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Electrical properties of cordierite obtained by non-hydrolytic sol–gel method

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Abstract

Cordierite ceramic material, due to its properties such as low thermal expansion coefficient, low dielectric constant and high specific resistivity, could be used as an insulating material in high-frequency electronics, as well as a substrate for integrated circuits and electronic modules. In this paper, cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) was synthesized by the non-hydrolytic sol–gel process combined with solvothermal treatment starting from aluminium chloride, TEOS and magnesium chloride dissolved in absolute ethanol. Crystallization of μ-cordierite from gel occurred at temperatures between 900 and 1000 °C and a higher calcination temperature resulted in the transformation of μ-cordierite to α-cordierite. Cordierite material obtained by sintering of powder in the temperature range from 1400 to 1450 °C showed values of the dielectric constants from 7.93 to 3.78 and values of dielectric loss tangents from 0.049 to 0.001.

Keywords: Cordierite; Sol–gel processes; Sintering; Dielectric properties

1. Introduction

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) is an important ceramics that founds various industrial applications. Due to its properties such as low thermal expansion coefficient ($\alpha = (1–2) \times 10^{-6}\,^{\circ}C^{-1}$), low dielectric constant ($\varepsilon = 5–6$) and high specific resistivity ($\rho > 10^{12}\,\Omega\,cm$), cordierite is a promising material in electronic industry, especially for high-frequency electronics. Microelectronic applications such as IC substrates and packages require good electrical insulation at high frequencies. Materials with high capacitance, C, cannot maintain electrical insulation at high frequency due to a decrease in capacitive resistance R_c, so it is necessary to employ ceramic materials with a low dielectric constant.[1] Cordierite is a potential material to replace alumina, traditionally used in the electronic industry.

The dielectric constant and the dielectric losses are parameters which represent the electrical efficiency of a material. These parameters could be minimized using materials with high purity and by controlling the particle size distribution, packing and sintering conditions. In this way, materials with very high electrical resistivity (ρ) and low dielectric constant (ε) at room temperature can be obtained.

It is difficult to produce dense cordierite ceramics by the solid-state reaction without sintering aids, because of the narrow sintering range near the incongruent melting point of cordierite. Sintering aids, on the other hand, degrade the dielectric properties. For that reason, recent studies on cordierite ceramics focused on the chemical synthesis of fine, reactive powders, which can be sintered at lower temperatures, without sintering aids. Sol–gel is a very attractive synthesis technique because of its ability to generate stoichiometric materials of high purity with good control over particle size.[2–4] Non-hydrolytic sol–gel processes[5–7] comprise the reaction between alkoxides and halides of certain elements (Al, Si, Ti and others), or between halides and organic oxygen compounds (ethers, aldehydes, ketones and others).

The aim of this study was the investigation of the influence of the sintering temperature on the dielectric properties of cordierite obtained by non-hydrolytic sol–gel method.

2. Experimental procedure

For the synthesis of cordierite gel, the following compounds were used: tetraethyl orthosilicate—TEOS ($(C_2H_5O)_4Si$)

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(Fluka), magnesium chloride ($MgCl_2$) (Fluka), aluminum chloride ($AlCl_3$) (Fluka) and absolute alcohol (C_2H_5OH) (Hemos). Reactants were of p.a. grade. The reactants were mixed in a stoichiometric ratio for cordierite (Mg:Al:Si = 2:4:5) in a glove box, and atmosphere of nitrogen. As a first step, $AlCl_3$ was dissolved in TEOS with intensive stirring. Then $MgCl_2$ was separately dissolved in absolute alcohol, stirring vigorously. This solution was added stepwise to the solution of aluminum chloride and TEOS. The mixture obtained this way, was heated in an autoclave at 150 °C for 3 h. The gel was dried at 100 °C, in a flow of nitrogen, and calcined at temperature 650 °C for 2 h.

Cordierite powder was first uniaxially pressed at 240 MPa in pellets with diameter 10 mm, then isostatically pressed at 400 MPa and sintered at 1400, 1430, 1440 and 1450 °C for 2 and 8 h, with heating rate 10 °C min^{-1}.

The relative linear shrinkage of the pressed pellet was determined using heat microscopy E. LEITZ, in an atmosphere of air, up to temperature of 1425 °C at a heating rate of 10 °C min^{-1}.

The densities of the sintered samples were determinated by the Archimedes method. The relative densities were calculated from the density of the α-cordierite (2.512 g/cm^3) as the theoretical density.

Capacity and dielectric loss tangent were measured at room temperature at frequencies 1 kHz, 10 kHz and 1 MHz using an impedance analyzer HP4271B (with data error of 1%). The specimens were polished to parallel surfaces and electrodes were silver painted. The values of the dielectric constant (ε) were calculated from the measurement of capacity using the following equation: $\varepsilon = Ch/\varepsilon_o S$, where C is the capacity (F), ε_o the vacuum permittivity (F/cm), h the thickness (cm), and S is the area of the sample (cm^2).

