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Novel cordierite nanopowders of new crystallization aspects and its cordierite-based glass ceramics of improved mechanical and electrical properties for optimal use in multidisciplinary scopes

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HIGHLIGHTS

- Novel α-cordierite nanoparticles (13.3–46.7 nm) prepared by co-precipitation route.
- The mechanism of μ-cordierite crystallization obeys the surface chemical kinetics.
- Phase transformation of μ-to α-cordierite greatly affects densification properties.
- The cordierite ceramics show good dielectric performance under *GHz* or *MHz* ranges.

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ABSTRACT

Nanocrystalline α-cordierite $Mg_2Al_4Si_5O_{18}$ powders have been synthesized via a novel and facile co-precipitation method using $MgCl_2.6H_2O$, $NaAlO_2$, $Na_2SiO_3.5H_2O$ as starting materials. XRD, SEM, HR-TEM and EDS techniques were employed to investigate the phase structure and crystal morphology of the synthesized powders at various annealing temperatures. The kinetics of cordierite crystallization was studied under non-isothermal conditions using Differential Thermal Analysis (DTA). The apparent activation energy (E_a) of μ-cordierite crystallization, calculated by modified Kissinger model was equal 286.1 K J mol^{-1} and comparable with the literature. The dielectric measurements revealed that the cordierite ceramic samples sintered at 1300 and 1350 °C could be successfully applied for electronic packaging under the *microwave* and *radiowave* frequency regions, respectively.

1. Introduction

Cordierite ($Mg_2Al_4Si_5O_{18}$) is one of the most attractive potential engineering ceramics which has unique and multidisciplinary properties, such as low thermal expansion coefficient ($\alpha = 1.5–4.0 \times 10^{-6}$ K^{-1}) [1–8], excellent thermal shock resistance [1–4,6–9], high refractoriness [2–4], good mechanical properties [2,6,10], chemical resistance [10–12], low dielectric constant and high quality factor [13–19]. Nanofabrication of such cordierite based glass ceramic materials has attracted a great attention during recent years. However, a wide range of wet synthesis routes, including Sol–gel [20–24], organic acid precursor [25,26] and co-precipitation [27–29] have been proposed for preparation of the cordierite nanopowders and/or ceramics. In comparison, the co-precipitation method is a relatively convenient wet chemical way for pre-cordierite nanopowders preparation. It provides good mixing of the starting materials and produce pre-cordierite powders with good chemical homogeneity, high chemical purity, fast chemical reaction rate and fine grain particle size, which are the most important factors in the preparation of dense sintered cordierite bodies having a stoichiometric composition and homogeneous microstructure [10,30,31]. Therefore, determining the starting raw material is one of the key factors that could considerably affect the precipitation and hydrolysis rates of the

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hydroxides gel mixture during the synthesis of cordierite precursor. Accordingly, our work is devoted to using the starting raw material of $NaAlO_2$ and Na_2SiO_3 (as new sources of Al and Si elements) [32,33] as well as the $MgCl_2$ (source of Mg element) to prepare the nanocrystalline α-cordierite powders via a facile co-precipitation method at low annealing temperatures for the first time. In addition, the new crystallization aspects of synthesized nanopowders will be systematically investigated in terms of phase structure, crystal morphology, particle size, and activation energy as well as the predicted reaction mechanism. Moreover, the sinterability improvement of the prepared cordierite ceramics will be discussed in a detailed study. Furthermore, optimizing the effect of sintering temperature relative to the mechanical and electrical properties will be considered in order to relate the obtained results into an optimal use of the cordierite ceramics.

2. Experimental

2.1. Chemicals

All the chemicals used in this study such as (magnesium chloride hexahydrate Sigma–Aldrich 99.9%, sodium aluminate Sigma–Aldrich 99.9%, sodium silicate pentahydrate Sigma–Aldrich 99.9%, and hydrochloric acid ADWIC 37%) were of analytical grade. Deionized water was used in the entire work.

2.2. Powder and ceramic preparations

2.2.1. Processing of cordierite nanopowders

Cordierite gel was synthesized by adding dilute hydrochloric acid solution to the solutions mixed of magnesium chloride, sodium aluminate and sodium silicate (stoichiometrically mixed together achieving the $2MgO{:}2Al_2O_3{:}5SiO_2$ ratio) until adjusting the pH at 7–7.5 and according to our previous published works [32–35]. The aqueous suspension was gently stirred for 15 min to achieve a good homogeneity and to attain a stable pH conditions. The formed gel is then filtered, washed thoroughly with deionized water and dried overnight at 105 °C in the oven. The samples of dried precursor powder were annealed at various temperatures (1000–1300 °C) and for 3 h with heating rate of 5 °C/min in an air atmosphere. The annealed cordierite samples were ground in an agate mortar with a pestle to be fully characterized. The overall co-precipitation reaction of cordierite precursor is expressed by the following chemical equation:

$$4\boldsymbol{NaAlO_2} + 2\boldsymbol{MgCl_2}\cdot 6\boldsymbol{H_2O} + 5\boldsymbol{Na_2SiO_3}\cdot 5\boldsymbol{H_2O} + 10\boldsymbol{HCl} \xrightarrow{\boldsymbol{pH}=7-7.5} 4\boldsymbol{Al}(\boldsymbol{OH})_3 + 2\boldsymbol{Mg}(\boldsymbol{OH})_2 + 5\boldsymbol{Si}(\boldsymbol{OH})_4 + 14\boldsymbol{NaCl} + 24\boldsymbol{H_2O} \quad (1)$$

