

Thermal and Electrical Properties of Alkoxy-derived Cordierite Ceramics

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Abstract

The thermal and electrical properties of alkoxy-derived cordierite ceramics are estimated. These properties are discussed in relation to the homogeneity and purity of the ceramics. The cordierite ceramics were prepared by sintering fine and homogeneous precursor powders. Previous papers demonstrate the high purity and homogeneity of the precursor powders and therefore, the cordierite ceramics should have the superior properties. It was found that the properties of the alkoxy-derived cordierite changed remarkably with sintering temperature or the crystalline phases. Because of residual stress and micro-cracking, the cordierite ceramics cannot have high flexural strength. However, the cordierite ceramics sintered at 1300°C had some superior properties, such as high thermal shock resistance (critical temperature difference of about 600°C), low thermal expansion and high electrical resistivity. This behavior is ascribed to the high purity and homogeneity of the resulting ceramics.

Es wurden die thermischen und elektrischen Eigenschaften der mit Alkoxy-abgeleiteten Kordierit-Keramiken bestimmt. Diese Eigenschaften werden in Verbindung mit der Homogenität und der Reinheit der Keramiken diskutiert. Die Kordierit-Keramiken wurden durch Sintern feiner und homogener Ausgangspulver hergestellt. Vorhergehende Veröffentlichungen belegen den hohen Reinheitsgrad und die Homogenität der Ausgangspulver, so daß diese Kordierit-

Keramiken verbesserte Eigenschaften aufweisen sollten. Es wurde festgestellt, daß sich die Eigenschaften Alkoxy-abgeleiteter Kordierite erheblich mit der Sintertemperatur oder dem Auftreten kristalliner Phasen verändern. Aufgrund innerer Spannungen und aufgrund von Mikrorissen weisen die Kordierit-Keramiken nur eine geringe Biegefestigkeit auf. Kordierite, die jedoch bei 1300°C gesintert wurden, besaßen zum Teil bessere Eigenschaften, wie eine hohe Thermoschockbeständigkeit (die kritische Temperaturdifferenz beträgt etwa 600°C), eine geringe Wärmeausdehnung und eine geringe elektrische Leitfähigkeit. Dieses Verhalten wird dem hohen Reinheitsgrad und der Homogenität der hergestellten Keramiken zugeschrieben.

On a mesuré les propriétés thermiques et électriques de céramiques cordiérites dérivés d'alcóolates. On discute ici de ces propriétés en les reliant à l'homogénéité et à la pureté des céramiques. Les matériaux cordiérite étaient préparés par frittage de poudres de précurseur fines et homogènes. De précédentes publications ayant mis en évidence le degré de pureté élevé et l'homogénéité de ces poudres de précurseurs, les céramiques cordiérite doivent ainsi posséder des propriétés supérieures. On a établi que les propriétés de la cordiérite dérivée de l'alcóolate dépendaient fortement de la température de frittage et des phases cristallines. Du fait de contraintes résiduelles et d'un phénomène de microfissuration, les céramiques cordiérites ne peuvent présenter des valeurs de contrainte à la rupture ou flexion élevées.

Les céramiques cordiérite frittées à 1300°C présentent toutefois certaines propriétés supérieures, comme une résistance élevée au choc thermique (différence de température critique d'environ 600°C), une dilatation faible et une haute résistivité électrique. Ce comportement est à imputer à la haute pureté et au degré d'homogénéité élevé des céramiques ainsi produites.

1 Introduction

Properties of ceramics depend upon purity, homogeneity and microstructure, including pores, boundaries and defects. Therefore, controlling these factors is indispensable in the preparation of the high-performance ceramics. The sol-gel process can offer a novel method to prepare the high-performance ceramics at low temperature. Especially by the alkoxide route, fine ceramic precursors with high purity and homogeneity can be prepared.^{1,2} The controlled hydrolysis and subsequent copolymerization of alkoxides allows the achievement of molecular design of the precursors.^{3,4} The powder compacts of the precursors can easily densify at low temperature.⁵ Further heating results in homogeneous crystallization to give high-performance ceramics.⁶

