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Electrical properties and thermal expansion of cordierite and cordierite-mullite materials

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Abstract

Commercially available cordierite and mullite powders were used to obtain cordierite and composite materials with mullite content up to 65 wt.% by attrition milling, uniaxial pressing and sintering. The employed cordierite powders were the coarse, medium and fine single granulometric fractions and the binary mixtures of them with 30, 50 and 70 wt.% of the smaller size component. Mullite powder employed in composites was a 7 h-attrition milled one. The dielectric constant (ε), dielectric loss tangent (tan δ), resistivity (ρ) and thermal expansion coefficient (α) were measured. The influence of the porosity, mullite and glassy phase contents and grain size in the electrical parameters was analyzed. The thermal expansion coefficient as a function of the composition was studied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cordierite; Electrical properties; Mullite; Thermal expansion

1. Introduction

Aluminosilicates offer certain advantages for use as packaging materials. Many aluminosilicate-based ceramics such as cordierite ($2MgO.2Al_2O_3.5SiO_2$) and mullite ($3Al_2O_3.2SiO_2$) have attracted much attention in recent years as substrate materials.[1–4]

Cordierite has low dielectric constant ($\varepsilon = 5$–6), high resistivity ($\rho > 10^{12}$ Ωcm), elevated thermal and chemical stabilities and very low thermal expansion coefficient ($\alpha = 1$–2×10^{-6} °C^{-1}).[2,5,6] These properties together with low processing costs characterise cordierite as a potentially available material to be used in replacement of the alumina substrates, traditionally employed in the electronic industry.[1–3] However, cordierite has the disadvantage of its very low average thermal expansion coefficient with respect to Si chip where microcircuits that carry out the logic and memory functions are built.[2] Moreover, cordierite materials are difficult to sinter by solid state process. Any sintering aids help the densification by liquid-phase process. Unfortunately, the electrical and thermal properties of cordierite are degraded by sintering aids.[7,8]

It has been showed that addition of mullite to cordierite allows tailoring the thermal expansion coefficient of composites matching that of Si preventing chip detachment and device failure.[2,9] However, the presence of mullite aggravates even more the sintering of the cordierite materials.

In order to obtain substrate materials that assemble the adequate properties,[2] a processing to dense materials with small grain size is required. The dielectric constant and the dielectric losses ('intrinsic' depending on the crystal structure and 'extrinsic' associated with impurities, microstructural defects, grain boundaries, porosity, microcracks and random crystallite orientation) represent a measurement of the electrical efficiency of the material. These parameters could be minimised using materials with high purity and controlling the particle size distributions, packing and sintering conditions. In this way, materials with very high electrical resistivities (ρ) at room temperature, that are required to diminish the current leakage between conductor lines, are obtained. Moreover, by improvement of the sinterability of the powders the sintering temperatures and the processing costs can be minimised.[10]

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The main objective of this paper is to evaluate the influence of mullite additions to commercial cordierite materials in which a glassy phase is present on the electrical properties and thermal expansion coefficient of the resulting composites.

2. Experimental procedure

2.1. Materials and processing

The starting materials were commercially available powders of cordierite (CORCR Baikowski, France) and mullite (MULCR Baikowski, France). Their mean particle sizes (Coulter LS 130) were 1.82 μm for the cordierite powder and 2.35 μm for the mullite and their specific surface areas, BET (Monosorb Quantachrome) were 3.4 and 2.3 m^2/g, respectively. The contents of the elements were determined by wet chemical analysis. The impurity level is less than 0.17 wt.% in cordierite powder and 0.3 wt.% in mullite one (Table 1). The real densities of cordierite, $\delta_{\mathrm{Rcordierite}} = 2.6$ g/cm^3 and mullite, $\delta_{\mathrm{Rmullite}} = 3.05$ g/cm^3 were determined by kerosene and He picnometries (Multipicnometry Quantachrome), respectively.

