

UDK 622.785;549.632

Influence of Prolonged Sintering Time on Density and Electrical Properties of Isothermally Sintered Cordierite-based Ceramics

A. Peleš^{1,*}, N. Đorđević², N. Obradović¹, N. Tadić³, V. B. Pavlović¹

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

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

³Faculty of Physics, University of Belgrade, Studentski Trg 12, 11000 Belgrade, Serbia

Abstract:

Mechanical activation is a commonly used and relatively fast and inexpensive procedure for sample preparation before the sintering process. Cordierite, a stoichiometric mixture of three different oxides ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) is a very attractive, widely used high-temperature ceramic material. The mechanical activation of the starting mixtures with 5.00 mass% TiO_2 was performed in a high energy ball mill during 10-80 min. The applied compaction pressure before the sintering process was 2t/cm^2 , based on our recent investigation. The sintering process was performed at 1350°C for 2h and 4h in air atmosphere. X-ray diffraction was used to analyze the phase composition of non-activated and 80 min activated samples, sintered for 2 and 4h, respectively. Scanning electron microscopy was performed to analyze the microstructure of both compacted and sintered samples. Atomic force microscope was used to investigate the surface of the sintered samples. This paper investigates the influence of prolonged sintering time on the densities of the sintered samples, along with electrical properties.

Keywords: Mechanical activation, Density, XRD, SEM, Electrical properties, AFM, Cordierite.

1. Introduction

Cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) based ceramics are widely used in various fields, from substrates for micro-electronic packaging industry to cookware, heat exchangers, glazes for floor tiles. Owing to the very low temperature thermal expansion coefficient ($20\cdot 10^{-7}/^\circ\text{C}$) and low relative dielectric constant (~ 5), these ceramics are also well known by their good thermo-mechanical, chemical and dielectric properties [1,2]. They can be applicable as materials that are exposed to sudden temperature changes [3-7] and also as a semiconducting bearers [8,9]. The temperature range of cordierite sintering is very narrow ($1300\text{-}1400^\circ\text{C}$).

Our previous investigations showed a significant influence of mechanical activation, as well as compaction pressure on starting mixtures (kaolin, quartz, magnesium oxide) on lowering of sintering temperature [10]. Mechanically activated components increased energy

*) Corresponding author: adriana.peles@itn.sanu.ac.rs

due to induced crystal defects compared to non-activated ones. During mechanochemical treatment, several processes occur: attrition of starting material, crystal lattice destruction, various defects formation, etc. All mentioned processes increase the chance that during heating, processes could be observed at lower temperatures than usual [11]. Furthermore, mechanical activation could affect the final electrical characteristics, so it is very important to approach and understand changes that get introduced into the system while milling.

In this paper, the authors used some starting conditions based on the previous investigation and tried to study the influence of sintering time on density, phase composition as well as on the microstructure along with electrical properties of sintered samples.

2. Experimental procedure

Mixtures of Mg(OH)₂, Al₂O₃, SiO₂ and TiO₂ (all p.a. purity) were used in these experiments. The cordierite ceramics starting mixture, MgO+Al₂O₃+SiO₂ in the 2:2:5 ratio, with the addition of 5.00 mass% TiO₂, were mechanically activated by grinding in a high-energy planetary ball mill. ZrO₂ vessels and balls were used with the powder to balls mass ratio of 1:40. The milling process was performed in air atmosphere for 10, 20, 40 and 80 minutes. The samples were denoted as K-0, K-10, K-20, K-40 and K-80, according to the milling time

The X-ray powder diffraction patterns after milling and sintering were obtained using a Philips PW-1050 diffractometer with λ Cu-K $_{\alpha}$ radiation and a step/time scan mode of 0.05°/1s. The morphology of the obtained powders and sintered samples were characterized by scanning electron microscopy (JEOL JSM-6390 LV). The powders were crushed and covered with gold in order to perform these measurements.