However, it is notoriously difficult to prepare the homogeneous precursors of silicates from alkoxides. Namely, the difference in the hydrolysis rate between silicon and the other alkoxides causes preferential hydrolysis.⁷ Yoldas⁸ proposed the partial hydrolysis method for glass formation. The method includes the direct reaction of aluminum alkoxides with the partially hydrolyzed bonds of silicon alkoxides. In this method, all other glass constituents can be introduced as alkoxides when silica constitutes more than half of the structure. Regardless of these results, the partial hydrolysis method from alkoxides is not used for ceramic processing. The present authors think the reasons are as follows: the partial hydrolysis of alkoxides and the following copolymerization of the partially hydrolyzed species are not controllable. Recently, the authors demonstrated a new process to prepare fine and homogeneous precursor powders with a cordierite composition.³ The method included partial hydrolysis of tetraethylorthosilicate (TEOS) and the double alkoxide method. Namely, the partially hydrolyzed TEOS reacted with the aluminum-magnesium double alkoxide to prepare a homogeneous precursor solution. Fine and homogeneous precursor powders with a stoichiometric composition were prepared by adding an excess of water to the

precursor solution. Powder compacts of the calcined precursor densify above 900°C followed by homogeneous crystallization. As a result, cordierite ceramics with a stoichiometric composition can be prepared at above 1200°C. The powder preparation, the sintering and the mechanical properties of the cordierite have already been reported.^{3,5,6} This paper describes the thermal and electrical properties of the alkoxy-derived cordierite ceramics. The properties of the ceramics are discussed in relation to the microstructures arising from the preparation process.

2 Experimental Procedure

2.1 Powder preparation and sintering

The powder preparation and the sintering have been described elsewhere.^{3,5} Homogeneous precursor powders were prepared by the copolymerization between partially hydrolyzed TEOS and the aluminum-magnesium double alkoxide. The partial hydrolysis condition of TEOS had a large effect on the homogeneity of the resulting precursor powders.³ Precursor powders prepared under the optimum condition were heat-treated at 800°C for 12 h to remove the residual organic component and water. Calcining temperature also affected the sintering behavior of the compacts.⁵ When the precursor powders were calcined above 900°C, full densification could not be achieved. The amorphous calcined powders were cold isostatically pressed and sintered at different temperatures up to 1450°C. The crystalline phases developed during sintering are listed in Table 1. The mechanical and the thermal properties of the resulting ceramics are summarized in Table 2.

2.2 Thermal properties

The specimens for the thermal expansion and the bending tests were cut into bars of 3 × 4 × 18 mm and 3 × 4 × 36 mm, respectively. The coefficients of thermal expansion (CTE) were measured by the push rod type dilatometer (the heating rate was

Table 1. Crystalline phases of the sintered compacts

Sintering temperature (°C)	Crystalline phases
900	μ-Cordierite
1000	μ-Cordierite > α-cordierite
1100	α-Cordierite > μ-cordierite
1200	α-Cordierite
1300	α-Cordierite
1400	β-Cordierite
1450	α-Cordierite

Table 2. Thermal and mechanical properties of alkoxy-derived cordierite ceramics

Sintering temperature (°C)	Flexural strength (MPa)	Young's modulus (GPa)	CTE × 10 ⁻⁷ (°C)	Poisson's ratio
900	61	79	47.4	0.26
1000	66	84	42.9	0.26
1100	—	—	27.7	—
1200	98	88	17.4	0.31
1300	100	87	15.7	0.31
1400	76	66	10.7	0.31
1450	56	76	12.7	0.31

5°C/min). The average values were calculated from the expansion length up to 800°C. The thermal stress, σ , developed in fast thermal quenching could generate cracks which degrade the fracture strength. It can be represented by the following equation:⁹

$$\sigma = \alpha \cdot E \cdot \Delta T / (1 - \nu)$$

where α , E , ΔT and ν are the coefficient of thermal expansion, Young's modulus, temperature difference and Poisson's ratio, respectively. Therefore, four-point bending tests before and after the quenching allow the critical temperature difference to be estimated. The specimens for the thermal shock tests were held at the testing temperatures for at least 30 min in a vertical furnace and then dropped into a container of water.

The thermal diffusivity was measured by the laser flash method. The relationship between thermal conductivity, κ , and thermal diffusivity, h , is represented by the following equation:

$$\kappa = h \cdot C_p \cdot D$$

where C_p is the specific heat and D is the density.