The cordierite starting powder with its initial granulometry and attrition milled powders were chosen as coarse C, medium M and fine F single fractions. The binary mixtures of them F/C, M/C and F/M were prepared in three ratios: 30/70, 50/50 and 70/30 wt.%.

Two sets of cordierite-mullite mixtures were prepared using attrition milled mullite: one of them by addition of 30 wt.% mullite to the cordierite matrices and the other with different proportions of milled mullite powder (0, 10, 15, 20, 25, 30 and 65 wt.%) into the F/C 50/50 cordierite matrix. These samples will hereafter be referred to as cordierite matrix-30M and M_0, M_{10}, M_{15}, M_{20}, M_{25}, M_{30} y M_{65} respectively.

The processing of materials and the characterisation of the sintered samples were described in a previous work.[11] As-received cordierite and mullite powders were attrition milled for 8 h ($D_{50} = 0.9$ μm; $S_E = 6.5$ m^2/g), 32 h ($D_{50} = 0.45$ μm; $S_E = 11.2$ m^2/g), and 7 h ($D_{50} = 1.3$ μm; $S_E = 6.4$ m^2/g), respectively. The preparation of cordierite and cordierite-mullite mixtures was performed by homogenizing the powders in the attrition mill (1045 rpm, 10 min); drying and sieving (37 mesh). Then, they were uniaxial pressed at 20 MPa without binders and sintered in an electrical furnace with $MoSi_2$ heating elements at 1450°C, 2 h using a slow firing schedule.[12]

Table 1
As-received cordierite and mullite powders wet chemical analysis (wt.%)

Chemical analysis (wt.%)	Cordierite	Mullite
W.L	0.004	0.13
Al_2O_3	36.9	72.7
SiO_2	49.4	27.2
MgO	12.32	0.008
Fe_2O_3	0.03	0.02
TiO_2	0.013	0.01
CaO	0.10	0.07
Na_2O	0.02	0.06
K_2O	0.004	0.003

The microstructures of the sintered materials were observed by scanning electron microscopy (SEM) on polished surfaces and thermally etched (20°C/min up to 1400°C, 30 min). The average grain size was determined by image analysis (Image-Pro Plus software) on the digitised SEM photographs. The apparent densities of the sintered materials (δ_S) were measured by Archimedes method and the relative density percentages (% δ_S/δ_R) were obtained using the real densities (δ_R) of the powders treated at 1450°C, 2 h calculated by the parallel mixing rule. For this calculus, the theoretical densities and the amounts of the phases present (cordierite, mullite and glass) were considered. These phases were determined by XRD (Philips, Cu K_α radiation at 40 kV and 30 mA) and FTIR (Bruker IFS25 fitted for Fourier transforms, using KBr pellets) after heating at sintering temperature (1450°C) and their amounts (84% cordierite, 10% mullite and 6% glass) were obtained by examining the isothermal section at the Al_2O_3–SiO_2–MgO system at this temperature.

2.2. Electrical properties and thermal expansion coefficient

Dielectric constant (ε), dielectric loss tangent (tan δ) and resistivity (ρ) measurements were made on disk-shaped samples (1.0 cm in diameter and 0.3 cm of thick). The specimens were polished to parallel surfaces and electrodes were silver painted.

Capacity and dielectric loss tangent were determined at room temperature in the range of 1 kHz–1 MHz, using an impedance analyser (Hewlett Packard HP 4284A LCR meter).

The ε values were calculated from the measurements of the capacity using the following equation: $\varepsilon = Cl/\varepsilon_0 A$, where C is the capacity (F), ε_0 the vacuum permitivity (F/cm), l the thickness (cm) and A (cm^2) the area of the sample.

