Processing and properties of dense cordierite ceramics obtained through solid-state reaction and pressure-less sintering

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Abstract

Sintering of pure cordierite $2MgO:2Al_2O_3:5SiO_2$, and cordierite with addition of 5 mass % TeO_2 was studied. Green bodies were prepared from powder mixtures mechanically activated in a high energy planetary mill, shaped by uniaxial (20 MPa) and cold isostatic pressing (1000 MPa). The pressure-less sintering of these specimens was performed at 1350 °C for 1 h. High relative density over 95 % of theoretical value was obtained through solid-state reaction and pressure-less sintering of powder activated for 40 minutes, and for the first time reported in the literature. Phase composition and microstructures of sintered samples were determined by XRD and SEM, coupled with EDS mapping. The real part of the complex relative permittivity of the samples was measured at 200 MHz. The loss tangent of all samples was below the resolution of the measurement setup. A strong correlation between the relative permittivity and the density agrees with previously published data.

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Introduction

Cordierite (2MgO·2Al$_2$O$_3$·5SiO$_2$) based ceramics are widely used in various fields, e.g. as substrates for micro-electronic packaging industry and cookware, heat exchangers, glazes for floor tiles, etc. Owing to relative low dielectric constant (~ 5) and very low CTE (<2·10^{-6} °C^{-1}), these ceramics are also well known by their good thermo-mechanical, chemical, and dielectric properties [1–3]. Due to their excellent resistance to the thermal shock they can be applicable as materials that are exposed to sudden temperature changes [4–8] and also as semi-conducting bearers [9, 10].

Cordierite is difficult to sinter due to its very narrow sintering temperature range (1300–1400 °C) [11]. Because a low temperature process is desirable, it is beneficiary to found functional aids which can allow easier process of sintering at lower temperature. The melting temperature of these additives should be lower than that of the precursors. In addition, the cationic radius should be larger than the radius of the metals in MAS to avoid the substitution into cordierite sites. Different components have been used as sintering aids, such as Cr$_2$O$_3$, ZrO$_2$, K$_2$O, TiO$_2$, Bi$_2$O$_3$, MoO$_3$, etc. [12, 13]. Also, TeO$_2$ fulfils the theoretical criteria of large atomic radius (142 pm) and low melting temperature 733 °C), therefore the experimental study of its influence on sintering and electrical properties of cordierite ceramics is needed and desirable.

Our previous study [14] shows that the mechanical activation of starting components (kaolin, quartz, magnesium oxide) has a significant impact on the decrease of the sintering temperature. It has been demonstrated that, compared to non-activated components, mechanically activated ones increase their energy due to induced crystal defects. During a mechanochemical treatment, several processes occur, such as attrition of the starting material, crystal lattice destruction, chemical reactions, the formation of various defects, etc. All of the mentioned processes increase the chance for reactions to occur at temperatures lower than usual [15]. Furthermore, mechanical activation could affect the final electrical characteristics; hence, it is very important to take into account and understand the changes that are introduced into the system during milling.

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According to our best knowledge, there have been no attempts to investigate the effect of mechanical activation along with TeO_2 addition, followed by pressure-less sintering for cordierite-based ceramics and investigation of all those parameters on densification, and physical-chemical properties. The main objective of this work is to investigate the effects of the mechanical activation, TeO_2 addition, and pressure-less sintering of cordierite-based material on its phase composition, microstructure, and electrical properties.

Materials and methods

Mixtures of MgO, Al_2O_3, SiO_2, and TeO_2 starting powders (all 99 % Sigma–Aldrich, p.a.) were used in these experiments. The mixtures of MgO+Al_2O_3+SiO_2 in the 2:2:5 molar ratio, with and without the addition of 5 mass % TeO_2, were mechanically activated by grinding in a high-energy planetary ball mill (Fritsch Pulverisette 5). ZrO_2 vessels and balls were used with the powder-to-balls mass ratio of 1:40. The milling process was performed in air for 10 and 40 minutes. The samples were denoted as MAS–0, MAS–10, MAS–40, MAS–0–Te, MAS–10–Te, and MAS–40–Te (according to activation time, and TeO_2 addition).

