

Reaction kinetics of mechanically activated cordierite-based ceramics studied via DTA

Nina Obradović¹ · Nataša Đorđević² · Suzana Filipović¹ · Smilja Marković¹ · Darko Kosanović¹ · Miodrag Mitrić³ · Vladimir Pavlović¹

Received: 19 August 2015 / Accepted: 24 October 2015 / Published online: 27 November 2015
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Abstract Since cordierite, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ (MAS), is a very useful high-temperature ceramic material, it is important to decrease its sintering temperature. In order to accelerate the process of sintering, 5.00 mass% MoO_3 was added to the starting mixtures. The mechanical activation of the starting mixtures was performed in a high-energy ball mill in time intervals from 0 to 160 min. After the activation, starting mixtures were sintered at 1300 °C for 2 h. In order to determine the impact of mechanical activation on particle size distribution and powders morphology, the mechanically treated powders were characterized by a laser light-scattering particle size analyzer and scanning electron microscopy. The phase composition of the starting mixtures and sintered samples was analyzed by the X-ray diffraction method. In order to determine temperature intervals of chemical reactions and phase transitions, differential thermal analyses (DTA) and thermo-gravimetric analysis were used. Kissinger's equation was employed to calculate apparent activation energies of various processes that occur within the system during heating. Based on the obtained DTA results, it was established that mechanical activation along with MoO_3 additive has influence on sintering temperature which was decreased for more than 100 °C, comparing to the literature data.

Keywords Mechanical activation · DTA–TG · Sintering · Kinetics · Cordierite

Introduction

Cordierite-based ceramics ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) are widely applied in many fields due to their mechanical as well as electrical properties. Very low-temperature thermal expansion coefficient ($20 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$) makes this material applicable in devices exposed to sudden temperature changes, such as heating element supports, refractory ceramics for furnaces, oven-ware [1–7]. Low value of dielectric constant (~ 5) and high specific resistivity nominates this ceramic for application in electronics as an insulating material for devices operating in high frequencies, filters, multilayer circuit boards, etc. [8].

There are a few known approaches to produce cordierite ceramics, such as sol–gel method [2, 9], preparation from preceramic risen [10], but the most often is solid-state reaction due to its simplicity, inexpensiveness as well as production of larger amount of products necessarily for detailed investigation or commercial processing [8, 11–13]. In order to overcome kinetic/diffusion constraints, deriving from distance of particles in powders, which is common in solid-state reaction and require high synthesis temperatures, mechanochemical activation is very useful method. Process of activation increase the diffusion rates of components in mixture across phase boundaries, leading to accelerated reaction [8, 14]. During mechanical treatment, several processes occur: attrition of starting material, crystal lattice destruction, introduction of defects, etc. All mentioned processes increase the chance that during heating, synthesis and/or sintering process could be observed at lower temperatures than usual [15].

✉ Nina Obradović
nina.obradovic@itn.sanu.ac.rs

¹ Institute of Technical Sciences of SASA, Knez Mihailova 35/IV, Belgrade 11000, Serbia

² Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franse d'Eperea 86, Belgrade 11000, Serbia

³ Vinča Institute of Nuclear Sciences, University of Belgrade, Mike Alasa 12-14, Belgrade 11000, Serbia

Beside mechanical activation, additives addition is often used method for improvement in reaction in powders mixtures. There are many efforts of improvement in solid-state reaction in cordierite, which reduces sintering temperatures by adding different kind of functional additives: yttria-stabilized zirconia, ceria, B_2O_3 , P_2O_5 , $2MgO \cdot B_2O_3$, etc. [8, 9, 16].

Influence of combined effect of mechanical activation and additives is interesting for investigation. In this paper, simultaneous effects of mechanical treatment and sintering additives were investigated through monitoring reaction kinetics of mechanically activated cordierite-based ceramics, doped with MoO_3 , via DTA.

Experimental

Mixtures of MgO , Al_2O_3 , SiO_2 and MoO_3 (all 99 % Sigma–Aldrich) were used in these experiments. The mixtures of $MgO + Al_2O_3 + SiO_2$ in the 2:2:5 molar ratio, with the addition of 5.00 mass% MoO_3 , were mechanically activated by grinding in a high-energy planetary ball mill. 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, 40, 80 and 160 min. The samples were denoted as C-1–C-5 (C-1 for non-activated mixture, C-5 for 160 min of activation process).