The pressure used in our experiments was 2t/cm² (approximately 200 MPa). The pressure was performed in a double-sided tool 6 mm in diameter (Hydraulic press RING 14, VEB THURINGER). The density of the specimens was calculated from measurements of their diameter, thickness, and mass. The theoretical density (TD) of mixture is 3.078 g/cm³ and is calculated based on the following equation:

$$\rho_{mixture} = \frac{m_{mixture}}{V_1 + V_2 + V_3 + V_4} \quad (1)$$

where: m – mass of the mixture (30.00 g), V₁, V₂, V₃ and V₄ – volumes of component 1 – Mg(OH)₂, component 2 – SiO₂, component 3 – Al₂O₃ and component 4 – TiO₂ in the mixture, calculated by usage of TD of each component.

The compacts were sintered isothermally at 1350°C, in air atmosphere for 2h and 4h, with heating rate of 10°C/min in a Lenton furnace.

The topography and roughness of samples were characterized using an atomic force microscope (AFM; Veeco Instruments, model Dimension V). Micrographs were obtained in tapping mode under ambient conditions, using TAP300 tips (resonant frequency 300 kHz, force constant 40 N/m). Roughness data were obtained using diNanoScope software (version 7.0). Scan sizes were 10x10 microns.

3. Results and discussion

Mechanically activated samples of cordierite with the addition of 5mass% TiO₂ were sintered for 2 and 4 hours at 1350°C. The density changes of the samples before and after sintering process were investigated. Density values of samples before and after sintering are shown in Tab. I for samples sintered for 2 hours, and in Tab. II for samples sintered for 4 hours. The results shown in Tabs I and II are consistent with the expected results. The density

of the samples was higher than the density of the starting material, also the density increased with prolonged sintering time.

Tab. I Mass and densities of green bodies and 2h sintered cordierite samples with addition of 5mass% TiO₂.

| activation time (min) | *m _o (g) | m _s (g) | **ρ _o (g/cm ³) | ρ _s (g/cm ³) |
|-----------------------|---------------------|--------------------|---------------------------------------|-------------------------------------|
| 0 | 0.2980 | 0.2845 | 2.001 | 1.990 |
| 10 | 0.2991 | 0.2845 | 2.070 | 2.145 |
| 20 | 0.2978 | 0.2839 | 2.048 | 2.178 |
| 40 | 0.2986 | 0.2845 | 2.039 | 2.184 |
| 80 | 0.2982 | 0.2856 | 1.962 | 2.168 |

Tab. II Mass and densities of green bodies and 4h sintered cordierite samples with addition of 5mass% TiO₂.

| activation time (min) | m _o (g) | m _s (g) | ρ _o (g/cm ³) | ρ _s (g/cm ³) |
|-----------------------|--------------------|--------------------|-------------------------------------|-------------------------------------|
| 0 | 0.2980 | 0.2840 | 1.975 | 2.011 |
| 10 | 0.2978 | 0.2835 | 2.072 | 2.160 |
| 20 | 0.2980 | 0.2843 | 2.035 | 2.204 |
| 40 | 0.2982 | 0.2842 | 2.050 | 2.202 |
| 80 | 0.2983 | 0.2853 | 1.968 | 2.178 |

*m_o, m_s - mass of sample before and after sintering process

**ρ_o, ρ_s - densities of sample before and after sintering process

In order to compare the results of changes in the density of samples before and after the sintering process, density variation $\Delta\rho$, ($\Delta\rho = \rho_s - \rho_o$), as a function of mechanical activation time for both sintering time, 2 and 4 hours, was analyzed. The results are presented at Fig. 1.

