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Crystallization behavior and sintering of cordierite synthesized by an aqueous sol–gel route

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Abstract

The purpose of the research was to investigate crystallization behavior and sintering of cordierite synthesized by a low-price aqueous sol–gel route starting from silicic acid and magnesium and aluminum salts. Viscous sintering of the gel occurred in the temperature range of 800–850 °C, followed by μ-cordierite crystallization at about 900 °C, which proves the homogeneity of the gel. Decreasing of μ-cordierite crystallinity in a wide temperature range prior to commencing of α-cordierite crystallization at about 1200 °C indicates reconstructive type of μ- → α-cordierite transformation. The transformation was fully completed at 1350 °C. The value of the Avrami parameter indicates that μ-cordierite crystallization was controlled by surface or interface nucleation, which implies that viscous sintering occurred in the primary gel particles, which leads to shrinkage, and thereafter nucleation occurred on the surface or interface of the particles. The overall activation energy of μ-cordierite crystallization was 382.0 kJ/mol. The sinterability of the powder obtained by calcination at 1300 °C, where well-crystallized α-cordierite was formed, was better than that of the powder obtained by calcination at 850 °C, where the most intensive shrinkage occurred before the onset of crystallization of μ-cordierite.

Keywords: A. sintering; A. Sol–gel process; D. Cordierite; Crystallization

1. Introduction

Dense cordierite-based ceramics are promising materials for technological applications due to their low thermal expansion and dielectric constant, and high chemical and thermal stability. Cordierite ceramics can be prepared by conventional methods, but it is difficult to sinter cordierite because of the narrow sintering range just below its incongruent melting point [1–3].

Some attempts have been made to improve the sinterability of cordierite by applying of sintering aid [4–8] or by using of cordierite powders with favorable sintering behavior [9–19]. Addition of sintering aid resulted in a decrease of the temperature of cordierite formation and an increase of the density of the sintered materials, but these aids, on the other hand, increase the thermal expansion coefficient and dielectric constant. Thus, the preparation of a homogeneous and fine cordierite powder that can bi sintered without sintering aids is considered to be highly desirable [8–19].

It is well known that the sol–gel method has the advantages of excellent control of the chemical composition and the possibility of reducing the sintering temperature [20]. In recent years, cordierite powders and materials have been produced by the sol–gel method using alkoxides [9,11,18,21,22], but the starting materials are very expensive and the fabrication processes are complicated. Colloidal processing [11,17,23–26] is considered an effective method for the preparation stoichiometric cordierite from starting materials that are cheaper than alkoxides and, at the same time, the sintering temperature is decreased and the density improved without the deterioration of the properties. It was shown that from colloidal, three-phase gels, crystallization of spinel and crystobalite (or quartz) occurred, which react forming α-cordierite [11,17,23–26], while from homogeneous monophasic gels obtained using alkoxides, μ-cordierite crystallizes which is then transform into α-cordierite [9,11,18,21,22].

In this work, cordierite was synthesized by a low-price sol–gel method, starting from silicic acid and magnesium and

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aluminum salts. Phase transformation and shrinkage during heating, the kinetic parameters of cordierite crystallization and the sintering behavior of cordierite powders were investigated.

2. Materials and methods

2.1. Synthesis

For the synthesis of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) powder, $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3\ 9H_2O$ were dissolved in an aqueous solution of silicic acid. The silicic acid was obtained by passing sodium silicate through a column filled with a cation exchanger in the H^+ form, whereby an exchange of the Na^+ ions from sodium silicate with the H^+ ions occurred. To prevent condensation, a 2% solution of silicic acid of pH ≈ 3.4 was used. The reactants were mixed in a stoichiometric ratio for cordierite and the mixture was gelled by heating and stirring with a magnetic stirrer. The obtained transparent gel was dried at 100 °C, ground and calcined at 600 °C for 2 h to remove all the thermal decomposition products. The obtained white powder was then calcined at different temperatures: 850, 900, 1000, 1100, 1200, 1300 and 1350 °C for 2 h in a programmable furnace under static air conditions.

2.2. Characterization

Differential thermal and thermogravimetric analysis (DTA and TGA) of the powder obtained by gel calcination at 600 °C was performed on an SDT Q600 instrument, up to a temperature of 1380 °C. The heating rate was 20 °C/min and Al_2O_3 was used as the standard. The sample mass was 5 mg.

The phase composition of the powders obtained by gel calcination at various temperatures was determined on an ITAL STRUCTURES APD 2000 diffractometer equipped with a back monochromator operating at a tube voltage of 40 kV and a tube current of 30 mA, using a copper cathode as the X-ray source ($\lambda = 0.15406$ nm), in the 2Θ angle range from 10° to 80°. A step size of 0.02° and a time per step of 0.5 s were used.

FTIR spectra of the dry gel and powders obtained by gel calcination were recorded on a MB BOMEM100 HARTMANN and BRAUN spectrometer, within the wave number range from 400 to 1250 cm^{-1}. The specimens were prepared with KBr at a mass ratio of specimen to KBr of 1:100.

The morphology of the gel was studied by scanning electron microscopy (SEM), using a Jeol JSM-5800 at 20 kV, and transmission electron microscopy (TEM), using a JEOL T-100. Prior to SEM analysis, the gel was coated with gold using a splutter coater. The sample for TEM analysis was prepared by dispersing the gel in ethanol and applying a drop of very dilute suspension onto carbon-coated grids.