The X-ray powder diffraction patterns were obtained using a Philips PW-1050 diffractometer with $\lambda Cu-K_\alpha$ radiation and a step/time scan mode of $0.05^\circ s^{-1}$. The measurements were taken on room temperature in air atmosphere.

The average particle size and particle size distribution were determined by a laser light-scattering particle size analyzer (PSA). The used instrument was Mastersizer 2000 (Malvern Instruments Ltd., UK) particle size analyzer based on laser diffraction, covering the particle size range of 0.02–2000 μm . For the PSA measurements, the powders were dispersed in distilled water, in ultrasonic bath (low-intensity ultrasound, at a frequency of 40 kHz and power of 50 W), for 5 min.

The morphology of the powders obtained after sintering was characterized by scanning electron microscopy (JEOL JSM-6390 LV). The pellets were cracked and covered with gold in order to perform these measurements.

The thermal behavior was determined by simultaneous TG–DTA (Setsys, SETARAM Instrumentation, Caluire, France) in the temperature range between 25 and 1400 $^\circ C$ under the air flow of 20 $mL min^{-1}$, in an Al_2O_3 pan. Experiments were done by heating rates of 5, 10, 20 and 30 $^\circ C min^{-1}$. Kissinger's equation was used to calculate activation energies of processes that occur within the system while heating.

The binder-free powders were compacted using the uniaxial double-action pressing process in an 8-mm-diameter tool (Hydraulic press RING, P-14, VEB THURINGER). The applied pressure was 392 MPa, and an amount of 0.3 g of powders was used for each pressed sample. The compacts were placed in an alumina boat and heated in a tube furnace (Lenton Thermal Design Typ 1600). The compacts were sintered isothermally at 1300 $^\circ C$ in air atmosphere for 120 min; the heating rate was 10 $^\circ C min^{-1}$. The density of specimens was calculated from the precise measurements of their diameter, thickness and mass.

Results and discussion

Diffraction pattern for C-1 mixture showed the presence of starting components [$Mg(OH)_2$, SiO_2 , Al_2O_3 , $AlO(OH)$, MgO and MoO_3]. All obtained intensities were identified by JCPDS cards [071–1126 for Al_2O_3 , 086–1628 for SiO_2 , 089–5108 for MoO_3 , 089–4248 for MgO , 083–0114 for $Mg(OH)_2$ and 074–1879 for $AlO(OH)$]. However, intensities of some peaks decreased with activation time, while some peaks are broadened which indicates that processes of crystal lattice destruction and amorphization have started (Fig. 1). Some $AlO(OH)$, MoO_3 and $Mg(OH)_2$ peaks may have not completely disappeared during activation process, but their concentration in the mixtures is too low to be detected using this technique. Although no new phases have been detected, our assumption is that the formation of new phases may have started, but those peaks are probably overlapped with SiO_2 peaks that are broadened. Due to great hardness of SiO_2 powder (crystal lattice energy is 13.125 $kJ mol^{-1}$), minor changes are notices within.

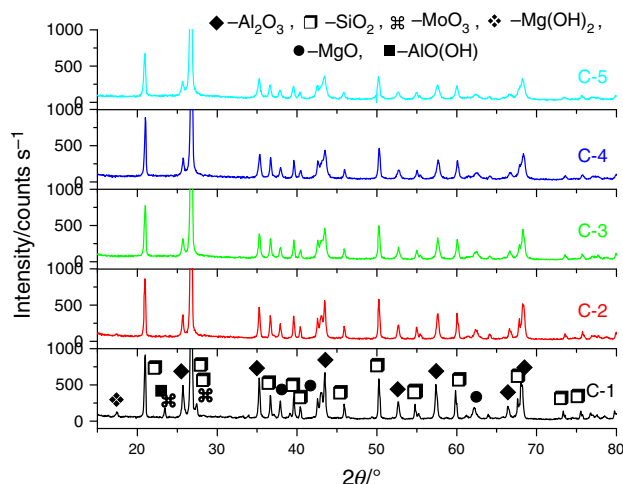


Fig. 1 XRD patterns of non-activated and mixtures activated 10–160 min

Particle size analysis, presented in Fig. 2, showed that average particle size $d(0.5)$, for non-activated mixture (C-1) is around 6 μm , while the value decreased with the increase in activation time (C-2). An exception from this behavior is noticed within powder C-3, where the particle size value is larger (around 9 microns). This type of behavior is consequence of agglomerates formation as a tendency of activated powder to decrease its surface energies. Average particle size for mixtures activated for 80 and 160 min is less than 5 μm . This is in accordance with XRD results, where destruction of crystal lattice was noticed as well as peak intensities decreasing as a function of prolonged activation time.

