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EXAMINATION OF INFLUENCE SINTERING TEMPERATURE ON MINERAL COMPOUNDS

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Abstract: Mineral materials, such as corundum, quartz and periclase are very often used in technological processes. Due to its characteristics, and chemical reaction in solid state, these minerals form very interesting and useful material, cordierite. The mineral ratio in this compound ($MgO : Al_2O_3 : SiO_2$) is 2:2:5. They form cordierite, electronic ceramic, which can be sintered in a narrow temperature range, at about 1375 °C. Composition of this electronic ceramics material is is $2MgO-2Al_2O_3-5SiO_2$ (MAS) and in this research 20% mass Bi_2O_3 was added in the aim of decrease the sintering temperature. The effects of sintering, the composition and morphology were followed by x-ray diffraction, scanning electron microscopy and EDS analysis, as a function of sintering temperature. MAS ceramics were sintered at 1000ºC, 1100ºC and 1200ºC.

Keywords: Ceramics, cordierite, x-ray diffraction, SEM, EDS

1 INTRODUCTION

Cordierite ($Mg_2Al_2Si_50_{18}$) is a very rare mineral in nature and where it occurs, it is found in small quantities. According to the systematization, based on the chemical composition, it belongs to the group of silicates. It is characterized by a low coefficient of thermal expansion, low electrical conductivity, high resistance to thermal shocks and high fire resistance (Babič, 2003). One of the applications of cordierite is the production of cordierite ceramics obtained from natural minerals such as talc, quartz, corundum, minerals of high-refractory clays, magnesium carbonate (Aćimović Pavlović et al., 2007). Due to its good properties, the application of cordierite has been constantly growing, so it was necessary to synthesize it in industrial conditions from oxides.

Magnesium oxide, MgO, occurs in nature in the form of periclase minerals. It is part of contact metamorphic rocks. It can be obtained from magnesite, $MgCO_3$, or dolomite

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$CaMg(CO_3)_2$. It is characterized by a high melting point of 2800 °C. That is why it is one of the components of refractory bricks (Babič, 2003). Al_2O_3 alumina is dehydrated alumina. They were obtained by the basic Bayer process, which consists of leaching bauxite with NaOH solution and subsequent separation of leached alumina. Alumina has a high melting point of 2072°C, so it is used as an insulator in blast furnaces (Vračar and Živković, 1993).

Quartz sand, SiO_2, is an unbound, loose rock, which basically consists of quartz grains. The use and quality of quartz sand are defined by its size, ie granulometric composition, then physical properties, as well as mineral and chemical composition. Quartz sand has a very large and wide application in various industries. Most of the produced quartz sand of different quality is used in construction (90-95% of world production). The remaining 5-10% is used in the industry of glass, ceramics, refractory bricks, then in certain metallurgical processes for obtaining metals and non-metals, in foundry, in the abrasive industry, chemical industry, etc. (Pavlica and Draškić, 1997).

Bi_2O_3 is added in order to lower the sintering temperature of cordierite ceramics. Bi_2O_3 is bismuth, one of the forms of bismuth in the Earth's crust, in addition to bismuth Bi_2S_3. Bismuth can also be formed as a by-product of extraction from ores of other metals such as ores of lead, copper, tin, molybdenum and tungsten. Bismuth oxide is used not only as an aid in sintering in technical ceramics, but also for the production of optical glasses and glass (Ojebuoboh, 1992; Klinikova et al, 2007).

Cordierite is material based on corundum, quartz and periclase. Sintered on high temperature (above 1350 °C) they make a chemical compound which have unique properties, such as low dielectric constants (~5) and low thermal expansion (20·10-7/ºC) (Moftah El-Buaishi et al., 2012). These properties make them suitable for a wide range of high-temperature applications. Due to remarkably properties, the uses are wide: catalytic converters, thermal insulation, components of portable electronic devices, kiln furniture. These properties make them suitable for a wide range of high-temperature applications (Obradović et al., 2012; Obradović et al., 2016) and semiconductors (Wadsworth and Stevens, 1992; Obradović et al., 2015; Obradović et al., 2016).

Cordierite is difficult to sinter because of the very narrow sintering temperature range (Obradović et al., 2012; Tumala, 1991) (1300-1400ºC). Because a low temperature process is desirable, it is necessary to found a functional adds which can allow easier process of sintering at lower temperature. The melting temperature of this aid should be lower than that of the precursors. In addition, the cationic radius should be much larger than the radius of the metals in MAS to avoid the substitution into cordierite sites. Different components have been used as sintering aid: Cr_2O_3, ZrO_2, K_2O, B_2O_3, TiO_2, Bi_2O_3 etc. (Knickerbocker et al., 1993; Djordjević et al., 2012). Bi_2O_3 has necessary criteria to form a liquid phase and support cordierite sintering, such as large radius and low melting temperature (825ºC). Bismuth oxide forms eutectics with magnesium, aluminum and silica.

