

Porous and Dense Cordierite Ceramic from Illite Clay

M Rundans¹, I Sperberga¹ and G Sedmale¹

¹Institute of Silicate Materials, Faculty of Material Science and Applied Chemistry,
Riga Technical University, Riga, Latvia

E-mail: maris.rundans@rtu.lv

Abstract. Ternary system MgO-Al₂O₃-SiO₂ contains many technically valuable crystalline phases such as enstatite, forsterite, spinel and cordierite. For most of these phases coefficient of thermal expansion (CTE) is extremely low (as low as $1.5 \cdot 10^{-6} \text{ K}^{-1}$) which allows for them to be used in conjunction with other thermally demanding materials like quartz, for example. Also, other important properties like their high mechanical strength and good dielectric permeability is of value for potential use in practical applications. Formation of cordierite from oxide powders takes place above 1350 °C. Rational preparation of such material requires modifications in synthesis rout, i.e., addition of flux forming agents or presence of volatile compounds. In this work the use of Latvian illite clay as partial raw material for preparation of both dense and porous cordierite ceramics was studied. No additional artificial flux and/or volatiles were used. Obtained dense and porous ceramic samples were tested for their phase composition, mechanical strength and porosity. It was determined that the use of illite clay of no less than 1/3 of total mass was enough to form both extremely dense and tough (compressive strength of about 400 MPa) and extremely porous (about 59% apparent porosity) materials by just adjusting thermal treatment regime. The X-Ray diffraction of the samples showed that formation of single-phase crystalline cordierite can also be achieved in relatively lower temperatures, e.g., as low as 1300°C.

1. Introduction

Modern ceramic materials created in the system MgO-Al₂O₃-SiO₂ has a broad range of applications in various fields, as this system can be found such refractory phases as enstatite (MgO·SiO₂), forsterite (2MgO·SiO₂), spinel (MgO·Al₂O₃), cordierite (2MgO·2Al₂O₃·5SiO₂), mullite (3Al₂O₃·2SiO₂), etc. [1]. These crystalline phases have low or even negative linear thermal expansion coefficient (CTE), high mechanical, chemical and thermal durability. For example, cordierite ceramics with its low CTE ($\alpha = 1.5 - 4.0 \cdot 10^{-6} \text{ K}^{-1}$) safely withstand sudden changes in temperature and is used as a refractory material [1,2]. These materials also have good dielectric properties and therefore are used for such purposes as the integrated circuits, electronic packing and others.

Naturally occurring magnesium aluminum silicate, such as cordierite and sapphirine are rareoccurring natural minerals, and therefore these crystalline materials must be obtained synthetically. The most widely used method is the high-temperature solid-state synthesis, rarely – sol-gel synthesis and glass melt re-crystallization. Various magnesium, aluminum and silicon oxides containing raw materials are used for the synthesis, of which the most common are talc and kaolin [3]. Dense cordierite ceramic material bulk density reaches 2.60 g/cm³, and compressive strength approaches 450 MPa [4]. Such materials may be acquired only from pure oxides, synthesizing them at temperatures above 1350 °C for several hours [5]. To reduce the required synthesis temperature, fluxing agents such as Bi₂O₃ are added to the oxide mixtures [6].

In this report obtaining and properties of high-temperature porous and dense ceramic materials using raw local Latvian Quaternary clay and quartz sand resources have been described.



2. Materials and methods

Mineral raw materials of Latvian origin - ground quartz sand ($\approx 98\%$ pur.) and carbonates-containing illite clay were used in pre-ceramic powder preparation; oxide composition of clay used is given in Table 1. By adjusting required stoichiometry with the help of MgCO_3 and $\text{Al}(\text{OH})_3$ ($> 99.99\%$ pur., Sigma Aldrich) green powders' compositions were matched to that of a cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$). These compositions are given in Table 2.

Table 1. Composition of illite clay in wt. %

SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	$\text{Na}_2\text{O}+\text{K}_2\text{O}$	Loss of ignition
51.0	16.5	2.4	6.8	6.3	5.0	11.4

Starting mixtures were carefully weighed and placed in an agate grinding containers and afterwards milled in water medium (1:1.6 ratio) for 2 hours in planetary ball mill. The sand was ground beforehand in similar way (3 hours in water medium) to the powdered state. After grinding all slurries were dried in oven at $60\text{ }^\circ\text{C}$ for 24 hours and crushed in a mortar into powders afterwards. Powderstate mixtures were dosed and pressed into cylindrical samples with varying height: diameter ratio (from 1:1 for use in compression testing to 1:5 for use in CTE testing) with the uniaxial hydraulic press (pressing pressure of 15 MPa). The samples were annealed in a furnace in normal atmosphere at maximum temperatures of 1200, 1250 and 1300 $^\circ\text{C}$ with heating rate of $6\text{ }^\circ\text{C}/\text{min}$ and dwell time of 3 hours.

