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# Low-temperature sintering, low-dielectric cordierite ceramic tapes for high frequency application

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**Abstract**

Cordierite is a promising material in the fields of high frequency multilayer ceramic components and ceramic package substrates. In this paper, cordierite green tapes were cast by aqueous tape casting with own formula. The characteristics of cordierite tapes such as phase transformation, sintering properties and dielectric properties were studied. Co-firing behavior of cordierite tape and Ag—Pd conductive metal was investigated tentatively. It was shown that the cordierite tapes can be sintered at 900 °C and the main crystalline phase is α- cordierite. The sintered tapes have good density, low dielectric constant ($\varepsilon$=3.4993; 2 GHz)and low dielectric loss (tg $\delta$=0.0063; 2 GHz). There is good co-firing compatibility between cordierite and Ag—Pd conductive metal in the sintering process. The low temperature sintering, low dielectric cordierite tapes can be used as a potential material for high frequency application.


*Keywords:* A. Tape casting; D. Cordierite; Characteristics; Ag—Pd; Co-firing

## 1. Introduction

With the development of electronic technology toward the directions of miniaturization, integrating, multi-dimension, high performance, surface modularization and high frequency, it becomes inevitable to produce multilayer ceramic components and ceramic package substrates suitable for high frequency application in the modern electronic information industry [1]. Generally speaking, ceramic materials with low sintering temperature, low dielectric constant and low dielectric loss are regarded as ideal ones for these fields [2]. However, the traditional dielectric materials such as Ni—Zn—Cu ferrite cannot meet the need of further increase of frequency above 300 MHz [3], so it is necessary to prepare new dielectric materials suitable for high frequency.

Cordierite ceramic material is taken as one of the most promising electronic materials with good dielectric properties, low sintering temperature, low coefficient of thermal expansion, etc [4]. However, high sintering temperature and narrow sintering temperature range of cordierite prepared by the traditional solid phase synthesis method severely limit its application. The co-firing behavior with conductive metal in low sintering temperature needs to be investigated as well. In order to expand the application of cordierite in the field of high frequency, cordierite prepared by wet chemical methods with low melting point additives is a viable option [5]. Aqueous tape casting is the preferred method for multilayer ceramic components and ceramic package substrates, so the good performances of green tapes are the guarantee of application.

In this work, low-temperature sintering, low-dielectric cordierite green tapes were cast by aqueous tape casting. The powders are prepared by sol—gel method and mixed with $Bi_2O_3$ additive. Ag—Pd conductive paste is used to form inner electrode. The characteristics of cordierite green tapes such as phase transformation, sintering performances, dielectric properties and the co-firing behavior with Ag—Pd conductive metal are researched.

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Table 1
Slurry formulation(wt%)

| Cordierite powders | PVA solution | PAAS solution | PEG4000 solution | Water and other additives |
|---|---|---|---|---|
| 18.2 | 36.4 | 9.1 | 8.6 | 27.7 |

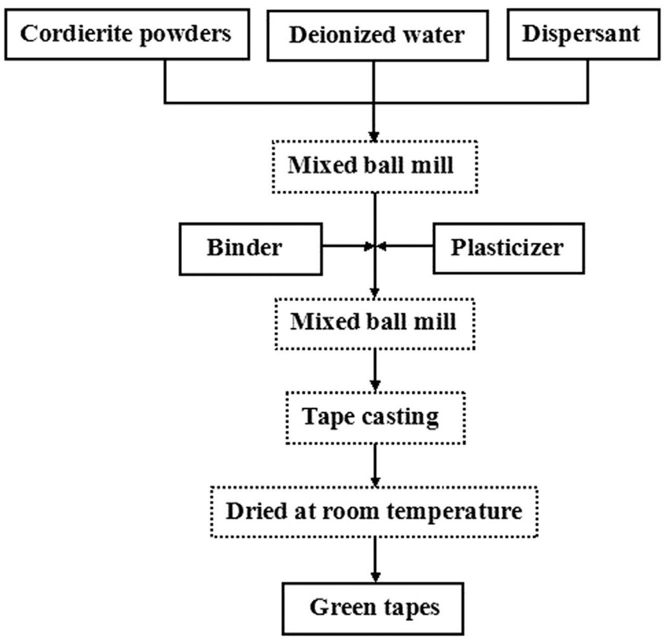


Fig. 1. Preparation process of cordierite green tapes.