The relative linear shrinkage of the compact of powder obtained by gel calcination at 600 °C was acquired using heating microscopy (E. LEITZ) up to 1430 °C, at a heating rate of 10 °C/min.

2.3. Kinetics

The crystallization kinetics of cordierite was studied on a gel previously calcined at 600 °C. The kinetic parameters were determined by differential thermal analysis under non-isothermal conditions at heating rates of 5, 10, 15 and 20 °C/min up to 1100 °C. The experiments were performed in the air, and Al_2O_3 was used as the reference material. The sample mass, in all cases, was 170 mg.

2.4. Sintering

The cordierite powders for the sintering investigation were obtained by gel calcination at a temperature where α-cordierite was formed or at a temperature where densification without crystallization of the silica-containing component occurred. So, dried and ground gel was calcined at either 1300 °C or 850 °C and then powders were ground for 3 h at 400 rpm in a mill with an alumina chamber using alumina balls. The so-obtained powders were uniaxialy pressed at 400 MPa and sintered at 1430 °C. The surfaces of the sintered materials were polished and thermally etched (1350 °C, 30 min with a heating rate of 20 °C/min) in order to observe their microstructures by SEM (Jeol JSM-5800).

The densities of the sintered samples were determined by the Archimedes method. The relative densities were calculated from the density of the α-cordierite (2.51 g/cm^3) as the theoretical density. The sintered samples were tested for microhardness and indentation fracture toughness. Microhardness (H) was measured with a Vicker's indenter. K_{IC} values were calculated using the formula [27]: $K_{IC} = 0.0824\ P{\cdot}c^{3/2}$, where P is the indentation load and c is the length of the induced radial crack.

3. Results and discussion

3.1. SEM and TEM of the dry gel

The morphology of the ground dried gel is shown in Fig. 1a, in which particles of irregular sizes and shapes can be seen. On the TEM image (Fig. 1b), primary particles of dry gel are observable. It is obvious that the dry gel is very porous, which implies that the dry gel contains high chemical energy.

3.2. Phase transformations during thermal treatment of the gel

The results of the DTA and TGA of the gel calcined at 600 °C for 2 h are given in Fig. 2. DTA and TGA were realized on calcined gel in order to eliminate all products of thermal decomposition and thus to enable a better registration of the phase transformations.

The endothermal peak at 125 °C on the DTA curve corresponds to desorption of physically absorbed water. This peak is accompanied by a relatively high weight loss, despite the previous calcination, which can be explained by high humidity adsorption from the air. The exothermal peak at

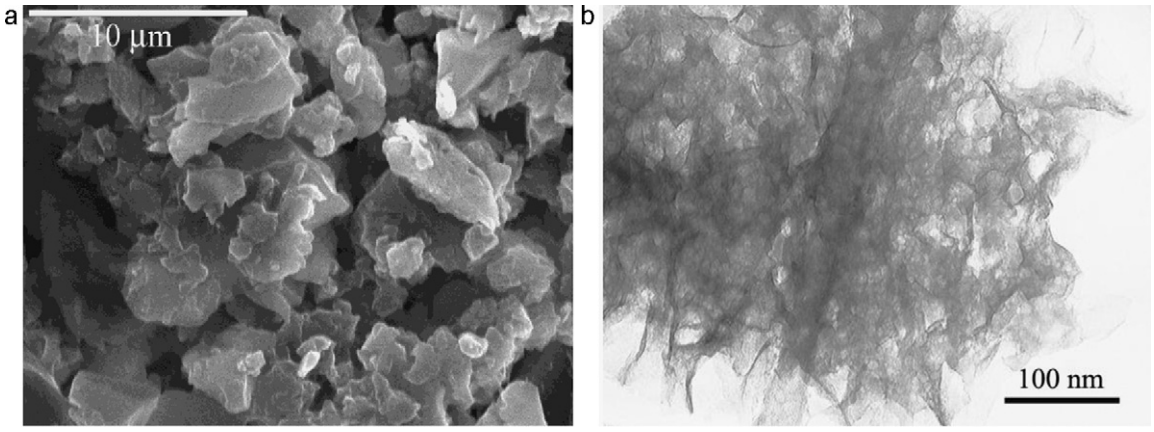

Fig. 1. (a) SEM of ground dry gel; (b) TEM of ground dry gel.

987 °C can be assigned to spinel and crystoballite crystallization, as in three-phase colloidal gels [11,17,23–26], or to μ-cordierite crystallization, as in monophase alkoxide-derived gels [9,11,18,21,22]. Thereafter, the peak at 1305 °C corresponds to α-cordierite formation by spinel and crystoballite reaction or by μ-cordierite transformation. Endothermal shifts in the DTA baseline prior to the crystallization peaks are evident on the DTA curve. The first shift (at 850 °C) corresponds to a gel → viscous liquid transition, *e.g.*, viscous sintering of the gel. It can be seen from Fig. 3 that intense shrinkage of the gel occurs in the temperature range of 800–900 °C, which confirms that the first endothermal shift in the DTA baseline corresponds to viscous sintering.

