Preparation and characterization of cordierite powders by water-based sol-gel method

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Received 3 November 2010; accepted 5 April 2011

Cordierite gel is synthesized by water-based sol-gel route, starting from basic magnesium carbonate and Al(NO₃)₃ inorganic solution dissolved in silica-ethanol sol. Crystallizing process of xerogels is confirmed by TG-DSC and X-ray diffraction. The µ-cordierite is formed firstly, then small amount of β-SiO₂ and Mg-Al spinel are identified, at the same time the sapphirine is formed through the chemical reactions from β-SiO₂ and Mg-Al spinel, and finally transformed to α-cordierite entirely. The obtained powders are analyzed by SEM and granularity analysis. The results show that more pure, fine and uniformly dispersed cordierite powders can be manufactured by water-based sol-gel method. The cordierite ceramics shown low dielectric constant (ε<5), low dielectric loss (tanδ<0.004) and low thermal expansion coefficient (α<1.85×10⁻⁶/°C).

Keywords: Water-based sol-gel method; Cordierite; Crystallizing process; Dielectric properties; Thermal expansion coefficient

Cordierite (Mg₂Al₄Si₅O₁₈), with almost the highest melting temperature (about 1460°C) among silicate glass-ceramics, has three polymorphic forms: a hexagonal high-temperature form, named indialite or α-cordierite (space group P6/mcc), an orthorhombic low-temperature form designed β-cordierite (space group Cccm) and a metastable form µ-cordierite, which is a solid solution with β-quartz structure. Due to its properties such as low dielectric constant and dielectric loss, very low thermal expansion coefficient and excellent thermal shock resistance it is used in electronic packaging materials, filters, heating elements, fairing, microwave/electromagnetic wave absorbing materials and so on. Therefore, it has been considered as a very promising electronic ceramic material.

Preparing cordierite by the conventional solid-state reaction has a long history and it has been widely used. Cordierite can be synthesized by sintering mixed simple compounds, such as oxides, hydroxides, carbonates or composite oxides, such as clay, talc, bauxite/siliceous earth. However, high sintering temperature needs range of firing temperature for only 30°C, and fluxing agent making electronic and chemical performance deteriorated greatly limits the use of solid-state reaction method.

In order to reduce the synthesis temperature and improve the powder properties, there are extensive use of co-precipitation, sol-gel route, carbon black method, mechano-chemical process and polymer network gel method. By comparison, the sol-gel method holds enormous advantages in homogeneity, size distribution, synthesis temperature and controlled composition, and over the last decade, it has always been a research hotspot in preparing advanced glass-ceramic materials. But the raw materials used in preparing cordierite by this method are pure ethyl silicate and alkoxide, which are expensive, and if controlling hydrolysis speed failed, precipitation will be observed.

In this study, an attempt has been made to prepare water-based solution, synthesize pure cordierite powders and characterize cordierite samples by a variety of analytical and test methods. Furthermore, this work promoted a possibility of mass-producing cordierite with a simple condition.

Experimental Procedure

Water-based sol-gel process flow

In order to synthesize cordierite gel, the compounds used are basic magnesium carbonate ((MgCO₃)₂·Mg(OH)₂·5H₂O), aluminum nitrate (Al(NO₃)₃), TEOS ((C₂H₅O)₄Si), absolute alcohol...
(C$_2$H$_5$OH), polyethylene glycol, HNO$_3$, which are of AR grade.

As the first step, basic magnesium carbonate and aluminum nitrate were dissolved in deionized water according to a stoichiometric ratio (Mg:Al=2:4) at 80°C and this solution was kept as precursor (A), and if the dissolution was incomplete, HNO$_3$ should be added. Then, the organic solution, kept as precursor (B), was made by TEOS, polyethylene glycol and absolute alcohol (C$_2$H$_5$OH) in a 3:1:3 volume ratio. Third, according to a stoichiometric ratio (Mg:Al:Si=2:4:5) precursor (A) was poured into precursor (B) with ceaseless stir to form the transparent sol. At last, after the sol was slowly dried overnight at 50°C and then at 120°C for 24 h, xerogels were obtained and these xerogels underwent calcination at 600-1380°C for 2 h.