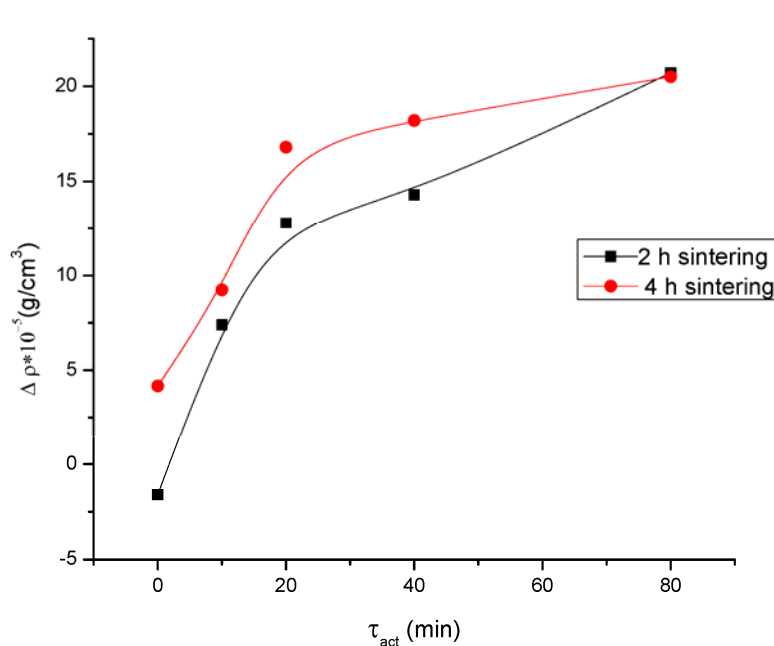


Fig. 1. Density changes as a function of mechanical activation time for cordierite samples sintered for 2h and 4h at 1350°C.

The curves show that $\Delta\rho$ of samples sintered for 2h and 4h increased rapidly in the first 20 minutes of mechanical activation, whereas the densities of samples sintered for 4h have a higher value. We expected these results if we have in mind the great energy that is introduced within the powder during milling process and the starting conditions (balls to powder mass ratio 40:1).

In the first 20 min of mechanical activation, the major changes are taking place in the starting powder material. It causes significant fragmentation and homogenization of the starting ingredients. Thus the activated samples during the sintering process show faster chemical reaction in the solid state and the density curve of the sintered samples as a function of activation time shows that the length of time of mechanical activation significantly increases the density of the obtained material. Samples sintered for 4 hours have a higher change in density than samples sintered for 2 hours. Samples sintered 2 and 4 hours exhibit changes in density sharply in the first 20 minutes of mechanical activation. After 20 min of activation time, density changes are still moving to higher values, but slower.

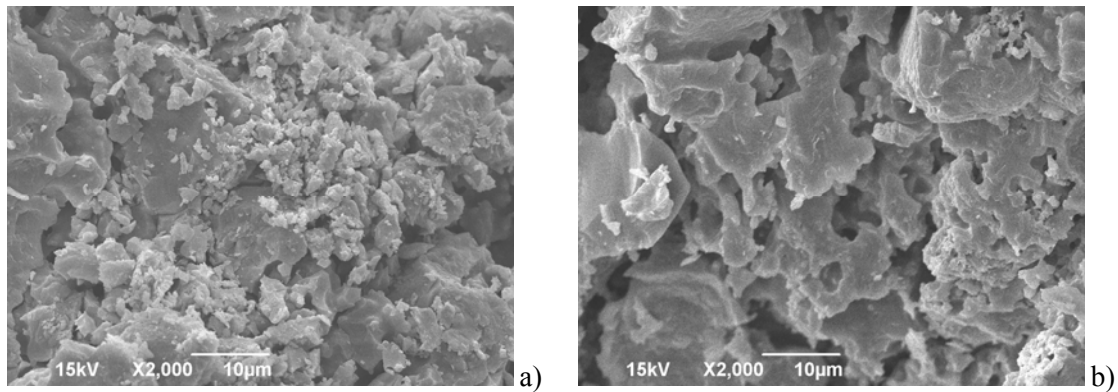


Fig. 2. SEM of non-activated samples sintered at 1350°C for a) 2h and b) 4h.

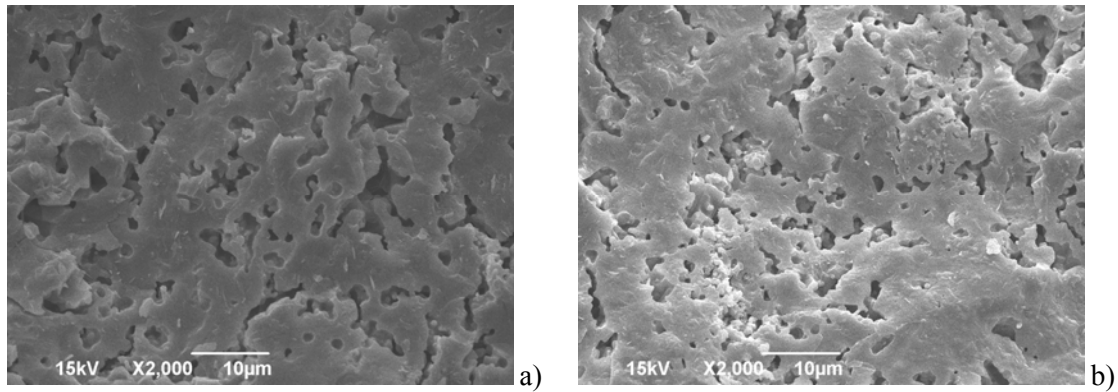


Fig. 3. SEM of mechanically activated samples for 80 minutes sintered at 1350°C for a) 2h and b) 4h.