It is assumed that the second shift (at 1225 °C) indicates some structural changes prior to α-cordierite formation, but this can be confirmed by X-ray diffraction analysis. In addition, it is assumed that the endothermal peak at 1350 °C does not corresponds to α-cordierite melting, because during the thermal-microscope analysis until 1430 °C, melting was not registered. It is possible that this peak indicates the formation of some liquid phase after α-cordierite formation, which is liquid for liquid phase sintering.

In order to determine the nature of the processes corresponding to the mentioned peaks and shifts, the phase composition of powders obtained by the gel calcination at 600, 850, 900, 1000, 1100, 1200, 1300 and 1350 °C were determined. The X-ray diffractograms of these powders are presented in Fig. 4.

The diffractograms of the powders obtained by gel calcination at 600 and 850 °C revealed that the gel remained amorphous up to 900 °C. At 900 °C, crystallization of the μ-cordierite and spinel phases appeared. The diffractograms of the powders obtained by gel calcination at 900, 1000 and 1100 °C show intense and sharp peaks corresponding to μ-cordierite and weak peaks corresponding to spinel. According to this, it may be said that the first exothermal peak on the DTA curve (at 987 °C) corresponds to μ-cordierite crystallization, because gel calcination during 2 h ensures crystallization at a lower temperature than in the DTA experiments due to inertia in the latter case. Crystallization of μ-cordierite at about 1000 °C is proof that the gel is monophasic and homogeneous. The presence of spinel indicates either non-stoichiometry or some inhomogeneity in the gel. On increasing the temperature from 900 to 1100 °C, the intensity of the peaks corresponding to spinel increased, while the peaks corresponding to μ-cordierite become lower and wider, which indicate a decrease in

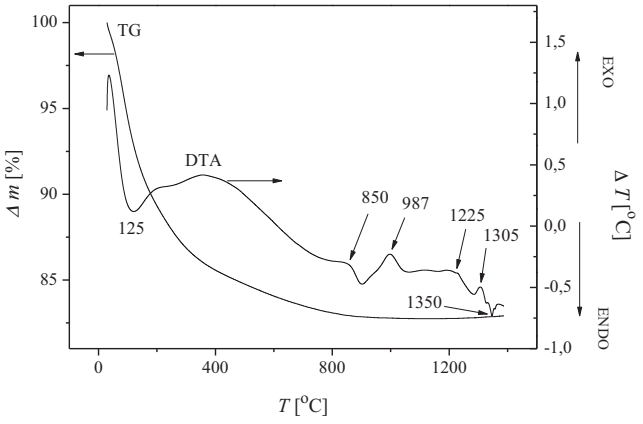

Fig. 2. DTA and TGA curves of a gel calcined at 600 °C for 2 h.

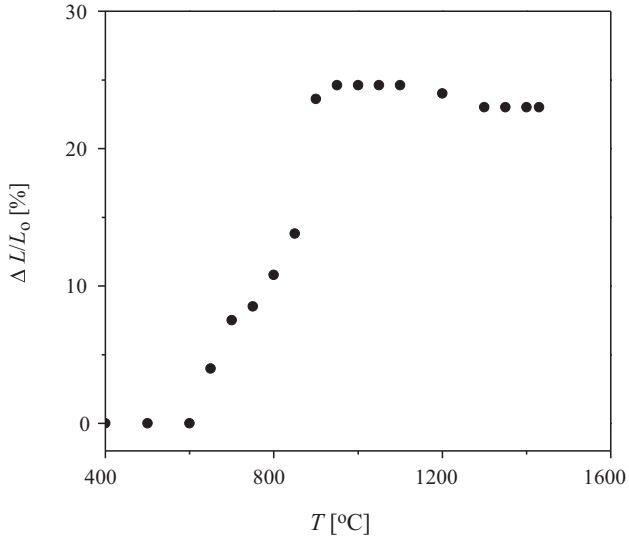

Fig. 3. Relative linear shrinkage of a calcined gel compact.

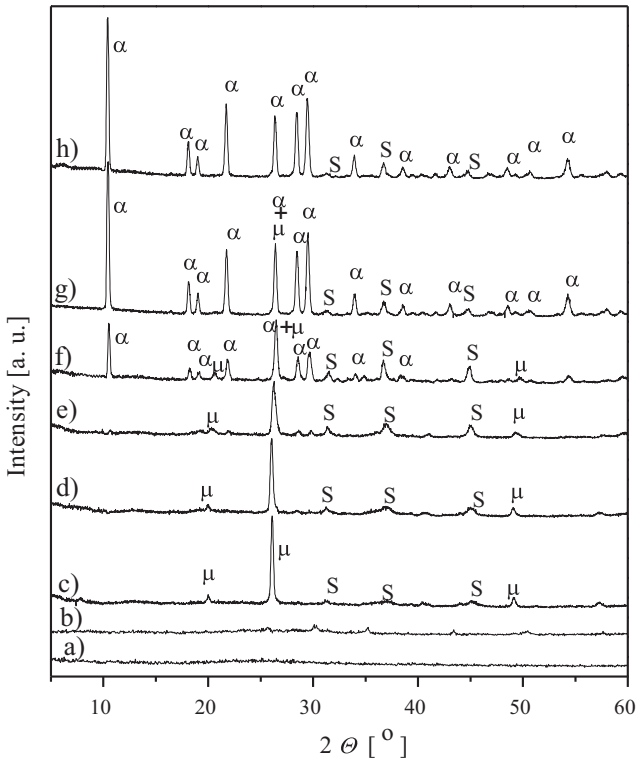

Fig. 4. X-ray diffractograms of the powders obtained by gel calcination at 600 °C (a), 850 °C (b), 900 °C (c), 1000 °C (d), 1100 °C (e), 1200 °C (f), 1300 °C (g) and 1350 °C (h) (S – spinel, α – α-cordierite, μ – μ-cordierite).

