and even sapphirine phases could be expected as trailing phases, especially, if synthesis temperature is 1200 °C or lower. However, calcium, alkali and iron containing crystalline phases began to melt above 1200 °C and formed a glassy phase, thus they are not detected within this X-ray analysis.

Sample N5 (obtained at 1300 °C) could be characterized as consisting of almost pure cordierite in its crystalline phase, as it can be seen in XRD (see Fig. 3), as the spinel phase in this case

was completely undetectable. However, sample A5 at the same synthesis temperature retained the same X-ray diffraction pattern, as did the samples that were synthesized in 1250 °C. They can be characterized as containing a very small amount of spinel phase which has not reacted to form cordierite yet.

B. Surface SEM Analysis of the Samples

Fig. 4 and Fig. 5 are comprised of SEM images of surface of samples at various magnifications. In Fig. 3 it can be seen that the samples that were synthesized at 1250 °C exhibit fine pore structure that can be measured to be in the range of couple of hundred micrometers. However, samples of N5 tend to have smaller pore sizes, the average being around 240 μm (calculated from 10 separate pore diameter measurements), while pores of samples of A5 are about twice the size. Similarly, pore walls are much closer to each other and are thinner in samples of A5. Pore shape is more pronounced spheroids for samples of A5 as well, while samples N5 (although retaining in ellipsoid shape) tended to be more irregular and had coarser pore form. Smaller and larger openings could be noticed in pore wall structure meaning that pores were not closed, but were instead interconnected. This property led to the assumption that these materials could be used as filters even without formation of artificial flow channels.