2 EXPERIMENTAL PROCEDURE

During this research following components were used: MgO (Euro Hemija, Belgrade), Al_2O_3 (Aluminijumski kombinat, Podgorica), SiO_2 (Bela Reka) and Bi_2O_3, p.a. (Reahim, Rusia). Chemical composition of starting compounds is given in Table 1. Three-component system MgO-Al_2O_3-SiO_2 has 2-2-5 compositions, and the amount of 20% Bi_2O_3 was added to the MAS system.

Table 1 Chemical composition of the raw materials

	incineration loss %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %
Al_2O_3	0,18	0,17	99,19	0,089	0,07	0,049	0,236	0,012
MgO	-	-	-	-	1,40	98,60	-	-
SiO_2	2,22	96,10	0,14	0,243	0,112	-	0,047	1,16

In the aim of homogenization of the powders, each mixture has been melted in the laboratory cylindrical mill with ceramic balls, model 13x10,5”, producer by VEB, during 5 minutes. Sintering samples were prepared in the tablet shape, with radius 8 mm and height 4 mm, pressuring under the pressure of $1 t/cm^2$. Sintering temperatures of the system were 1000 ºC, 1100 ºC and 1200 ºC.

X-ray powder diffraction (XRPD) technique was used for identification and definition of the unit-cell parameters. XRPD analysis was performed using the Philips PW1710 diffractometer; with Cu Kα radiation (40kV, 30mA), step scan 0.25s, 0.02° 2θ, *d* range from 5° to 85°2θ.

The microstructures of the sintered samples were observed using scanning electron micrograph (SEM) “Joel” with microsonde (increasing range 500, 1000, 2000, 10.000 and 20.000x). SEM and energodispersion elementary analyses were done on the sintered sample fracture.

3 RESULTS AND DISCUSSION

$MgO \cdot Al_2O_3 \cdot SiO_2/Bi_2O_3$, sintering temperature: 1000 ºC and 1100 ºC

X-ray diffraction analyses of the system $MgO \cdot Al_2O_3 \cdot SiO_2$ with 10% Bi_2O_3 sintered at 1000ºC did not show the presence of cordierite (Fig 1). Based on the analysis and the obtained results, it is concluded based on the presence of $MgSiO_3$ (enstatite) that the sintering process started (according to the formation of this interphase compound), but that not enough temperature was reached for the formation of cordierite.

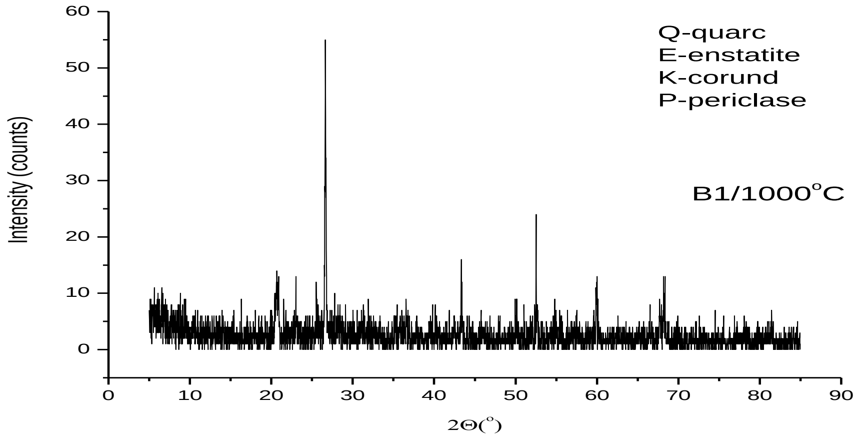

Figure 1 X-ray diffractograme of MAS/Bi2O3 sintered at 1000ºC

The X-ray diffraction analyses of the system sintered at 1100ºC (MAS/ Bi_2O_3) showed the reflections of low intensity characteristics for cordierite (in the Figure 2. the picks marked with star). The microphotographs of the sample MAS/Bi_2O_3 sintered at 1100ºC showed continual structure with hollows (Figure 2.). The present lonely grains are probably untreated components from the starting mixture. SEM showed that at the sintering temperature the homogenous structures in morphological sense were produced, EDS analyses proved the same (Fig. 4. and 5. shows the intensity of the elements present based on EDS analysis, as well as mass % and atomic %).

