Preparation low dielectric constant material of cordierite with polyacrylamide gel method

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Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) received much attention during the past decades due to its low dielectric constant, high resistivity, low thermal coefficient and high chemical and mechanical stability. These properties together with low processing cost characterized cordierite as materials with extensive applications in the electronic industry. For example, cordierite has been used as the multilayer ceramic substrate for electric devices in integrated circuits [1–3], and magnetic disk substrate for high storage capacity [4].

However, One of the difficulties encountered with the preparation of cordierite ceramics using conventional processes, i.e., via direct crystallization of the melt is the narrow temperature band for sintering which is located just below the incongruent melting point (1450 °C) of pure cordierite [5, 6]. The narrow temperature interval demands reasonably well-controlled temperature conditions during densification. Hence, to solve this problem, sol-gel process has become a very attractive synthesis technique for processing cordierite. This is mainly because of its ability to generate powders of high surface area, high intrinsic energy and consequently high sinterablility, which allow a broadening of the sintering range [7]. However, in the multicomponent reactant system of cordierite, the different hydrolysis rates of the reactant easily caused inhomogeneity in the resultant oxides. To overcome such limits, several approaches have been attempted, including matching of hydrolysis rates by chemical modifications with chelating ligands [8] or partial prehydrolysis of an alkoxide [9]. So the process of sol-gel synthesizing cordierite becomes complex.

The present paper reports a simple method of polyacrylamide gel to prepare cordierite powders. The as-synthesized cordierite dielectric properties variations with temperatures were also measured.

In this study, silicic acid instead of usual TEOS (tetraethylorthosilicate) was used for preparing the powder precursor. Silicic acid was obtained by passing the sodium metasilicate aqueous solution (4 wt%) through a column filled with solid ion exchange resin (H^+ form). The solution was diluted to 1:20 molar ratio of silicic acid to distilled water, then solid aluminum and magnesium nitrates were added to the aqueous silicic acid solution in amount according to the molar ratio of Al:Mg:Si equal to 2:2:5. This solution was then added by acrylamide, N,N′–methylenc bisacrylamide and 2,2′ azobisisobuty-rinitrite as monomer, cross-linking agent and initiator respectively. The transparent solution could be formed under stirring. The solution was cured at 75 °C in water bath until acrylamide polymerized, then the homogeneous, transparent and brittle gel was resulted. The smashed gels were turned into xerogels by drying in an oven at 80 °C for 12 hr. The powder precursors were obtained by calcining the xerogels in a muffle furnace at 500 °C for 5 hr. The obtained powder precursors were pressed to form pellet under a uniaxial pressure 20 MPa and sintered at 800–1200 °C for 4 hr.

Phase transition of the precursor were identified by XRD (D/Max-III, Japan) using CuK_α radiation. The morphologies of the cordierite pellets were examined by scanning electron microscopy (SEM, Hitachi S-3500), and a chemical analysis was carried out by energy-dispersive X-ray spectroscopy (EDS, Oxford INCA). The dielectric properties of the pellets sintered at 1200 °C were measured by Impedance Analyzer (HP4192A).

For the formation process of the cordierite gel system, there have been many controversies so far [10]. To investigate the crystallization process of the gel, the pellet samples were sintered at different temperatures for 4 hr. Fig. 1 shows the XRD patterns of the pellet sample sintered at different temperatures. From the Fig. 1, we can see that all compositions were amorphous after the calcination at temperature below 800 °C for 4 hr, and the predominant crystalline phase was sapphirine phase at 900 °C. When temperature reached 1000 °C, the phases of μ-cordierite appeared, and coexisted with a little phase of sapphirine. It could be

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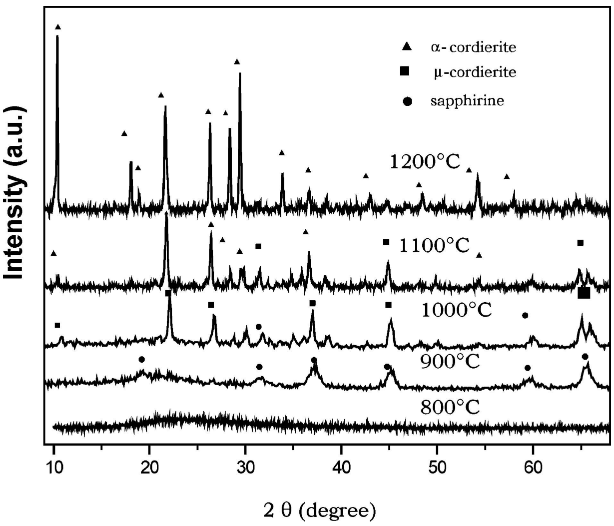

Figure 1 The XRD patterns of the pellets samples calcined at different temperatures for 4 hr.