2.3 Electrical properties

The specimens were cut into plates (12.0 × 12.0 × 1.05 ± 0.01 mm) and polished to parallel mirror-like planes. Platinum paste was used as an electrode. The capacity of the specimens were measured by LCR meter (YHP, LF impedance analyzer model 4192 A) and a stray capacitance was corrected. The dielectric constant, ϵ_r , can be calculated by the following equation:

$$\epsilon_r = C \cdot d / \epsilon_0 \cdot S$$

where C , d , ϵ_0 and S are the capacity, the distance between electrodes, the permittivity and the area of the electrode, respectively. The resistivity, ρ , and the dielectric loss, $\tan \delta$, were estimated by the following equations:

$$\rho = R \cdot d / S$$

$$W = \pi \cdot f \cdot V^2 \cdot C_0 \cdot \epsilon_r \cdot \tan \delta = k \cdot f \cdot V^2 \cdot CLF$$

where R , W , C_0 , f , V , k and CLF are electrical resistance, AC loss, capacity of the electrostatic capacitor, the frequency, the applied voltage, a constant and capacity loss factor, respectively.

3 Results and Discussion

3.1 Thermal expansion

The average CTE of the alkoxy-derived cordierite ceramics decreased with the sintering temperature and almost levelled off above 1200°C (Fig. 1). As shown in Table 1, the residual μ -cordierite and/or intergranular glassy phase are responsible for the higher CTE. The CTE decreased enormously at 1400°C. Hirose *et al.*¹⁰ reported that CTE values of dense cordierite ceramics prepared by hot-pressing of cordierite glass powders scattered in a wide range because of the micro-cracks arising from hexagonal to orthorhombic transformation. In this study, hexagonal to orthorhombic transformation or Al/Si ordering¹¹ is also accelerated at this temperature (Fig. 2). Therefore, the low CTE at 1400°C is ascribed to the micro-cracking. The hysteresis of the thermal expansion curve shows the existence of the micro-cracks (Fig. 3). However, it seems that the pseudo-hexagonal variety likely to be developed in

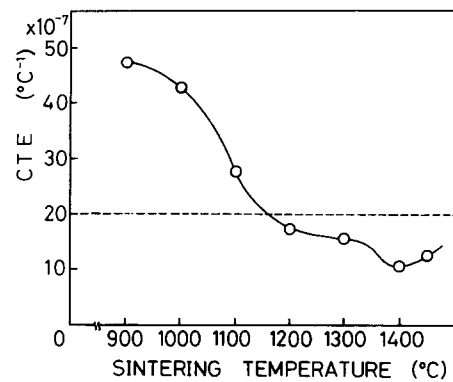


Fig. 1. The average coefficients of the thermal expansion (CTE) of the sintered cordierite ceramics.

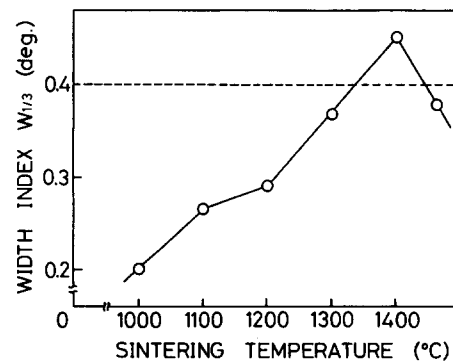


Fig. 2. Width indices of the sintered cordierite ceramics. β -Cordierite has a width index of more than 0.4.

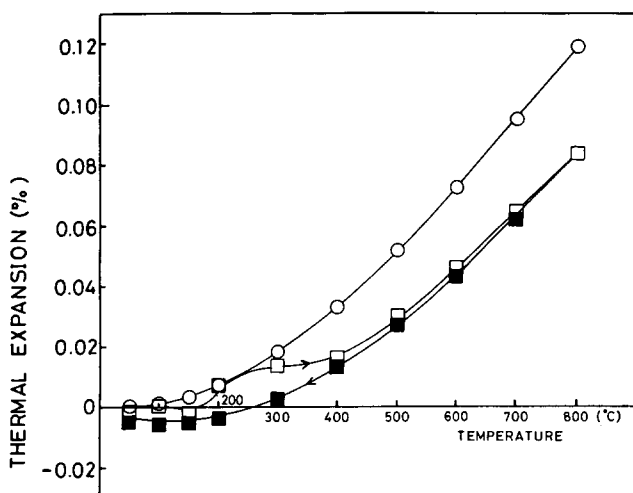


Fig. 3. Thermal expansion behavior of the cordierite ceramics sintered at 1300°C (○) or 1400°C (□, ■) for 2 h.

