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 aids which can allow easier sintering process at lower temperature. The influence of MoO$_3$ on the preparation process of cordierite ceramics was investigated. 2MgO-2Al$_2$O$_3$-5SiO$_2$ was researched by sintering followed binary systems: MgO/MoO$_3$, Al$_2$O$_3$/MoO$_3$ and SiO$_2$/MoO$_3$ (all sintered at 850°C and 1100°C, sintering time 2h). Composition of these systems was 80 mass% of oxide and 20 mass% MoO$_3$. The effects of sintering, the composition and morphology were followed by X-ray diffraction and SEM microscopy. It has been found that MoO$_3$, beside liquid phase, forms intermediary unstable compounds with MgO and Al$_2$O$_3$, which is the significance information for further research. MAS ceramics were sintered with 20 mass% MoO$_3$ at 1100°C, 1200°C and 1300°C, during 2h.

Keywords: Cordierite, Sintering, MoO$_3$, XRD, SEM.

1. Introduction
Cordierite (2MgO-2Al$_2$O$_3$-5SiO$_2$) 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].

Cordierite 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
Because a low temperature process is desirable, it is necessary to found 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: Cr$_2$O$_3$, ZrO$_2$, K$_2$O, B$_2$O$_3$, TiO$_2$, Bi$_2$O$_3$ etc [13]. MoO$_3$ has necessary criteria to form a liquid phase and support cordierite sintering, such as large atomic radius of 145 pm and low melting temperature (795ºC). Molybdenum trioxide forms eutectics with magnesium and aluminum.

2. Experimental procedure

In these experiments, authors used powders of MgO, Al$_2$O$_3$, SiO$_2$ and MoO$_3$ (all p.a.). First part was 20 mass% MoO$_3$ and 80 mass% of other oxides. Second part was 20 mas% MoO$_3$ and 80 mass% of MAS ($2\text{MgO}+2\text{Al}_2\text{O}_3+5\text{SiO}_2$). 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 MoO$_3$ were sintered isothermally at 850 and 1100ºC in an air atmosphere for 2 hours and a heating rate of 10ºC/min. Those samples were denoted as AM1 for Al$_2$O$_3$+MoO$_3$ sintered at 850ºC 2h; AM2 for Al$_2$O$_3$+MoO$_3$ sintered at 1100ºC 2h; MM1 for MgO+MoO$_3$ sintered at 850ºC 2h; MM2 for MgO+MoO$_3$ sintered at 1100ºC 2h; SM1 for SiO$_2$+MoO$_3$ sintered at 850ºC 2h; SM2 for SiO$_2$+MoO$_3$ sintered at 1100ºC 2h.

MAS with MoO$_3$ were sintered isothermally at 1100, 1200 and 1300ºC in an air atmosphere for 2 hours and a heating rate of 10ºC/min. Samples were denoted as MASM1 for MAS+MoO$_3$ sintered ad 1100ºC for 2h; MASM2 for MAS+MoO$_3$ sintered ad 1200ºC for 2h and MASM3 for MAS+MoO$_3$ sintered ad 1300ºC for 2h.

X-ray powder diffraction patterns after sintering were obtained using a Philips PW-1050 diffractometer with $\lambda$Cu-K$_\alpha$ radiation and a step/time scan mode of 0.05 ºs.

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 (Al$_2$O$_3$+MoO$_3$ sintered at 850ºC 2h) and b) AM2 (Al$_2$O$_3$+MoO$_3$ sintered at 1100ºC 2h). Besides starting oxides, Al$_2$(MoO$_4$)$_3$ 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 1100ºC.

Results presented on Fig. 2. are XRD patterns for a) MM1 (MgO+MoO$_3$ sintered at 850ºC 2h) and b) MM2 (MgO+MoO$_3$ sintered at 1100ºC 2h). MM1 pattern shows MgO, MoO$_3$ and intermediary compound MgMoO$_4$. On the other hand, MM2 shows no MoO$_3$ peaks because the reaction between starting components is completed, therefore MgO and MgMoO$_4$ are the only detected phases, with greater intensities.
Results presented on Fig. 3, are XRD patterns for a) SM1 (SiO$_2$+MoO$_3$ sintered at 850°C 2h) and b) SM2 (SiO$_2$+MoO$_3$ sintered at 1100°C 2h). SM1 pattern shows SiO$_2$ along with intermediary compound MoO$_3$(H$_2$O)$_2$. Contrary to that, SM2 shows no MoO$_3$(H$_2$O)$_2$, but Mo$_8$O$_{23}$ phase. There are no peaks of MoO$_3$. 

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

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

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.

Micrograph presented on Fig. 4. c) shows very large MgO grain covered with small MoO$_3$ 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 MoO$_3$ are no longer present. Fig. 4. e) presents clearly defined edgy shaped grains of SiO$_2$. No chemical reaction was observed. Higher sintering temperature leads to phase transformation of MoO$_3$, while grain shapes of SiO$_2$ remain.
Results presented on Fig. 5. are XRD patterns for a) MASM1 (MAS+MoO$_3$ sintered at 1100°C 2h), b) MASM2 (MAS+MoO$_3$ sintered at 1200°C 2h) and c) MASM3 (MAS+MoO$_3$ sintered at 1300°C 2h). MASM1 pattern contains SiO$_2$, Al$_2$O$_3$, MgAl$_2$O$_4$ and MgMoO$_4$. MASM2 and MASM3 show no presence of Al$_2$O$_3$. 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 MoO$_3$ at 1100°C makes a liquid phase which should leads to faster cordierite formation. This amount of additive didn’t lead to cordierite formation at this temperature and it is shown that MoO$_3$ do not posses 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 patters.
Fig. 6. SEM micrographs of a) MASM1, b) MASM2 and c) MASM3.

4. Conclusions

Based on obtained results, we can conclude:
- $\text{Al}_2\text{O}_3$ makes intermediary compounds with $\text{MoO}_3$ at 850 and 1100°C for 2h ($\text{Al}_2(\text{MoO}_4)_3$ and $\text{Al(OH)}_3$);
- $\text{MgMoO}_4$ is detected after sintering MgO and $\text{MoO}_3$ at 850 and 1100°C for 2h;
- $\text{SiO}_2$ did not make any intermediary compounds with additive; $\text{MoO}_3$ made some compounds.
- $\text{MoO}_3$ 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, $\text{MoO}_3$ makes a liquid phase during sintering process. We can conclude that $\text{MoO}_3$ 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