

Influence of Pore on Dielectric Constant of Cordierite Ceramics Prepared by Sol-Gel Process

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Cordierite ceramics with low dielectric constants were obtained through sol-gel techniques using as metal alkoxides. The powders for the sintered cordierite ceramics were prepared by hydrolysis of metal alkoxides with ethanol and distilled water. In the hydrolysis, the mole ratio of HCl/TEOS was controlled by changing the amount of HCl as a catalyst. The sol-gel derived powders were dried, pressed, and fired at 1300°C. The dried powders were calcined at 800°C for 3 hours to remove residual organics. The fired bodies with different dielectric constants were obtained by using HCl adjusted to various mole ratios of HCl/TEOS in the process. The variation of the amount of HCl catalyst led to a significant influence on dielectric constant, which was attributed to the formation of pores in the sintered body. Especially, the porosity of the sintered body influenced the dielectric constants.

Key words : Sol-gel, Cordierite, Dielectric constant

I. Introduction

Preparation of chemically homogeneous cordierite powders was investigated using alkoxide precursors, because the alkoxy-derived gel powders are very fine and reactive.¹⁾ Cordierite ceramics are of interest to the electronic packaging industry as potential multilayered substrate materials because of their low dielectric constants, relatively low coefficients of thermal expansion and high volume resistivities. Especially, the low dielectric constant is an important factor because a material with low dielectric constant has a great advantage for high-speed integrated circuit substrates. It is well known that dielectric constant is related to porosity.²⁾ Fujii *et al.*³⁾ achieved dielectric constant of 1.53 from 80% porosity SiO₂ synthesized by foaming silica sol. Yarbrough *et al.*⁴⁾ used colloidal silica sol mixed with polyvinyl alcohol to produce SiO₂ thick films having large pore size distribution (100~1000 nm) and dielectric constant of 1.95~2.50. Yarbrough *et al.*⁴⁾ also produced silica/void composites having the porosity of 40~70% based on the dielectric mixing rules. Since the air has the dielectric constant of 1, pores in the ceramic structure may be used to control dielectric constant.^{5,6)} Little work has been done on producing porosity controlled cordierite bodies for low dielectric constant via sol-gel process.

In the present work, we reported on the preparation of porosity controlled cordierite ceramic with low dielectric constant, using HCl as a catalyst in sol-gel process. This paper also described the effect of HCl/TEOS mol ratio on porosity and dielectric constant in the cordierite body.

II. Experimental

Fig. 1 illustrates the experimental procedure for preparing cordierite ceramic via sol-gel process. Al(OC₂H₅)₃, Mg(OC₂H₅)₂, and Si(OC₂H₅)₄ were used as the raw materials. The reagents having the stoichiometry of cordierite were dissolved in solvents of ethanol and distilled water. Al(OC₂H₅)₃ and Mg(OC₂H₅)₂ were reacted to make a double alkoxide. The solution was refluxed at 80°C for

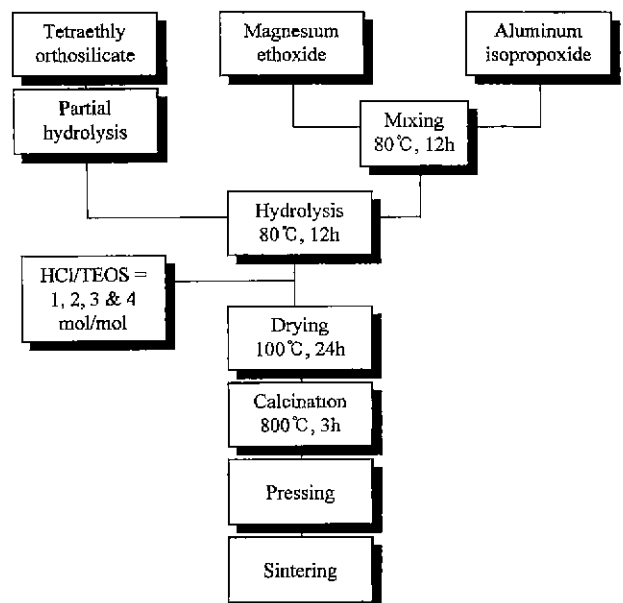


Fig. 1. Schematic diagram for preparation of cordierite body from alkoxides.