The SEM analysis was performed using scanning electron microscopy JEOL-T20, operated at an accelerating voltage of 19 kV. The powders were previously fumed with the Pd–Pt alloy.

3. Results and discussion

The phase transformations of cordierite gel synthesized by non-hydrolytic sol–gel method combined with solvothermal treatment, as well as kinetics of these transformations were described previously.[8] Crystallization of μ-cordierite from the amorphous phase occurs at 967 °C while transformation μ → α-cordierite occurs at 1202 °C. The formation of α-cordierite by the reaction of amorphous SiO_2 and spinel takes place at 1257 °C. Spinel crystallization occurs at the same temperature interval as in the crystallization of μ-cordierite.

The relative linear shrinkage of the pressed calcined cordierite powder heated up to 1425 °C is presented in Fig. 1. From this curve, the densification of the cordierite pellet from 800 to 1000 °C can be observed. The shrinkage up to 1000 °C is a consequence of densification by the viscous flow mechanism, which is precluded by the crystallization of μ-cordierite from the amorphous phase.[2,9] The shrinkage continues from 1200 to 1300 °C, where μ → α-cordierite transformation occurs. The shrinkage in this temperature range is probably a consequence of the differences in the densities of μ- and α-cordierite.

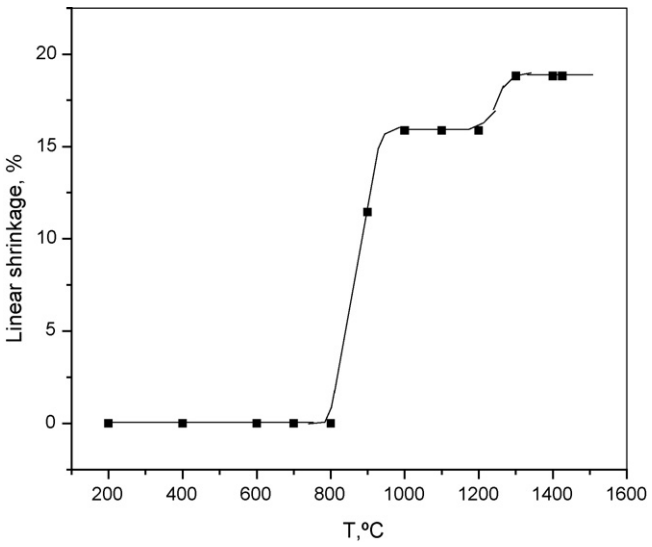

Fig. 1. The relative linear shrinkage of cordierite powder calcined at 650 °C.

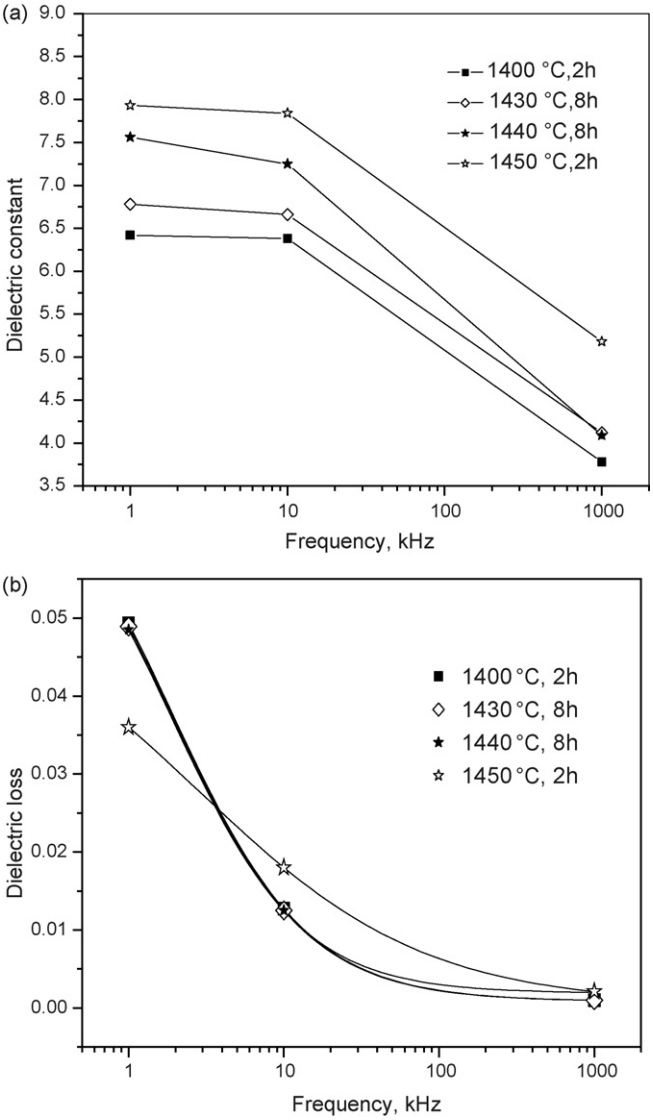

Fig. 2. The dependencies of the dielectric constant (a) and the dielectric loss (b) on the frequency for the cordierite samples sintered at different temperatures.