## 2. Experimental procedure

Green tapes are prepared by aqueous tape casting with cordierite powders as raw materials, sodium polyacrylate (PAAS), polyvinyl alcohol (PVA) and polyethylene glycol (PEG4000) act as dispersant, binder and plasticizer, respectively. The cordierite powders used in the slurry are prepared by the sol—gel method with 5 wt% $Bi_2O_3$ added. The powders have a certain particle size distribution and the average particle size is about 600 nm. Based on the previous research [6], the slurry composition is shown in Table 1. The tape casting process is shown in Fig. 1.

The thickness of cordierite green tapes cast above is about 100 μm. The tapes are cut into square shapes (20 mm × 20 mm). 10 layers of cut pieces are laminated regularly under 5 MPa at ambient temperature for 3 min. Ag—Pd conductive paste (Ag:Pd: 70:30, firing peak: 900—1150 °C) is used to form inner electrode. The Ag—Pd conductive paste is screen printed on the upper surface of a cut piece and laminated with another one. The phase transformation is analyzed by X-ray diffraction (XRD, PW3040/60, Panalytical BV, Holland). The densities of sintered samples are measured by the Archimedes method. The linear shrinkage is determined by geometrical measurements before and after firing. The dielectric properties of the samples are measured by a Network Analyzer (E5071C, Agilent, USA) in the frequency range of 500 MHz—2 GHz. The surfaces and cut cross-sections of sintered samples are characterized by taking micrographs with a Scanning Electron Microscope (SEM, S4800, Hitachi, Japan). The element distribution is observed by an Energy Dispersive Spectrometer (EDS, Hitachi, Japan) which is attached to the SEM.

## 3. Results and discussion

### *3.1. Phase transformation and sintering properties*

XRD patterns of cordierite tapes sintered at different temperatures are shown in Fig. 2. Plenty of α-cordierite phase is precipitated at 850 °C, and little μ-cordierite phase is detected at the same time. The main phase is α-cordierite at 900 °C. A little β-cordierite appears at 950 °C, while the main phase is still α-cordierite. In Contrast to the traditional solid phase synthesis method, the sintering temperature of cordierite is largely reduced. Powders prepared by the sol—gel method have lower particle size, higher inner energy, higher surface area and activity; all these characteristics can reduce the sintering temperature [4,7,8]. In addition, $Bi_2O_3$ as sintering aids promotes the liquid phase sintering and accelerates the density of cordierite tapes at relatively low temperature [9—11].

Surface SEM micrographs of cordierite tape sintered at 900 °C are shown in Fig. 3. The upper surface of the sintered tape is very compact and almost without cracks and pores. And the bottom surface is the same as the upper one. It is shown that the cordierite tape can be sintered at 900 °C and is of good density.

The relationship between sintering temperature and shrinkage and density of cordierite tape sintered at different temperatures is shown in Fig. 4. The variation tendency of the shrinkage and density with temperatures is basically the same. The shrinkage (a curve) increases rapidly with rising sintering temperature before 850 °C. However, the rate decreases between 850 °C and 900 °C. The maximum shrinkage (35.2%) appears at 900 °C. The shrinkage, basically no longer changes after 900 °C (the shrinkage is 35.0% at 950 °C). Similarly, the density of sintered cordierite tape also increases gradually with the rising of sintering temperature and

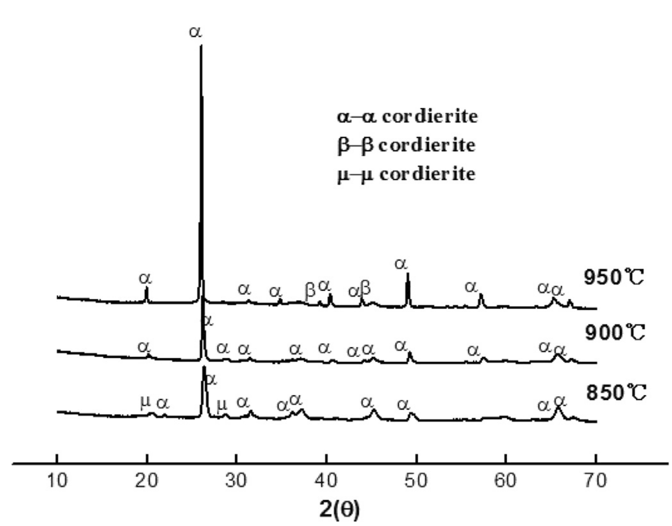


Fig. 2. XRD patterns of cordierite tapes sintered at different temperatures.

