



## Structural characteristics of cordierite/steatite ceramics sintered from mixtures containing pore-forming organovermiculite

M. Valášková<sup>a,b,\*</sup>, J. Zdrávková<sup>a,b</sup>, J. Tokarský<sup>a,b</sup>, G. Simha Martynková<sup>a,b</sup>, M. Ritz<sup>c</sup>, S. Študentová<sup>d</sup>

<sup>a</sup>Nanotechnology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, CZ-708 33 Ostrava-Poruba, Czech Republic

<sup>b</sup>IT4Innovations Centre of Excellence, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, CZ-708 33 Ostrava-Poruba, Czech Republic

<sup>c</sup>Regional Material and Technology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, CZ-708 33 Ostrava-Poruba, Czech Republic

<sup>d</sup>Department of Analytical Chemistry and Material Testing, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, CZ-708 33 Ostrava-Poruba, Czech Republic

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### Abstract

The preceramic mixtures appropriate to the composition of cordierite are composed of talc, kaolinite and vermiculite (Ver), and/or organovermiculite (Ver-org) as a pore-forming agent. The preceramic mixtures for sintering at 1300 °C were prepared in two different ways, loosely in crucibles and compressed into pellets. Structural characterization of cordierite/steatite ceramic was performed using X-ray powder diffraction (XRD), FTIR spectroscopy, scanning electron microscopy analysis and porosity measurement. The ceramic samples showed (1) bimodal meso-macropore size distribution and unimodal macropore size distribution, when the preceramic mixtures included Ver and Ver-org, respectively, and (2) higher porosity when sintering mixtures occurred in crucibles in comparison with pellets. The XRD patterns and quantitative XRD phase analysis revealed cordierite/steatite ceramics in the composition of indialite (IND) and two orthorhombic forms of enstatite: protoenstatite (PEN) and orthoenstatite (OREN). All cordierite/steatite samples contained a greater amount of PEN than OREN and a slightly higher quantity of IND when sintered in crucibles compare to pellets. The ceramic samples prepared from the preceramic mixtures with twice the amount of Ver-org contained a high quantity of IND (91 vol%), PEN (about 9 vol%) and no OREN. The unit cell parameter *c* in comparison with the pure IND was about 0.001–0.003 nm shorter at all INDs. The pore-forming Ver-org supports structural substitution of cations during crystallization of IND with the substitution  $\text{Ca}_{0.50}\text{Mg}_{1.50} \rightarrow \text{Ca}_{0.25}\text{Mg}_{1.75}$ . The IR spectra in the 400–1600  $\text{cm}^{-1}$  region confirmed the presence of cordierite and steatite.

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### 1. Introduction

Ceramic bodies containing a high content of cordierite have excellent thermal shock and low dielectric loss properties making them suitable for a wide range of high-temperature and electronic applications. Steatite ceramics have good electrical properties and high mechanical strength, and therefore are particularly used for low or high voltage electrical application.

Several works have shown that steatite ceramics have higher thermal expansion coefficient values than those of cordierite, and, furthermore, cordierite ceramics have a higher thermal shock resistance than steatite [1,2]. Steatite and cordierite are the major components of the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  ternary system. Study of the system led to the synthesis of the magnesium aluminum silicate at the composition  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  and introduction the term cordierite  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  [3]. The  $\alpha$  form is a hexagonal polymorph of  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  and distinct from natural orthorhombic cordierite [4,5]. Occurrence of  $\alpha$  form crystals in fused sediments in India led to calling the new mineral indialite [6]. The structure of cordierite consists of six-membered rings of corner-shared Si and Al tetrahedra linked by

\*Corresponding author at: Nanotechnology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, CZ-708 33 Ostrava-Poruba, Czech Republic. Tel.: +420 597321573.

E-mail address: [marta.valaskova@vsb.cz](mailto:marta.valaskova@vsb.cz) (M. Valášková).

additional tetrahedra and octahedra. The stacking of the rings along the *c* axis forms large cavities parallel to the [001] [4]. Water, carbon dioxide, argon, helium, alkaline earth and alkali metal ions have been found in the cavities [7]. The prediction of the structure of cordierites with the  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ge}^{4+}$  brought new findings, that those dopants in small amounts (1–2%) may enter the channels along the *c* axis or substitute Si–Al in tetrahedra or Mg in octahedra [8]. The solid solution limit of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  sites in the structure of cordierite was studied on the calculated unit cell parameters of the compounds ranging from the  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  to the  $\text{Mg}_{2-x}\text{Ca}_x\text{Al}_4\text{Si}_5\text{O}_{18}$  [9].

Steatite ceramics with the formula  $\text{MgSiO}_3$  may include four polymorphic forms [10,11]. Orthorhombic forms are enstatite and protoenstatite (PEN). PEN is stable after heating at 1300 °C, and upon cooling inverts to either monoclinic low clinoenstatite (CLEN) or orthoenstatite (OREN). Above 980 °C, low CLEN inverts reversibly to high clinoenstatite [12]. The structure of  $\text{MgSiO}_3$  consists of two nonequivalent chains, where one half of the  $\text{Mg}^{2+}$  cations occupy symmetrical (or regular) octahedral positions, while the second half occupies irregular octahedral positions. This structural characteristic allows half of the  $\text{Mg}^{2+}$  to be replaced by  $\text{Ca}^{2+}$  [13,14].