Table 2. Compositions of prepared powder samples in wt. %

Sample	Illite clay	Sand	MgCO_3	$\text{Al}(\text{OH})_3$
C0	-	44.1	21.5	34.4
C25	18.7	32.0	19.0	30.3
C50	33.2	22.5	17.0	27.3

Crystalline phase composition was determined with powder XRD using Rigaku Ultima, Japan apparatus ($\text{Cu K}\alpha$ radiation; scanning rate of $4\text{ }^\circ/\text{min}$ and 2θ range of $5\text{-}50^\circ$). Apparent porosity and volume density was determined using Archimedes method. Compressive strength (in MPa) was tested using ToniNorm by Zwick (Germany) test plant. Samples M25 (1300 $^\circ\text{C}$) and M50 (1250 and 1300 $^\circ\text{C}$) were taken polished surface. Sample CTE was determined in temperature range of $20\text{ - }1000^\circ\text{C}$ and heating rate of $10^\circ\text{C}/\text{min}$. using horizontal dilatometer (Linseis L76 Platinum Series, Germany).

3. Results and discussion

3.1. X-ray diffraction

All samples containing the illite clay (C25 and C50) have cordierite as main crystalline phase. This phase had already formed at 1200 $^\circ\text{C}$, in contrast to the sample C0 – composition without illite clay content (Figure 1). It indicates that the required cordierite synthesis temperature has been reduced when using illite clay. Samples without clay content, by contrast, begins to form cordierite only above 1200 $^\circ\text{C}$ (Figure 2). Spinel and anorthite are formed as secondary phases. Anorthite crystalline phase above 1200 $^\circ\text{C}$ begins to melt and forms the glassy state, thus it is not detected at higher temperatures. Samples without clay additive retain both modifications of SiO_2 (quartz and cristobalite) as well as sapphirine throughout all of the temperature range of synthesis. On the contrary – samples of composition C50 can be characterized as consisting of crystalline cordierite as it can be seen in XRD (Figure 2) + glassy phase only.

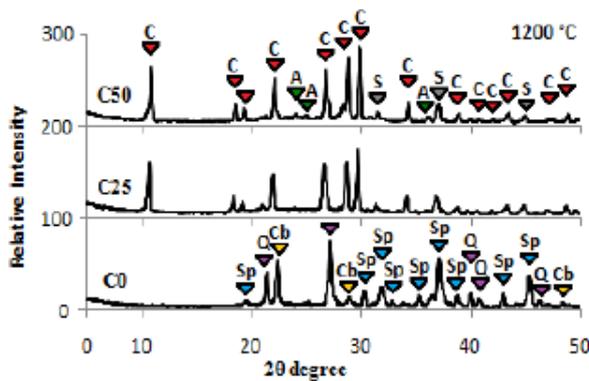


Figure 1. XRD of samples C0, C25, C50 at 1200°C. C – cordierite, A – anorthite, S – spinel, Q – quartz, Cb – cristobalite, Sp – sapphirine

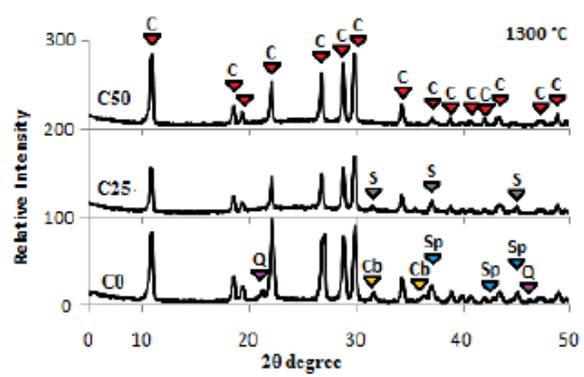


Figure 2. XRD of samples C0, C25, C50 at 1300°C. C – cordierite, S – spinel, Q – quartz, Cb – cristobalite, Sp – sapphirine

3.2. Sample porosity and compressive strength

Results of hydrostatic weighting as well as compressive strength testing are summarized in Table 3. As can be seen, the sample C50 which is obtained at highest temperature (1300°C) are extremely porous and sponge-like as it is evident from the high water absorption (58.80%) and high porosity (96.71%) with sample pore walls being of less than 1 mm thickness. However, samples obtained from the same composition at 1250 °C are also porous, but the sample pore size is much smaller, measured in microns range as well as wall thickness being greater. In both cases, the pore size and the layout is relatively homogeneous, but the pore size and the quantity significantly affects both the sample compressive strength, i.e., highly porous, sponge-like sample C50/1300 compressive strength is below 5 MPa, but the sample C50/1250 compressive strength is sufficient for practical uses.