the present materials is not true beta, which exists only above about 1400°C. The dense cordierite ceramics with low CTE can be obtained at 1200°C or 1300°C. Furthermore, the CTE of the cordierite ceramics sintered at 1300°C is in good agreement with the mean value ($1.57 \times 10^{-6} \text{ K}^{-1}$) calculated from the axial expansion coefficients:

$$\alpha = (2\alpha_a + \alpha_c)/3$$

where α is an average thermal expansion coefficient, and α_a and α_c are the linear thermal expansion coefficients along the a -axis and the c -axis, respectively. Cordierite polycrystals prepared by the different methods show different thermal behavior. The thermal expansion behavior apparently depends upon thermal history, microstructures and compositions.¹² In addition, cordierite has a small axial thermal expansion of opposite sign and a negative expansion perpendicular to a plane defined by vertex-linked tetrahedra.¹³ Therefore, grain growth in a cordierite polycrystal causes a change in the energy balance between stored elastic mismatch energy in each grain, and the energy required to crack a grain boundary.¹⁴ As a result, high-temperature sintering leads to the micro-cracking in a cordierite polycrystal. The good agreement of CTE of the 1300°C sintered ceramics with that of the calculated value shows the high purity and homogeneity.

3.2 Thermal shock resistance and thermal conductivity

Thermal shock resistance is considered to be a most important property for high-temperature structural ceramics. The critical temperature difference, ΔT_c , is one criterion of the property. Below this temperature

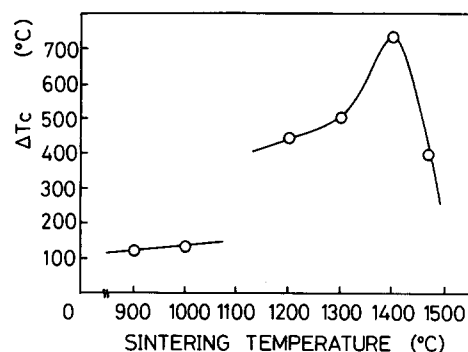


Fig. 4. The critical temperature difference, ΔT_c , of the cordierite ceramics calculated from the thermal and mechanical properties.

difference, the strength of the ceramics does not degrade by rapid cooling. In this paper, the critical temperature difference, ΔT_c , was calculated by the following equation:⁹

$$\Delta T_c = \sigma_c(1 - \nu)/(\alpha \cdot E)$$

where σ_c , E , α and ν are the four-point bending strength, Young's moduli measured by the Knoop indentation method,¹⁵ the average CTE and Poisson's ratio. Figure 4 shows that the highest thermal shock resistance is expected at the 1400°C firing. However, this is ascribed to the reduced flexural strength, Young's modulus⁶ and low CTE arising from the micro-cracking (Table 2). In the present paper, the thermal shock resistance of the dense α -cordierite ceramics (sintering at 1300°C) was determined (Fig. 5). It was found that ΔT_c is as high as 600°C. This superior thermal shock resistance, compared with that of conventional cordierite ceramics, is due to the high purity and homogeneity of the ceramics with no glassy phase. However, the reduced strength and Young's modulus resulted in the difference between the measured and the calculated ΔT_c . The strength of the pure and dense cordierite ceramics is calculated to be about 190 MPa if the Young's modulus is 140 GPa,⁶ because the strength changes in proportion to the square root of Young's modulus. This suggests that

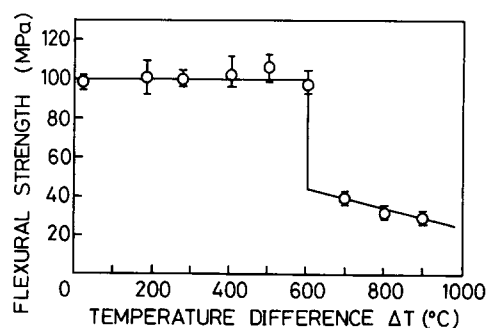


Fig. 5. The flexural strength of the 1300°C sintered cordierite ceramics after quenching.

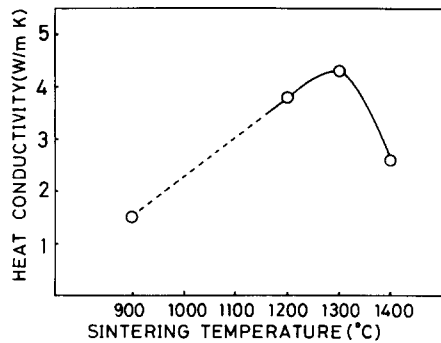


Fig. 6. Thermal conductivity of the cordierite ceramics sintered at different temperatures.

unhealed micro-cracks exist in the ceramics even at 1300°C firing.

