

UDK 549.632; 622.785

Sintering of Cordierite in the Presence of MoO₃ and Crystallization Analysis

N. Đorđević¹, N. Obradović², D. Kosanović^{2*)}, M. Mitrić³, V. P. Pavlović⁴

¹Institute for Technology of Nuclear and Other Raw Mineral Materials, Franchet d'Esperay st. 86, 11000 Belgrade, Serbia

²Institute of Technical Sciences of SASA, Knez Mihailova 35/IV, 11000 Belgrade, Serbia

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

⁴Faculty of Mechanical Engineering, University of Belgrade, Belgrade, Serbia

Abstract:

Cordierite (MAS) is difficult to sinter because of the very narrow sintering temperature range (1300-1400°C). Because a low temperature process is desirable, it is necessary to find functional ads which can allow easier sintering process at lower temperature. The influence of MoO₃ on the preparation process of cordierite ceramics was investigated. 2MgO-2Al₂O₃-5SiO₂ was researched by sintering followed binary systems: MgO/MoO₃, Al₂O₃/MoO₃ and SiO₂/MoO₃ (all sintered at 850°C and 1100°C, sintering time 2h). Composition of these systems was 80 mass% of oxide and 20 mass% MoO₃. The effects of sintering, the composition and morphology were followed by X-ray diffraction and SEM microscopy. It has been found that MoO₃, beside liquid phase, forms intermediary unstable compounds with MgO and Al₂O₃, which is the significance information for further research. MAS ceramics were sintered with 20 mass% MoO₃ at 1100°C, 1200°C and 1300°C, during 2h.

Keywords: Cordierite, Sintering, MoO₃, XRD, SEM.

1. Introduction

Cordierite (2MgO-2Al₂O₃-5SiO₂) is a technically important ceramic which is applied in a great variety of areas. Cordierite and cordierite based glass ceramics, well known because of their low dielectric constant, high resistivity, elevated thermal and chemical stability and very low thermal expansion coefficient, are promising materials for electronic applications. Due to its lower processing costs and its better electrical properties, cordierite is an alternative material to be used as substrate in replacement of alumina, conventionally employed in the electronic industry [1-3].

Ceramic bodies with high cordierite content have excellent thermal shock resistance. They also have low dielectric constants (~5) and low thermal expansion coefficient (20·10⁻⁷/°C) [4]. These properties make them suitable for a wide range of high-temperature applications [5-9] and semiconductors [10,11].

Cordierite is difficult to sinter because of the very narrow sintering temperature range

*) Corresponding author: darko.kosanovic@itn.sanu.ac.rs

(1300-1400°C) [12]. Because a low temperature process is desirable, it is necessary to find functional ads which can allow easier process of sintering at lower temperature. The melting temperature of these ads 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: Cr₂O₃, ZrO₂, K₂O, B₂O₃, TiO₂, Bi₂O₃ etc [13]. MoO₃ has necessary criteria to form a liquid phase and support cordierite sintering, such as large atomic radius of 145 pm and low melting temperature (795°C). Molybdenum trioxide forms eutectics with magnesium and aluminum.

2. Experimental procedure

In these experiments, authors used powders of MgO, Al₂O₃, SiO₂ and MoO₃ (all p.a.). First part was 20 mass% MoO₃ and 80 mass% of other oxides. Second part was 20 mass% MoO₃ and 80 mass% of MAS (2MgO+2Al₂O₃+5SiO₂). Mixtures were homogenized by mixing in ball mill during 2 minutes.

The binder-free powders were compacted using a uniaxial double action pressing process in an 8 mm diameter tool (hydraulic press RING, P-14, VEB THURINGER). Compacts were placed in an alumina boat and heated in a tube furnace (Lenton Thermal Design Typ 1600).