Figs. 2. and 3. represent scanning electron micrographs of sintered powders. Non-activated powder sintered for 2 hours (Fig. 2. a) shows fine-grained structure, defined grain sintered material, and high porosity between grains. The surface is rough. The particles of the starting material were homogenized, but the extension of time of sintering (Fig. 2. b) at a temperature of 1350°C leads to further convergence of grain, and the reaction sintering process allows better contact of the starting particles. This leads to the formation of larger agglomerates. The porosity of the obtained product is lower than the previous sample sintered for 2h, but still very high. Defined grains are much less conspicuous. Blocks of agglomerates

are formed, due to a longer sintering time. Samples which were mechanically activated for 80 minutes showed a significantly smoother texture.

Porosity was significantly smaller, and was practically a negligible difference in the appearance between the surface of samples sintered for 2 and 4 hours (Fig. 3. a) and b)). The defined grain of the starting powder material flow is not visible. Based on the SEM images, we can see a significant influence of mechanical activation on the sintering process, and the impact of the length of the sintering process on the cordierite sample set.

XRD patterns of samples non-activated and activated for 80 min and sintered for 2h and 4h at 1350°C are shown in Figs. 4. and 5. All obtained intensities were identified by JCPDS cards (084-1220 for cordierite, 083-2241 for TiO₂ rutile, 074-0201 for SiO₂, 089-7717 for alumina and 084-0377 for magnesium aluminum oxide).

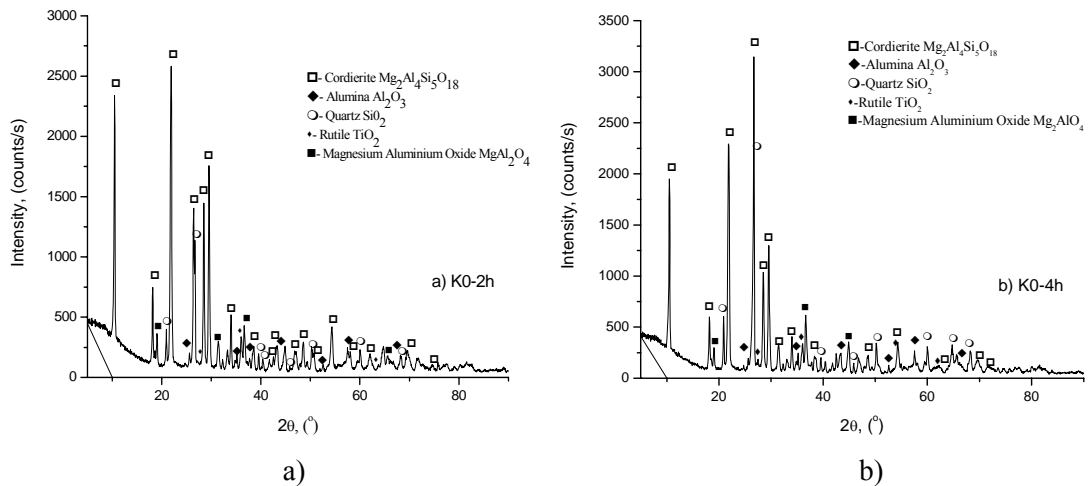


Fig. 4. XRD patterns of non-activated samples sintered at 1350°C for a) 2h and b) 4h.