The green bodies in the shape of cylinders (diameter 14 mm, height 4 mm) were prepared by uniaxial pressing at 20 MPa, followed by cold isostatic pressing at 1000 MPa. Sintering was performed at 1350 °C, with a heating rate of 10 °C min^{-1} and dwell time of 1 h. The apparent densities and the ratio of open porosity of sintered samples were determined by Archimedes method in distilled water (EN 623–2).

The X-ray powder diffraction patterns were obtained using a Philips PW-1050 diffractometer with λCu-K$_\alpha$ radiation and a step/time scan mode of 0.05 ° s^{-1}. The measurements were performed at the room temperature in air atmosphere.

The morphology of the sintered samples was characterized by the scanning electron microscopy (JEOL JSM-6390 LV). The samples were crushed and covered with gold in order to perform these measurements.

Raman spectra of all powders, recorded in the 200–1100 cm^{-1} range, were collected with a LabRAM HR Evolution system which employed Cobolt Blues™ 473 nm solid state laser with power of 1 mW at the sample surface. All the measurements were realized using a spectrometer

equipped with a grating having 1800 lines mm^{-1}, a 100 x microscope objectives and acquisition of 20 s/10 cycles.

The measurements of the relative permittivity of the sintered samples, metallized on the top and bottom with silver, were performed using an Agilent E5061A network analyzer. The samples were placed in a coaxial chamber [16]. The reflection coefficient of the chamber was measured by the analyzer and the relative complex permittivity of the samples was extracted using electromagnetic models.

Results and discussion

The phase compositions of the non-activated and activated samples after the sintering process without addition of TeO_2 are presented in Figure 1. The XRD pattern of the initial non-activated sintered sample indicates that several phases – $Mg_2Al_4Si_5O_{18}$, SiO_2, Mg_2SiO_4, $\alpha-Al_2O_3$, and $MgSiO_3$ – are present within MAS-0 sintered mixture. The formation of cordierite began even during the sintering of the starting mixture, although significant amounts of the starting phase SiO_2 and intermediate compound $MgSiO_3$ are present. The phase $MgSiO_3$ is no longer present in the sintered samples MAS-10 and MAS-40, which means that the intermediate compound reacted further and produced increased amounts of cordierite (from 63.6 % for MAS-10 to 69.8 % for MAS-40) and decreased amounts of Mg_2SiO_4 and Al_2O_3 phases (from 17.1 % for MAS-10 to 13 % for MAS-40, and 5.6 % for MAS-10 to 2.4 % for MAS-40, respectively). The diffraction patterns of the activated and sintered samples, besides well crystallized sharp peaks of cordierite, show small amount of $ZrSiO_4$ (approx. 2.5 %) due to the high-energy ball milling in ZrO_2 jar with balls made of the same material.

Figure 1. XRD patterns of sintered MAS-0, MAS-10, and MAS-40 samples.

The phase compositions of the non-activated and activated samples with addition of TeO_2 after the sintering process are presented in Figure 2. All phases that are present in the sintered mixture MAS-0, are detected in the mixture MAS-0-Te as well, with the presence of some TeO_2,

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namely in the sample MAS-40-Te. Also, the presence of $ZrSiO_4$ phase is identified in the activated and sintered samples, along with the absence of the intermediate compound $MgSiO_3$, present only in the non-activated sintered mixture. The only difference with respect to the sintered mixtures without TeO_2 is the absence of SiO_2 phase in the MAS-40-Te sample. The identification of the obtained reflections was carried out using JCPDS cards (075-1439 for cordierite, 082-1403 for SiO_2, 089-1625 for Mg_2SiO_4, 081-2267 for α-Al_2O_3, 011-0273 for $MgSiO_3$, 083-1375 for $ZrSiO_4$, and 052-1005 for γ-TeO_2).

Figure 2. XRD patterns of sintered MAS-0-Te, MAS-10-Te, and MAS-40-Te samples.