12 hours. The TEOS was partially hydrolyzed to prepare a mixed solution. The mixed solution of TEOS and the double alkoxide was stirred for 12 hours to obtain complete mixing. In hydrolysis, the mole ratio of HCl/TEOS was varied in order to change the amount of HCl as a catalyst, which was adjusted to 1, 2, 3, and 4. Water was used twice the stoichiometric amount of water required for complete hydrolysis and condensation. Each material (25 g) obtained from the process was dried at 100°C for 24 hours, calcined at 800°C for 3 hours, and heat-treated at various temperatures for 2 hours to investigate the powder properties. A part of the samples calcined at 800°C for 3 hours was uniaxially pressed at 750 kg/cm² in a 10 mm diameter steel die. The green compact was sintered in air at 1300°C. The heating rate was 5°C/min and held 2 hours at 1300°C.

Dielectric constant and porosity of the sintered sample were determined using impedance analyzer and mercury porosimeter. DTA was used to investigate the phase transformation. Crystalline phases were identified by an X-ray diffractometer with Cu K α radiation and Ni filter. TEM was also used to observe the powder characteristics. The structure of the powders were analyzed by FTIR. The viscosity of the cordierite solutions were determined using viscometer.

III. Results and Discussion

Fig. 2 shows the TEM micrographs of powders dried at 100°C. Particles are of about 0.1 μ m, but they are partially agglomerated. The dried powders catalyzed with different HCl/TEOS ratios (1 and 4) showed a similar morphology. But the agglomeration of the powder catalyzed with 1 mole ratio was larger than the powder catalyzed with 4 mole ratio.

Fig. 3 shows the change in viscosity of the cordierite solution with time. The viscosity of the cordierite solution abruptly increased in a shorter time when a smaller amount of catalyst for hydrolysis was added. The increase in the viscosity with time suggested the increase of polymerization. And they are aggregated to form large particles as reaction progresses. On the other hand, the acid catalyzed hydrolysis-polycondensation of cordierite results in the formation of short chain-like polymer when the catalyst concentration is high.

Fig. 4 shows the infrared spectra of the powder (HCl/TEOS=1, 2 mol/mol) dried at 100°C at 24 hours. The absorption band at 1600 cm⁻¹ is assigned to the banding H-O-H vibration of water. The band at 1020 cm⁻¹ is attributed to the Si-O-Al bond. The absorption bands at 540 cm⁻¹ and 680 cm⁻¹ are attributed to the Al-O or Mg-O bonds.⁹ It is apparent that a number of the aluminum ions replace silicon in the tetrahedral unit to form Si-O-Al net work structure.¹⁰

The DTA curves at a heating rate of 10°C/min for powders dried at 100°C are shown in Fig. 5. All samples