Figure 3 represents SEM micrographs of non-activated mixture and mixtures activated for 10, 40, 80 and 160 min. Initial non-activated mixture is a submicron powder composed of large number of particles various in shape and size. Attrition is noticed within powder activated 10 min. SEM C-3 represents agglomerates 5 micron in size covered by smaller particles, more uniform and regularly shaped. Micrographs (d) and (e) indicate at further attrition of agglomerates that were formed during prolonged mechanical activation.

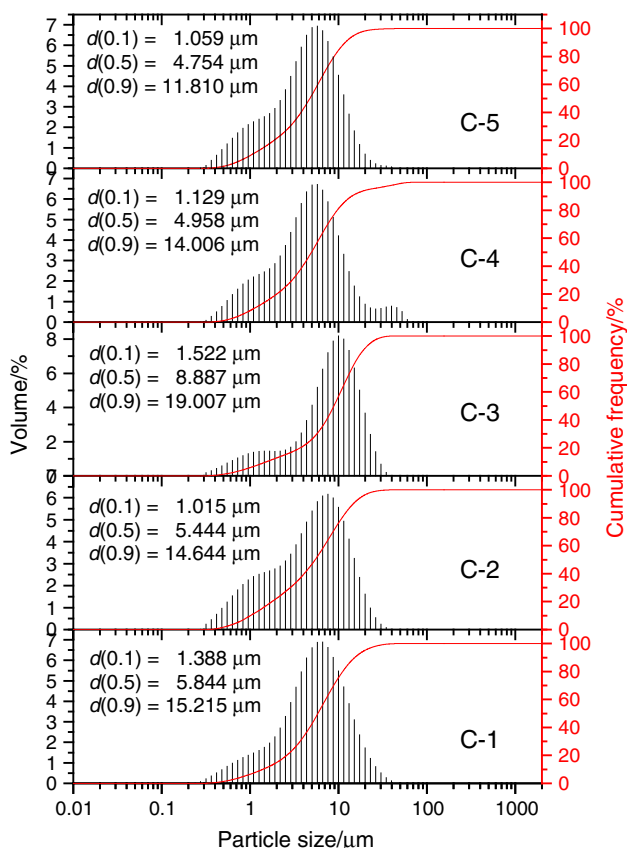


Fig. 2 Particle size analysis of mixtures non-activated and activated for 10–160 min

The milling process produces significant changes in the DTA–TG curves. Curves of non-activated and mixtures activated 10–160 min, with 10 $^{\circ}\text{C min}^{-1}$ heating rate, are shown in Figs. 4 and 5. All samples have well-defined DTA peaks. The first one is a strong endothermic peak at around 100 $^{\circ}\text{C}$, which belongs to humidity evaporation. Second is a weak endothermic peak at around 400 $^{\circ}\text{C}$ corresponding to the dehydroxylation of Al_2O_3 -based compounds [12]. A second important endothermic peak is observed in C-1, centered at 574 $^{\circ}\text{C}$, corresponding to the structural $\alpha \rightarrow \beta$ phase transition in crystalline SiO_2 [17]. This peak has a tendency to decrease its area when milling. In C-5, it becomes reduced to a small hump. Afterward, a small exothermic effect at 1045 $^{\circ}\text{C}$ appears in the mixture without treatment. This peak is due to the transformation of the non-crystalline structure of the SiO_2 -based compounds into a spinel or premullite phase [16]. This peak gradually shifts to lower temperatures with the increase in the grinding time. The fact that the premullite phase does not appear as a crystalline phase using XRD must be taken into account. Furthermore, exothermic peak centered at 1170 $^{\circ}\text{C}$ for C-1 and shifted to lower temperatures for activated samples (around 1120 $^{\circ}\text{C}$) could be attributed to mullite formation [11]. A reduction in the temperature can be observed for all activated samples. This is due to the reduction in the energy necessary to destroy the crystalline structure of the system. The energy supplied by the planetary mill causes structural disorder, through the distortion or breakage of the crystalline structure. This is evident from the reduction in the intensities of XRD peaks.