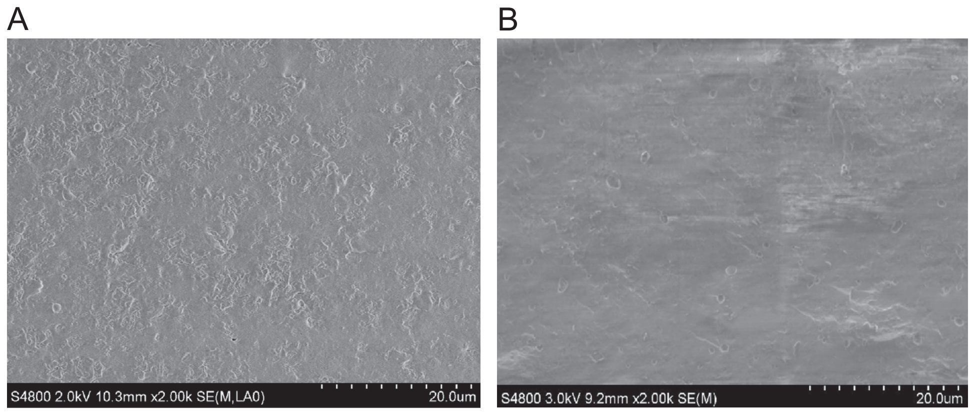


Fig. 3. Surface SEM micrographs of cordierite tape sintered at 900 °C for 5 h: A: upper surface, and B: bottom surface.

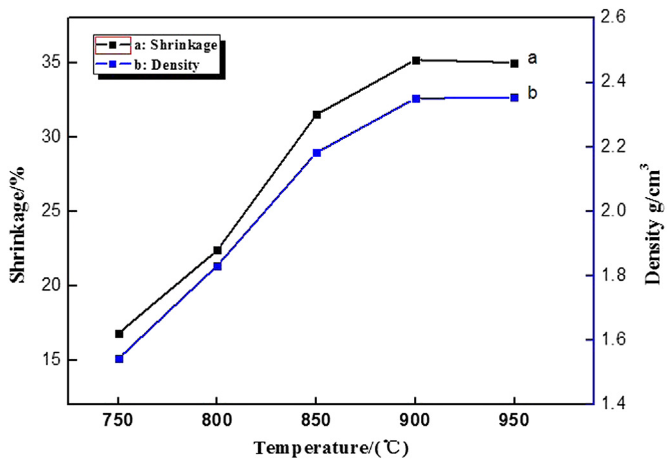


Fig. 4. Shrinkage and density of cordierite tape sintered at different temperatures.

a higher value (2.352 g/cm$^3$) appears at 900 °C (b curve). On further increasing the sintering temperature, the change is not obvious. According to the results above, the cordierite tape has good density at 900 °C.

Cross-section SEM micrograph of the laminate sintered at 900 °C is shown in Fig. 5. It can be seen that the cordierite tapes bonded well with each other and no delaminations, cracks and pores are visible in the interface. The shrinkage and density of the laminate sintered at 900 °C are also measured. Compared to the single tape, the shrinkage of the sintered laminate decreases to 31.0% at 900 °C. The density of the sintered laminate is about 2.351 g/cm$^3$ at 900 °C and there is almost no obvious change. The reduction of shrinkage may be caused by the constraint of each layer of cordierite tapes. The close density with the single tape sintered at 900 °C shows that the bond quality of each layer is good.