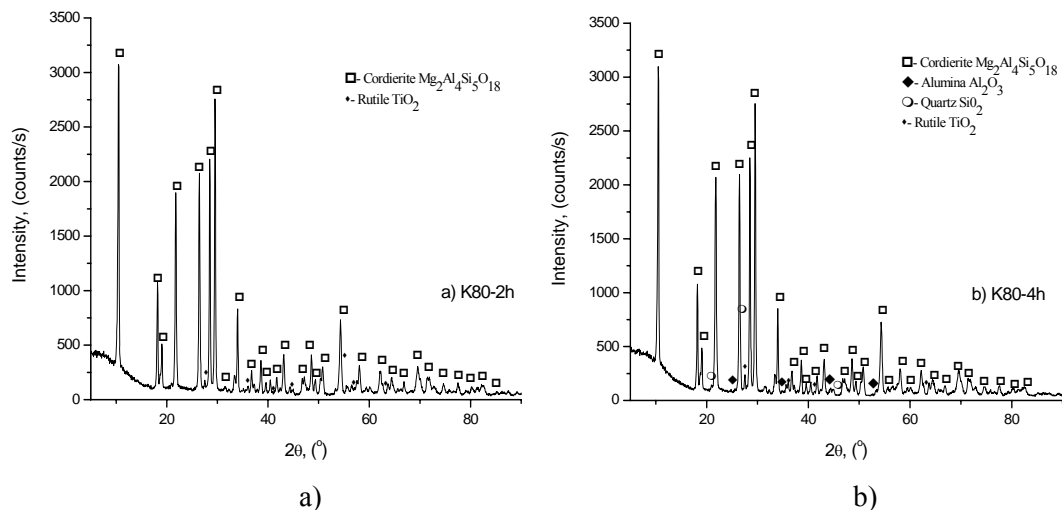


Fig. 5. XRD patterns of samples activated 80 min sintered at 1350°C for a) 2h and b) 4h.

XRD analysis of non-activated samples sintered 2 and 4 hours shows a presence of cordierite formation as well as the remains of the starting oxides. Corundum (Al₂O₃), quartz (SiO₂) and MgAl₂O₄ and TiO₂ rutile were detected. Comparing the diffraction patterns of non-activated samples, sintered 2 and 4 hours, it can be seen that the sample sintered 4 h have higher amounts of cordierite (66% compared with 60% cordierite sintered for 2 hours). The remains of the starting oxides are reduced with the prolonged sintering of the starting material.

Diffraction patterns which are mechanically activated 80 minutes (Fig. 5.) had significantly greater responses compared to non-activated sintered samples. The sample which was sintered for 2 hours showed practically insignificant traces of the starting oxides corundum (2.4%) and quartz (0.9%) and (95.4%) cordierite phase. The sample sintered for 4 hours has no remaining traces of the starting oxides (except rutile TiO_2 content of 2% additives whose presence was expected). Cordierite is present in an amount of 98%, which can be considered a fully completed reaction during the sintering process.

Tab. III Electrical properties of cordierite after sintering at 1350°C for a) 2h and b) 4 h as a function of milling time (0 – 80 min).

| a) | | | b) | | |
|----|------|--------------|----|------|--------------|
| 2h | C | ϵ_r | 4h | C | ϵ_r |
| 0 | 0.71 | 3.7418 | 0 | 0.77 | 4.0973 |
| 10 | 0.88 | 4.6468 | 10 | 0.82 | 4.3248 |
| 20 | 0.88 | 4.6734 | 20 | 0.84 | 4.5167 |
| 40 | 0.80 | 4.3363 | 40 | 0.92 | 4.9741 |
| 80 | 0.83 | 4.6462 | 80 | 0.82 | 4.5992 |

Tab. III presents the results of measured capacitance. Electrical properties of the obtained materials were monitored as a function of time of mechanical activation and prolonged sintering time. From these data the value of the dielectric constant was calculated. Electrical measurements were in great accordance with results given previously in the paper regarding XRD patterns. It is obvious that the milling and sintering time have influence on the capacitance and dielectric constant values. Two areas are visible: the first one for samples activated 0 – 20 minutes, and the second for samples activated 20 – 80 min. Both the capacitance and dielectric constant rapidly increase with the first 20 minutes of activation, whereby more significant changes in the sample sintered for 2 hours. After 20 minutes of mechanical activation changes in capacitance and dielectric constant are smaller. Data value for the dielectric constant of the sintered samples for 2 and 4 hours range from 3.74 to 4.97, as expected.