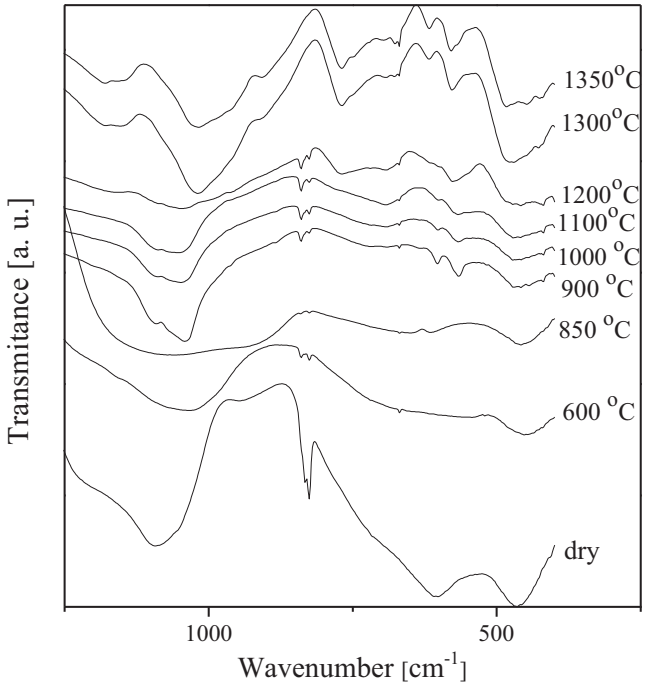

Fig. 5. FTIR spectra of the dry gel and the powders obtained by gel calcination at 600, 850, 900, 1000, 1100, 1200, 1300 and 1350 °C.

crystallinity. μ-Cordierite crystallinity decrease in a wide temperature range prior to α-cordierite crystallization indicates reconstructive type of transformation (structural rearrangement) [28], meaning that bonds are broken and atoms are rearranged. Obviously, it is required for the μ-cordierite structure to partially destroy prior to comencing of α-cordierite crystallization, so the new α-phase will form out of this disordered structure. Accordingly, it can be assumed that endothermal shift at 1225 °C corresponds to transition temperature of disordered structure from which α-cordierite crystallization occurs (peak at 1305 °C).

The diffractogram of the powder obtained by gel calcination at 1200 °C shows peaks correspond to μ- and α-cordierite, indicating that the α-cordierite formation started at temperatures below 1200 °C, while the DTA results exhibited a peak corresponding to the μ- → α-cordierite transformation appeared at about 1300 °C. It is obvious that during calcination for 2 h, the transformation occurred at a lower temperature than during the DTA experiments. The slight expansion of the gel compact in the temperature interval 1100–1300 °C (Fig. 3) can be explained by μ- → α-cordierite transformation, because the density of α-cordierite is smaller than that of μ-cordierite. On calcination for 2 h at 1300 °C, the transformation μ- → α-cordierite was almost completed, while at 1350 °C, it was fully completed. The peaks corresponding to α-cordierite on the diffractogram of the powder obtained by calcination at 1350 °C are intense and sharp, which indicate good crystallinity of the obtained powder. This result confirmed that the endothermal peak at 1350 °C does not correspond to cordierite melting. In addition, there are no peaks corresponding to mullite, which means that incongruent melting of cordierite did not occur.

The results of FTIR spectroscopy of the dry gel and the powders obtained by gel calcination at 600, 850, 900, 1000, 1100, 1200, 1300 and 1350 °C are illustrated in Fig. 5.

Bands corresponding to Si–O bonds are evident in the FTIR spectra of the dry gel [16–19]: a broad band with a minimum at about 1090 cm^{-1}, a shoulder at about 1200 cm^{-1} and bands at 605 cm^{-1} and 465 cm^{-1}. The band at 826 cm^{-1} corresponds to nitrate ions from the $Mg(NO_3)_2$ and $Al(NO_3)_3$ used in the synthesis. The position of the band corresponding to Si–O bonds at about 1090 cm^{-1}, as in pure silica gel, indicates that bonds Si–O–M (M = Al, Mg) did not form in the dry gel. Thus, it can be supposed that Si–O–Si chains were formed during gelation and hydrated aluminum and magnesium ions remained incorporated between these chains. In the FTIR spectrum of the sample obtained by gel calcination at 600 °C, the shoulder at about 1200 cm^{-1} disappeared and the band at about 1090 cm^{-1} shifted to lower wavenumbers (1040 cm^{-1}), indicating Si–O–M bonds (M = Al, Mg) formation. The FTIR spectrum of the sample obtained by gel calcination at 850 °C indicates transient state before μ-cordierite formation at 900 °C. The same bands are evident in the spectra of the powders obtained by gel calcination at 900, 1000 and 1100 °C, but intensities of the bands at 1090 and 1040 cm^{-1} decreased with increasing temperature. The FTIR spectrum of the powder obtained by gel calcination at 1200 °C indicates that the transformation μ→α-cordierite had commenced: a band at 770 cm^{-1} corresponding to the six-member ring in the α-cordierite structure is evident in the spectrum. In addition, there are changes in the positions and intensities of the bands at 1090 and 1040 cm^{-1}. By comparing the spectra of the powders obtained by gel calcination at 900,

1000, 1100 and 1200 °C, it seems that the transformation of μ- to α-cordierite occurred by a continuously changing structure with increasing temperature. This is in accordance with results of X-ray diffraction analysis, *i.e.*, with decreasing intensities the μ-cordierite peaks with increasing temperature. The FTIR spectra of the powders obtained by gel calcination at 1300 and 1350 °C are typical for a well-ordered cordierite structure.

