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Microwave sintering of mullite–cordierite precursors prepared from solution combustion synthesis

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Abstract

Mullite–cordierite composite was synthesized using the solution combustion synthesis method and glycine as a fuel and aluminum nitrate, magnesium nitrate and colloidal silica as the reagents. The effect of fuel to oxidizer ratio on the combustion behavior, as well as chemical composition and morphology of the formed powders was investigated. All synthesized powders were amorphous with submicron particle size. It was found that the change of fuel to oxidizer ratio had no effect on synthesis of this composite without heat treatment. The smallest particle size of composite powder was obtained as 302 nm for ratio less than 1 (rich of fuel). Mullite, cordierite and spinel were detected after microwave heating at 1200 and 1400 °C. Mullite and cordierite were detected as the only crystalline phases when the stoichiometric ratio of fuel to oxidizer was chosen and this composite obtained the highest density of 2.61 g/cm^3.

Keywords: B. Composite; D. Cordierite; D. Mullite; Combustion synthesis

1. Introduction

Silicate based compounds such as mullite and mullite–cordierite have excellent high temperature mechanical properties, good chemical stability and low thermal expansion coefficient [1–3]. In the recent years, these compounds have been used in electronic packing applications due to their low thermal expansion coefficient compared to Si chips and low dielectric constant. Also, other advantages of using silicates are, allowing a selection of relatively wide range values of dielectric constant and thermal expansion by producing bodies consisting of two or more phases. These structures can also offer advantages of improved mechanical properties [4,5]. Due to numerous difficulties related to ceramic processing, many researchers have resorted to the use of chemical synthesis method, in order to reduce synthesis and sintering temperature of mullite and cordierite composites [6]. Recently, much attention has been devoted towards the preparation of these materials with fine particles and higher reactivity, in order to reduce the sintering temperature. One of these chemical synthesis methods is the solution combustion synthesis. This is an effective method for the synthesis of nanoscale materials and oxidic ceramics [7,8]. This process is based on mixing of fuel such as glycine and urea and metal nitrates. Nitrates oxidize easily and organic fuels act as reducing agents. An external heat is needed to ignite the reaction [7,8].

Mullite–cordierite composites were prepared by sol–gel methods [9] and solid state mixing [10–12]. To the best of our knowledge, there are few reports on the solution combustion synthesis of this composite and only Gopichandran et al. [4] has reported the preparation of this composite with urea fuel.

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In this study, mullite–cordierite composite was prepared by solution combustion synthesis, using glycine as fuel. The effect of fuel to oxidizer ratio on synthesis, sintering and the dielectric properties of composites was examined.

2. Experimental procedures

Al $(NO_3)_3 \cdot 9H_2O$ (99% Merck), Mg $(NO_3)_2 \cdot 6H_2O$ (99% Merck) and a commercially colloidal silica (30 wt% solid) were used as starting materials. Glycine (98.5%, Merck) was used as the fuel, a redox reaction was established and the amount of fuel was calculated according to the propellant chemistry criteria [13]. In this case, the reaction was adapted using the equivalent valence of reactants. By considering the valences of C=+4, H=+1, O=−2, N=0, Al=+3, Si=+4, the oxidizing and reducing valences for reactants are shown in Table 1.

The chemical reaction equation for the formation of mullite–cordierite composite can be expressed as follows:

$$2Mg(NO_3)_2 \cdot 6H_2O + 10Al(NO_3)_3 \cdot 9H_2O + 7SiO_2 + nC_2H_5NO_2 \rightarrow Al_6Si_2O_{13} + Mg_2Al_4Si_5O_{18} + (102 + 2.5n)H_2O + 2nCO_2 + (17 + 0.5n)N_2 \quad (1)$$

The amount of fuel (n) can be calculated from balance of valences

$$\sum v_i n_i = 0 \quad (2)$$

where v_i and n_i are equivalent valences and number of moles of each component, respectively. The amount of fuel for stoichiometric reaction was calculated as 18.9.

