Influence of Mechanical Activation on Electrical Properties of Cordierite Ceramics

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Abstract:
The goal of the presented research was to find a possible correlation of the process parameters and functional properties of cordierite based ceramic materials. A three-component oxide mixture was prepared containing MgO+Al₂O₃+SiO₂ in the 2:2:5 ratio with the addition of 10% Bi₂O₃. Mixtures were mechanochemically activated 5 and 240 minutes in a mill with ceramic balls, and sintered at temperatures from 1173-1573K. Structural transformations were determined by the XRD method. Quantitative measures of the functional sample properties, capacity Cc and electrical resistance Rρ as well as tangens of dielectric loss angle tg α were used. The results obtained proved that there is a correlation between mechanochemical activation and properties of cordierite ceramics.

Keywords: Cordierite, Mechanochemical activation, Electrical properties

Introduction

The low temperature expansion coefficient, low dielectric constant and good mechanical properties give cordierite ceramics a wide application in the high temperature field [1-4]. Cordierite ceramics form during the process of sintering in a narrow temperature ‘window’ (Δt > 283 K) at temperatures above 1573 K. The purpose of this research was to find values of process parameters in order to decrease the cordierite forming temperature and to improve the desirable properties of the obtained ceramics. For that reason, mechanochemical activation of components was chosen as one of the possible ways to lower sintering temperatures [5-7].

Additives can also decrease the process reaction temperature during sintering. Application of additives should improve the contact between reacting components during the sintering process. Additives with a lower melting point than the reacting components temperature should enable the formation of a liquid phase in the system, and improve contacts between mixture components [8]. It is also important that the additive ionic radius should be high enough not to upgrade itself into the crystal structure of cordierite.

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**Experimental procedure**

In the presented research technical quality oxides MgO (purity 98.60%, Euro Hemija, Beograd), Al₂O₃ (purity 99.19%, Aluminijumski kombinat Podgorica), SiO₂ (purity 96.10%, Bela Reka) and Bi₂O₃ (purity 99.98%, Reahim) were used. The melting point of Bi₂O₃ is close to 1093°C. The mixture of MgO+Al₂O₃+SiO₂ in the 2:2:5 ratio, with addition 10% Bi₂O₃, was mechanochemically activated. Activation periods were 5 and 240 minutes (mixtures designated B1 and B6) in acylindrical ceramic mill with balls (VEB, model 13x10.5’’) [9]. Tab. I presents sample designations and corresponding milling times.

Activated samples were prepared in the form of tablets with a radius of 8mm and 4mm high, compacted with a pressure of 1t/cm². Samples activated 240 minutes were sintered at temperatures of 1173K, 1273K, 1373K, 1473K and 1573K (samples B6). Samples activated for 5 minutes were sintered at temperatures of 1273K and 1373K (sample B1).

Sintered samples were analyzed using X-ray diffraction on a “Philips” PW-1710 device, with a curved graphite monochromator and scintillated counter. Intensities of diffracted CuKα X-ray radiation (λ=11.54178Å) were measured at room temperature in 0.02 2θ intervals and 0.25s time intervals in the range of 5° to 85° 2θ. The working voltage of the Rö tube was 4kV and the current was 3mA, with a collimator angle of 1° and with 0.1mm, [10].

Capacity [Cₜ], resistance [Rₜ], and tgδ, measurements were done on a Impedance/gain-Phase Analyzer, Hewlett Packard model 4194A, in the frequency range of 0.99-1kHz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Milling time (min)</th>
</tr>
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<tbody>
<tr>
<td>B1</td>
<td>5</td>
</tr>
<tr>
<td>B2</td>
<td>15</td>
</tr>
<tr>
<td>B3</td>
<td>30</td>
</tr>
<tr>
<td>B4</td>
<td>60</td>
</tr>
<tr>
<td>B5</td>
<td>120</td>
</tr>
<tr>
<td>B6</td>
<td>240</td>
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</table>

**Results and Discussion**

XRD analysis of the experimental cordierite mixture activated 5 minutes and sintered at 1273K (B1/1273K) did not detect the presence of cordierite. XRD analysis of the same sample sintered at 1373K (B1/1373K) detected the presence of indialite (cordierite modification) traces. Larger amounts of indialite were detected in samples activated 240 minutes and sintered at 1373K (B6/1373K). XRD diffractograms of B1 and B6 samples sintered at 1373K are presented on the Fig. 1.