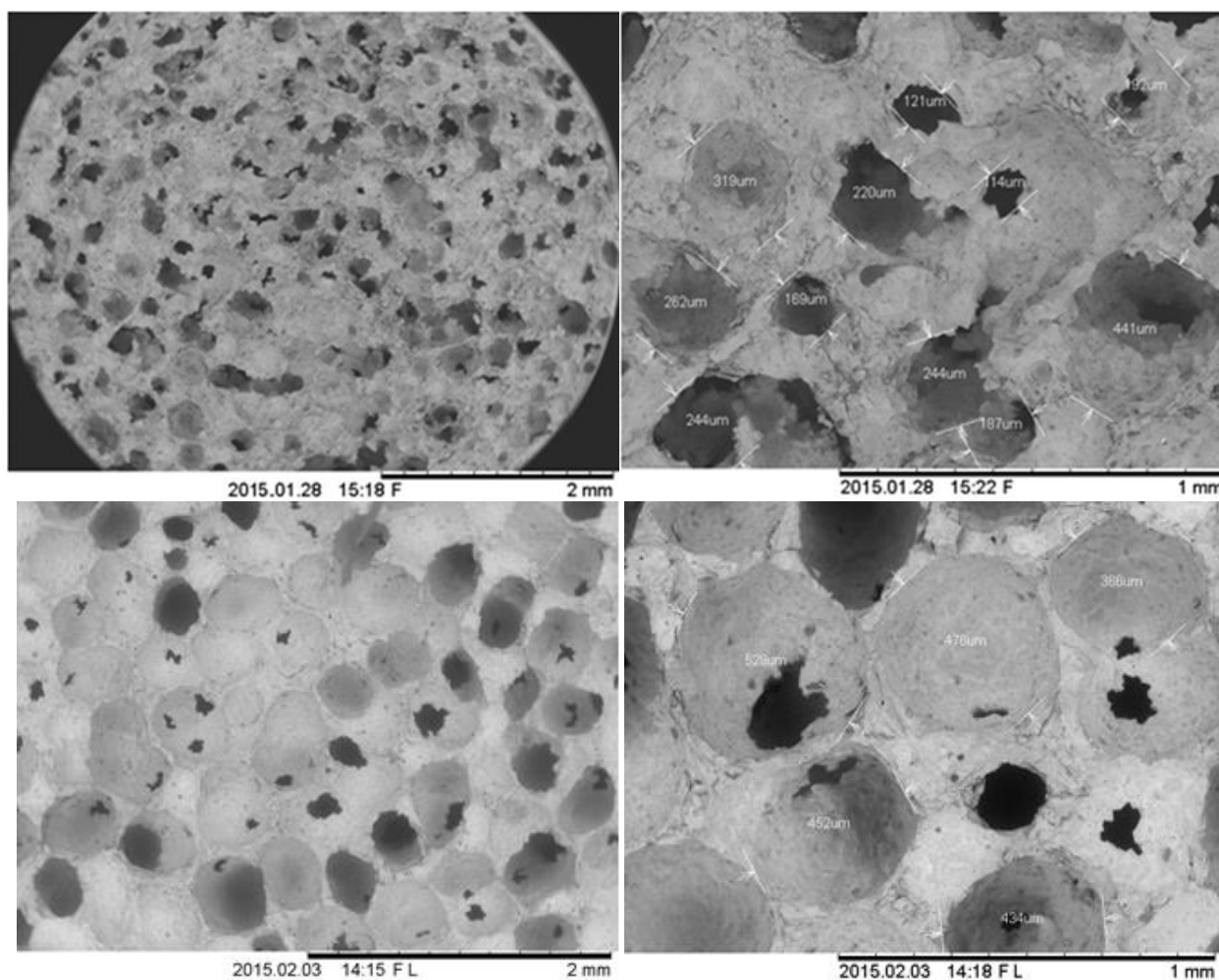


Fig. 4. SEM images of samples N5 (a, b) and A5 (c, d) synthesized at 1250 °C.

As it can be seen in Fig. 5, pore size of both compositions was drastically increased when the maximum synthesis temperature is increased only by 50 °C. In these conditions pore size of both samples was in millimeter range with pore wall thickness measurable in micrometers. Pore type also seemed to be spherical without noticeable elongation. Upon closer look on the complexion of the material surface (Fig. 5 b), a noticeable hexagon-shaped darker areas could be seen; these were surrounded with lighter colored shapeless mass. Since α -cordierite has a hexagonal lattice structure and since these samples contain almost only cordierite crystalline phase, it could be deduced that the darker hexagon-shaped areas were indeed cordierite grains that were surrounded by a glassy phase.

Similarly, the same areas could be seen for samples A5 (Fig. 5 d) as well. However, for these samples cordierite grains

were smaller and less hexagon-shaped with a much larger proportion of enveloping glassy phase. Pore walls in both of these samples remained perforated, yet openings were fewer and smaller.

C. Sample Porosity and Compressive Strength

Results of hydrostatic weighting as well as compressive strength testing results were summarized in Table III. As it was displayed visually before, both of the highest temperature (1300 °C) samples were extremely porous and sponge-like; this was evident from their high porosity values as well. However, samples obtained at 1250 °C were also porous, but the sample pore size was much smaller, measured in micrometer range and also wall thickness was greater.