In order to estimate the dielectric constants of the composites by the mixing rule, the dielectric constants at 1 MHz of cordierite (coarse single fraction, C sintered at 1450°C, 2 h) and mullite (attrition milled powder sintered at 1700°C, 2 h) materials were determined. Experimental values were divided by a factor $(1-P)$, where P is the pore fraction, obtaining the following values at zero porosity, $\varepsilon^0_{\mathrm{cordierite}} = 6.2$ and $\varepsilon^0_{\mathrm{mullite}} = 8.4$. The obtained ε^0 value of mullite is only slightly greater than that reported by Giess et al.,[13] although, this value results higher than those usually reported in literature.[6,9,14] The presence of a higher level of impurities in the mullite powder indicated by chemical analysis could produce an increase in the mullite ε^0 value.

Resistivities of the samples were determined using a Phitronic power supply (0–60 V, 0–1.5 A) and a Keithley 614 electrometer.

Thermal expansion coefficients (α) were determined employing an Adamel Lhomargy dilatometer in a temperature range of 50–1000°C at a heating rate of 5°C/min. The analysed specimens were bars of $2.5 \times 0.6 \times 0.3$ cm prepared by uniaxial pressing at 20 MPa and sintering at 1450°C, 2 h. The average values were calculated from the expansion length up to 900°C.

3. Results and discussion

3.1. Densification and microstructural analysis

The composition of the composite materials were located in the crystallisation field of mullite and in the cordierite-mullite-glass compatibility triangle on a line that connects the starting compositions of cordierite ($SiO_2 = 50$ wt.%; $Al_2O_3 = 37$ wt.% and $MgO = 13$ wt.%) and mullite ($SiO_2 = 27.2$ wt.%; $Al_2O_3 = 72.8$ wt.%) commercial powders in the isothermal section at 1450°C at the Al_2O_3–SiO_2–MgO system.[11] Also, the composition of the glassy phase (63% SiO_2, 25% Al_2O_3 and 12% MgO) and the cordierite, mullite and glassy phase amounts were obtained from this isothermal section. The amount of cordierite diminished (from 84 to 9 wt.%) while the amount of glass increased (from 6 to 27 wt.%) with higher mullite content (from 10 to 64 wt.%).

The densification degree ($\%\delta_S/\delta_R$) of the studied materials was calculated as the ratio of the apparent density (measured by water immersion) and the real density calculated by the parallel mixing rule ($\delta_{M0} = 2.57$ g/cm^3; $\delta_{M10} = 2.62$ g/cm^3; $\delta_{M15} = 2.64$ g/cm^3; $\delta_{M20} = 2.67$ g/cm^3; $\delta_{M25} = 2.69$ g/cm^3; $\delta_{M30} = 2.7$ g/cm^3; $\delta_{M65} = 2.89$ g/cm^3).

For calculation, the theoretical densities of the cordierite (δ_{th} cordierite $= 2.52$ g/cm^3) and mullite (δ_{th} mullite $= 3.16$ g/cm^3) and the glass density (2.51 g/cm^3) measured by kerosene picnometry were considered.

The densification degree reached by sintering of the single fractions[11] of cordierite and their composites with 30 wt.% mullite increased in the order $C < M < F$ (from 94.16 to 97.27% for cordierite and from 95.56 to 98.15% for cordierite-30% mullite) in agreement with the increment in the green densities. Regarding the densification degree of the binary mixtures[11] (F/C, M/C and F/M) of cordierite and their composites, a simple order was not obtained; not always the best green densities produced higher final densities. The obtained relative densities were only slightly greater or similar to those reached with the materials prepared with the single fractions. The higher values were obtained for F/M 70/30 (98.05%) and F/M 70/30–30M (98.52%).

It can be seen that as the percentage of mullite increased, the densification degree of the materials showed a no linear increment from $M_0 = 95.72\%$ to $M_{65} = 97.58\%$[11] indicating that mullite does not produce an inhibitor effect on the densification of this commercial cordierite powder in disagreement with some reported data.[15,16] This fact has been explained taking into account the composition of the glassy phase and the increment of this amount with the added mullite content since a liquid-phase sintering mechanism is operating. In all the studied materials, the final grain size was smaller than the initial particle size, this fact strongly supports the assumption that the sintering in presence of a liquid phase occurs almost exclusively through primary and secondary (particle–particle) rearrangements.