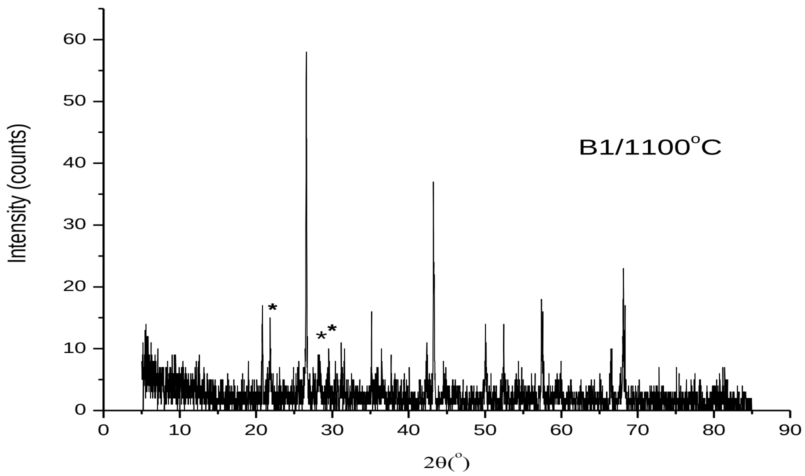

Figure 2 X-ray diffractogram of MAS/Bi_2O_3 sintered at 1100ºC

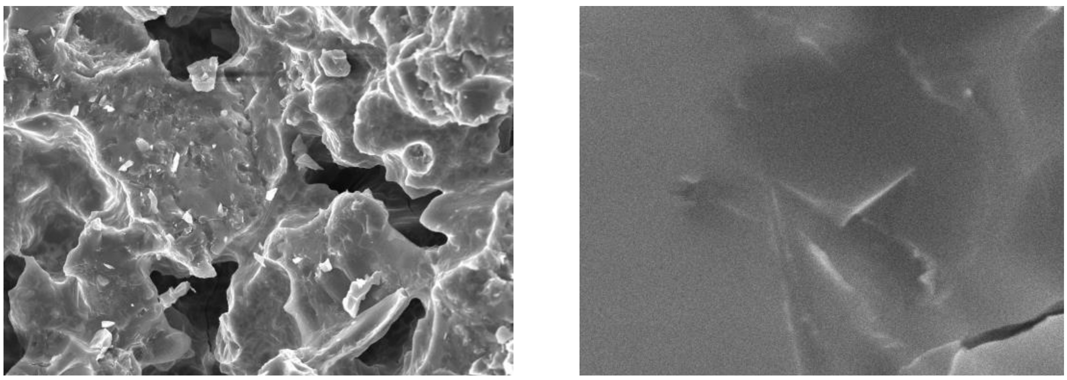

Figure 3 SEM microphotographs of the sample MAS/Bi_2O_3 sintered at 1100ºC (1000x and 20000X)