The ceramic samples were prepared using the powders calcined at 600°C for the measurement of dielectric properties and thermal expansion coefficient. The powders were granulated using 5wt% PVA solution and pressed at 20 MPa to 10 mm diameter and 1 mm thick disks. Then the disks were sintered at 1200-1380°C for 2 h.

Characterization of phase and properties

DSC-TG was carried out on 20 mg dried gels in N$_2$ atmosphere with a NETZSCH STA 449C thermal analyzer at a heating rate of 10°C/min with precision of ±1°C. The XRD analyses were carried out using a Philips XPert diffractometer within the range of 2θ=8-70° with Cukα radiation. Microstructures of the calcined powders were observed using a Hitachi S-530 SEM. Average linear thermal expansion coefficient from room temperature to 600°C was measured in air at a heating rate of 10°C/min using a NETZSCH DIL 402C dilatometer. Electrical properties of ceramic samples were measured by an impedance analyzer LCR analyzer (HP4278A) at 1 MHz and 1 Vrms.

Results and Discussion

TG-DSC analysis

Thermal analysis was carried out to investigate the decomposition and phase evolution of cordierite dried gels. Figure 1 shows the TG-DSC curves of xerogels in the range 0-1400°C. The endothermic peak appeared in the range 0-250°C, corresponding to 35% weight loss, which can be attributed the evaporation of absorption water. The first exothermic peak appeared at 383°C, leading to a weight loss of 18% resulted from the oxidation of residual organic groups and release of weak bonding organic groups. The TG data shown little weight loss when the temperature was higher than 383°C and the weight became constant at the temperature higher than 800°C with a total weight loss of 53%. The second obvious exothermic peak, corresponding to the formation of μ-cordierite, appeared in a range from 984 to 1018°C and the third obvious exothermic peak appeared at 1310°C duo to the appearance of α-cordierite. Two weak exothermic peaks were observed at 1202°C and 1235°C, which were attributed to the crystalline phase change.

XRD analysis

XRD analysis was carried out to study the phase evolution of the dried gels in the calcination process. Figure 2 shows the XRD patterns of the dried gels calcined at 700, 1200, 1250, 1300, 1350 and 1380°C, respectively.
respectively. As can be seen in the figure, an amorphous phase was formed at the sintering temperature lower than 700°C. When the temperature rose to 1200°C, μ-cordierite and some Mg-Al spinel appeared. According to DSC and XRD figures, when the temperature increased to 1250°C, β-SiO₂ peaks were observed and sapphirine was produced through the chemical reactions of β-SiO₂ and Mg-Al spinel. The XRD pattern at 1300°C shows that most of μ-cordierite had transformed into α-cordierite, however, there were still some β-SiO₂ and sapphirine left, and only characteristic peaks of α-cordierite (PDF No. 12-0235) appeared at 1350°C. While the temperature was increasing from 1350 to 1380°C, no change appeared, hence the optional calcination temperature for cordierite by water-based sol-gel route was 1350°C. Therefore we can summarize the crystallization process: first μ-cordierite appeared, then β-SiO₂ and Mg-Al spinel, which formed sapphirine, and α-cordierite became the only phase at last. In comparison with the result of Ghitulica^{12}, this process was different from what occurred in the conventional solid-state reaction and wet-chemical method, but the same was that α-cordierite will be obtained at a relatively high temperature.

Microstructure analysis of cordierite powders

Figure 3 shows the SEM images of cordierite powders (sintered at 1350°C for 3 h/ball-milled for 36 h) without and with the process that the xerogels were ball-milled for 36 h before calcination, respectively. Comparing Fig. 3a showing a average grain size about 5 µm with Fig. 3b showing a average grain size less than 2 µm, we will see ball-milling xerogels had great influence on the grain size. This may be due to the different mechanical strength between α-cordierite crystal phase and xerogels amorphous phase. The α-cordierite powders with small average grain size (Fig. 4) was due to that its xerogels with low strength had been ground into smaller powders before crystallization.

Figure 4 shows the size distribution corresponding of cordierite powders without and with ball-milling.