3.3. Kinetics of μ-cordierite crystallization

The DTA curves of the powder obtained by gel calcination at 600 °C for 2 h, at heating rates of 5, 10, 15 and 20 °C/min, are shown in Fig. 6. The exothermal peak corresponding to μ-cordierite crystallization shifts towards higher temperatures as the heating rate increases.

Based on the data presented in Fig. 6, the Avrami parameter n was determined by the method of Ozawa [29–31]. To determine this parameter, the data on the degree of crystallization (α) at different temperatures and heating rates (Q) were used and from the slope of the dependence of log (–ln (1–α)) on log Q for a given temperature, the value of n was determined. The degree of crystallization (α) at a given temperature was determined [32] from the ratio of the area of the part of the peak up to a given temperature to total peak area.

The values of the parameter n at temperatures 955, 959, 962, 964 and 966 °C, are presented in Table 1. The mean value of the Avrami parameter n for the crystallization of μ-cordierite was 0.86.

The mean value of the Avrami parameter n, which was close to 1, indicates interface controlled crystallization of μ-cordierite with a constant nucleus number and one-dimensional growth or surface nucleation [17–19,33]. This value is considerably different from the value obtained for the crystallization of μ-cordierite from alkoxy-derived cordierite gel, obtained by a hydrolytic sol–gel process [18]. In that case, μ-cordierite crystallize from homogenous monophasic gel, with constant nucleation rate and three-dimensional growth ($n = 4$). On the other hand, the value of the Avrami parameter, $n = 2.23$, for the crystallization of μ-cordierite from a gel obtained by a non-hydrolytic sol–gel method [19] indicates the simultaneous contribution of different mechanisms: homogeneous nucleation and three-dimensional crystallite growth due to homogeneity of the gel and surface crystallization due to submicron particles of the gel. Bearing in mind the value of the Avrami parameter n obtained in this work and the results presented in Fig. 3, it can be said that viscous sintering occurred in the primary gel particles, which led to shrinkage (Fig. 3), and thereafter nucleation occurred on the surface or interface of the particles. Then, the μ-cordierite crystals grew towards the center of the particles.

Table 1
Values of the Avrami parameters n at various temperatures.

T [°C]	n
955	0.88
959	0.84
962	0.91
964	0.84
966	0.83

The overall activation energy of μ-cordierite crystallization can be calculated by the Kissinger equation [31,34]. Fig. 7 presents the dependence of ln Q/T_p^2 on $1/T_p$, from which the slope, E_a/R, $E_a = 382.0$ kJ/mol, was obtained. This value is much lower than that determined for alkoxide sol–gel processed μ-cordierite [17,35], probably because of the surface instead volume nucleation. However, the obtained value is higher than the value obtained for μ-cordierite crystallization from high cordierite glass (303.5 kJ/mol) [36].

3.4. Sinterability of the cordierite powders

In order to investigate the influence of calcination temperature on sinterability, the dry gel was calcined at

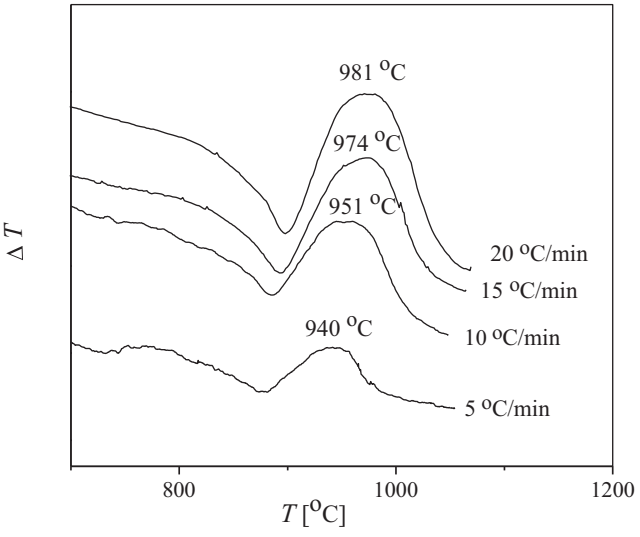

Fig. 6. DTA curves at heating rates of 5, 10, 15 and 20 °C/min of the powder obtained by gel calcination at 600 °C for 2 h.