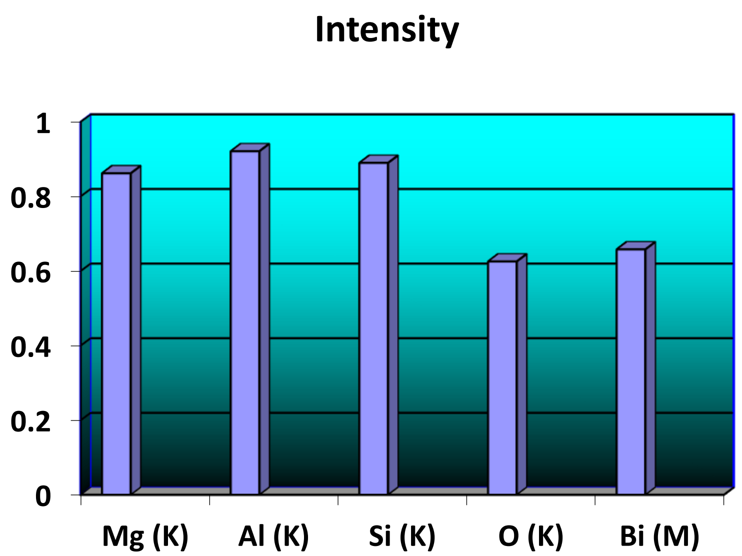

Figure 4 EDS MAS/Bi_2O_3 at 1100ºC, Intensity

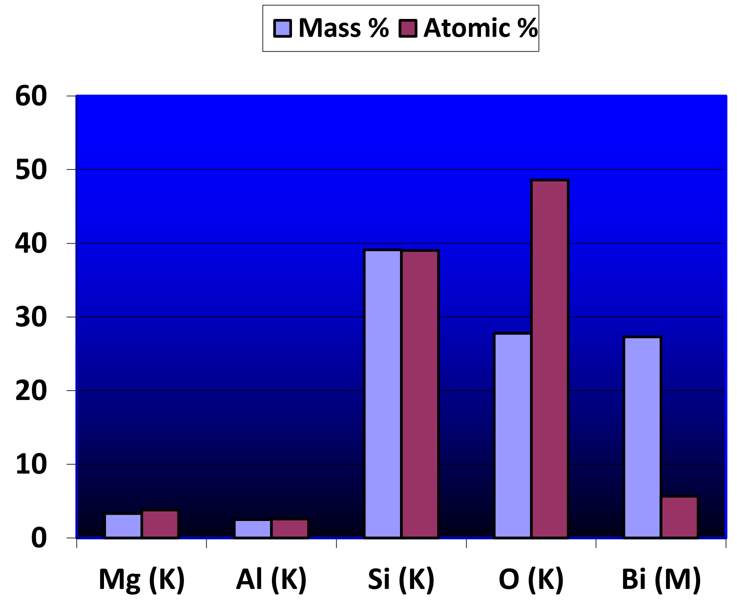

Figure 5 EDS MAS/Bi_2O_3 at 1100ºC, Mass % and Atomic %

MgO·Al$_2$O$_3$·SiO$_2$/Bi$_2$O$_3$, sintering temperature: 1200ºC

After the sintering process of MAS/Bi$_2$O$_3$ system, at 1200 ºC, X-ray diffraction analyses showed the presence of indialite, which is the hexagonal form of cordierite.

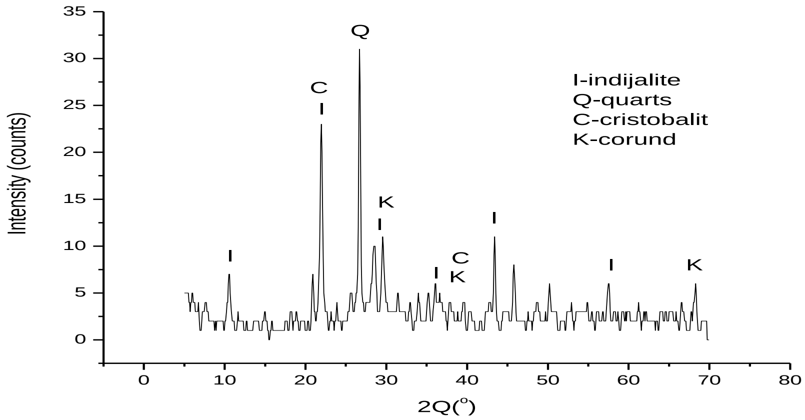

Figure 6 X-ray diffractogram of MAS/Bi$_2$O$_3$ sintered at 1200ºC

Beside the indialite, the presented phases in the sample were quarts, cristobalite and corund. The results of analysis indicate that the presence of Bi$_2$O$_3$ has enabled chemical reaction between the components. Although a temperature of 1375 ºC is required to obtain the final product, thanks to the presence of a liquid phase (bismuth oxide melts at 820 ºC) which enabled contact between the components that form cordierite, the form of the final product (indiate) was obtained.

The presented X-ray diffraction analyses of the MAS sample with 10% Bi$_2$O$_3$ sintered at 1000ºC, 1100ºC and 1200ºC did not show the presence of unstable compounds that were found by analysis of the samples MgO/Bi$_2$O$_3$ and Al$_2$O$_3$/Bi$_2$O$_3$. Bi$_2$O$_3$ is primary added as functional component to provide flux phase in the sintering system. In the more-component system, Bi$_2$O$_3$ obviously makes intermediary compounds and transports the ions (Mg^{2+} and Al^{3+}) to SiO$_2$. At this way, Bi$_2$O$_3$ can make influence on the mechanism of the reaction in the complex system.

4 CONCLUSION

In the aim of researching the reactions of cordierite synthesis, MgO, Al$_2$O$_3$, SiO$_2$/Bi$_2$O$_3$, sintered at 1000ºC, 1100ºC and 1200ºC. The results showed existing of the liquid phase at 820ºC (the melting temperature of Bi$_2$O$_3$). The unstable compounds defended through the liquid phase, which allowed (from the two aspects) the acceleration of the reaction in the more-component system.

Sintered MAS system with Bi_2O_3, the presence of cordierite was detected. The lowest temperature on which indialite was detected (the hexagonal form of cordierite) was 1100ºC. At 1200ºC indialite was the most presented component. With this research it was shown that presence of Bi_2O_3 in the starting MAS mixture decrease the sintering temperature for ~170ºC, comparing the temperature of forming cordierite ceramics from the mixture without functional adds.

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