Table 1
The densities of the cordierite samples sintered at different temperatures

Sintering temperature (°C)	Density of sample (g/cm^3)	Relative density (%)
1400	2.17	86.3
1430	2.17	86.3
1440	2.20	87.5
1450	2.26	90.0

The densities of cordierite pellets sintered at different temperatures are presented in Table 1. The densities of the samples increase with increasing sintering temperature.

The dependencies of the dielectric constant and the dielectric loss on the frequency for cordierite samples sintered at different temperatures are presented in Fig. 2a and b, respectively.

From Fig. 2a, it can be observed that the dielectric constant decreases with increasing frequency from 1 kHz to 1 MHz for all the samples. This can be explained by the fact that increasing frequency induces weakening or disappearing of ionic polarization and, consequently, the decrease of dielectric constant values. The dielectric losses (Fig. 2b), corresponding to dielectric constant measurements, were also decreasing at higher frequency from 0.049 at 1 kHz to 0.001 at 1 MHz. According to some authors,[10] ion migration polarization loss and electronic polarization loss may exist at low frequency, while at high frequency the ion vibrations may be the only source of the dielectric loss. Additionally, the dielectric constants increase with increasing sintering temperature. At lower sintering temperatures, the porosity is higher which can be observed in Fig. 3a and b where the micrographs of the samples sintered at 1400 and 1450 °C, are presented. From these images, it is obvious that with increasing sintering temperature, a denser microstructure is obtained, but some porosity remains. The lower values of the dielectric constant at 1400 °C can be assigned to a higher content of air ($\varepsilon = 1$) in the pores present in the cordierite sintered body.

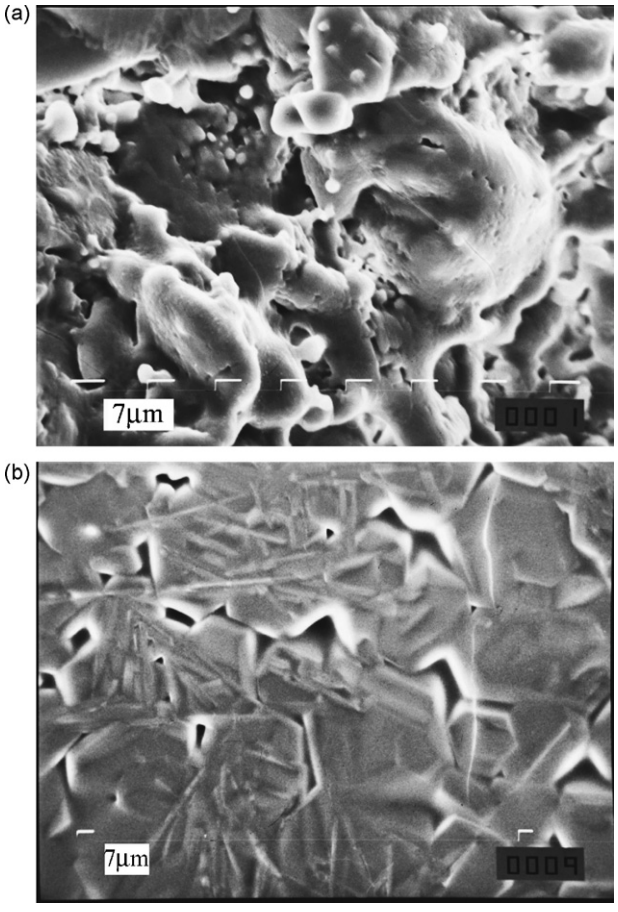

Fig. 3. The micrographs of cordierite sintered at 1400 °C (a) and 1450 °C (b).

4. Conclusion

The present work demonstrates that cordierite can be synthesized using a non-hydrolytic sol–gel method combined with solvothermal treatment, by the reaction of metal chlorides and an alkoxide precursor. The dielectric constant of obtained cordierite material depends on the sintering temperature and varies from 3.78 at 1400 °C to 5.18 at 1450 °C at 1 MHz. The dielectric loss of 0.001 and the dielectric constant of 5.18 at 1 MHz, show that this cordierite ceramic is promising for high-frequency electronic application.

Acknowledgment

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