Figure 6 shows the change in the thermal conductivity of the ceramics with sintering temperature. The thermal conductivity increased with a sintering temperature up to 1300°C and reached as high as 4.5 W/mK. Thus these pure and homogeneous cordierite ceramics have higher thermal conductivity than conventional cordierite ceramics. The following argument explains why. The thermal conductivity in ceramics is predominated by the phonon-phonon interaction and scattering.¹⁶ In the same way, glasses, with their completely non-crystalline structure, have a very low thermal conductivity because the phonon mean free path is limited to the order of interatomic distances by the random structure. Therefore, the presence of glass phase in the cordierite ceramics has a large effect on the thermal conductivity. The impurity scattering also influences the thermal conductivity of the ceramics. The high thermal conductivity of the cordierite ceramics sintered at 1300°C is ascribed to the absence of the glassy phase and impurities.

For the case of finite heat transfer rate where the thermal diffusivity enters through the Biot modulus, the thermal shock resistance, R' , is nearly proportional to thermal conductivity, κ , expressed by the following equation;⁹

$$R' \doteq \sigma \cdot (1 - \nu) \cdot \kappa / (\alpha \cdot E) \doteq \Delta T_c \cdot \kappa$$

The above equation shows that the thermal conductivity has a significant effect on the apparent ΔT_c . Namely, materials with high thermal conductivity permit rapid temperature equalization and reduce thermal stresses. The good thermal conductivity of the 1300°C sintered cordierite thus also contributed to the good thermal shock resistance.

3.3 Dielectric constant

Recently, cordierite has been a candidate for integrated circuit substrates with a low dielectric constant and high electrical resistivity.¹⁷ Because of

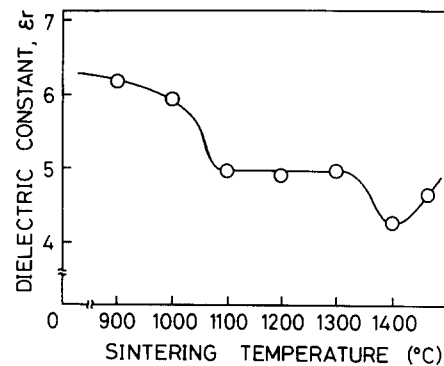


Fig. 7. Dielectric constant of the cordierite ceramics sintered at different temperatures.

the superior electrical properties of cordierite ceramics, the propagation delay of the signal decreases when using this substrate compared with alumina substrates. The propagation delay is expressed by the following equation:

$$T_{pd} = (\epsilon_0 \cdot \epsilon_r)^{1/2} \cdot V_c$$

where T_{pd} is the propagation delay, ϵ_0 is the permittivity, ϵ_r is the dielectric constant and V_c is a velocity of light in vacuum. Therefore, a material with a low dielectric constant has a great advantage for high-speed integrated circuit substrates. Figure 7 shows the relationship between dielectric constant and sintering temperatures. From Fig. 7, the dielectric constant of μ -cordierite is considered to be about 6. At 1100°C, the amount of the residual μ -cordierite was sufficiently small (about 10% by weight) such that the dielectric constant of the sintered compact is almost the same as α -cordierite. However, the dielectric constant of the cordierite ceramics containing μ -phase (1000°C and 1100°C firing) varied with frequency (Fig. 8).

The reasons are as follows: the electric charge adjusts itself instantaneously to any change in voltage in an ideal capacitor. However, in a real ceramic, there is an inertia-to-charge movement

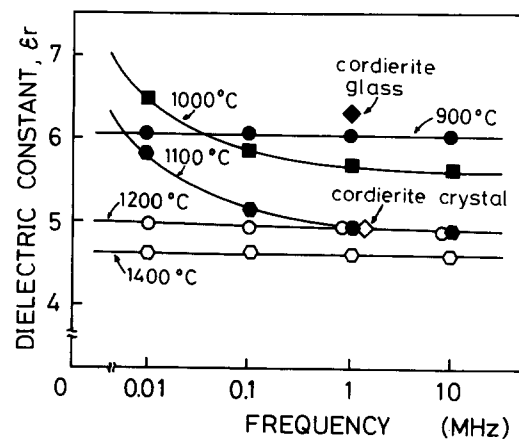


Fig. 8. Changes in the dielectric constant of the cordierite ceramics sintered at different temperatures with frequency.

that shows up as a relaxation time for charge transport. This causes a frequency dependence of the dielectric constant. In addition, space charges have a large effect on the total polarization at low frequencies.

The reduced dielectric constant of cordierite ceramics sintered at 1400°C may be ascribed to the increased porosity.