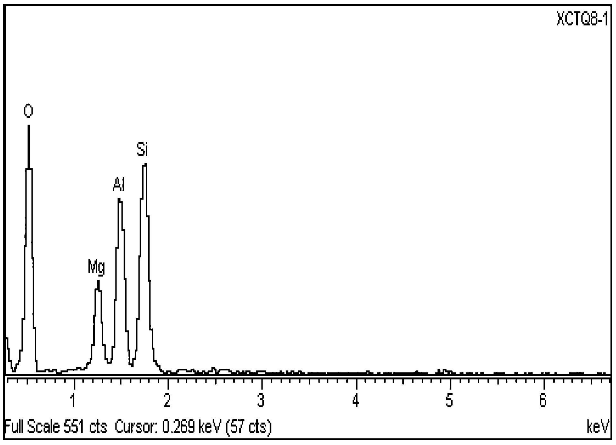

Figure 3 Surface analysis of EDX.

attributed to that sapphirine transit to μ-cordierite by reaction with amorphous SiO_2 at about 1000 °C. When temperature reached 1100 °C, α-cordierite appeared in compositions and μ-cordierite still coexisted, but the phase of sapphirine disappeared. So it was thought that the metastable μ-cordierite phase began to transform into stable α-cordierite phase at about 1100 °C. After the sample was sintered at 1200 °C for 4 hr, the predominant crystalline phase was α-cordierite, and there was little other phase. Therefore, the crystallization process can be considered as following sequence: amorphous $\rightarrow$ sapphirine $\rightarrow$ μ-cordierite $\rightarrow$ α-cordierite. In above temperature ranges, other silicate compounds, such as spinel, mullite and cristobalite were not crystallized from amorphous phase. This may be attributed to that sapphirine phase first crystallized from amorphous phase, and reduced the chances of forming other silicate compounds [3]. Compared with the method of solid reaction at 1450 °C [5, 6], the synthesized temperature of polyacrylamide gel method could be decreased by 250 °C.

Fig. 2 displays the surface microstructure of the sample sintered at 1200 °C for 4 hr. The coalescence of grains was easily observed in the picture, and the pore with size of 4–5 μm distributed uniformly in the cordierite matrix. This may be the one of reasons that cordierite matrix exhibits a low dielectric constant, because the pore have a low value of dielectric constant of atmosphere ($\varepsilon = 1$) [2]. The chemical composition of the cordierite was determined using energy-dispersive X-ray spectroscopy. Fig. 3 indicates that the composite are composed of Si, Al, Mg and O. The molecular ratios of Si, Al, Mg and O in several test spots calculated from the EDX data are all proximately 5:4:2:18, which are in good agreement with the stoichiometric ratio of $Mg_2Al_4Si_5O_{18}$. This result indicated that the distribution of Si, Al, Mg and O was homogeneous in the products synthesized by polyacrylamide gel method.

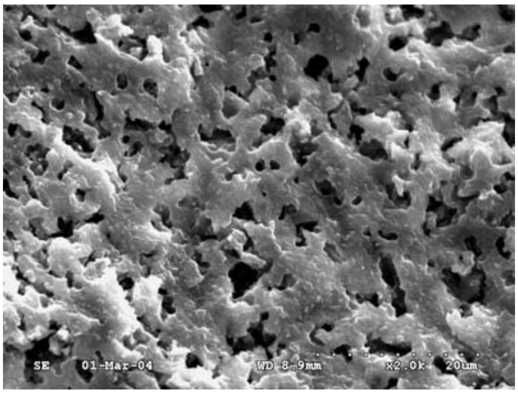

Figure 2 SEM microstructure of the fracture surface.

Fig. 4 shows the variations of the dielectric constant and loss tangent versus frequency at different test temperatures. From Fig. 4, we can see the dielectric constant and the tangent loss deceased sharply with increasing frequency when measuring frequency lower than 1 MHz at all test temperatures, but they decreased slowly when frequency ranged from 1 to 4 MHz. The decrease of the dielectric constant with increasing frequency may be attributed to that the ionic polarization and orientational polarization gradually weakened or disappeared with increasing frequency, and the decrease of the tangent loss with increasing frequency was mainly due to the ions migration polarization loss and the electronic polarization loss may exist at low frequency, while at high frequency the ion vibrations may be the only source of the dielectric loss [2, 11].