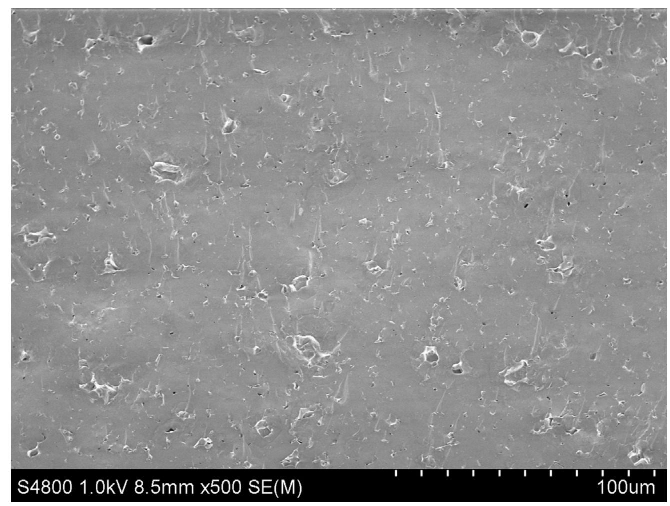


Fig. 5. Cross-section SEM micrograph of the laminate sintered at 900 °C for 5 h.

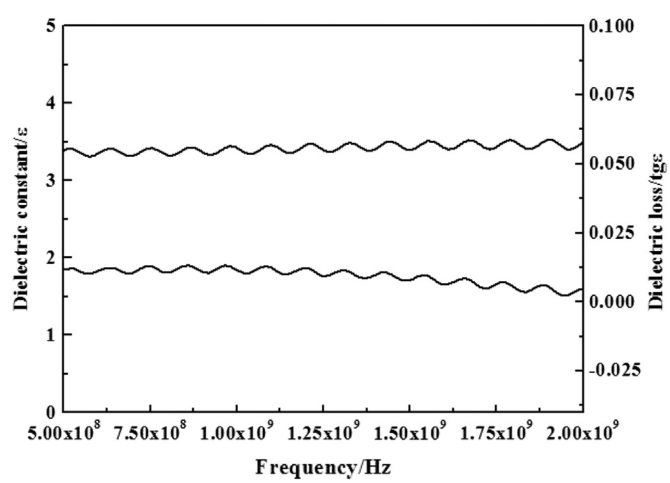


Fig. 6. Dielectric constant and dielectric loss of cordierite tape sintered at 900 °C for 5 h.

### 3.2. Dielectric properties

Dielectric properties are the main influencing factors of dielectric materials for high frequency application. Low dielectric constant is helpful to reduce the accompanied capacitance and relaxation time of signal transmission, and low dielectric loss favors the reduction of the leakage conductive flow of ceramic substrates [12]. Dielectric constant and dielectric loss of cordierite tape sintered at 900 °C are shown in Fig. 6. The dielectric constant has a slight fluctuation with the increase of frequency. The variation of dielectric constant is not obvious. The dielectric constant of the sintered tape is 3.4993 at the frequency of 2 GHz.

