Influence of mechanochemical activation on the sintering of cordierite ceramics in the presence of Bi_2O_3 as a functional additive

N. Obradović^{a,*}, N. Đorđević^b, S. Filipović^a, N. Nikolić^c, D. Kosanović^a, M. Mitrić^d, S. Marković^a, V. Pavlović^a

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

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

^c Institute for Multidisciplinary Research, Kneza Višeslava 1a, 11000 Belgrade, Serbia

^d Vinča Institute of Nuclear Sciences, Mike Alasa 12-14, 11000 Belgrade, Serbia

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ABSTRACT

Due to its outstanding electrical characteristics, such as the low temperature expansion coefficient, low dielectric constant and good mechanical properties, cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, is a very attractive high-temperature ceramic material. In order to accelerate the process of sintering, 2.50 mass% Bi_2O_3 has been added to the starting mixtures. Liquid phase sintering caused by the presence of bismuth-oxide lowers the temperature of cordierite formation. The mechanical activation of the starting mixtures (0–56 min in vibro-mill) additionally lowers sintering temperatures. The sintering process was performed at 1200, 1300, 1350 and 1400 °C, for 2 h. The particle size analysis (PSA) was employed in order to determine the changes in the particle size of the mechanically treated powders. The phase composition of the starting powders and sintered materials was analyzed by the X-ray diffraction method. Furthermore, scanning electron microscopy (SEM) was used in the analysis of the powder morphology.

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1. Introduction

Cordierite, whose chemical composition is $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, is one of the phases of the ternary MgO – SiO_2 – Al_2O_3 system, along with mullite, cristobalite, tridymite, enstatite, forsterite, sapphirine etc. [1]. Cordierite is widely used in glass–ceramic compositions for manufacturing multilayer circuit boards, catalytic converters, filters, kiln furniture, and thermal insulation materials [2]. Furthermore, because of the outstanding thermo-mechanical, chemical and dielectric properties of cordierite glass ceramics, they have been in use for decades in various fields, ranging from substrates for micro-electronic packaging industry to cookware, heat exchangers and, more recently, glazes for floor tiles. Despite extensive research carried out in the fields of crystallization behavior, kinetics and properties of these glass ceramics, they are still under study [3]. Mullite glass ceramics have also attracted some attention in recent years because of their low thermal expansion, high mechanical strength and optical characteristics, and they have found diverse applications like dental porcelains, ceramic matrix composites and materials used in laser technology.

There are several methods to synthesize cordierite, such as solid-state reaction, sol-gel and crystallization from glass. Among

these methods, sintering of oxide powders under the temperature between 1250 and 1350 °C through solid-state reactions or crystallization of glass powders is the most conventional, as reported by V. K. Marghussian et al. [4]. The same authors have established that the fabrication of cordierite–mullite composites via the conventional sintering route is very difficult because of the high refractoriness of these two materials (especially mullite). The addition of any sintering aids could adversely affect the thermal and electrical properties of the composite material.

Different processes remarkably influence the reactivity of the solids [5]. Mechanical treatments are important as long as they can help produce changes in the texture and structure of the solids, causing the particle size reduction and decreasing the reaction sintering temperature [6]. Additives can also decrease the temperature of the reaction process during sintering [7]. The application of additives should improve the contacts between reacting components. Therefore, cordierite is mixed with bismuth-oxide, which cannot be incorporated into the crystal lattice of cordierite because of its greater atomic radii [8]. The authors attempted to study the influence of both mechanical activation and additive usage on the cordierite formation during an isothermal sintering process at various temperatures.

2. Experimental procedure

Mixtures of MgO (98.60%, Euro Hemija), Al_2O_3 (99.19%, Aluminiumski kombinat, Podgorica), SiO_2 (96.10%, Bela Reka) and Bi_2O_3

* Corresponding author. Tel.: +381 11 20 27 203.

E-mail address: nina.obradovic@itn.sanu.ac.rs (N. Obradović).

(99.98%, Reahim) were used in these experiments. A chemical analysis of the initial components was performed by AAS, Analyst 300. The mixture of $\text{MgO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$ in the 2:2:5 ratio, with the addition of 2.50 mass% Bi_2O_3 , was mechanically activated by grinding in a high-energy vibro mill (KHD Humboldt Wedag A.G., Germany, MH954/3). The construction of the mill is made of specially constructed bearing with a horizontal cap of the vessel. The rotation of the electromotor with the power of 0.8 kW is transformed into vibrations which are directly connected with the milling vessel. The working elements are within the vessel – two free concentric rings made of steel, 3 kg in weight. The working elements make one-third of vessel's volume – the reactor. The amount of the milled powders was 150 g. The milling process was performed in air for 7, 14, 28 and 56 min. The samples were denoted as K2.5-0 to K2.5-56, according to the milling time and 2.50 mass% Bi_2O_3 additions.