Values of the apparent densities and ratio of open porosity of the sintered samples, determined by Archimedes method, are given in Table 1. The lowest density is obtained for the non-activated sample with TeO_2 addition (2.21 g·cm^{-3}), while the highest value is obtained for the sample activated for 40 minutes and sintered without TeO_2 (2.60 g·cm^{-3}), which makes it very dense. According to literature data, there are many papers dealing with dense cordierite ceramics. A recent paper by D. Redaoui et al. reports samples with apparent density 2.50 g·cm^{-3} obtained from naturally occurring clay minerals, milled for 20 hours in wet media, calcined for 24 h, and then sintered at 1250 °C [17], and Neto&Moreno reported even the density 2.58 g·cm^{-3} for cordierite ceramics obtained for samples produced from mechanically activated kaolin/talc/alumina powders and sintered at 1350 °C for 1 h [18]. In this regard the density of the ceramics obtained in this work is according to our best knowledge the highest density reported for cordierite based ceramics obtained after mechanical activation and pressure-less sintering. Moreover, these samples did not contain open pores (see Table 1) so we have reached the relative density above 95 % of theoretical density of this composition [19]. The densities of the sintered samples with TeO_2 are slightly lower with respect to the samples without it, anyway also the doped sample activated for 40 minutes reached high apparent density (2.56 g·cm^{-3}) together with minimal content of open pores. Due to its low melting point (733 °C), TeO_2 should serve as a transient liquid-phase sintering aid [20] in the initial and intermediate sintering stage and due to its low boiling point (1250 °C) evaporate from the sample before reaching the final sintering stage. For a better evaluation of the proposed transient liquid-phase sintering mechanism the use of different TeO_2 concentration would be necessary.

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Table 1. Apparent density and relative open porosity of sintered samples.

A scanning electron micrograph, along with EDS mapping of the sintered sample MAS-0 is presented in Figure 3. During the sintering of the non-activated powder, formation of irregularly shaped pores is noticed, although there are some parts where spherical pores are visible as well. Uneven phase distribution is present, along with sintered particles that were not part of agglomerates in the initial powder.

Figure 3. a) SEM, b) EDS mapping of MAS-0 sintered sample.

Prolonged activation for 40 minutes, followed by sintering, led to a completely sintered and dense sample, with a homogeneous structure, presented in Figure 4. The mapping image indicates an even and homogeneous phase distribution. No spherical (closed) pores are detected, indicating very high relative density of the sample.

Figure 4. a) SEM, b) EDS mapping of MAS-40 sintered sample.

Contrary to the MAS-0 sample, sintering of MAS-0-Te sample showed melting and formation of a liquid phase during the sintering regime. The micrograph presented in Figure 5 indicates parts of the microstructure where some sintered powder particles are coated with the liquid phase, which enables process of mass transport. The mapping shows that Te is distributed along the grains of the sintered material, either as the residual TeO_2 or dissolved in the matrix.

Figure 5. a) SEM, b) EDS mapping of MAS-0-Te sintered sample.

Finally, continual parts that are well sintered are visible within the sintered sample activated for 40 minutes with addition of TeO_2, as seen in Figure 6. Besides, a porous structure is still present, with contact necks that are strengthened during sintering. This microstructure indicates the final sintering stage due to the presence of the closed porosity (see Table 1). The microstructure of the initial powder activated 40 minutes with TeO_2, was non-uniform and

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sintering of that kind of a structure leads to formation of non-uniformly shaped pores. TeO_2 phase remains on the grain boundaries, while the part of the liquid phase remains within the sintered sample.

Figure 6. a) SEM, b) EDS mapping of MAS-40-Te sintered sample.