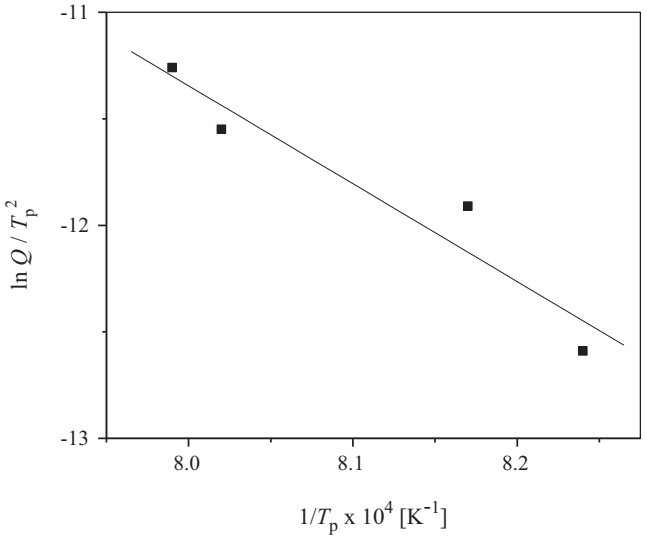

Fig. 7. Dependence of ln Q/T_p^2 on $1/T_p$ for the peak corresponding to μ-cordierite crystallization.

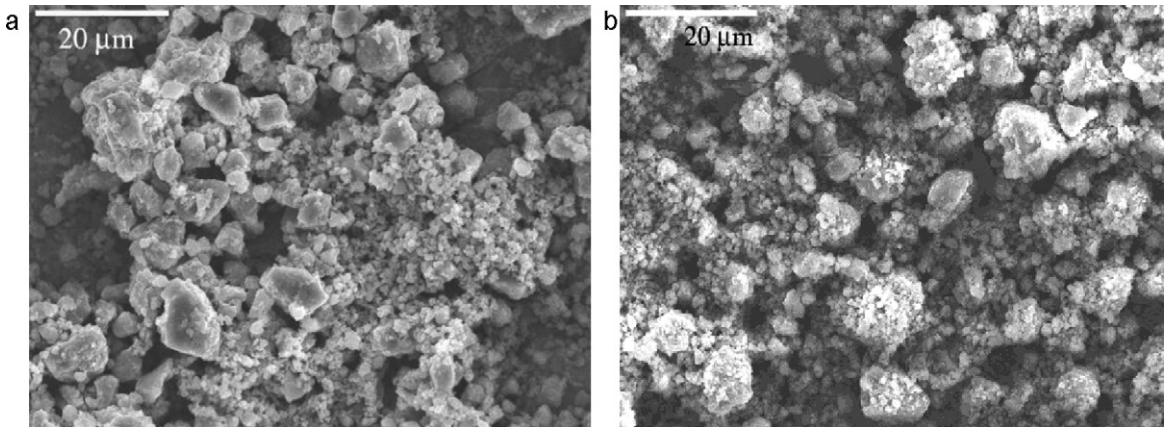

Fig. 8. SEM micrographs of the powders obtained by grinding for 3 h of the gels calcined at: (a) 850 °C and (b) 1300 °C.

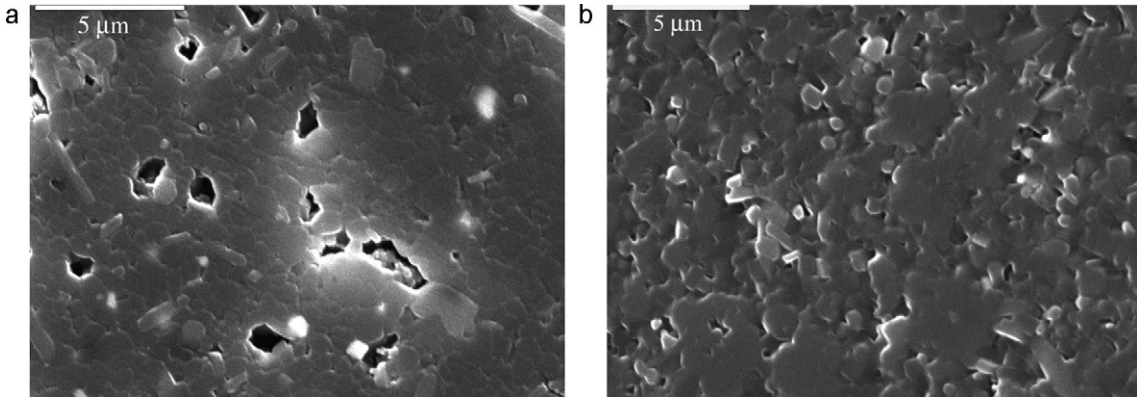

Fig. 9. SEM micrographs of polished and thermally etched surface of cordierite materials obtained by sintering at 1430 °C of compacts of powder obtained by gel calcination at: (a) 850 °C and (b) 1300 °C.

850 °C, the temperature at which the most intensive shrinkage (densification) occurs before the onset of crystallization of μ-cordierite (Figs. 3 and 4), and at 1300 °C, the temperature at which α-cordierite is formed. The SEM micrographs of the powders obtained by gel calcination at 850 and 1300 °C and subsequent grinding for 3 h are presented in Fig. 8. It can be seen that both powders contained nearly spherical particles, the dimensions of which are about 1 μm, but also larger particles of about 10 μm. Hence, the obtained powders had a bimodal distribution of particle sizes.