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

The average particle size, particle size distribution, and the nature of agglomerates were determined by a 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 X-ray powder diffraction patterns after milling and sintering were obtained using a Philips PW-1050 diffractometer with $\lambda\text{Cu-K}\alpha$ radiation and a step/time scan mode of $0.05^\circ/1\text{ s}$.

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 4 t/cm^2 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 1200, 1300, 1350 and 1400 $^\circ\text{C}$ in air atmosphere for 120 min; the heating rate was $10\text{ }^\circ\text{C/min}$. The density of specimens was calculated from the measurements of their diameter, thickness and mass.

3. Results and discussion

The micrographs of the starting powders (not shown in this paper) indicate that Al_2O_3 particles have irregular shapes, showing

Fig. 1. Scanning electron micrographs of (a) K2.5-0, (b) K2.5-7, (c) K2.5-14, (d) K2.5-28 and (e) K2.5-56.

Table 1

A chemical analysis of the initial components, obtained by AAS.

Composition	Alumina, (%)	Magnesia, (%)	Silica, (%)
SiO ₂	0.17	–	96.10
Al ₂ O ₃	99.19	–	0.14
Fe ₂ O ₃	0.09	–	0.24
CaO	0.07	1.40	0.11
MgO	0.05	98.60	–
Na ₂ O	0.24	–	–
K ₂ O	0.01	–	1.16
LOI	0.18	–	2.22

an agglomeration tendency. The Bi₂O₃ powders consist of small-sized particles with a tendency to form aggregates and agglomerates. Furthermore, the MgO powder has polygonal agglomerates 20 × 10 μm in size, while SiO₂ has no agglomerates, though it does show irregularly shaped particles. The scanning electron micrographs of the non-activated and activated mixtures are presented in Fig. 1. The non-activated mixture consists of the starting powders, uniformly distributed. The mixture activated for 7 min shows particles that have retained their shapes as well as some comminuted particles gathered around bigger ones. Further attrition is observed in the powder activated for 14 min; particles become spherical and the presence of heterogeneous agglomerates is also noticed. A 28-minute milling led to the accumulation continuing of smaller particles over the bigger ones, while the SEM image presented in Fig. 1 (e) indicates the attrition of bigger particles. The powders used in this investigation are pro analysis except for the SiO₂ powder. The chemical analysis of the initial components performed using an atomic absorption spectrophotometer is presented in Table 1.

Fig. 2. Cumulative and frequency distribution curves for (a) K2.5-0, (b) K2.5-7, (c) K2.5-14, (d) K2.5-28 and (e) K2.5-56.

Fig. 2 shows the frequency distribution and cumulative distribution curves of all samples. Fig. 2 (a) shows that the K2.5-0 particle size distribution consists of the starting particles of about 10 μm in size. The seven- and fourteen-minute activations showed three differently sized particles: about 2 μm, about 10 μm and about 70 μm, respectively, corresponding to the attrition of the starting powders and a small number of “big” particles, agglomerates, which serve as the nuclei around whose surface smaller particles gather. Further milling led to additional decrease in the particle size, showing distributions around 2.5 μm; these measurements are in a great accordance with the given micrographs.

This is, also, in accordance with the X-ray analysis. The X-ray diffraction patterns of the starting mixtures are given in Fig. 3 (a). The X-ray diffraction patterns of non-milled and milled powders are given in Fig. 3 (b). K2.50-0 is the X-ray pattern of the non-milled starting mixture containing SiO₂, Al₂O₃, MgO and Bi₂O₃. Mechanical activation led to the attrition of powder particles and further lowering of peak intensities. Furthermore, after 56 min of activation, some Al₂O₃ and MgO peaks disappeared, SiO₂ peaks were additionally lowered, though no new cordierite phase was noticed. The identification of all of the obtained reflections has been performed using the JCPDS cards (86–1629 for quartz low SiO₂, 74–1730 for Bi₂O₃, 75–0921 for korund Al₂O₃ and 74–1225 for MgO).

Fig. 3. XRD patterns of (a) starting oxides and (b) non-milled and milled powder mixtures.

Fig. 4. Densities obtained after sintering at various temperatures.