The developed microstructures analysed by SEM[11] were very similar, as much in the cordierite materials as in the composites up to 30 wt.% mullite. Homogeneous microstructures with equiaxial grains of similar submicron size (0.3–0.52 μm) and mainly intergranular pores with spherical shape and sizes close to grain diameters were observed and there were no morphological differences to distinguish between the cordierite and mullite grains. Additionally, a few elongated grains (aspect ratio ≈ 1.9) attributed to mullite growing in presence of a liquid phase were observed. Significant differences can be observed in the microstructure of the composite formulated with 65 wt.% mullite. This sample presented faceted grains with a higher amount of elongated grains (larger aspect ratio ≈ 3) and few equiaxial ones (0.54 μm). Also, the observed porosity is manifestly higher than that of the other cordierite–mullite materials in agreement with its smaller calculated relative density.

3.2. Electrical properties

3.2.1. Influence of the frequency on dielectric constant and dielectric loss tangent

In Fig. 1 the dielectric constant and dielectric loss tangent dependencies on frequency for the cordierite (F/C 50/50) and composites M_{30} and M_{65} are shown.

Both, in the cordierite and in the composites, ε did not show an important dependence with the frequency in all the range studied (Fig. 1a). The observed behavior can be attributed to the possible low time delay for signal propagation.[17] This fact indicates that the electric charge adjusts itself instantaneously to any change in voltage.

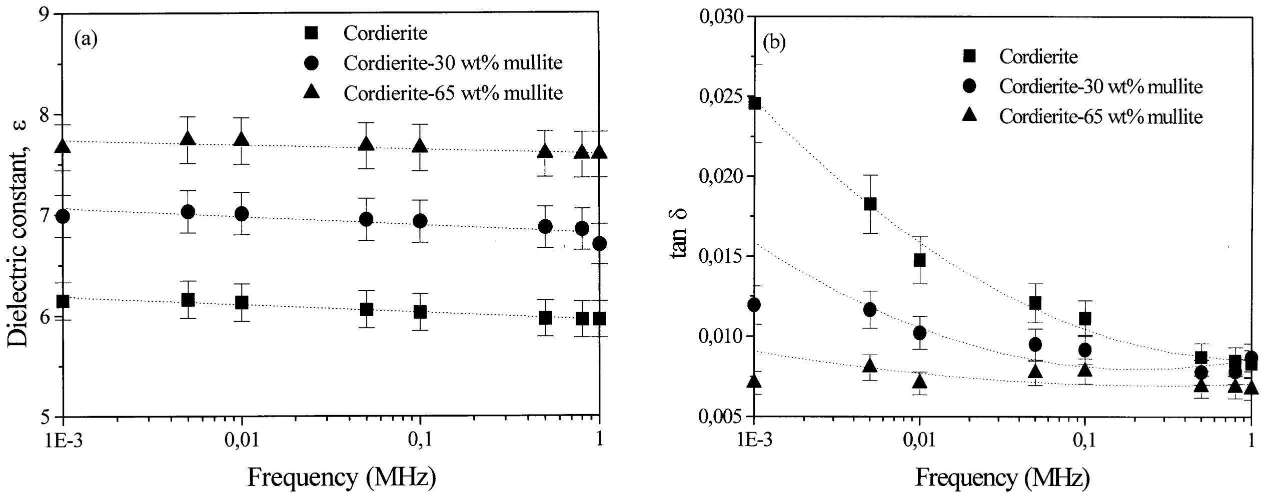

Fig. 1. (a) Dielectric constant, ε and (b) dielectric loss tangent, tan δ as a function of the frequency.