Starting oxides with MoO₃ were sintered isothermally at 850 and 1100°C in an air atmosphere for 2 hours and a heating rate of 10°C/min. Those samples were denoted as AM1 for Al₂O₃+MoO₃ sintered at 850°C 2h; AM2 for Al₂O₃+MoO₃ sintered at 1100°C 2h; MM1 for MgO+MoO₃ sintered at 850°C 2h; MM2 for MgO+MoO₃ sintered at 1100°C 2h; SM1 for SiO₂+MoO₃ sintered at 850°C 2h; SM2 for SiO₂+MoO₃ sintered at 1100°C 2h.

MAS with MoO₃ were sintered isothermally at 1100, 1200 and 1300°C in an air atmosphere for 2 hours and a heating rate of 10°C/min. Samples were denoted as MASM1 for MAS+MoO₃ sintered at 1100°C for 2h; MASM2 for MAS+MoO₃ sintered at 1200°C for 2h and MASM3 for MAS+MoO₃ sintered at 1300°C for 2h.

X-ray powder diffraction patterns after sintering were obtained using a Philips PW-1050 diffractometer with λ Cu-K α radiation and a step/time scan mode of 0.05 °/s.

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

3. Results and discussion

Results presented on Fig. 1. are XRD patterns for a) AM1 (Al₂O₃+MoO₃ sintered at 850°C 2h) and b) AM2 (Al₂O₃+MoO₃ sintered at 1100°C 2h). Besides starting oxides, Al₂(MoO₄)₃ is detected on both diffraction patterns, and Al(OH)₃ is present on higher sintering temperature. It was noticed that intermediary compound along with oxides have more pronounced peaks at 1100°C.

Results presented on Fig. 2. are XRD patterns for a) MM1 (MgO+MoO₃ sintered at 850°C 2h) and b) MM2 (MgO+MoO₃ sintered at 1100°C 2h). MM1 pattern shows MgO, MoO₃ and intermediary compound MgMoO₄. On the other hand, MM2 shows no MoO₃ peaks because the reaction between starting components is completed, therefore MgO and MgMoO₄ are the only detected phases, with greater intensities.

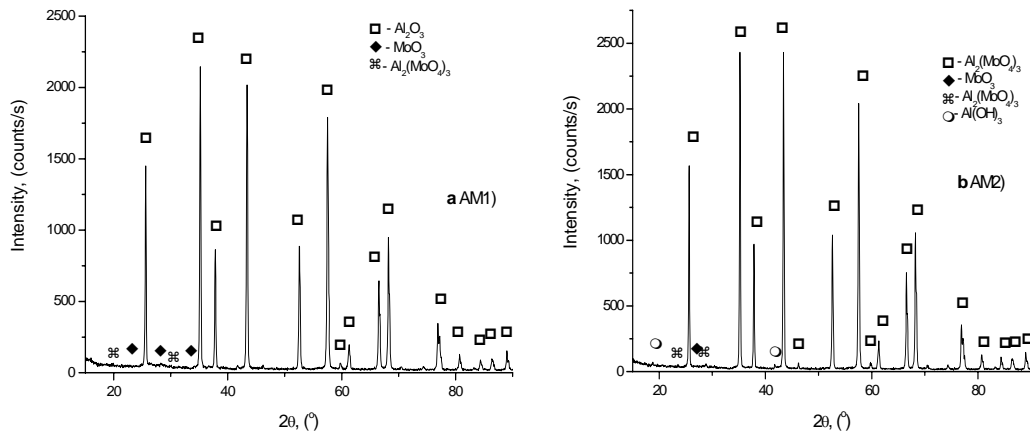


Fig. 1. XRD patterns of a) AM1 and b) AM2.