We investigated the influence of sintering time and the influence of activation time by AFM. Due to pictures we made by AFM we can see that roughness of our samples decrease with sintering time and activation time. On the Fig. 6. a) we can see the non-activated sample sintered for 2h (Image roughness is 1039 nm) and has greater roughness than the sample sintered at 1350° for b) 4h (Image roughness is 763 nm). On the Fig. 7. we can see sample activated for 80 minutes and sintered for a) 2h and b) 4h, and the same influence of activation and sintering time are noticed. Image roughness for sample sintered for 2h is 611 nm, and for the sample sintered for 4h is 352 nm.

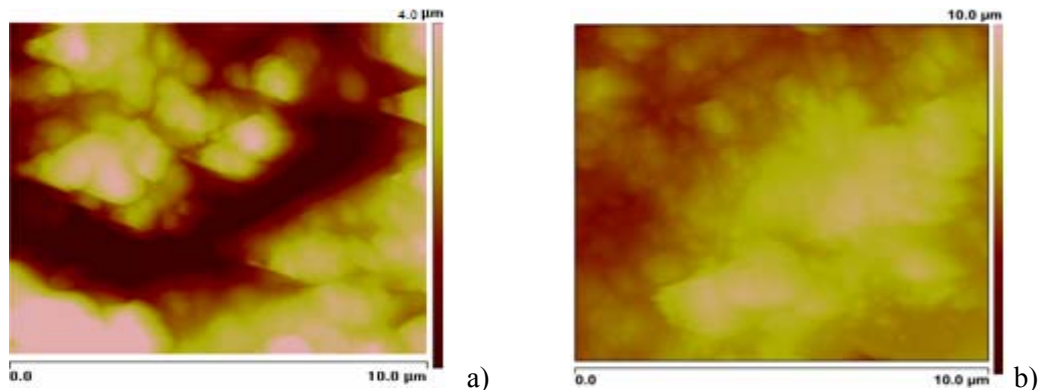


Fig. 6. AFM of non-activated samples sintered at 1350°C for a) 2h and b) 4h.

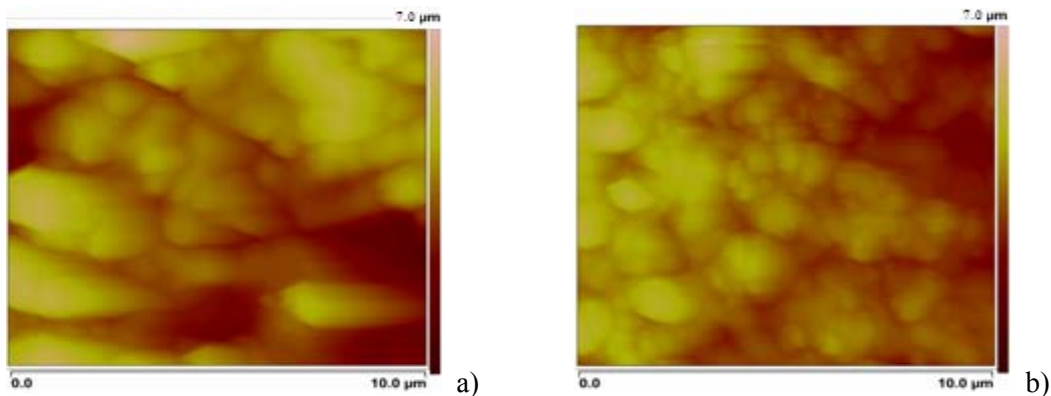


Fig. 7. AFM of 80 minutes activated samples and sintered at 1350°C for a) 2h and b) 4h.

4. Conclusions

Investigation results shows that sintering time, as well as mechanical activation, has influence on the final characteristics of the sintered material. The results that justify prolonged sintering time are:

- Longer sintering time increases the density variation of the sintered samples. The time of mechanical activation has also influence on the density changing of the samples, and increases with increasing sintering time.

- At the same sintering temperature, samples activated 80 minutes have a higher percentage of reacted starting material compared to samples that have not been activated. For samples that were sintered 4 hours and 80 minutes activated starting components were not found. Cordierite ceramics was obtained in an amount of 98%. The remaining 2% is TiO₂ rutile, which was added to the starting mixture as an additive.

- SEM results shows that samples which were mechanically activated for 80 minutes showed a significantly smoother texture. Porosity was significantly smaller than non-activated samples surface, and was practically a negligible difference in the appearance between the surface of samples sintered for 2 and 4 hours.