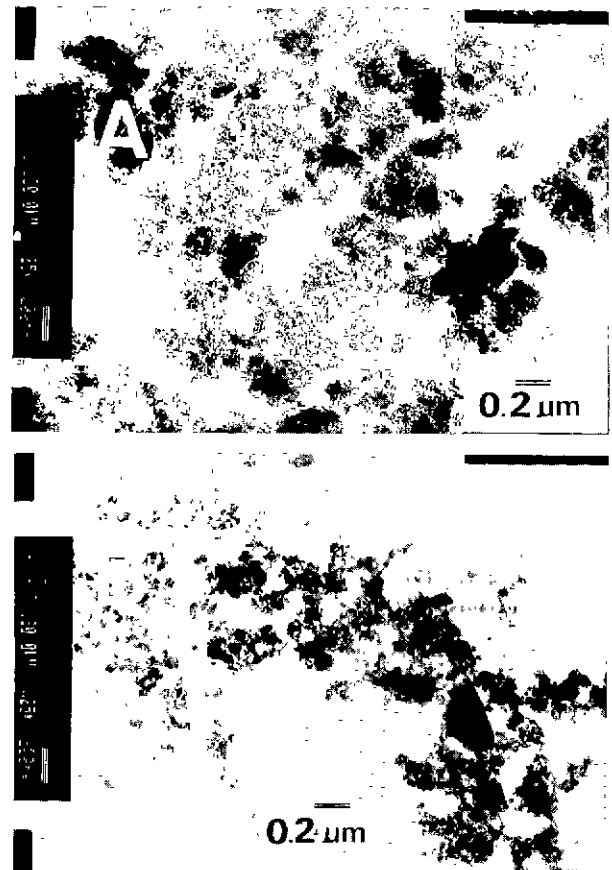


Fig. 2. TEM micrographs of powders dried at 100°C for 24 hours, catalyzed with different HCl/TEOS mol ratios: (A) HCl/TEOS=1 mol/mol and (B) HCl/TEOS=4 mol/mol.

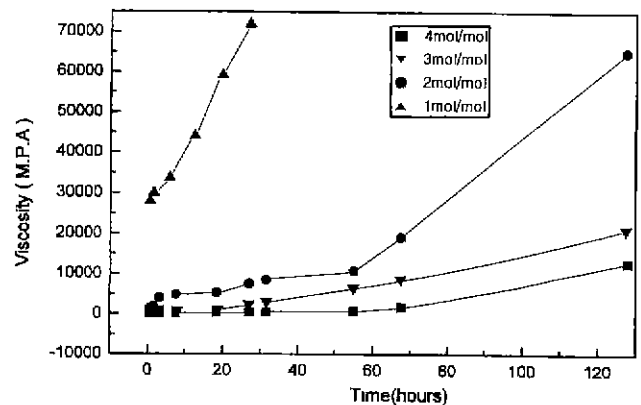


Fig. 3. The viscosity of the cordierite solution with time, catalyzed with different HCl/TEOS mol ratios.

catalyzed with different HCl/TEOS mole ratios have two exothermic peaks. The first peaks at temperatures, ranging 917-921°C corresponded to the crystallization of metastable μ -cordierites. The second peaks were observed at temperatures between 1020°C and 1040°C. These peaks were due to the formation of α -cordierite phases. The crystallization temperature of α -cordierite increases with an increase in HCl/TEOS mol ratio as shown in the

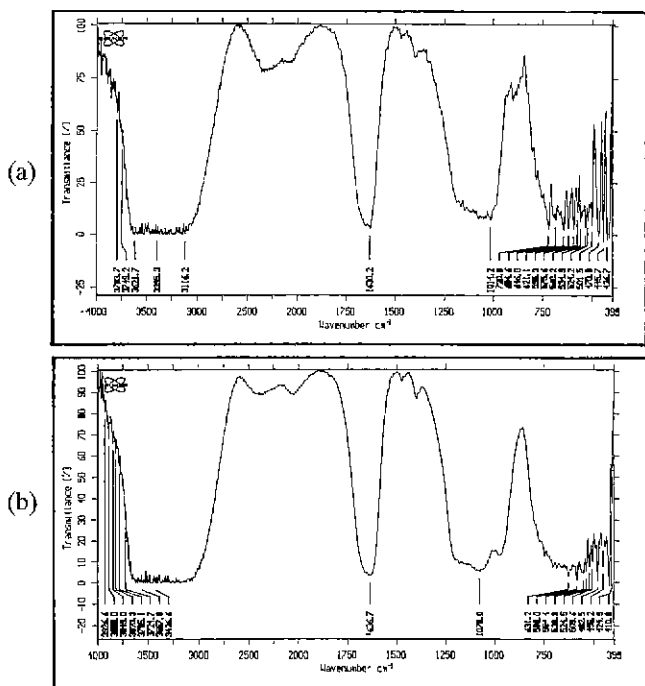


Fig. 4. IR spectra of powders dried at 100°C for 24 hours. A: HCL/TEOS=1 mol/mol, B: HCL/TEOS=1 mol/mol.