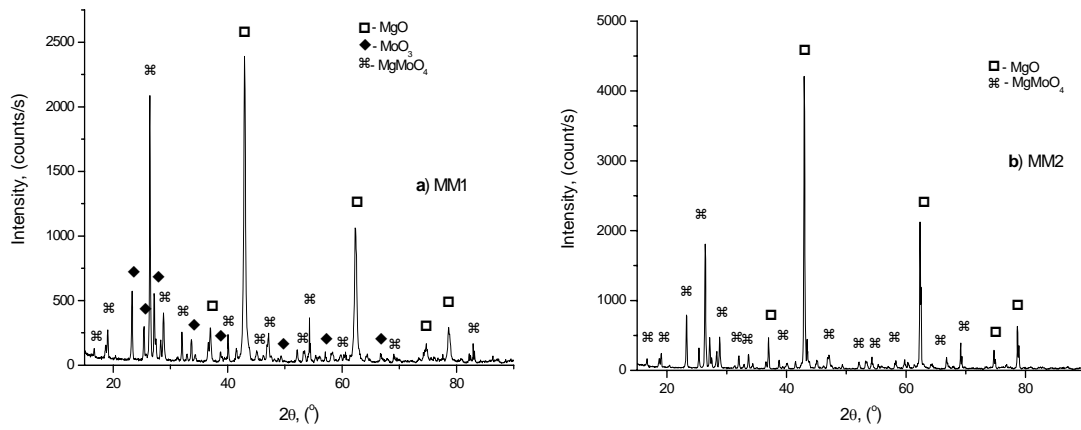


Fig. 2. XRD patterns of a) MM1 and b) MM2.

Results presented on Fig. 3. are XRD patterns for a) SM1 ($\text{SiO}_2 + \text{MoO}_3$ sintered at 850°C 2h) and b) SM2 ($\text{SiO}_2 + \text{MoO}_3$ sintered at 1100°C 2h). SM1 pattern shows SiO_2 along with intermediary compound $\text{MoO}_3(\text{H}_2\text{O})_2$. Contrary to that, SM2 shows no $\text{MoO}_3(\text{H}_2\text{O})_2$, but Mo_8O_{23} phase. There are no peaks of MoO_3 .

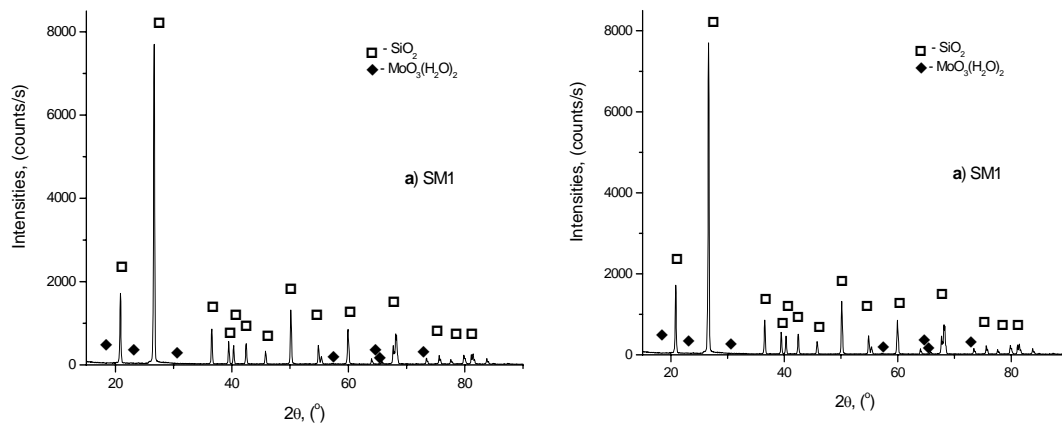


Fig. 3. XRD patterns of a) SM1 and b) SM2.

Fig. 4. presents SEM micrographs of sintered samples. The AM1 micrograph showed grains that are not clearly formed. Starting sintering stadium is observed. Sample AM2 shows grains that are clearly visible, and higher sintering temperature has influence on more pronounced grain boundaries and better shaped grains.