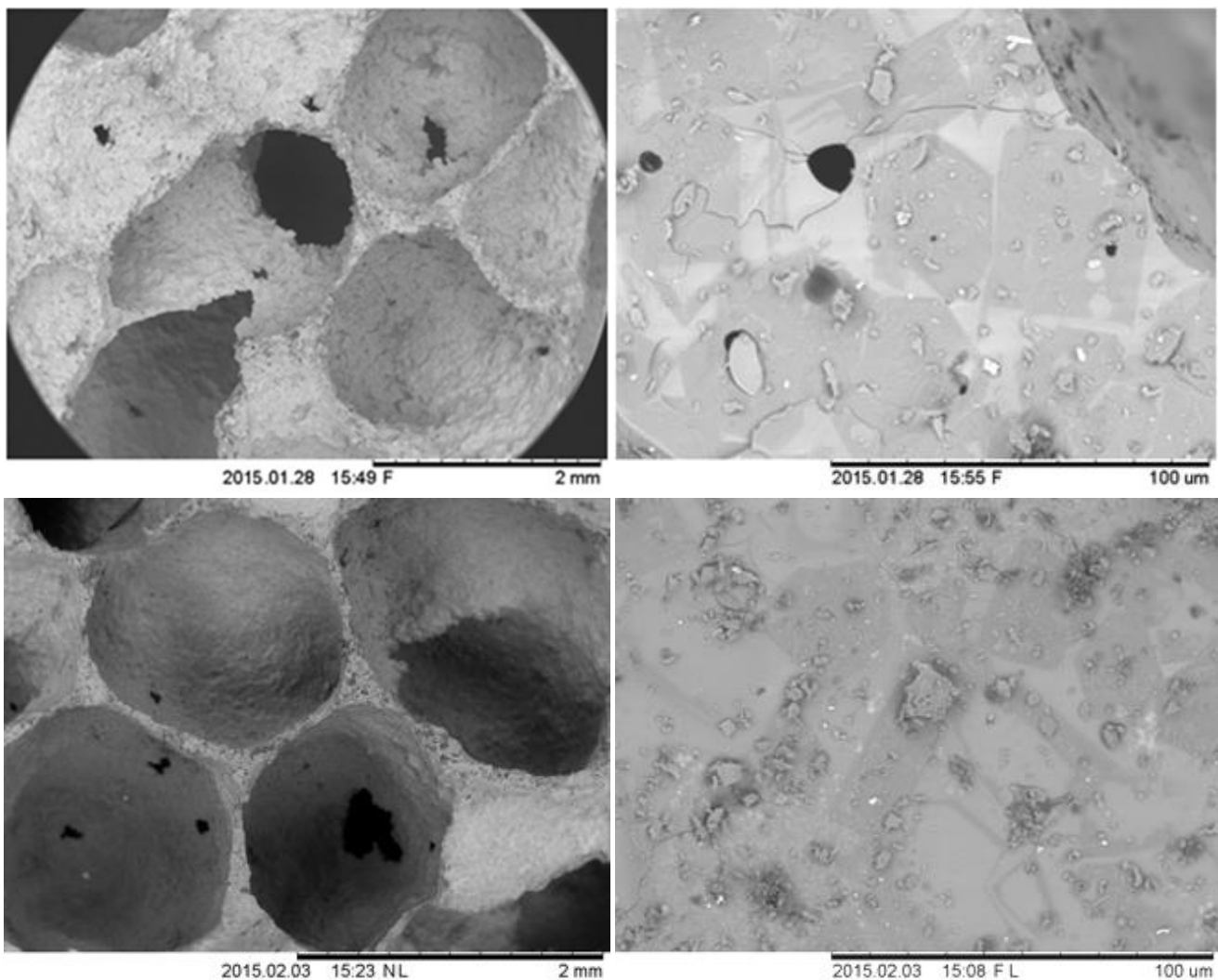


Fig. 5. SEM images of samples N5 (a, b) and A5 (c, d) synthesized at 1300 °C.

TABLE III

DENSITY, APPARENT POROSITY AND COMPRESSIVE STRENGTH OF THE SAMPLES N5 AND A5.

Sample	Density, g/cm ³	Apparent porosity, %	Compressive strength, MPa
N5 1250 °C	1.46	29.17	20.52
A5 1250 °C	1.25	39.03	16.48
N5 1300 °C	1.02	58.80	< 5.0*
A5 1300 °C	0.92	63.91	< 5.0*

*— undetectable

Unlike conventional cases of ceramic sintering, the density of the samples was decreasing with the increase of synthesis temperature. Since overall porosity and pore size had increased, the solid phase/pore ratio was reduced to a point where samples of the highest synthesis temperature had density near/below the density of water, thus making them rather lightweight.

In both cases, pore size and layout is relatively homogeneous, but pore size and quantity significantly affects both compressive strength of samples, i. e., highly porous, sponge-like samples N5 and A5 1300 °C had compressive strength below 5 MPa; this limits their practical use. But samples obtained at 1250 °C had sufficient compressive strength to enable them to be available for a wider variety of uses.

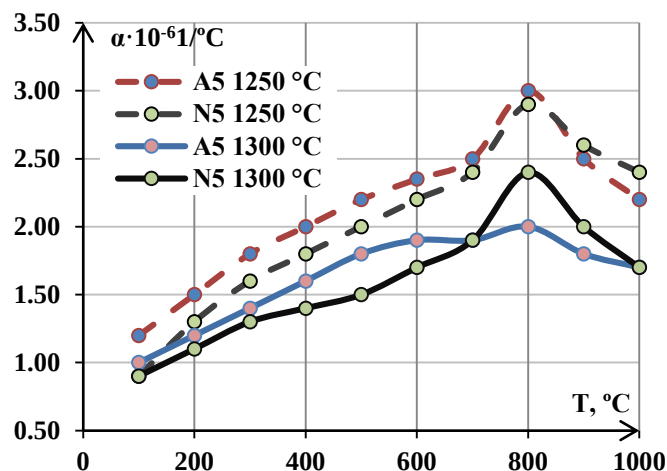


Fig. 6. Coefficient of thermal expansion (CTE) of the samples in dependence on temperature.