- Electrical investigation shows the influence of mechanical activation time and sintering time on values of capacitance and dielectric constant. Both capacitance and dielectric constant rapidly increase with first 20 minutes of mechanical activation. Data value for the dielectric constant of the sintered samples 2 and 4 hours range from 3.74 to 4.97, which is in accordance with literature data.

- AFM results shows that samples which were mechanically activated for 80 minutes showed a significantly smoother texture. Image roughness is in decrease with mechanical activation time as well as sintering time.

Acknowledgement

This research was performed within project 172057OI funded by the Ministry for Education and Science of the Republic of Serbia.

5. References

1. A. I. Kingon, R. F. Davis, Engineer Materials Handbook, Vol. 2. "Ceramics" edited by S. J. Schneider, Jr., ASM International Metals Park, OH, (1991) 758.
2. N. Obradovic, N. Djordjevic, S. Filipovic, N. Nikolic, D. Kosanovic, M. Mitric, S. Markovic, V. Pavlovic, Powder Technology 218 (2012) 157.
3. V. J. Powers, C.H. Drummond, Ceram. Eng. Sci. Proc. 7 (1986) 969.
4. I. Warsworth, R. Stevens, J. Eur. Ceram. Soc. 9 (1992) 153.
5. M. Pinero, M. Atik, J. Zarzycki, J. Non-Cryst. Solids 147–148 (1992) 1523.
6. D. Kervadec, M. Coster, J.L. Chermant, Mater. Res. Bull 27 (1992) 967.
7. N. Clausen, G. Petzow, J. Phys. (Paris), 47 (1986) 693.
8. R. R. Tumulala, J. Am. Ceram. Soc. 74 (1991) 895.
9. S. H. Knickerbocker, A. H.Kumar, L. W. Herron Am. Ceram. Soc. Bull. 72 (1993) 90.
10. N. Djordjevic, N. Obradovic, S. Filipovic, J. Zivojinovic, M. Mitric, S. Markovic, Tehnika – Novi materijali 21 (2012) 3, 329.
11. N. Đorđević, M.M. Ristić, Lj. Pavlović, M. Lazić, J. Stojanović, TEOTES, IV konferencija "Teorija i tehnologija sinterovanja" (2001) 25.
12. J. S. Reed, Introduction to the Principles of Ceramic Processing, Wiley, New York (1988) 158.
13. G. L. Messing, C. J. Markhoff, L. G. McCoy, J. Am. Ceram. Soc., 61 (1982) 857.
14. I. Shapiro, Adv. Powder Metall. Part. Mater., 3 (1994) 41.
15. J. K. Beddow, Particulate Science and Technology, Chemical Publishing Co.,Inc. New York, (1980), 285.
16. R. M. German, Particle Packing Characteristics, Metal Powder Industries Federation, Princeton, New Jersey, (1989) 59.
17. R. Panelli, F. A. Filho, Powder Tech., 114 (2001) 255.
18. N. Obradovic, S. Stevanovic, M. Mitric, M. V. Nikolic, M. M. Ristic, Science of Sintering, 39 (2007) 241.

Садржај Механичка активација је брза и јефтина процедура која се обично користи за припремање узорака пре процеса синтеровања. Кордијерит, стехиометријска мешавина три различита оксида ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) је веома атрактиван, и широко коришћен високотемпературни керамички материјал. Почетна смеша са 5.00 масених % TiO_2 је механички активирана у високоенергетском млину са куглицама у временском интервалу од 10- 80 минута. Пре процеса синтеровања узорци су испресовани под притиском од 2t/cm^2 , базирано на нашем пређашњем истраживању. Узорци су синтеровани на температури од 1350°C у периоду од 2 и 4 сата у атмосфери ваздуха. Дифракцијом X зрака је установљена фаза неактивираних и узорака активираних 80 минута, синтерованих 2 и 4 сата, респективно. Скенирајућом електронском микроскопијом је анализирана микроструктура оба синтерована узорка. Микроскопом атомских сила смо анализирали површину оба узорка. Овај рад испитује утицај продуженог времена синтеровања на густину синтерованих узорака, као и електричне особине.

Кључне речи: Механичка активација, Густина, XRD, SEM, Електричне особине, AFM, Кордијерит.