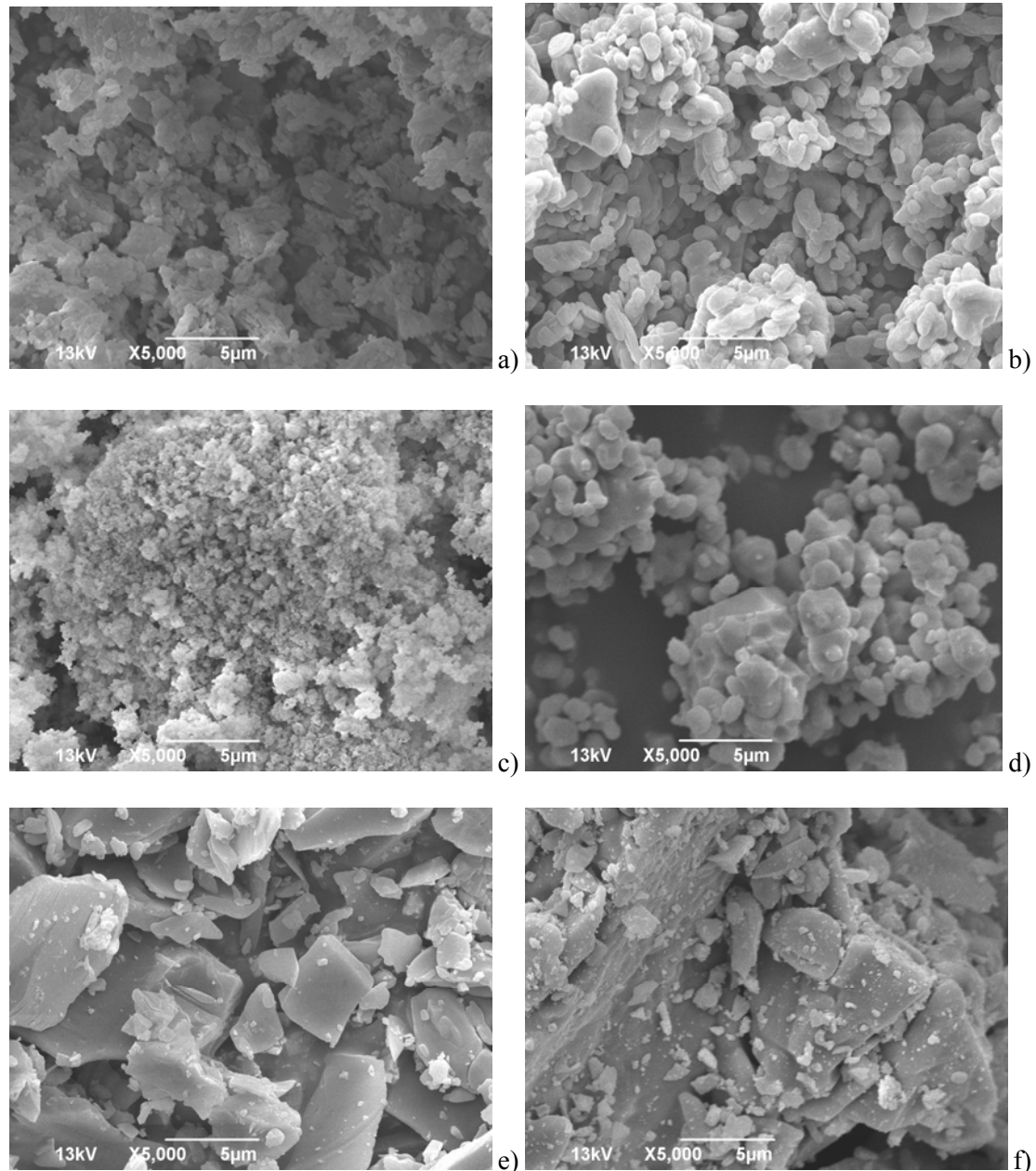


Fig. 4. SEM micrographs of a) AM1, b) AM2, c) MM1, d) MM2, e) SM1 and f) SM2.

Micrograph presented on Fig. 4. c) shows very large MgO grain covered with small MoO₃ grains that are on its surface. Higher sintering temperature leads to chemical reaction and more uniform grain size of both components. Small grains that belong to MoO₃ are no longer present. Fig. 4. e) presents clearly defined edge shaped grains of SiO₂. No chemical reaction was observed. Higher sintering temperature leads to phase transformation of MoO₃, while grain shapes of SiO₂ remain.