The SEM micrographs of polished and thermally etched surfaces of cordierite materials obtained by powder pressing and sintering at 1430 °C are presented in Fig. 9. In both cases, the grain sizes are the same as the sizes of the smaller initial particles (about 1 μm). As the microstructure of the sample obtained from the gel calcined at 1300 °C is more uniform and pore-free than the one calcined at 850 °C, it seems that in this case, the larger particles were destroyed and more effectively packed during pressing and sintering. The presence of pores between the fully densified areas in the case of the sample obtained from the gel calcined at 850 °C indicates that the agglomerates were not destroy during pressing and that densification during sintering occurred inside the large particles, while densification between the agglomerates did not occur. Obviously, harder agglomerates are formed by calcination at temperatures at which viscous sintering occurs without crystallization than in the case where α-cordierite crystallize.

Table 2
Relative density (ρ/ρ_T), microhardness (H) and fracture toughness (K_{IC}) of sintered cordierite materials.

Cordierite material obtained from the gel calcined at:	ρ/ρ_T (% TD)	H (GPa)	K_{IC} (MPa m$^{1/2}$)
850 °C	94	6.84	3.62
1300 °C	96	7.47	3.81

Properties of obtained sintered cordierite materials are presented in Table 2. Material obtained from the gel calcined at 850 °C has worse mechanical properties due to lower density and presence of large pores.

4. Conclusion

Starting from silicic acid and magnesium and aluminum salts, a homogeneous monophasic cordierite gel was obtained, which was proved by μ-cordierite crystallization at about 900 °C. In temperature range of 800–850 °C, viscous sintering

of the gel without μ-cordierite crystallization occurred. According to the XRD and FTIR results, μ- → α-cordierite transformation took place in a wide temperature range, and α-cordierite appeared at about 1200 °C. On calcination for 2 h at 1350 °C, the transformation μ- → α-cordierite was fully completed.

The mean value of the Avrami parameter for μ-cordierite crystallization, which is close to 1, indicates interface controlled crystallization with a constant number of nuclei and one-dimensional growth or surface nucleation. Accordingly, it was concluded that viscous sintering occurred in the primary gel particles, which led to shrinkage, and thereafter, nucleation occurs on the surface or interface of the particles. Due to surface nucleation, the overall activation energy of μ-cordierite crystallization (382.0 kJ/mol) was lower than in the cases where volume nucleation occurs.

The sinterability of the powder obtained by calcination at 1300 °C, where well-crystallized α-cordierite was formed, was better than that of the powder obtained by calcination at 850 °C, where the most intensive shrinkage occurred before the onset of μ-cordierite crystallization. Based on the microstructure of sintered materials, it was concluded that harder agglomerates were formed by calcination at temperatures where viscous sintering occurred without crystallization than in the case where a crystallized powder was obtained.

References

[1] M.A. Camerucci, G. Urretavizcaya, A.L. Cavalieri, Sintering of cordierite based materials, Ceram. Int. 29 (2003) 159–168.

[2] S. Taruta, T. Hayashi, K. Kitajima, Preparation of machinable cordierite/mica composite by low-temperature sintering, J. Eur. Ceram. Soc. 24 (2004) 3149–3154.

[3] M.A. Camerucci, G. Urretavizcaya, A.L. Cavalieri, Mechanical behavior of cordierite and cordierite-mullite materials evaluated by indentation techniques, J. Eur. Ceram. Soc. 21 (2001) 1195–1204.

[4] L. Kostić-Gvozdenović, T. Janaćković, M. Tecilazić-Stevanović, D. Janaćković, Effect of ZnO as additive on the sintering and synthesis of cordierite-mullite ceramics, in: G. Ziegler, H. Hausner (Eds.), Euro-Ceramics II, vol. III: Electroceramics and Ceramics for Special Applications, Deutsche Keramische Gesellshaft e.V, Cologne, 1993, pp. 2431–2435.

[5] R.W. Dupon, R.L. McConville, D.J. Musolf, A.C. Tanous, M.S. Thompson, Preparation of cordierite below 1000 °C via bismuth oxide flux, J. Am. Ceram. Soc. 73 (1990) 335–339.

[6] M.T. Malachevsky, J.E. Fiscina, D.A. Esparza, Preparation of synthetic cordierite by solid-state reaction via bismuth oxide flux, J. Am. Ceram. Soc. 84 (2001) 1575–1577.

[7] S. Mei, J. Yang, J.M.F. Ferreira, Microstructural evolution in sol–gel derived P_2O_5-doped cordierite powders, J. Eur. Ceram. Soc. 20 (2000) 2191–2197.

[8] K. Sumi, Y. Kobayashi, E. Kato, Low-temperature fabrication of cordierite ceramics from kaolinite and magnesium hydroxide with boron oxide additions, J. Am. Ceram. Soc. 82 (1999) 783–785.

[9] H. Suzuki, K. Ota, H. Saito, Preparation of cordierite ceramics from metal alkoxides (part 1)—preparation and characterization of the powder, J. Ceram. Soc. Jpn. (Yogyo-Kyokai-Shi) 95 (1987) 163–169.

[10] H. Suzuki, K. Ota, H. Saito, Preparation of cordierite ceramics from metal alkoxides (part 1)—sintering, J. Ceram. Soc. Jpn. (Yogyo-Kyokai-Shi) 95 (1987) 170–175.