Figure 7 presents Raman spectra of cordierite-based ceramics in the range of wavenumbers of 200–1100 cm^{-1}. Beside cordierite peaks, in the Raman spectra of the non-activated sintered samples peaks of SiO_2 (cristobalite), Mg_2SiO_4 (ringwoodite), $MgSiO_3$ (enstatite), and Al_2O_3 are also pronounced [21–24], which is in a good accordance with the results obtained using XRD measurements (see Figures 1 and 2). From the Raman spectra, it can be assumed that there is also a possible existence of $MgAl_2O_4$ in the samples, but the fact that major lines of this spinel overlap with lines of some other present phases, especially with the most intensive lines of the SiO_2 and Al_2O_3, impedes precise assessment [24]. The presence of $MgAl_2O_4$ phase wasn't explicitly detected using XRD measurement, but the overlapping of its diffractions with Mg_2SiO_4 diffractions could influence the XRD estimations to some extent, as well. The Raman spectra pointed out that the share of mentioned non-cordierite phase's decreases with the activation time, which is followed by the increase in amount of cordierite. The influence of the mechanical activation is most visible in decrease of the reflections at ~230 cm^{-1} and ~416 cm^{-1}, relative to the strongest cordierite peak. The change is prominent even for the sample activated for 10 minutes, and is more pronounced with prolonged activation time. The position of the peak assigned to the superposition of the strongest lines of SiO_2, Al_2O_3 and $MgAl_2O_4$ phases is shifted towards lower frequencies, from 416 cm^{-1} to 407 cm^{-1}, with the increase of the activation time. The strongest cordierite peak indicates the existence of the orthorhombic modification of Mg-cordierite phase, present in spectra of the non-activated sintered samples. The existence of that modification is manifested in clearly visible asymmetry of the strongest peak and its partial splitting, where the line at ~ 564 cm^{-1} occurs along with the shoulder on the side of higher frequencies (575–585 cm^{-1}) [25]. That trend is more noticeable in the samples with TeO_2 addition. The appearance of the asymmetry and splitting of the cordierite peak is related to Al–Si ordering within the cordierite structure (with bending vibration of T_26, T_21, and T_23 units), as well as with simultaneous stretching vibrations of the M and T_26 sites in the structure [26]. The asymmetry is markedly

reduced for prolonged activation time and cordierite peaks can be assigned predominantly to the hexagonal modification in these samples.

Figure 7. Raman spectra of sintered samples MAS-0, MAS-10, MAS-40, MAS-0-Te, MAS-10-Te, and MAS-40-Te (C – cordierite, E – enstatite $MgSiO_3$, RW – ringwoodite Mg_2SiO_4, A – alpha-Al_2O_3, SiO_2 – cristobalite, S – spinel $MgAl_2O_4$, and Z – $ZrSiO_4$).

Although the origin of peaks at ~ 703 cm^{-1} and ~ 901 cm^{-1} in non-activated sintered samples is not known precisely, it is assumed that the first one could be assigned to the existence of δ(O-Al-O) vibrations, while the other one corresponds to Si-O-Si (Al) vibrations [27]. Two most intensive lines of TeO_2 phase contribute to the peaks at ~ 226 cm^{-1} and 660 cm^{-1}, in samples with TeO_2 addition. With the extended activation time, the presence of $ZrSiO_4$ peak at ~ 354 cm^{-1} is noticed, so we concluded that this phase is also present within the peaks at 438 cm^{-1} and 1006 cm^{-1}, although those peaks dominantly originate from the cordierite phase.

The results for the real part of the complex relative permittivity (dielectric constant) of the samples, measured at 200 MHz, are shown in Table 2. The loss tangent for all samples was very small, below the resolution of the measurement setup (< 0.005).

Table 2. Real part of complex relative permittivity of sintered samples.

There is a strong correlation between the relative permittivity and the density (resp. residual porosity), which agrees with our previous results [28, 29], when the relative permittivity follows the trend of the density changes (see Table 1). Furthermore, if we compare the changes in densities with the activation time, an increase of the density with the prolonged milling time is noticed, owing to a lower porosity and a more compact structure which is observed as changes in the microstructures (see Figures 3–6). This suggests that the higher density and the homogeneity of the morphology are dominantly responsible for the higher permittivity of the samples. The better packaging the starting powder, of activated and hence more reactive particles, facilitated sintering. Strengthening of grain boundaries occurred, and consequently the relative density increased [29]. According to available physical models, porous materials exhibit similar dielectric characteristics

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as composites, where the porosity (air) is considered to be one of their components [30]. Figure 8 shows results from three sets of measurements of cordierite-based ceramics. The data are clustered around the fitting curve for mixtures (logarithmic linear approximation of the Lichtenecker's model) [31], given by $\frac{\ln \varepsilon_r'}{\ln \varepsilon_{r\,max}'} = \frac{\rho}{\rho_{max}}$, where the relative permittivity of one component (air) is 1, and $\varepsilon_{r\,max}' = 6$ is the relative permittivity of the second component at the highest density (when no open porosity is present) $\rho_{max} = 2.6$ g·cm^{-3}. Note that $\varepsilon_{r\,max}'$ and ρ_{max} are our estimates, because reliable data were not available in the literature. This model was selected because it gives a better prediction of permittivity of multi-phase materials than other models (e.g., Maxwell-Garnett) [32].