3.4 Electrical resistivity

Since ceramic insulators for integrated circuit substrates must have high resistivity and a low loss factor, these properties of the 1300°C sintered cordierite were measured.

In general, the resistivity of the ceramics decreases with temperature because ionic conductivity increases exponentially with temperature. In addition, impurities such as lithium or sodium have a great effect on the insulating property. For these reasons, cordierite ceramics prepared by the conventional method have a low T_c value of about 450°C. The T_c value means the temperature at which the resistivity of the insulator decreases to below $10^6 \Omega\text{cm}$ in a one-minute DC voltage test. In contrast with the conventional cordierite ceramics, however, the alkoxy-derived cordierite is expected to have higher resistivity because of its high purity and homogeneity. In practice, the T_c value of the alkoxy-derived cordierite is considered to be about 1200°C or above, because a DC resistivity is considered to be an AC resistivity at the frequency of 0 KHz. Therefore, the value was estimated by extrapolating the resistivity measured by applying an AC voltage (Fig. 9).

As well as the resistivity, the energy loss is

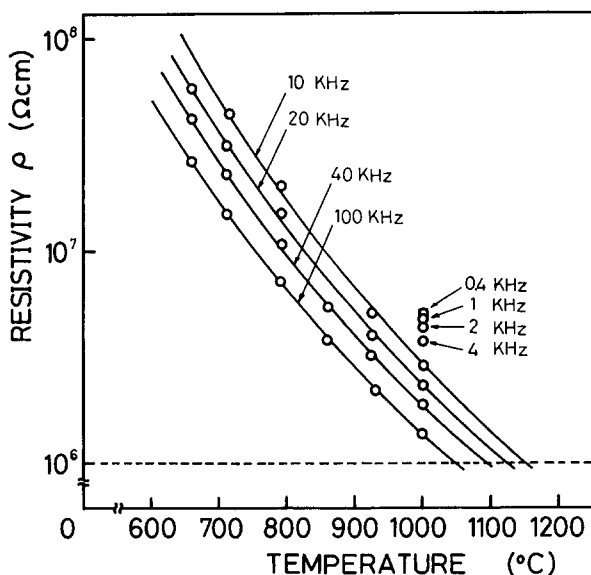


Fig. 9. Change in the resistivity of the cordierite ceramics sintered at 1300°C with temperature.

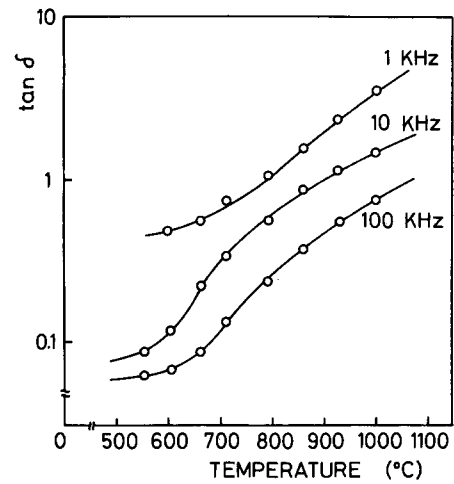


Fig. 10. Change in the dielectric loss of the 1300°C sintered cordierite ceramics with temperature.

important in AC circuit designs not only because it represents a lack of efficiency but also because electrical energy losses change the impedance of the circuit. Since the capacity loss factor, CLF, is proportional to the dielectric loss, $\tan \delta$, the change in $\tan \delta$ with temperature is shown in Fig. 10. The value of $\tan \delta$ also increased with increasing temperature. This may be due to the increased ionic conduction at high temperature. The frequency dependence of $\tan \delta$ is ascribed to the time lag for the ionic mobility.

4 Conclusions

The thermal and electrical properties of alkoxy-derived cordierite ceramics depends upon the crystalline phases developed. High-temperature sintering enhances the crystallization and α to β transformation. The residual μ -cordierite and/or amorphous phase have a large effect on the properties of the ceramics. As a result, pure and dense α -cordierite ceramics, including no other phase, have superior properties as follows:

- (1) Low thermal expansion (coincides with the mean value calculated from the axial expansion coefficients).
- (2) High thermal shock resistance (critical temperature difference of about 600°C).
- (3) High thermal conductivity of about 4.5 W/m K.
- (4) Low dielectric constant of about 5 (coincides with that of the single crystal).
- (5) High electrical resistivity.

In addition, the alkoxy process offers a low-temperature sintering of dense cordierite ceramics.

These results show the great advantage of the alkoxy-derived cordierite ceramics over conventional ones.

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