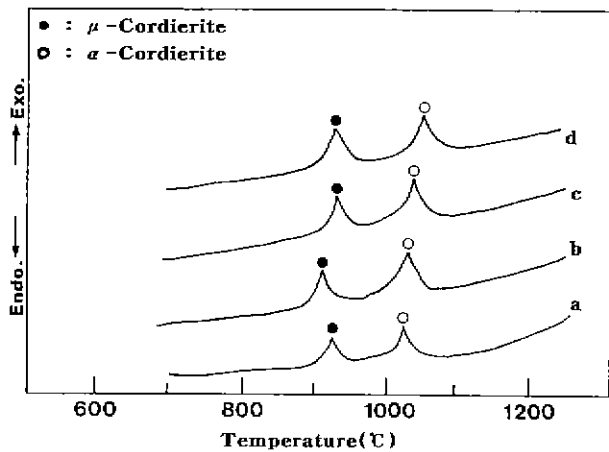


Fig. 5. DTA curves of powders dried at 100°C, catalyzed with different HCL/TEOS mol ratios : a, b, c and d denote sample catalyzed with HCL/TEOS mol ratios 1, 2, 3 and 4 respectively.

DTA curves. The results were confirmed by X-ray diffraction analysis.

Fig. 6 shows the X-ray diffraction patterns of the samples (HCL/TEOS=4 mol/mol) dried at 100°C for 24 hours and calcined at various temperatures for 2 hours. The sample heat-treated at 1000°C shows small crystalline peaks, the intensity of which increases with increasing heat-treatment temperature. Most of the peaks observed below 1100°C can be assigned to the μ -cordierite phase, and at 1200°C this transformation to the α -cordierite phase. At 1300°C, the peaks due to the crystallization of α -cordierite phase are observed.

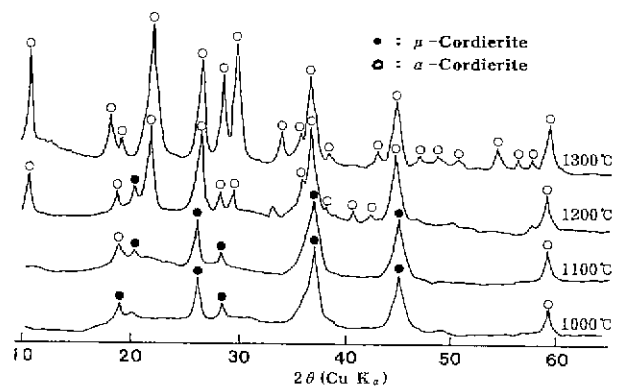


Fig. 6. XRD diffraction patterns of powder (HCL/TEOS=4 mol/mol) dried at 100°C and heat-treated at different temperatures.

Fig. 7 shows the pore size distribution of samples sintered at 1300°C as function of HCL/TEOS mol ratio. It shows that the maximum pore size is 9194Å and the minimum pore size is 648Å. It is interesting to note that all samples catalyzed with different HCL/TEOS mole ratios showed a similar pore size distribution. However, the volume fraction of each pore size was different from HCL/TEOS mol ratios.