With respect to dielectric loss tangent, one diminution in the measured values with the increasing frequency was observed in all the studied materials (Fig. 1b) to attain a constant value above 0.050 MHz. For this reason, 1 MHz was fixed as the frequency for the electrical measurements in order to make sure that the electrical parameters remain constant with the employed frequency. This frequency is in the range where the most important contribution to the dielectric losses occurs by a relaxation mechanism, since the conduction losses are small at frequencies greater than 100 Hz at room temperature.[18,19]

3.2.2. *Effect of the porosity*

The influence of the porosity ($\%P=100-\%\delta_S/\delta_R$) of the cordierite and cordierite–30% mullite materials on the ε and tan δ was studied.

Sintered materials with different porosities were designed by controlling the green particle packings obtained from the single fractions and the formulated binary granulometric mixtures.

In order to evaluate the variation of the dielectric constant with the porosity, both the parallel ($\varepsilon=\Sigma\ \varepsilon_i V_i$) and the series ($1/\varepsilon = \Sigma V_i/\varepsilon_i$) models were considered. In these expressions ε is the dielectric constant of the composite, V_i and ε_i represent the volume fraction and dielectric constant of i component, respectively. Whether, one of the phase is the porosity ($\varepsilon_i=1$ and $V_i=P$), the mentioned equations reduce to $\varepsilon=\varepsilon_m - P(\varepsilon_m - 1)$ for parallel model and $\varepsilon = \varepsilon_m/[P(\varepsilon_m - 1) + 1]$ for series model.

Fig. 2 shows the dependence of the dielectric constant on the porosity of cordierite (Fig. 2a) and cordierite–30wt.% mullite (Fig. 2b) and also the values obtained assuming the parallel and series models. In both materials, a slight linear decreasing of the dielectric constant can be assumed with the increasing porosity if a 90% confidence limits is considered in F-test for significance of regression. This effect is due to the contribution of the pores with a lower value of dielectric constant ($\varepsilon=1$) than that of the matrix. The higher values of the composites can be attributed to their lower porosity and to the presence of a greater amount of mullite (phase with higher ε) in the composites with respect to cordierite materials. For both materials, the best fitting for the experimental values was obtained employing the parallel model. This suggests that the structure of the materials can be associated to an arrangement of capacitive elements in parallel. The results are in agreement with the data reported by Anderson et al.[9] and in dissent with those achieved by Mussler et al.[6] for similar systems.

Some simple models that indicate a linear dependence of the tan δ with porosity fail to predict a null value of tan δ for fully dense ceramics in which sources of loss exist as the random grain orientation and the grain boundaries. Different mathematical expressions considering the loss due to porosity in an additional term have been proposed:[20]

$$\tan\delta = (1-P)\tan\delta^0 + AP^n \tag{1}$$

$$\tan\delta = (1-P)\tan\delta^0 + BP[P/(1-P)]^{2/3} \tag{2}$$

where tan δ^0 is the loss tangent of the fully dense material and A and B are constants.

The expression (2) is obtained from (1) assuming that the power of P is approximately 2/3. Since a pore volume to the power of 2/3 has dimensions of area, it suggests that the loss may be related to the surface area of the pore volume.

Fig. 3 shows the dependence of the dielectric loss tangent values on the porosity for the cordierite and cordierite–30 wt.% mullite and the corresponding fitting curves using Eqs. (1) and (2). In both materials the dielectric loss tangent increases with the porosity (con-