[11] A.M. Kazakos, S. Komarneni, R. Roy, Sol–gel processing of cordierite: effect of seeding and optimization of heat treatment, J. Mater. Res. 5 (1990) 1095–1103.

[12] K. Sumi, Y. Kobayashi, E. Kato, Synthesis and sintering of cordierite from ultrafine particles of magnesium hydroxide and kaolinite, J. Am. Ceram. Soc. 81 (1998) 1029–1032.

[13] R. Ianos, I. Lazau, C. Pacurariu, Solution combustion synthesis of α-cordierite, J. Alloys Compd. 480 (2009) 702–705.

[14] R. Goren, H. Gocmez, C. Ozgur, Synthesis of cordierite powder from talc, diatomite and alumina, Ceram. Int. 32 (2006) 407–409.

[15] C. Ghitulica, E. Andronescu, O. Nicola, A. Dicea, M. Birsan, Preparation and characterization of cordierite powders, J. Eur. Ceram. Soc. 27 (2007) 711–713.

[16] Dj. Janaćković, V. Jokanović, Lj. Kostić-Gvozdenović, S. Zec, D. Uskoković, Synthesis and formation mechanism of submicrometre spherical cordierite powders by ultrasonic spray pyrolysis, J. Mater. Sci. 32 (1997) 163–168.

[17] R. Petrović, Dj. Janaćković, S. Zec, S. Drmanić, Lj. Kostić-Gvozdenović, Phase-transformation kinetics in triphase cordierite gel, J. Mater. Res. 16 (2001) 451–458.

[18] R. Petrović, Đ. Janaćković, S. Zec, S. Drmanić, Lj Kostić-Gvozdenović, Crystallyzation behavior of alkoxide-derived cordierite gel, J. Sol–Gel Sci. Technol. 28 (2003) 111–118.

[19] I. Janković-Častvan, S. Lazarević, D. Tanasković, A. Orlović, R. Petrović, Đ. Janaćković, Phase transformation in cordierite gel synthesized by non-hydrolitic sol–gel route, Ceram. Int. 33 (2007) 1263–1268.

[20] J.D. Mackenzie, Applications of sol–gel methods for glass and ceramics processing, in: L.L. Hench, D.R. Ulrich (Eds.), Ultrastucture Processing of Ceramics Glasses and Composites, John Wiley & Sons, New York, 1984, pp. 15–26.

[21] R. Salmon, E. Matijević, Preparation of colloidal magnesium–aluminum–silicates by hydrolysis of a mixed alkoxide, Ceram. Int. 16 (1990) 157–163.

[22] M. Okuyama, T. Fukui, C. Sakurai, Effects of complex precursors on alkoxide-derived cordierite powder, J. Am. Ceram. Soc. 75 (1992) 153–160.

[23] M.G.M.U. Ismail, H. Tsunatori, Z. Nakai, Preparation of mullite-cordierite composite powders by the sol–gel method: its characterizatics and sintering, J. Am. Ceram. Soc. 73 (1990) 537–543.

[24] M. Awano, H. Takagi, Y. Kuwahara, Grinding effect on the synthesis and sintering of cordierite, J. Am. Ceram. Soc. 75 (1992) 2535–2540.

[25] M. Awano, H. Takagi, Synthesis of cordierite and cordierite–$ZrSiO_4$ composite by colloidal processing, J. Mater. Sci. 29 (1994) 412–418.

[26] R. Petrović, Dj. Janaćković, B. Božović, S. Zec, Lj. Kostić-Gvozdenović, Densification and crystallization behaviour of colloidal cordierite-type gel, J. Serb. Chem. Soc. 66 (2001) 335–343.

[27] A.G. Evans, E.A. Charles, Fracture toughness determinations by indentation, J. Am. Ceram. Soc. 59 (1976) 371–372.

[28] H. Yanagida, K. Koumoto, M. Miyayama, The Chemistry of Ceramics, John Wiley & Sons Ltd., Chichester, 1996.

[29] T. Ozava, Kinetics of non-isothermal crystallization, Polymer 12 (1971) 150–158.

[30] J.A. Augis, J.E. Bennett, Calculation of the Avrami parameters for heterogeneous solid state reactions using a modification of the kissinger method, J. Therm. Anal. 13 (1978) 283–292.

[31] H. Yinnon, D.R. Uhlmann, Applications of thermoanalytical technicues to the study of crystallization kinetics in glass-forming liquids, Part I: theory, J. Non-Cryst. Solids 54 (1983) 253–275.

[32] K. Matusita, S. Sakka, Kinetic study of crystallization of glass by differential scanning calorimetry, Phys. Chem. Glasses 20 (1979) 81–84.

[33] D.R. Mc Farlane, M. Fragoulis, Theory of devitrification in multicomponent glass forming systems under diffusion control, Phys. Chem. Glasses 27 (1986) 228–234.

[34] I.W. Donald, The crystallization kinetics of a glass based on the cordierite composition studied by DTA and DSC, J. Mater. Sci. 30 (1995) 904–915.

[35] B.C. Lim, H.M. Jang, Crystallization kinetics and phase transformation characteristics in seeded monophasic cordierite gel, J. Mater. Res. 6 (1991) 2427–2433.

[36] K. Watanabe, E.A. Giess, Crystallization kinetics of high-cordierite glass, J. Non-Cryst. Solids 169 (1994) 306–310.