Cordierite is formed at sintering temperatures above 1573K [10] with no additives, so the influence of mechanochemical activation and additive is clearly visible. Activation decreases the size of the mixture particles and increases the free active particle surface. This has direct influence on the kinetics of sintering.
The kinetics of cordierite formation in the experimental samples obtained at higher temperatures was analyzed. XRD diffractograms of samples sintered at temperatures 1473K and 1573K, where even more amounts of indialite were detected, are presented in Figs. 2 and 3.

**Fig. 1** XRD analysis of samples B1/1373K and B6/1373K

**Fig. 2** XRD diffractogram of B6/1473K
Fig. 3 XRD diffractogram of B6/1573K

The obtained decrease of the sintering temperature is presented graphically on fig. 4.

Fig. 4 Temperature changes in the process of cordierite sintering with no additives as a function of the activation time

The performed experiments proved the stated assumption that mechanochemical activation has an influence on the cordierite forming temperature.

Simultaneously, functional properties of the obtained experimental samples were measured. Capacity measurements $C_c$ of the samples activated 5 and 240 minutes as a function of the sintering temperature are presented on Fig. 5. It is visible that the increase of sintering temperature induces the increase of capacity with visible gradient change in the
range 1373-1573K. This could be explained with the fact that in this temperature range, reaction and indialite formation induce changes in the base mixture. At the same time the sample density increases, which has an influence on increasing the conductivity.

The capacity difference of samples activated for 5 and 240 minutes is also visible. While the absolute capacity values for both samples are almost the same, the influence of activation pretreatment is evident.

Simultaneously, while the capacity increases, the resistance of the samples decreases, Fig. 6. The decrease of electric resistance values is evident in samples obtained at higher sintering temperatures, which could be explained with a higher amount of reacted components of the base mixture and increased product density, which leads to decrease of the electric resistance, compared to the same samples sintered at lower temperatures.

For the samples activated 5 minutes and the sintering temperature range from 1373K to 1573K a slight increase of resistivity was detected that is probably due to measurement error, not changes in the material. Resistance measurements of sample B6 were in close correlation with capacity measurements for the same sample [10].
The influence of mechanochemical activation is reflected in lower resistance values for samples activated 240 minutes, compared to samples activated for 5 minutes.

Dielectric loss, $\tan \delta$, which was measured, did not show any significant differences between samples (2.1 and 2.2) regardless of the activation period or the sintering temperature.

The obtained functional properties of cordierite ceramics did differ from the values determined for samples obtained by the classical sintering process.

Conclusions

Effects of mechanochemical activation and sintering temperature on electrical properties of cordierite ceramics were analyzed. Traces of indialite (cordierite modification) were determined by XRD at the sintering temperature of 1373K. Higher amounts were detected at the same sintering temperature when the activation period was 240 minutes. The amount of produced indialite increased as the sintering temperature increased, and the highest gradient was between 1373K and 1573K.

Values of electric properties as a function of the activation period indicated that the activation pretreatment has an influence on the product properties. The capacity increased for the longer activation period and sintering temperatures of 1373K to 1573K, which is in correlation with structural analysis.

Sample resistance measurements showed a decrease of the values obtained for higher sintering temperatures and for longer activation periods.

The obtained results prove the activation time influence on the formation temperature of cordierite ceramics, with no significant changes in electrical properties of the product.

References


Садржај: Циљ овог истраживања је био да испита могуће корелације функционалних својстава кордијеритне керамике у функцији од припреме полазне смеше.
Трокомпонентни систем састава $\text{MgO}+\text{Al}_2\text{O}_3+\text{SiO}_2$ у односу 2:2:5 је припремљен са додатком 10% $\text{Bi}_2\text{O}_3$. Смеша је механохемијски активирана 5 и 240 минута у млину са керамичким куглама и синтерована у температурном опсегу од 1173-1573К. Структурне трансформације су праћене рендгеноструктурном анализом. Квантитативне промене функционалних својстава узорака праћене су мерењем капацитивности $C_c$, електричне отпорности $R_\rho$ и тангенса угла диелектричних губитака. Резултати су доказали корелацију између механохемијске активације и својстава кордијеритне керамике.

**Кључне речи:** кордијерит, механохемијска активација, електрична својства.