Within the range 1150–1400 $^{\circ}\text{C}$ (Fig. 4b), a series of exothermic effects were detected. De Aza et al. [18] using a high-sensitivity equipment found two exothermic peaks at 1275 and 1357 $^{\circ}\text{C}$, both corresponding to the formation of cordierite. In our case, the first peak can be detected in the C-1 sample centered at 1260 $^{\circ}\text{C}$ and shifted to lower temperatures (around 1200 $^{\circ}\text{C}$) when milling, having a tendency to increase the intensity, corresponding to μ -cordierite formation. In the activated samples, the exothermic peak for C-1 at 1328 $^{\circ}\text{C}$ which shifts to temperatures of about 1290 $^{\circ}\text{C}$ is assigned to the formation of α -cordierite [19].

The analysis of the TG curves (Fig. 5) confirms the behaviors observed by DTA since the dehydroxylation is accompanied by the corresponding mass losses.

The C-1 sample presents three mass loss steps well defined at 200, 400 and 1200 $^{\circ}\text{C}$, which are in accordance with the DTA peaks described, corresponding to water evaporation, dehydroxylation process and MoO_3 evaporation [20], respectively.

Kissinger's equation [21] was employed to calculate apparent activation energies of various processes that occur within the system while heating:

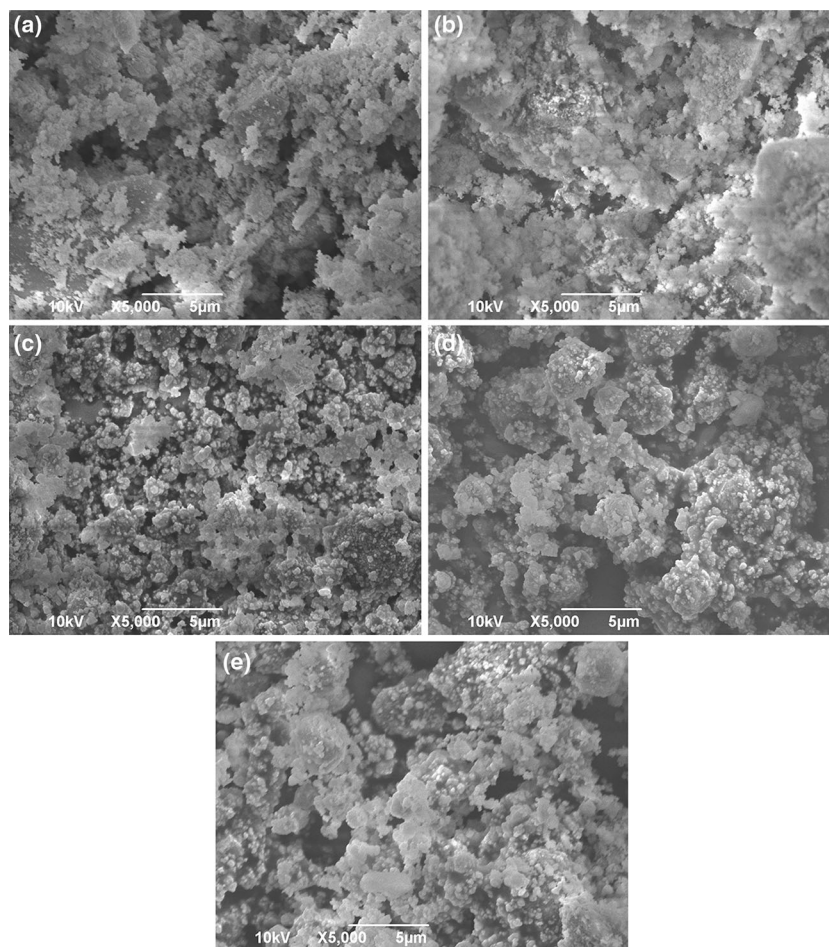


Fig. 3 SEM micrographs of samples **a** C-1, **b** C-2, **c** C-3, **d** C-4 and **e** C-5

$$\ln\left(\frac{\beta}{T_p^2}\right) = C - \frac{E_a}{R} \cdot \left(\frac{1}{T_p}\right) \quad (1)$$

where β is a constant heating rate (5, 10, 20 and 30 °C min⁻¹), T_p is the maximal absolute temperature at which the reaction peak/maximum occurs, R represents an ideal gas constant 8.314 J mol⁻¹ K⁻¹, C is a constant and E_a is the activation energy. Values of activation energies are given in Table 1.