The overall preparation equation for cordierite formation by annealing the dried gel powder could be described as follow:

$$4\boldsymbol{Al}(\boldsymbol{OH})_3 + 2\boldsymbol{Mg}(\boldsymbol{OH})_2 + 5\boldsymbol{Si}(\boldsymbol{OH})_4 \xrightarrow{\Delta} 2\boldsymbol{Al_2O_3}\cdot 2\boldsymbol{MgO}\cdot 5\boldsymbol{SiO_2} + 18\boldsymbol{H_2O} \quad (2)$$

2.2.2. Processing of cordierite ceramic pellets

Pellets of cordierite samples were prepared by annealing the aforementioned dried precursor at 700 °C for 2 h at rate of 5 °C/min in an air atmosphere, firstly. Secondly, the annealed glass precursor was ground in an agate mortar with a pestle. Thirdly, the ground powders of certain amount was compacted by the uniaxially dry pressing technique in a 15 mm diameter steel die at a pressure of 3 metric tons. Finally, the formed compacts were sintered at different temperatures (1200–1350 °C) for 5 h with heating rate of 5°/min in an air atmosphere to get the cordierite ceramic pellets.

2.3. Characterization

X-ray powder diffraction (XRD) was carried out on a model Bruker AXS diffractometer (D8-ADVANCE Germany) with Cu Kα (λ = 1.54056 Å) radiation, operating at 40 kV and 40 mA. The diffraction data were recorded for 2θ values between 10° and 70° and the scanning rate was 3° min^{-1} or 0.02°/0.4 s. Thermal analysis (TG/DTA) was performed under air atmosphere from room temperature to 1300 °C with different heating rates (5–30 °C/min) using (TGA, Model Q50, V6.1 series, TA Instruments, USA). Scanning electron microscopy was investigated by a SEM (JEOL-JSM-5410 Japan). High Resolution Transmission Electron Microscopy (HR-TEM) was recorded with a TECNAI G2 S-Twin microscope operating at 200 kV, equipped with energy dispersive spectroscopy, EDS (EDAX PV 9900, EDAX International, Inc.) The expansion-shrinkage measurements were achieved using an Adamel Lhormergy 1/128 inch apparatus (Instrument SA, Longjumeau). The density and porosity of each sintered sample were measured by Archimedes method. Microhardness tests were evaluated by means of Vickers Microhardness Tester, INDENTEC-HWDN-7 Japan (2 kg normal load applied for 15 s) as an average of 6 measurements.

Dielectric properties were measured using a network impedance analyzer (Agilent-E4991A, USA). This was responsible for the generation and reception of signals in the frequency range of 1 MHz–3 GHz. The electrodes of dielectric cell were made of gold (Au). The classic parallel plate method was used in the test fixture to determine the dielectric permittivity and loss tangent of the material. The parallel plate capacitor procedure involves placing the ceramic sample coated with silver paste in between two circular plates; the load was then measured by LCR. The real part of the complex relative permittivity (ε') was calculated from the capacitance and the imaginary part of the complex relative permittivity (ε'') was calculated from the measurement of the dissipation factor. A calibration procedure performed on the test fixture using an OPEN, SHORT and a known LOAD state before the DUT was measured as this reduces the errors in the system. The Agilent software was used to convert the measured data into permittivity values.

3. Results and discussion

3.1. Crystal structure investigation

The phase structures of the cordierite precursor annealed from 1000 to 1300 °C for 3 h were investigated by X-ray diffraction analysis (XRD). Fig. 1 indicates that the α-cordierite was not detected in samples annealed at 1000 and 1100 °C for 3 h. At these temperatures, sapphirine $Mg_{3.5}Al_9Si_{1.5}O_{20}$ (ICDD: 21-0549), enstatite $MgSiO_3$ (ICDD: 75-1093), spinel $MgAl_2O_4$ (ICDD: 77-0435) and μ-cordierite $MgAl_2SiO_3$ (ICDD: 14-0249) were identified in the XRD patterns as the raw materials of the precursor did not completely react with each other to produce the desired phase structure. Meanwhile, the two polymorphs α- and μ-cordierites were concurrently evolved by annealing the precursor at 1200 °C. In addition, a small amount of spinel was also detected in the sample. However, by increasing the annealing temperature up to 1300 °C, α-cordierite $Mg_2Al_4Si_5O_{18}$ (ICDD: 89-1485) appeared as the main phase, while the μ-cordierite $MgAl_2SiO_3$ (ICDD: 14-0249) and spinel becoming the minor phases. Such obtained results were in good agreement with experimental evidence gathered elsewhere