Fig. 4. shows the densities obtained after a two-hour sintering process at 1200, 1300, 1350 and 1400 °C. The maximum change of the density is observed in powders activated for 14 min. It is clearly visible that the sintering process entered the final stage for the samples sintered at higher temperatures. A temperature of 1200 °C is not an adequate sintering temperature; higher temperatures are required for higher densities. The compacts activated for 56 min and sintered at 1300–1400 °C for 2 h reach the maximum density values.

Scanning electron micrographs of the samples activated for 56 min and sintered at various temperatures for 2 h are presented in Fig. 5. SEM (a) indicates that 1200 °C is a relatively low sintering temperature which leads to multiphase systems with an open porosity and two kinds of particles: bigger polygonal blocks 4–6 μm in size and smaller ones, 1.5–2.5 μm in size tending to make agglomerates. SEM (b) shows a significant mass transport with two different phases within. Also, the presence of the liquid phase sintering is noticed: the cracks between the blocks of 4–6 μm in size are filled with a liquid phase,

while smaller particles are sintered within agglomerates. SEM (c) refers to the sintering process between the liquid phase and large blocks, leading to their strengthening and breakage through grains. The liquid phase has not yet reacted with smaller grains. The growth of both smaller and larger particles is noticed in the SEM images (d), along with a closed porosity.

The phase diagram of the ternary MgO–SiO₂–Al₂O₃ system is presented in Fig. 6. One can conclude that several phases are present within the system: mullite, tridymite, enstatite, forsterite, sapphirine, spinel, cordierite, etc. A pink mark on the diagram represents the composition used in our experiments.

The samples activated and sintered at 1200–1400 °C for 2 h, presented in Fig. 7 do not have the same structure, which is in accordance with the obtained SEM micrographs. The XRD pattern of the sample activated for 56 min and sintered at 1200 °C for 2 h indicated that several phases – SiO₂, mullite and cordierite – are present within the K2.5-56 sintered mixture. The formation of the mixed cordierite and mullite phase has begun during the sintering at 1200 °C, although a significant amount of the starting SiO₂ phase is still present. It can be noticed that a larger amount of the mullite phase is present. On the contrary, the XRD pattern of the sample obtained at 1300 °C indicates a pure cordierite–mullite phase, without the presence of the starting phases. Further increase in the sintering temperatures led to a better recrystallization and an increase in peak intensities, although the phase structure of cordierite–mullite remained. The identification of the obtained reflections has been carried out using the JCPDS cards (86–1629 for SiO₂, 89–1487 for cordierite and 79–1457 for mullite).

4. Conclusion

The effects of mechanical activation and 2.50 mass% Bi₂O₃ additions on the formation of cordierite during the sintering process were analyzed. Based on our previous investigation [9], mechanical activation led to the homogenization of powder particles, the comminuting of particles, and after this period, the introduced energy was used to

Fig. 5. Scanning electron micrographs of samples activated for 56 min and sintered at: (a) 1200, (b) 1300, (c) 1350 and (d) 1400 °C, for 2 h.

Fig. 6. Phase diagram of the ternary MgO–SiO₂–Al₂O₃ system.

induce changes in the crystal structure, which resulted in the emergence of defects, initially on the surface of the crystal lattice, and then inside. A reduction of the particle size allows to lower the temperature at which the reaction begins, since it favors crystal growth and, consequently, the crystallization rate [10].

The powders activated for 56 min and sintered at 1300–1400 °C for 2 h reached the maximum density values, near 1.92 g/cm³ and entered the final sintering stage, as shown by the curve saturation on the density diagram. On the other hand, the addition of bismuth-oxide, owing to a lower melting temperature (850 °C), leads to liquid phase sintering. Having in mind its greater atomic radius, it cannot be incorporated into the cordierite crystal lattice; therefore it acts as a catalyst, increasing the reaction velocity. According to the literature

data, this has influence on sintering temperatures lower than 1365 °C, [4]. The sintering at 1200 °C for 2 h led to the formation of a cordierite–mullite phase, along with the SiO₂ starting phase. Furthermore, the XRD patterns of the mixtures sintered at higher temperatures suggest that we have obtained a pure cordierite–mullite phase ceramic material. Finally, the addition of 2.50 mass% Bi₂O₃ accompanied by a relatively short milling time of 56 min led to a decrease in temperatures of both the formation of cordierite and its sintering process.

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Fig. 7. XRD patterns of mixtures activated for 56 min and sintered at various temperatures for 2 h.