The first peak at 1045 °C for C-1 and lower for activated samples corresponds to the transformation of the non-crystalline structure of the SiO₂-based compounds into a spinel or premullite phase. The second peak at 1260 °C for C-1 and lower for treated samples is assigned to cordierite formation. And the third peak centered at 1325 °C for non-activated sample and lower for activated samples is due to α -cordierite formation.

Table 1 shows apparent activation energies for various processes. It is clearly indicated that with prolonged milling

time, obtained values decrease. Mechanical energy introduced into the system during the mechanical treatment lowers energy necessary for enactment of appropriate processes. For example, energy necessary for cordierite formation is 212 kJ mol⁻¹ for non-activated sample and decreases to 70 kJ mol⁻¹ for the longest activated sample. Powder become more reactive due to the increase in specific surface area and number of contacts between particles which lead to the decrease in energy needed for reactions.

An exception to this tendency is noticed for α -cordierite formation. The highest value of activation energy is observed for sample activated 40 min, which could be correlated with existing agglomerates. In Fig. 2, distribution of sample C-3 shows the value $d(0.9) = 19 \mu\text{m}$. Reaction of such agglomerated powder is significantly more difficult owing to less number of contacts between particles, which leads to the increase in energy necessary for this mentioned process.

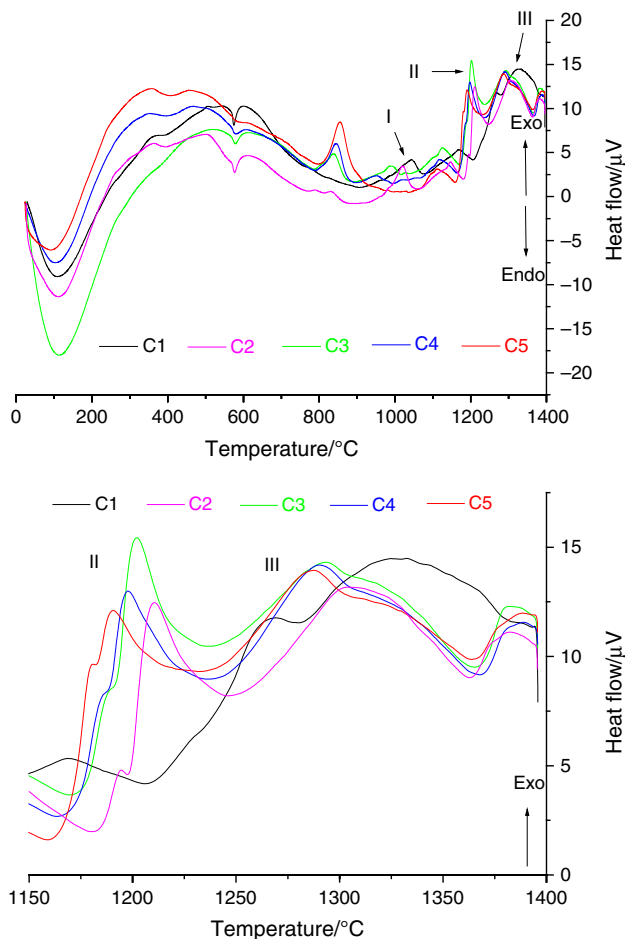


Fig. 4 a DTA curves of non-activated and mixtures activated 10–160 min, with 10 °C min⁻¹ heating rate b DTA curves of non-activated and mixtures activated 10–160 min with enlarged temperature interval 1150–1400 °C, with 10 °C min⁻¹ heating rate