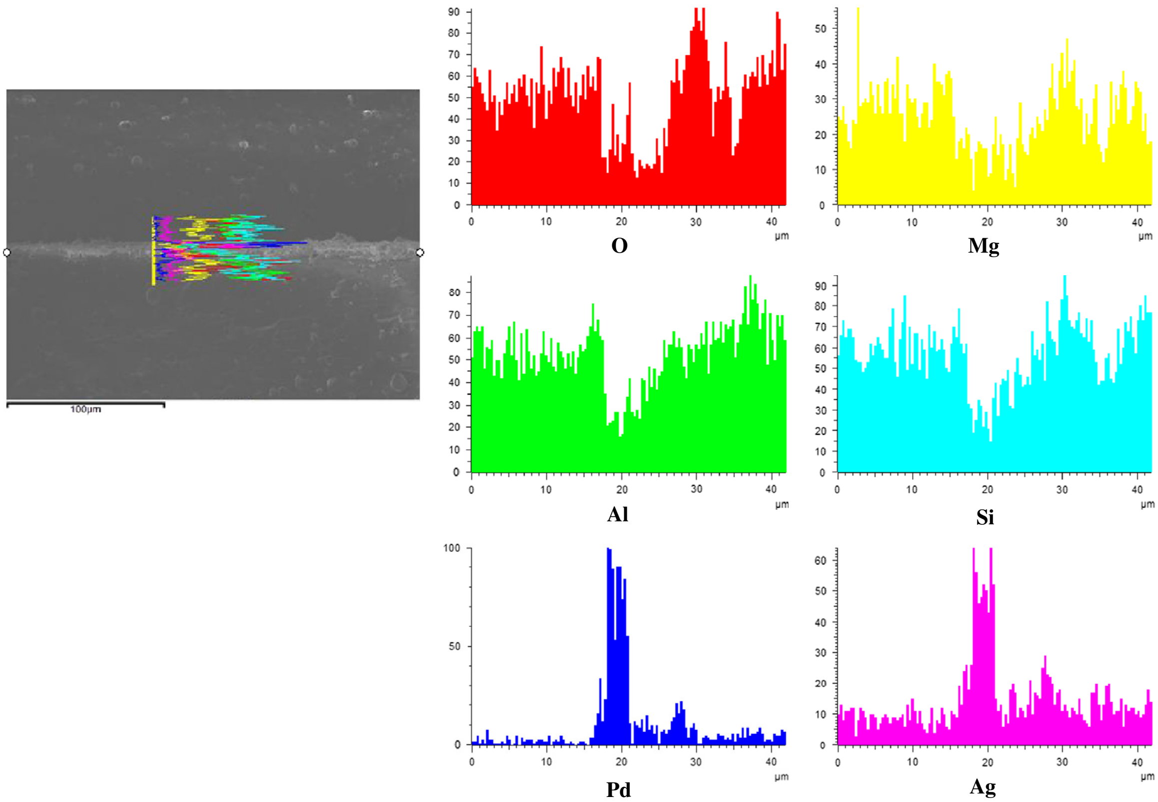


Fig. 7. Co-firing interface SEM micrograph of cordierite and Ag—Pd electrode at 900 °C for 5 h and distribution images of each element.

The dielectric loss also has a slight fluctuation with the increase of frequency, but a tendency to decrease appears. The dielectric loss is 0.0063 in the frequency of 2 GHz.

### 3.3. *Co-firing behavior with Ag—Pd conductive metal*

Co-firing behavior of cordierite and Ag—Pd is investigated tentatively. Co-firing interface of cordierite and Ag—Pd inner electrode and distribution of each element are shown in Fig. 7. It can be seen that a distinct white region appears between the cordierite layers. It is the so called Ag—Pd conductive layer. Ag—Pd conductive layer spreads neatly and combines well with cordierite layers. The whole co-firing interface is very compact without cracks and pores. It indicates that the sintering shrinkage of cordierite layer and Ag—Pd inner electrode is consistent and the two materials have good co-firing compatibility. By line scanning of EDS, the distribution of each element is acquired. On the whole, most of the elements have a uniform distribution. Elements of oxygen (O), magnesium (Mg), aluminium (Al) and silicon (Si) contained in the cordierite are still located in the cordierite layers. The main elements of conductive layer are still Ag and Pd. However, all the elements have a small migration after co-firing. Small amounts of oxygen, magnesium, aluminium and silicon migrate to the conductive layer. Similarly, a few silver (Ag) and palladium(Pd) migrate to the cordierite layers. All element migration especially the migration of palladium is very slight. The slight element migration is normal and it may be caused by the factor of substrate. The printing process and the application of pressure during lamination before co-firing can also lead to the diffusion of Ag—Pd. The results above show that the cordierite tapes prepared can be co-fired with Ag—Pd. No chemical reaction takes place between the two materials which can guarantee the stability of the performance of cordierite for high frequency application.

## 4. Conclusions

The green tapes cast by aqueous tape casting have low sintering temperature and the main phase of cordierite tapes sintered at 900 °C is α-cordierite. The sintered tapes have good density as well as low dielectric constant ($\varepsilon=3.4993$; 2 GHz) and dielectric loss (tg $\delta=0.0063$; 2 GHz). The tapes can be co-fired with Ag—Pd conductive metal at low temperature and there is good co-firing compatibility in the sintering process. The low sintering temperature, good sintering properties, low dielectric constant and dielectric loss, and good co-firing compatibility with Ag—Pd conductive metal make cordierite a great potential material for high frequency applications.

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