Figure 8. Measured relative permittivity as a function of density, along with logarithmic fitting curve. The first set of samples is from [28] and the second set is from [29].

Conclusions

In the present study, cordierite-based ceramics materials were prepared using mechanical activation followed by pressure-less sintering. The phase composition, microstructure, and electric properties of the bulk materials were characterized systematically. The most important conclusions are:

(1) Pressure-less sintering of investigated powders leads to cordierite formation. The formation of cordierite began even during the sintering of the non-activated starting mixture, with SiO_2 and $MgSiO_3$ phases. The phase $MgSiO_3$ is no longer present in the sintered samples MAS-10 and MAS-40, meaning that the intermediate compound reacted further and produced increased amounts of cordierite. MAS-10 and MAS-40 sintered samples, besides well crystallized sharp peaks of cordierite, show small amount of $ZrSiO_4$ due to the contamination during high-energy ball milling. The phase composition of sintered samples with TeO_2 remains, but the presence of TeO_2 is noticed. Raman analysis confirmed that the share of non-cordierite phase's decreases with the activation time, which is followed by the increase in cordierite amount, where

for prolonged activation time cordierite peaks can be assigned predominantly to the hexagonal modification.

(2) The lowest density of 2.21 g·cm^{-3} is obtained for the non-activated sample with TeO$_2$ addition, whereas the highest value of 2.60 g·cm^{-3} is obtained for the sample activated for 40 minutes and sintered. According to authors' best knowledge, it is the highest reported density of cordierite based ceramics obtained after mechanical activation and pressure-less sintering. The absence of open porosity indicates the value of relative porosity over 95 %. The densities of the sintered samples with TeO$_2$ were slightly lower with respect to the samples without it, anyway also the doped sample activated for 40 minutes reached high apparent density (2.56 g·cm^{-3}) together with minimal content of open pores. For a better understanding of transient liquid-phase sintering mechanism the systems with different TeO$_2$ concentrations will be studied.

(3) The microstructures showed homogeneous phase distribution of dense MAS-40 sample with no open porosity present, indicating that final sintering stage was reached. The density has the dominant influence on the dielectric permittivity (lowest value 4.96 was obtained for MAS-0-Te sample, and 5.55 is for MAS-40 sample) with a loss tangent below 0.005.

Acknowledgement

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Table 1. Apparent density and relative open porosity of sintered samples

Sample	Apparent density (g/cm³)	Relative open porosity (vol. %)
MAS-0	2.45	10.8
MAS-10	2.32	12.0
MAS-40	2.60	0.0
MAS-0-Te	2.21	18.5
MAS-10-Te	2.29	13.5
MAS-40-Te	2.56	0.5

Table 2. The real part of complex relative permittivity of sintered samples

Sample	ε_r'
MAS-0	5.24
MAS-10	4.99
MAS-40	5.55
MAS-0-Te	4.96
MAS-10-Te	4.96
MAS-40-Te	5.54

Figure Captions

Figure 1. XRD patterns of sintered MAS-0, MAS-10, and MAS-40 samples.

Figure 2. XRD patterns of sintered MAS-0-Te, MAS-10-Te, and MAS-40-Te samples.

Figure 3. a) SEM, b) EDS mapping of MAS-0 sintered sample.

Figure 4. a) SEM, b) EDS mapping of MAS-40 sintered sample.

Figure 5. a) SEM, b) EDS mapping of MAS-0-Te sintered sample.

Figure 6. a) SEM, b) EDS mapping of MAS-40-Te sintered sample.

Figure 7. Raman spectra of sintered samples MAS-0, MAS-10, MAS-40, MAS-0-Te, MAS-10-Te, and MAS-40-Te (C – cordierite, E – enstatite $MgSiO_3$, RW – ringwoodite Mg_2SiO_4, A – alpha-Al_2O_3, SiO_2 – cristobalite, S – spinel $MgAl_2O_4$, and Z – $ZrSiO_4$).

Figure 8. Measured relative permittivity as a function of density, along with logarithmic fitting curve. The first set of samples is from [28] and the second set is from [29].

15kV   X5,000   5μm

15kV   X5,000   5μm

Si Al Mg O Electron

15kV   X5,000   5μm

Te Si Al Mg O Electron

15kV   X5,000   5μm