Jiane et al. [13] suggested a model for calculating the fuel to oxidizer ratio using elemental stoichiometric coefficient (Φ_e). This parameter is defined as shown in Eq. (3).

$$\Phi_e = \frac{\sum (\text{Cofficient of oxidizng elements}) \times (Valences)}{\sum (\text{Cofficient of reducing elements}) \times (Valences)} \quad (3)$$

The molar ratio between nitrate and glycine is stoichiometric when $\Phi_e = 1$, for $\Phi_e > 1$ and $\Phi_e < 1$, the mixtures are fuel lean and fuel rich, respectively.

In the present study, in order to investigate the effect of oxidizer to fuel ratios on the properties of the final products, the elemental stoichiometric coefficients (Φ_e) with values of 0.6, 0.8, 1, and 1.38 were used.

At first, aluminum nitrate, magnesium nitrate and glycine were separately dissolved in minimum amount of water. Then, colloidal silica was diluted and added drop wise to aluminum nitrate solution under continuous stirring condition. Thereafter, magnesium nitrate and glycine solution were added. A Petri dish vessel containing the resultant solution was heated at 350 °C on a hot plate. At first, a highly viscous transparent gel-like precursor was obtained and then the combustion reaction was initiated. After the combustion reaction, the voluminous products were easily crumbled and subjected to calcination at 700 °C for 2 h in air. The particle size of calcined powders was measured by zeta sizer (model 3000HS_A, Malvern, England). The specific surface area was obtained by BET (Belsorp mini II). Calcined powders were compacted at a pressure of 250 MPa and sintered in a microwave furnace (900 W, 2.45 GHz) at 1200 and 1400 °C. Phase composition of synthesis powders and bulk products were investigated by X-ray diffraction (Philips PW 3710) using CuK_α radiation (λ=0.154 nm). The morphology of calcined powders and sintered samples was characterized by SEM (Stereo Scan S360) and Vega Tescan. The density of samples were measured by Archimedes' method. Dielectric constant measurement were carried out on disc-shaped samples (9–10 mm diameter and ≈2 mm thickness). All measurements were made at room temperature and 1 MHz on a LCR meter (LCR-811G LCR). Dielectric constant was calculated using the following equation:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \quad (4)$$

where C is the capacitance of the material, d is the thickness of the pellet and A is the area of cross-section, ε_r and ε_0 are the dielectric constant and permittivity of free space, respectively.

3. Results and discussion

Fuel to oxidant ratio is one of the most important parameters in determining the properties of synthesis powder such as crystallite size, morphology, degree and nature of agglomeration. Reaction was conducted at different fuel to oxidizer ratios, so that they were carried out using quantities of glycine different from the stoichiometric amount (reaction mixture 1) up to 50 and 100% in excess (reaction mixtures 2 and 3) and 25% at less (reaction 4), as with their elemental stoichiometric coefficient (Φ_e) summarized in Table 2.

However, Table 3 shows the value of formation of enthalpy and specific heat of compounds. As the data implies, the enthalpies of the possible reactions during the combustion process can be calculated (Table 4).

Based on the reaction RS3 (Table 4), it can be seen that the process of formation of this composition is highly endothermic, therefore a fuel is necessary to provide reaction

Table1
The oxidizing and reducing valences of reactants.

Valences	Materials
−10	$Mg(NO_3)_2 \cdot 6H_2O$
−15	$Al(NO_3)_3 \cdot 9H_2O$
0	SiO_2
+9	$C_2H_5NO_2$
−2	NH_4NO_3

Table 2
Amount of fuel or elemental stoichiometric coefficients used in this study.

Sample	1	2	3	4
Glycine	18.9	28.3	23.6	14.2
% Excess or less	–	100	50	−25
ϕ_e	1	0.6	0.8	1.38