Fig.4(a)–(c) also show that the dielectric constant and the tangent loss increased with increasing test temperature, and the obtained cordierite ceramics displays a low dielectric constant and low dielectric loss tangent at low temperature. The values of dielectric constant and dielectric tangent loss were only 3.82 and 1.8×10^{-3} at 25 °C and 4.0 MHz, which was close to the reported value [2]. When temperature increased from 25 to 200 °C at 0.05 MHz, the value of dielectric constant increased from 3.96 to 7.83 and dielectric loss tangent increased from 0.033 to 0.628. So the temperature has a significant influence on the dielectric properties of the cordierite materials. The increase of the dielectric constant with temperature was attributed to the increasing of electronic, ionic and orientational polarizability with increasing temperature, and the increase of the tangent loss with increasing temperature

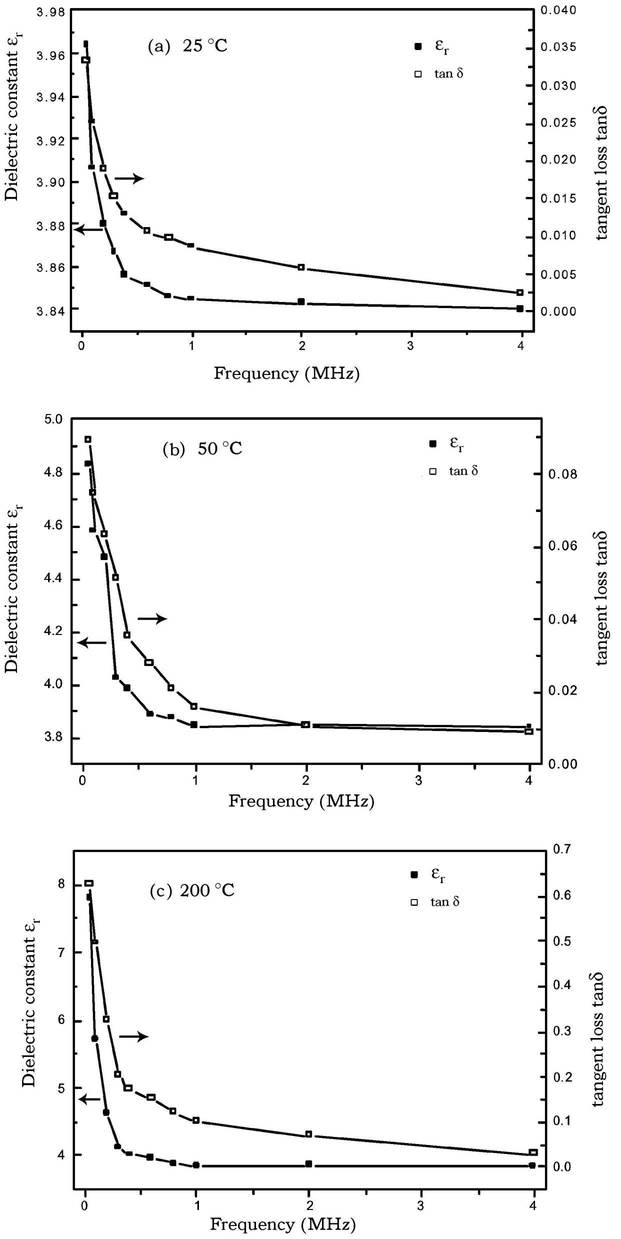

Figure 4 The variation of cordierite dielectric constant and tangent loss versus frequency and temperature.

was due to rapid increasing of the relaxation loss and the conduction loss with increasing temperature [2, 11].

From the above experimental result, we can summarize as follows. The cordierite could be prepared by the polyacrylamide gel method using silicic acid as starting materials. Compared with the method of solid reaction, the synthesized temperature of polyacrylamide gel method could be decreased by 250 °C. During the sintering process, sapphirine phase was first crystallized from amorphous phase, then transformed into μ-cordierite phase, and μ-cordierite phase finally was transformed into α-cordierite at 1200 °C. The synthesized α-cordierite exhibited excellent electric properties at low temperature. The temperature and frequency have significant influence on the dielectric properties of cordierite. The dielectric constant and dielectric loss tangent of cordierite decreased with increasing test frequencies, and the dielectric constant and dielectric loss tangent increased with test temperature.

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