Results presented on Fig. 5. are XRD patterns for a) MASM1 (MAS+MoO₃ sintered at 1100°C 2h), b) MASM2 (MAS+MoO₃ sintered at 1200°C 2h) and c) MASM3 (MAS+MoO₃ sintered at 1300°C 2h). MASM1 pattern contains SiO₂, Al₂O₃, MgAl₂O₄ and MgMoO₄. MASM2 and MASM3 show no presence of Al₂O₃. Sintering temperatures of 1200 and 1300°C lead to cordierite formation. Higher temperature caused greater amount of cordierite phase.

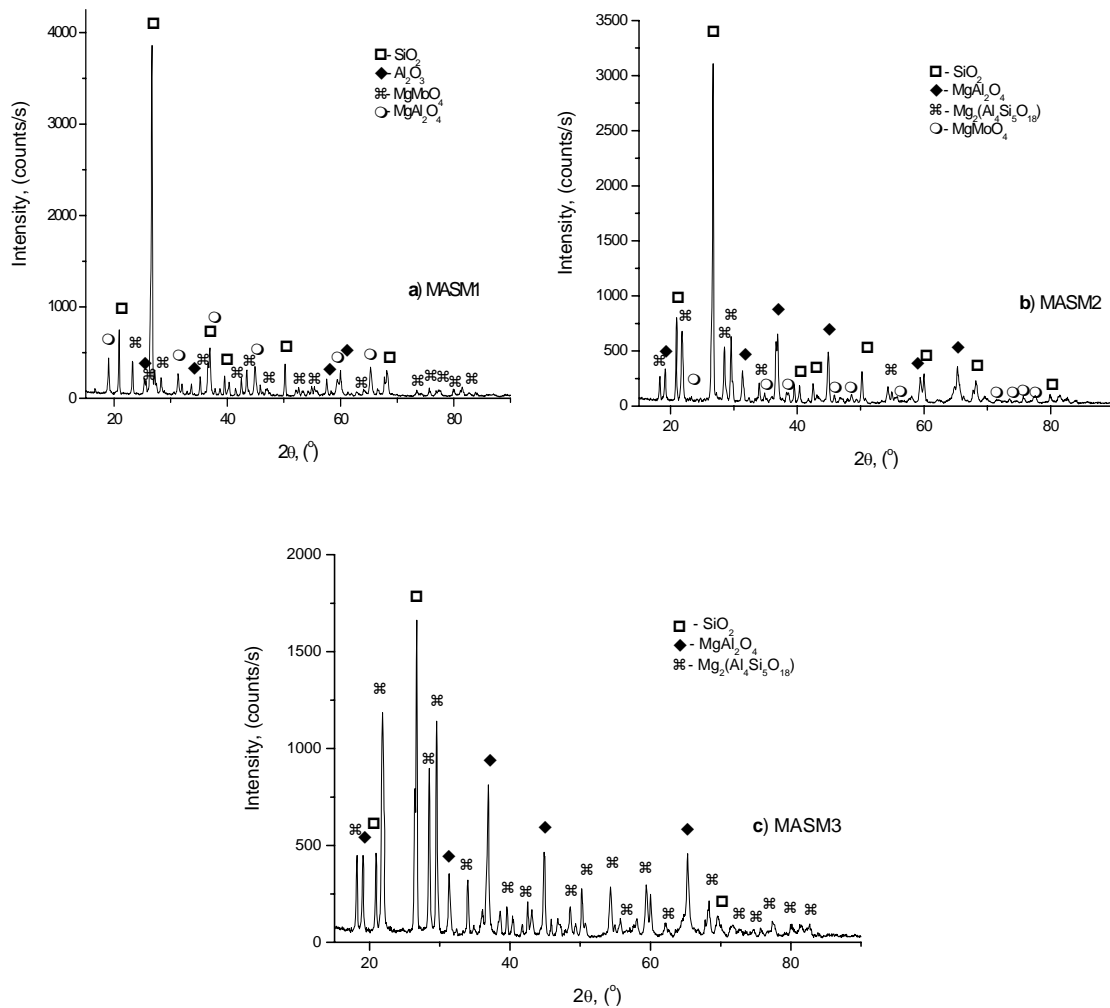


Fig. 5. XRD patterns of a) MASM1, b) MASM2 and c) MASM3.