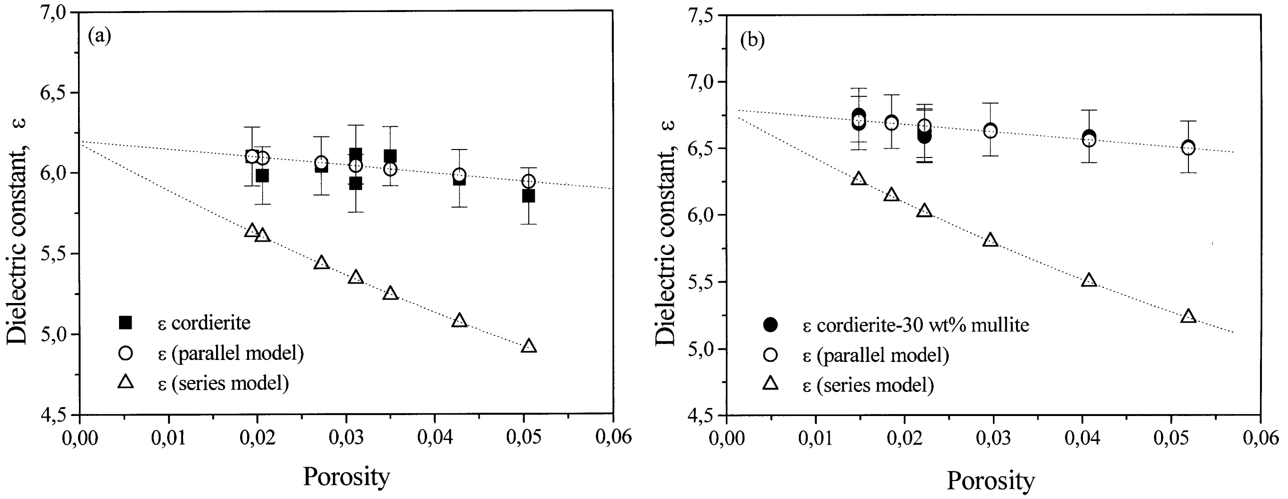

Fig. 2. Dependence of the dielectric constant, ε with the porosity of (a) cordierite and (b) cordierite–30 wt.% mullite materials.

sidering a 95% confidence limits), showing higher values for the composites than those obtained for the cordierite materials. Additionally, the increment in the tan δ in the whole studied porosity ranges resulted lower for the composites than that registered for the cordierite materials. This difference (in the slope) could be related to a change in the environment of the pore surfaces, since the solid matrix is cordierite or cordierite–30 wt.% mullite, respectively. The narrow porosity range that these materials exhibited permit a good fitting with the two models. The obtained fitting parameters are the following: for cordierite materials, Eq. (1): $n=1$–1.5; tan $\delta^0=0.0049$-0.0056; $A=0.16$–0.45 and Eq. (2): tan $\delta^0=0.0057$; $B=0.51$; for cordierite–30 wt.% mullite, Eq. (1): $n=1.1$; tan $\delta^0=0.0084$; $A=0.055$ and Eq. (2): tan $\delta^0=0.0088$; $B=0.24$.

The effect of the grain size distribution on the electrical parameters (ε and tan δ) was considered insignificant. This effect could be attributed to the very small variation of the grain sizes developed in all the sintered cordierite and composites (0.3–0.52 μm).

3.2.3. *Effect of the increasing mullite content*

The dependence on the composition of the dielectric constant (ε), dielectric loss tangent (tan δ) and resistivity (ρ) was studied employing the cordierite matrix F/C 50/50.

In order to analyse the effects of the increasing mullite content on the dielectric constant, the influence of the porosity was eliminated. ε Was extrapolated to zero porosity (ε^0) dividing these values by the factor $(1-P)$ considering that the experimental values of the dielectric constant as a function of the porosity fit with the parallel model.

In Fig. 4 the experimental values normalized to zero porosity (ε^0) and the corresponding values calculated from the parallel and series mixing rules are shown as a function of the increasing mullite content. By removing

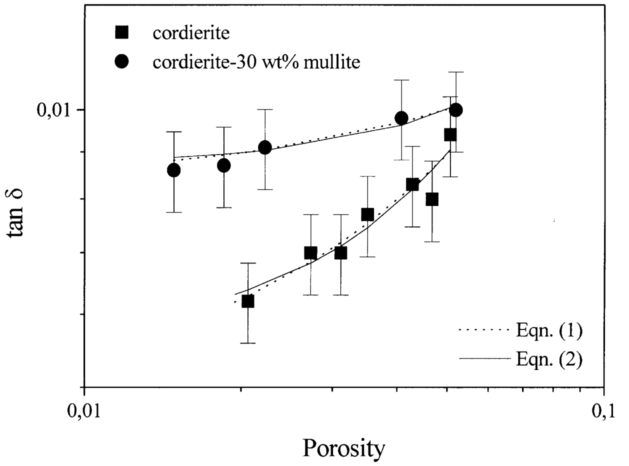

Fig. 3. Dependence of the dielectric loss tangent (tan δ) with the porosity of cordierite and cordierite–30 wt.% mullite materials and fits to the models (1) and (2).