Meanwhile, samples annealed at 1200°C are extremely dense as it can be seen from their compressive strength values reaching as high as nearly 400 MPa for composition C25. This value is close to the theoretical value of dense cordierite; it also far outclasses strength of pure cordierite composition samples C0 at this temperature as the presence of illite clay has improved clay-containing sample densification rate.

Table 3. Water absorption, density and compressive strength of samples

Sample	Apparent porosity, %	Density, g/cm ³	Compressive strength, MPa
C0/1200	25.2	1.70	43
C0/1250	10.4	2.06	148
C0/1300	1.1	2.35	154
C25/1200	1.1	2.55	117
C25/1250	1.2	2.38	399
C25/1300	4.8	2.23	110
C50/1200	0.9	2.46	390
C50/1250	29.2	1.46	21
C50/1300	58.8	1.02	~ 5

3.3. Coefficient of thermal expansion

Results of CTE testing are visualized in Figure 3. Sample which does not contain cordierite crystalline phase has very high coefficient that ranges at about $7.5 - 9.0 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (not displayed). On the contrary, each of the other samples which contain cordierite shows a satisfactory small value of CTE with largest being for samples obtained at 1200°C. Generally, CTE value lowers with both increasing amount of clay and temperature of synthesis reaching as low as $1.2 - 2.4 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for sample C50 synthesized at 1300. Slight increase is detected for samples without clay C0 at around 600 °C which could be contributed to α - β quartz transition impact as this phase is present only in these samples as shown in XRD. For samples with clay content rapid increase in CTE is observed at 800°C followed by a decline afterwards and could be explained with the presence of anorthite rich glassy phase.

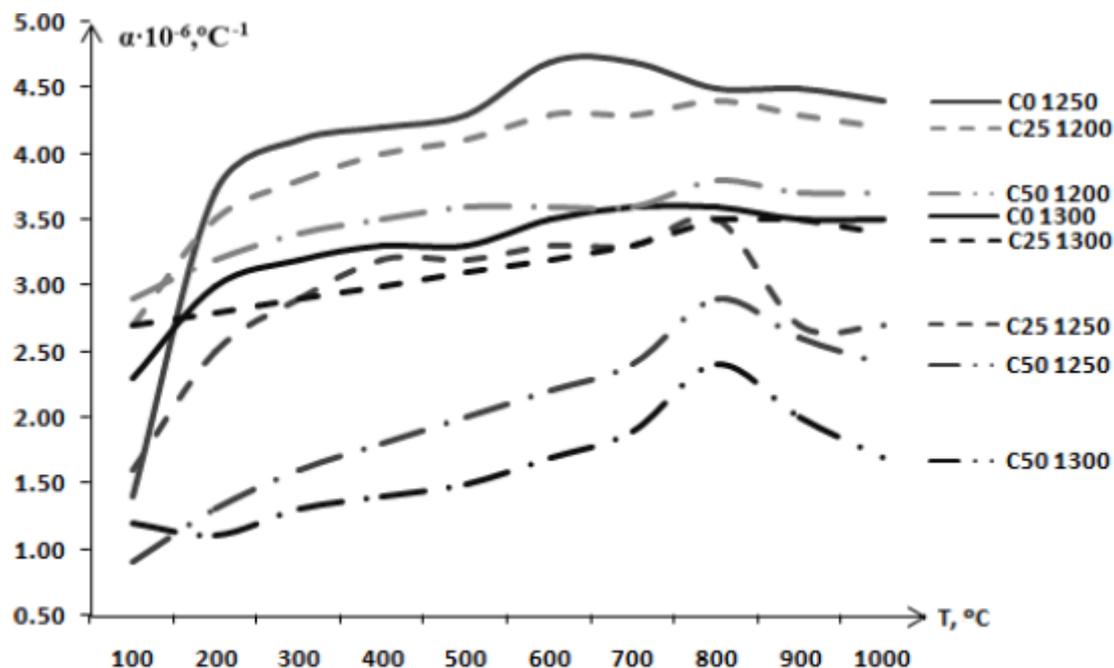


Figure 3. CTE for samples C0, C25 and C50 synthesized at temperatures 1200, 1250, 1300°C.

4. Conclusions

In this work both dense and highly porous cordierite containing ceramic materials were obtained using mineral raw materials of Latvia – illite clay and quartz sand. Dense cordierite ceramic samples were obtained at 1200°C reaching compressive strength of 400 MPa while highly porous material was obtained at 1300°C. Coefficient of thermal expansion is satisfactory small for every ceramic sample with composition of 1/3 clay content (C50) being the lowest and thus most beneficial for practical use.

References

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