SEM micrographs of MASM1, MASM2 and MASM3 are presented on Fig. 6.

Non-homogenous structure is observed on Fig. 6. a). Presence of MoO₃ at 1100°C makes a liquid phase which should lead to faster cordierite formation. This amount of additive didn't lead to cordierite formation at this temperature and it is shown that MoO₃ does not possess very low level of catalyst properties. Higher sintering temperature led to formation of a new cordierite phase which is clearly visible on SEM b) and c). Plane formations of new phase are noticed along with dense structure. After sintering at 1300°C for 2h, a great amount of cordierite is formed, which is in accordance with XRD patterns.

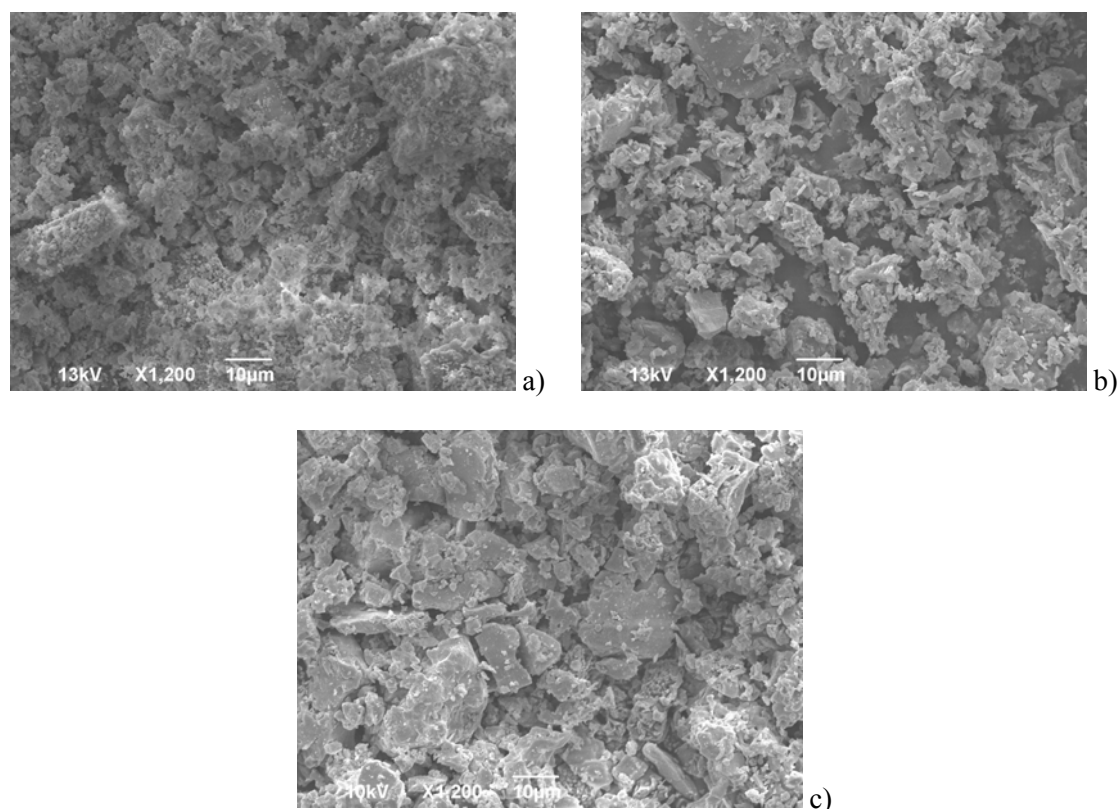


Fig. 6. SEM micrographs of a) MASM1, b) MASM2 and c) MASM3.