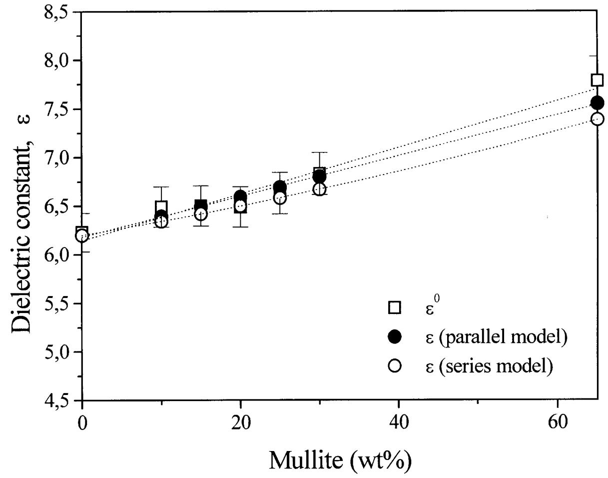

Fig. 4. Dielectric constant at zero porosity, ε^0 and values calculated from the parallel and series mixing rules as a function of the mullite content.

the effect of the porosity, the dielectric constant presents a significant linear increment (taking a 95% confidence limits) because of the increase of mullite and glassy phase contents (phases with ε higher than that of the cordierite) in the composition range studied. It must be mentioned that the dielectric constant of the glass can be relatively high due to the presence of Mg and Al. Furthermore, the wetting angle between cordierite ($\theta = 18°$) or mullite ($\theta = 23°$) and the glass permit its penetration along grain boundaries[12] and influences on the dielectric constant values.

The better fit of the experimental extrapolated data was obtained with the parallel model in agreement with published data.[9,14] Values calculated using the series model were always lower than the experimental data. Also, it can be seen that experimental data are slightly higher than the values calculated from the parallel mixing rules being this effect notably stronger for the composite with 65 wt.% of mullite. One possible explanation for this fact could be given taking into account the morphology of the developed grains. It has been reported that materials with faceted and elongated grains, as those observed in the composite with 65 wt.% mullite, presented higher dielectric constant than that registered in materials with equiaxial grains.[13] In our system, it must be also considered that two kinds of mullite appear: the commercial mullite added as the second phase and the one produced from the incongruent melting of the cordierite at 1450°C given mullite plus a liquid. These mullites of different origins can develop grains with unlike size and morphology. As it was said before, any influence of the grain size on the dielectric constant values due to the very narrow variation range in the grain size analysed was discarded.

In respect to the variation of the dielectric loss tangent with the mullite content, the obtained tan δ values are shown in Fig. 5. By increasing the mullite content up to 20 wt.% the dielectric loss tangent increases continuously and then it decreases until the corresponding mullite value. Taking into account the effect of the diminution of the porosity and the increasing amounts of glass, in opposition to the effect of the mullite content increase, an explanation of these results could be given. In those materials with cordierite matrix, the tan δ values arise from a balance between the increasing amount of mullite content and the effect of lower porosity and the higher glass content. Whereas, in the material whose matrix mainly consists of mullite (65 wt.% mullite), the significatively high glass content in this composite and the very different developed microstructure can prevail on the deleterious effect of higher mullite content in agreement with data reported by Anderson et al.[9]