![Fig. 3—SEM image of cordierite powders (a) without ball-milling xerogels procedure and (b) with ball-milling xerogels procedure](image1)

![Fig. 4—Particle size distribution of cordierite powders (a) without ball-milling xerogels procedure and (b) with ball-milling xerogels procedure](image2)
xerogels procedure. Without ball-milling xerogels procedure, particle size distribution of cordierite powders was not uniform (Fig. 4a). There were quite a number of powders with the size between 2.5~4.5 \( \mu \text{m} \). Cordierite powders with ball-milling xerogels procedure was found to be uniform (Fig. 4b) with particle size of 90\% \( d (0.9) \) of the cordierite ranging between 0.6 and 1.8 \( \mu \text{m} \). It had an average particle size of 1.05 \( \mu \text{m} \), median volume diameter (D50) of 1.33 \( \mu \text{m} \) and specific surface area (BET) of 1.72 \( \text{m}^2/\text{g} \), respectively. Thus, it was found that ball-milling xerogels had a good impact on cordierite powder size, shape and size distribution.

**Microstructure, dielectric properties and thermal expansion coefficient analysis of ceramics samples**

SEM images of cordierite ceramics sintered at temperatures 1200\(^\circ\)C, 1250\(^\circ\)C, 1300\(^\circ\)C, 1350\(^\circ\)C and 1380\(^\circ\)C for 2 h are shown in Fig. 5. As the sintering temperature was increased from 1200\(^\circ\)C to 1300\(^\circ\)C, pores being obvious at 1200\(^\circ\)C (Fig. 5a) were
gradually eliminated until 1300°C. But when the sintering temperature was increased to 1350°C and 1380°C, a few pores appeared again.

The dielectric constant and dielectric loss of the ceramics sintered at different temperatures were measured (Fig. 6). As can be seen from Fig. 6, the dielectric constant monotonously decreased from 5.13 to 4.51 along with the sintering temperature increased in the temperature region 1200-1350°C, but while the sintering temperature was increasing to 1380°C, the dielectric constant(≈4.50) was almost unchanged, which was attributed to the only existed α-cordierite phase in ceramics, because the dielectric constant was mainly determined by phase composition. These dielectric constant values agree very well with the value (≈5) reported in literature. It is observed that the dielectric loss of sample increased with increasing sintering temperature to 1300°C at first, and then declined thereafter, which was mainly due to the change of ceramics compactness. The dielectric loss tanδ≈0.004 of the sample sintered at 1350°C was at a low level, where as Chen reported the dielectric loss tanδ≈0.006. The dielectric constant (ε) and dielectric loss (tanδ) for samples sintered at 1350°C have been found to be 4.51 and 0.0028, respectively, which indicate the suitability for substrate applications.

In order to investigate cordierite ceramics’ thermal expansion coefficient, cuboid-shaped samples were sintered at 1350°C using the powders pre-sintered at 600°C. Figure 7 shows the thermal expansion coefficient of cordierite as a function of temperature between room-temperature and 600°C with the heating rate 10°C/min. Using the following function, the thermal expansion coefficient was determined, i.e.,

$$\alpha = \frac{1}{L_o} \times \frac{\Delta L_t - \Delta L_{t_0}}{t - t_0} + 0.57 \times 10^{-6} \ (1/°C)$$

Where 0.57×10^{-6}°C is the thermal expansion coefficient of quartz glass in the thermal expansion instrument. Through the calculation, the thermal expansion coefficient of the cordierite sample in this study is 1.85×10^{-6}°C and Acimovic et al. has reported a thermal expansion coefficient α≈2.65×10^{-6}°C (20-1000°C).

Conclusions
The pure cordierite powders and glass-ceramics have been prepared successfully by water-based sol-gel technique. Detailed analysis was carried out using TG-DSC, XRD, SEM and granularity analysis. The dielectric properties and thermal expansion coefficient of the samples were also measured. Crystallizing process of xerogels was revealed and the optimal route for preparing cordierite powders was proposed, for example, pre-sinter xerogels at 600°C/ball-mill for 36h/calcine at 1350°C/ball-mill again for 36 h. The powders had a homogeneous size distribution (particle size<2μm), and our cordierite ceramics shown low dielectric constant (ε<5), low dielectric loss (tanδ<0.004) and low thermal expansion coefficient (α<1.85×10^{-6}°C), which were comparable with the results by Chen. Thus, the results depicted a possibility of mass-producing pure cordierite powders with a simple condition.
Acknowledgement

This study is supported by “the Fundamental Research Funds for the Central Universities”, UESTC (ZYGX2009J035).

References