Fig. 8 shows the porosity and dielectric constant, respectively, of samples dried at 100°C, calcined at 800°C, pressed at 750 kg/cm² and sintered at 1300°C, as a func-

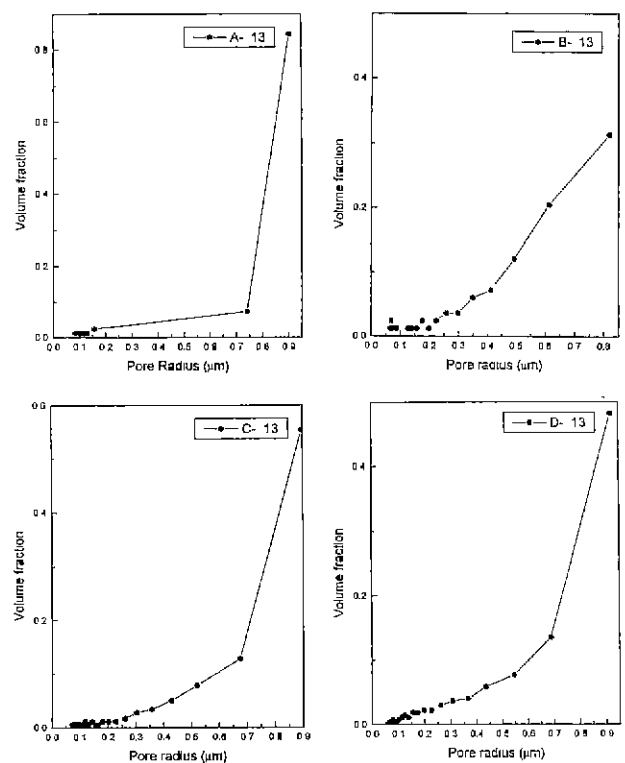


Fig. 7. Pore size distribution of samples heat treated at 1300°C, catalyzed with different HCL/TEOS mol ratios : A, B, C and D denote sample catalyzed with HCL/TEOS mol ratios 1, 2, 3 and 4 respectively.

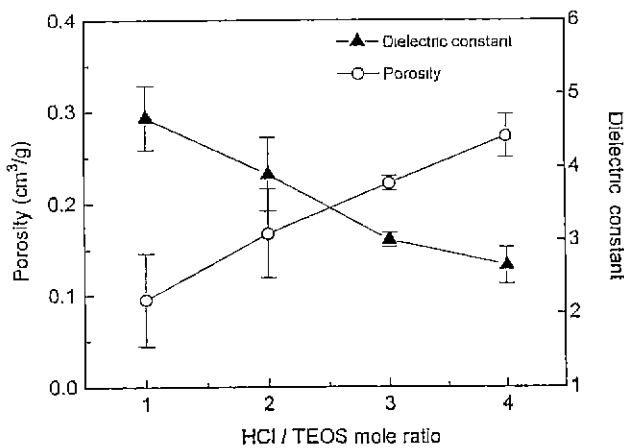


Fig. 8. Porosities and dielectric constants of 1300°C sintered HCl/TEOS mol ratios.

tion of HCl/TEOS mole ratio. It is interesting to note that the sample catalyzed with low HCl/TEOS mole ratio shows lower porosity and higher dielectric constant than those of sample catalyzed with the HCl/TEOS mole ratio. The reduced dielectric constant of cordierite ceramics at 1300°C is due to the increased porosity.¹¹⁾ The observed variations in porosity and dielectric constant may be ascribed to differences in the level of condensation resulting from hydrolysis, by HCl-catalyzed reaction. Further studies on the reaction mechanism are currently being in progress.

IV. Conclusions

Here we draw the following conclusions:

(A) Precursor powders for cordierite have been prepared by the copolymerization between partially hydrolyzed TEOS and the aluminum-magnesium double alkoxide, using HCl as a catalyst.

(B) Cordierite ceramics with various dielectric constants can be obtained by using HCl adjusted to various

mol ratios of HCl/TEOS in the sol-gel process.

(C) The dielectrics constant decreases with the increase of HCl/TEOS mol ratio. The reduced dielectric constant of cordierite ceramics sintered at 1300°C is ascribed to the increased porosity.

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