4. Conclusions

Based on obtained results, we can conclude:

- Al₂O₃ makes intermediary compounds with MoO₃ at 850 and 1100°C for 2h (Al₂(MoO₄)₃ and Al(OH)₃);
- MgMoO₄ is detected after sintering MgO and MoO₃ at 850 and 1100°C for 2h;
- SiO₂ did not make any intermediary compounds with additive; MoO₃ made some compounds.
- MoO₃ did not lead to cordierite formation at 1100°C for 2h as expected. Cordierite phase is detected at 1200°C. Larger amounts of MAS are observed at 1300°C.
- Beside the fact that no traces of cordierite are detected at 1100°C, MoO₃ makes a liquid phase during sintering process. We can conclude that MoO₃ can be used to decrease sintering temperature and cordierite formation for more than 150°C.

Acknowledgement

The results presented in this paper are a part of Project OI 172057 financed by Ministry of Education, Science and Technology Development of Republic of Serbia and Project F/198, funded by the Serbian Academy of Science and Arts.

5. References

1. R.R. Tumulala, Ceramic and glass-ceramic packaging in the 1990s, J. Am. Ceram. Soc. 74 (5) (1991) 895–908.
2. M.A. Subramanian, D.R. Corbin, U. Chowdhry, Better ceramic substrates through zeolites, Bull. Mater. Sci. 16 (6) (1993) 665–678.
3. S.H. Knickerbocker, A.H. Kumar, L.W. Herron, Cordierite glass-ceramics for multilayer ceramic packaging, Am. Ceram. Soc. Bull. 72(1) (1993) 90–95.
4. A.I. Kingon, R. F. Davis, Engineer Materials Handbook, vol. 2. “Ceramics and Davis” edited by S. J. Schneider, Jr. (ASM International Metals Park, OH, 1191).
5. V.J. Powers, C.H. Drummond, Ceram. Eng. & Sci. Proc. 7 (1986) 969.
6. I. Warsworth, R. Stevens, J. Eur. Ceram. Soc. 9 (1992) 153.
7. M. Pinero, M. Atik, J. Zarzycki, J. Non.crist. Solids. 147–148 (1992) 1523.
8. D. Kervadec, M. Coster, J.L. Chermant, Mater. Res. Bull 27 (1992) 967.
9. N. Clausen, G. Petzow, J. de Physique (Paris), Colloque C1 suppl. To 47 (1986) 693.
10. R.R. Tumulala, J. Amer. Ceram. Soc. 74 (1991) 895.
11. S.H. Knickerbocker, A.H.Kumar, L.W. Herron Amer. Ceram. Soc. Bull. 72 (1993) 90.
12. A. Peleš, N. Đorđević, N. Obradović, N. Tadić, V. B. Pavlović, "Influence of prolonged sintering time on density and electrical properties of isothermally sintered cordierite-based ceramics", Science of Sintering, 45 (2013).
13. K. Kondo, M. Okuyama, Y. Shibata, “Advances in ceramics”, Vol. 19, edited by J. B. Blum and R. Cannon (American Ceramic Society Inc., Ohio, 1986).

Садржај Кордијерит (MAS) је тешко синтеровати због врло уског температурног опсега синтеровања (1300-1400°C). Обзиром да је нискотемпературни процес пожељан, неопходно је пронаћи функционалне адитиве који омогућавају лакши процес синтеровања на нижој температури. Утицај MoO_3 на процес припреме кордиеритне керамике је испитиван. $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ (MAS) је истражена синтеровањем следећих бинарних система: MgO/MoO_3 , $\text{Al}_2\text{O}_3/\text{MoO}_3$ и $\text{SiO}_2/\text{MoO}_3$ (сви синтеровани на 850°C и 1100°C, у току 2h). Састав ових система чини 80 мас% оксида и 20 мас% MoO_3 . Ефекти синтеровања, састав и морфологија праћени су дифракцијом X зрака и SEM микроскопијом. Утврђено је да MoO_3 , поред течне фазе, чини интермедијарна нестабилна једињења са MgO и Al_2O_3 , што је битна информација за даље истраживање. MAS керамике синтероване су са 20 мас% MoO_3 на 1100°C, 1200°C и 1300°C, током 2h.

Кључне речи: Кордијерит, Синтеровање, MoO_3 , XRD, SEM.