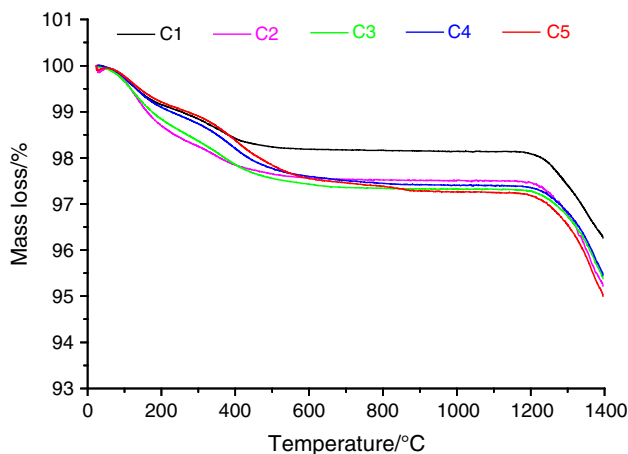


Fig. 5 TG curves of non-activated and mixtures activated 10–160 min

Table 1 Activation energies for various processes obtained by Kissinger’s equation

Peak	$E_a/kJ mol^{-1}$				
	C-1	C-2	C-3	C-4	C-5
I	337.815	245.295	243.917	215.316	–
II	211.903	166.084	158.488	77.154	70.096
III	370.506	672.146	1562.212	650.109	616.369

Figure 6 shows XRD patterns of activated and sintered samples. As it can be seen from presented diffractograms, single-phase system was not achieved. Cordierite is a major occurred phase along with minor share of $MgAl_2O_4$, SiO_2 and Al_2O_3 . Formation of spinel $MgAl_2O_4$ is caused by the presence of MgO and Al_2O_3 agglomerates in starting powder mixtures, incurred during the mechanical treatment. Furthermore, should be noted that few peaks of quartz is superimposed to the intensive peaks of cordierite so identification is not trivial and easy. Sharper and intensive peaks of cordierite indicate that reaction sintering along with crystallization take place during heating treatment. Presence of other phases indicates that reaction is not completed yet.

Figure 6 presents changes in microstructure of activated samples sintered at 1300 °C for 2 h. As it can be noticed, all samples show very high porosity, which is in correlation with very low values of relative densities (shown in Table 2, from 73 to ~77 % TD). Low densities about 77 % usually characterize cordierite ceramic [22]. Even cordierite

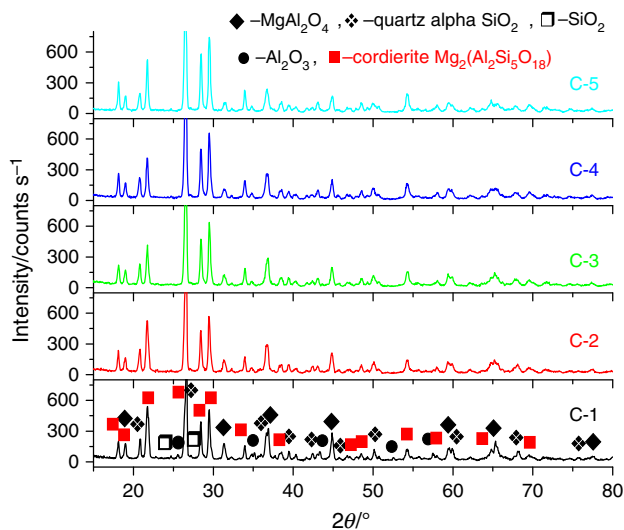


Fig. 6 XRD patterns of non-activated and activated mixtures sintered at 1300 °C for 2 h

Table 2 Densities of samples sintered at 1300 °C for 2 h

sample	$\rho_s/\%TD$
C-1	74.42
C-2	76.57
C-3	76.77
C-4	75.49
C-5	73.15

TD theoretical density (2.51 g cm^{-3})

obtained using other synthesis methods, such as obtaining from preceramic polymers, does not reach higher densities than 80 % of TD [10]. At micrograph of samples activated for 40 and 80 min, note the large compact areas which are consequence of sintering within the agglomerate of starting powders. Present open porosity along with low-density values indicates first or early medium sintering stage for these samples (Fig. 7).

Conclusions

Simultaneous action of effects, mechanical treatment as well as additives addition were investigated through monitoring reaction kinetics of mechanically activated cordierite-based ceramics, doped with MoO_3 , via DTA.