D. Coefficient of Thermal Expansion

Results of CTE testing are shown in Fig. 6. All of the samples showed a satisfactorily small value of CTE; samples obtained at 1250 °C had the largest value. Generally, CTE value lowers with both the increase of amount of clay and temperature of synthesis, reaching as low as $0.8 \cdot 10^{-6}$ – $2.4 \cdot 10^{-6}$ 1/°C for sample N5 1300 °C throughout the whole range of tested temperatures.

Rapid increase in CTE for the samples was observed at 800 °C, followed by a decline afterwards; it could be explained with the presence of Ca- and alkali-rich glassy phase.

IV. CONCLUSION

In this work highly porous cordierite-containing ceramic materials were obtained using mineral raw materials from Latvia as main ingredients — carbonate clays and quartz sand.

X-ray diffraction analysis revealed that cordierite was the main crystalline phase in all samples and spinel was a leftover impurity in most samples; it was completely undetectable in at least one sample (N5 1300 °C). Anorthite crystalline phase was not detected in any samples, indicating that this component was transformed to a glassy phase.

Surface analysis and hydrostatic weighting revealed that all samples were highly porous and rather lightweight, with thin pore walls and therefore had small resistance to compressive forces. Coefficient of thermal expansion was satisfactory small for every ceramic sample, ranging from $1.0 \cdot 10^{-6}$ 1/°C to $3.0 \cdot 10^{-6}$ 1/°C throughout the whole tested temperature range. CTE was smaller for samples that were obtained at the highest synthesis temperature; however, the influence of the Ca- and alkali-rich glassy phase was still felt, especially at 800 °C.

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Māris Rundāns, Ingunda Šperberga. Poraina kordierīta keramika no dabiskiem māliem.

Keramikas materiāliem, kas veidoti sistēmā $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ir plašs pielietojums dažādās jomās. Tā tas, piemēram, ir termiski stabilajai fāzei kordierītam ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$). Kordierīta keramika ar tās zemo termiskās izplešanās koeficientu — TIK ($\alpha \approx 1,0\cdot 10^{-6}\text{--}4,0\cdot 10^{-6} \text{ } 1/^{\circ}\text{C}$) droši iztur straujas temperatūras izmaiņas, tāpēc tā var tikt izmantota kā ugunsizturīgs materiāls.

Dabā kordierīts ir reti sastopams minerāls, tādēļ šis kristāliskais materiāls ir jāiegūst sintētiski. Visplašāk izmantotā metode ir augsttemperatūras cietfāžu sintēze, retāk — sola-gēla sintēze un rekristalizācija no stiklveida kausējuma. Sintēzei tiek izmantotas dažādas magnija, alumīnija un silīcija oksīdus saturošas izejvielas, no kurām visbiežāk lietotās ir talka un kaolīns. Lai samazinātu nepieciešamo sintēzes temperatūru, oksīda maisījumiem tiek pievienoti dažādi kušņi, piemēram, B_2O_3 .

Šajā pētījumā ieguva augsti porainus kordierīta keramiskos materiālus, izmantojot vietējās izejvielas — karbonātu mālu un kvarca smiltis. Ieguva dažādas porainības materiālus, mainot sintēzes temperatūru. Rentgenfāžu analīzes rezultāti liecināja, ka šie materiāli saturēja kordierītu kā galveno kristālisko fāzi. Porainībai palielinoties, tā tieši ietekmēja spiedes stiprību, to ievērojami samazinot. Iegūto materiālu termiskās izplešanās koeficienti bija zemi (ne augstāki par $3,0\cdot 10^{-6} \text{ } 1/^{\circ}\text{C}$ visā pētītajā temperatūras diapazonā), neskatoties uz poru un stiklveida fāzes klātbūtni.