Industrial production of cordierite ceramics is based on the use of the natural high quality refractory clays. Standard cordierite preceramic mixture, which is composed of kaolin, talc and technical grade alumina has a narrow sintering interval. The additives such as alumina, magnesium carbonate, quartz and other oxides are incorporated to the cordierite mixtures in order to achieve better shape, strength, temperature resistance, and other properties of the material [15]. The preceramic mixtures with addition of the alumina ( $\text{Al}_2\text{O}_3$ ) at 1200–1250 °C show a reaction of alumina with the enstatite, as well as reaction with the excess silicon oxide. Therefore, cordierite ceramics contain an increased amount of Al–Mg-spinel at the expense of enstatite and an additional mullite phase [16]. Cordierite ceramics prepared from halloysite and talc [17], and from kaolinite and talc [18] were used as automotive catalysts that promote purifying exhaust gas. The effect of vermiculite addition to the preceramic mixtures on the changes in properties of the cordierite ceramics was discussed in several works [19–23].

The steatite ceramics are produced by dry pressing, extrusion, casting and semi wet pressing using talc (about 80–90%), plastic clay (about 5–10%) and a flux melting agent (about 5–10%). The flux ( $\text{BaO}$ ,  $\text{BaCO}_3$ ,  $\text{ZnO}$ , etc.) enables the development of a melting phase during sintering and influences the electrical characteristics [24]. The steatite glass-ceramic (GCs) materials with a wide sintering range were developed using a glass powder of the  $\text{MgO}$ – $\text{BaO}$ – $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$  system [25]. The enstatite GCs in the ternary  $\text{MgO}$ – $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$  system was sintered using tetragonal zirconia as a nucleation agent [26].

Steatite/cordierite ceramic in the composition of clinoenstatite, protoenstatite, cordierite, forsterite and a very small amount of quartz was sintered from the powders of cordierite (as a reinforcement material) and steatite [27]. Authors found

that the cordierite addition contributes to the negative relative densities and the thermal expansion coefficient of the steatite-based ceramics. The high purity cordierite/steatite ceramics were sintered from the clay mixtures containing talc, kaolinite and vermiculite [28]. The authors investigated the effect of vermiculites from different commercially available deposits in the preceramic mixtures on the sintering and ceramics properties. The results unambiguously confirmed dependency of porosity and the progress of indialite crystallization on the alkali  $\text{Na}^+$  and  $\text{K}^+$  present in the structure of vermiculites. It was also found that the sintering manner of the preceramic mixtures in pellets and crucibles influenced the porosity in ceramics and their quantitative indialite and steatite composition.

The aim of the present work was to prepare and characterize the cordierite/steatite ceramics that are not currently often studied from preceramic clay mixtures at 1300 °C with organovermiculite as a pore-forming additive. Talc, kaolinite and vermiculite (Ver) or organovermiculite (Ver-org) in the preceramic mixtures of the appropriate composition of cordierite were prepared loosely in crucibles and under pressure to pellets. Structural characterization of cordierite/steatite ceramic was performed using the X-ray powder diffraction (XRD), FTIR spectroscopy, scanning electron microscopy (SEM) analysis and porosity measurement.

## 2. Materials and methods

The clay minerals kaolinite (from LB Minerals, s.r.o., Czech Republic), talc KT5 (from Koltex Color, s.r.o., Czech Republic) and vermiculite (from the Paraiba region of Brazil, a superfine particle size fraction (0–2 mm) from Grena, s.r.o., Czech Republic) were used in the preceramic mixtures. Octadecylamine (ODA),  $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ , (97%, melting point 55–57 °C) was purchased from Sigma-Aldrich, Co. The clay minerals were sieved and a particle size fraction of less than 40  $\mu\text{m}$  was used in the preceramic clay mineral mixtures. The vermiculite was ground in a planetary ball mill Fritsch Pulverisette 7 before sieving. Each milling was carried out with a 10 g sample for 15 min in the wolfram carbide mill chamber of 50  $\text{cm}^3$  capacity with 3 (78.7 g) grinding balls (13 mm diameter) and the rotation speed of 250 rpm. Organovermiculite (ODA/Ver named Ver-org) was prepared using the melt-intercalation of ODA to Ver (the weight ratio ODA: Ver=4:1) at 80 °C for 24 h [29].

The clay mineral preceramic mixtures were prepared from the talc, kaolinite and vermiculite close to the oxide composition of cordierite  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  (Table 1). The mixtures named A and B contained the amount of kaolinite of approximately 50 wt%, and a different quantity of talc (40 wt% and 20 wt%, respectively) and vermiculite (13 and 30 wt%, respectively). The counterpart mixtures named A-org and B-org contained a higher amount of Ver-org, calculated on the quantity of pure vermiculite. Finally, the mixtures were homogenized in a rotary mixer, and then milled in the planetary mill for 15 min.

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