XRD results indicate no new phase formation although intensive decrease in peak's intensities along with amorphization and peak broadening has been noticed. Particle size analysis indicates the attrition of starting powders. The increase in particle size is observed for sample activated 40 min, indicating the presence of agglomerates, followed by SEM micrographs. DTA has given us characteristic temperatures for various well-described processes occurring in the system during heating up to 1400 °C. Based on Kissinger's equation, activation energies for spinel or premullite phase formation, cordierite and α -cordierite formation were calculated. Decrease in activation energy for the first process from 338 to 215 kJ mol^{-1} and for the

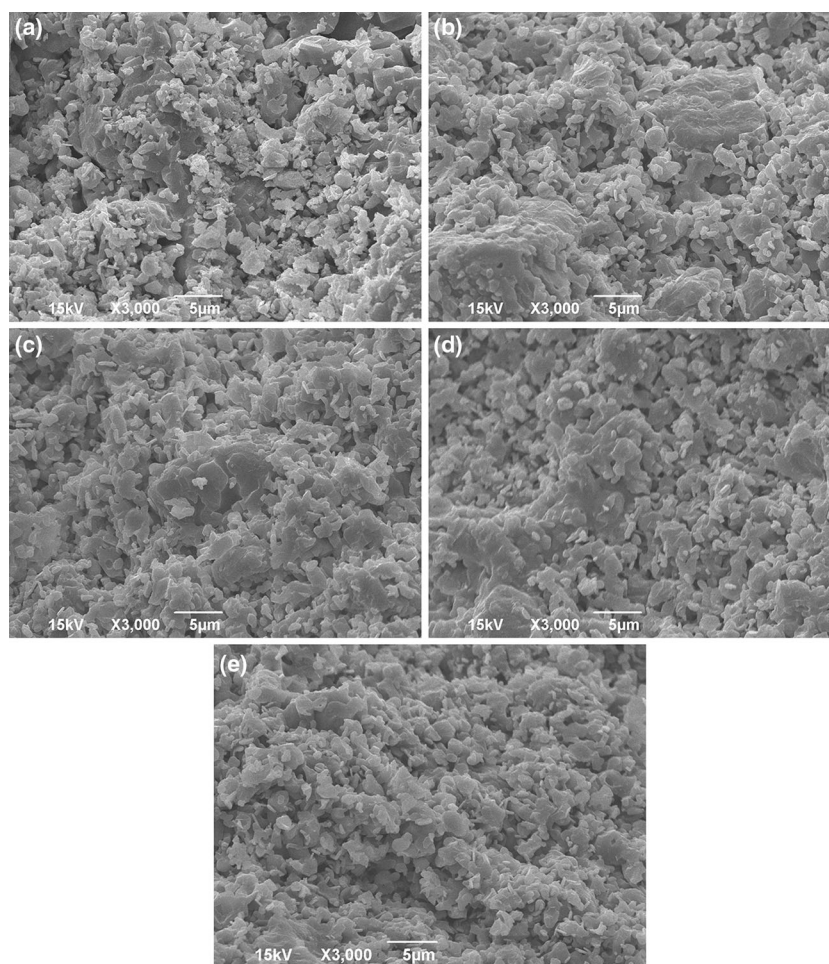


Fig. 7 SEM micrographs of samples **a** C-1, **b** C-2, **c** C-3, **d** C-4 and **e** C-5, sintered at 1300 °C for 2 h

second one from 212 to 70 kJ mol⁻¹ is correlated with the increase in powder reactivity which is caused by introduced mechanical energy. An exception for process of α -cordierite formation was attributed to agglomerate existence. Comparing to the literature data, it was established that mechanical activation with MoO₃ addition leads to the decrease in sintering temperature for more than 100 °C.

Thermal treatment did not lead to single-phase formation. Beside cordierite as a major phase, XRD patterns showed minor share of MgAl₂O₄, SiO₂ and Al₂O₃ phases. Densities exceed 70 % of TD, which is common for this type of ceramic material.

Acknowledgements This research was performed within the project 172057, funded by the Ministry for education, science and research development of the Republic of Serbia and project F-7/II funded by the Serbian Academy of Sciences and Arts.

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