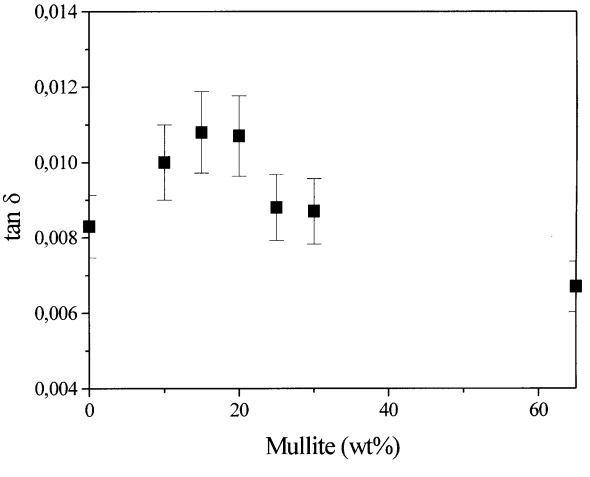

Fig. 5. Dielectric loss tangent, tan δ of cordierite–mullite composites.

On the other hand, there are numerous discrepancies with respect to the tan δ dependence on the grain size in the published results. Some authors[20] have determined an increase of the dielectric loss tangent with the diminution of the grain size due to an increment of the amount of the grain boundaries. But, other researchers[20,21] determined that it decreases or does not depend on the grain size. As in the case of the dielectric constant, the effect of the grain size on the tan δ was considered negligible.

No significative differences were appreciated in the resistivity (ρ) values for the studied cordierite materials and composites. Moreover, the reached experimental values (3–4×10^{11} Ωcm) are in the limit of the range required for its use as substrate. The last result can be attributed to the presence of impurities and glassy phase locates in the grain boundaries.

3.3. Thermal expansion coefficient

In order to estimate the amount of mullite that allows us to obtain a composite thermal expansion coefficient close to that of silicon ($\alpha = 3$–3.5×10^{-6} °C^{-1}) the models of Turner and Kerner[22] were employed. For the calculus, the experimental values determined for cordierite ($\alpha_{\text{cordierite}} = 2.2 \times 10^{-6}$ °C^{-1}) and mullite ($\alpha_{\text{mullite}} = 6 \times 10^{-6}$ °C^{-1}) were considered and the bulk (K) and shear (G) modulus of both phases were taken from the literature.[13] The better fitting of thermal expansion coefficients was obtained with 30 wt.% mullite by assuming the model of Turner and with 35 wt.% mullite with the model of Kerner.

In Table 2, the experimental average values of thermal expansion coefficients (α) of M_0; M_{30}; M_{65} and M_{100} materials are given. The cordierite–30 wt.% mullite composite exhibits a thermal expansion coefficient in the range of the silicon coefficient ($\alpha = 3$-3.5×10^{-6} °C^{-1}). A close correlation between the experimental values and the Turner and Kerner predictions was obtained. In agreement with data reported by Mussler et al.,[6] in the cordierite–mullite materials with mullite contents lower

Table 2
Average thermal expansion coefficient (α) of cordierite, cordierite–30 wt.% mullite, cordierite–65 wt.% mullite and mullite materials

Materials	$\alpha \times 10^{-6}$ (°C^{-1})
M_0	2.2
M_{30}	3.6
M_{65}	5.0
M_{100}	6.0
Si[a]	3.5

[a] Value taken from literature.[2]

than 35 wt.%, the thermal expansion is controlled by the cordierite, phase with the lower α.

4. Conclusions

Cordierite and cordierite–mullite materials to use as substrates in electronic were obtained from commercial powders by processing control. The cordierite material with the granulometric composition 70 wt.% fine and 30 wt.% medium particles exhibited the best electrical properties. The addition of 30 wt.% mullite to cordierite materials allowed to obtain composites whose thermal expansion coefficient matched with that of silicon. Moreover, this mullite content did not cause an important damage in the electrical properties; assembling the composite with the same matrix than the cordierite material the best required properties for its use as substrate.

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