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Fabrication and properties of cordierite based glass/AlN composites by sol–gel and pressureless sintering

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Abstract

In this study, the effect of AlN content on the crystallization behavior of cordierite based glass, was firstly investigated. Results show that μ-cordierite appeared in the composites with high AlN content even at high temperatures, which implied that the AlN may broad the crystallization temperature range of μ-cordierite and depress the transformation of μ→α-cordierite. The crystallization temperature of α-cordierite was about 980 °C for the pure glass and the temperature increased with AlN content for composites, but the crystallization temperature of μ-cordierite had reverse trend. The composites owned excellent bending strength when the AlN content was 20 wt%. With increasing of AlN content, the dielectric loss was increased which was caused mainly by the structural loss and the appearance of μ-cordierite, but the dielectric constant had crosscurrent. It was observed that the composites were beneficial in producing LTCC material which can be highlighted with high strength, low shrinkage and good dielectric properties at 1 MHz.

Keywords: C. Dielectric properties; Cordierite-based glass; Crystallization; Microstructure

1. Introduction

Cordierite are promising materials in different branches of industry, because of their low dielectric constant, low thermal expansion coefficient, high resistivity and chemical stability [1–3]. Cordierite based glass can be obtained by solid state reaction or sol–gel methods [4,5]. But the cordierite glass–ceramics are difficult to sinter, due to its narrow sintering range. Because of the excellent controlling of the chemical composition and the possibility of reducing the sintering temperature, sol–gel process has been widely used to prepare cordierite based glass [6,7]. By adding a series of nucleation, the cordierite based glass can be sintered below 1000 °C which was favor to LTCC materials. The properties of cordierite based glasses, obtained by solid state reaction methods, with nucleating agents such as CeO_2, V_2O_5 and B_2O_3 had been studied extensively [8–10], however, the report on properties and crystallization behavior of cordierite based glass made by sol–gel techniques was rare [11].

LTCC materials were used to make electronic substrates for high density integrated devices packaging usually consist of low-melting glass and ceramic fillers [12]. The properties of the LTCC materials are determined by the filler materials and the glass. There have been several studies for using various ceramics as fillers including $CaCu_3Ti_4O_{12}$, Si_3N_4, BN and Li_2O [13–15]. There are a number of works have been done on the cordierite based glass/AlN composite, however, the studies about the cordierite-AlN composite prepared by sol–gel process is really rare. As a report example, Chen and co-workers [16] reported that cordierite/AlN composites were prepared by hot pressure sintering at 1000 °C with a pressure of 40 MPa in vacuum atmosphere, the composites possessed excellent mechanical properties such as high density, bending

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strength and fracture toughness, however, the dielectric properties and crystallization behavior of the composites were not investigated.

In this work, the cordierite based glass was prepared by sol–gel method and the composites with different AlN content were sintered at 950 °C in N_2 atmosphere for 4 h. The effects of AlN content on the crystallization, shrinkage, mechanical and dielectric properties of the cordierite glass/AlN composites were investigated.

2. Experimental procedure

2.1. Glass powder preparation

Sol-gel process was used to prepare cordierite glass powder. The following reagents were used as raw material, including $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, B_2O_3 and P_2O_5 and tetraethoxy silane (TEOs). The mole ratio of $Al(NO_3)_3 \cdot 9H_2O$:$Mg(NO_3)_2 \cdot 6H_2O$:TEOs was 2:2:5. 2.5 wt% B_2O_3 and 2.5 wt% P_2O_5 were used as fluxing and nucleating agent respectively. $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, B_2O_3 and P_2O_5 were mixed and dissolved in deionizer water and stirred for 2 h to obtain the clear solution. TEOs was mixed with ethanol and stirred for 2 h. The two solutions were mixed in room temperature and stirred for 4 h, then put the mixture into the oven at 60 °C to form dried gel. The dried gels were calcined in air at 600 °C for 2 h. The calcined gel was milled using planetary ball milling with the speed of 350r/min for 4 h to get the glass powder.

2.2. Sample preparation

Cordierite based glass powders got from above process and AlN powders were mixed in ethanol for 24 h and then dried at 80 °C in oven to get the mixture. The mixture were uniaxially pressed at 20 MPa to get disk pellets in 50 mm diameter die. The pellets were sintered at different temperatures in N_2 atmosphere for 4 h with heating rate of 10 °C/min.

2.3. Measurements of material properties

The calcined temperature and the corresponded reaction of the dried gels were determined by TG (thermo gravimetric analysis). Glass transition temperature (Tg) and crystallization temperature of the composites were measured using DTA (differential thermal analysis, STA 409C/CD, Netzsch Co., Germany) with the heating rate of 10 °C/min. The crystalline phase was identified by X-ray diffractometer using CuKa radiation. Linear shrinkage of the samples was measured by measuring the size of the sample before and after sintering. The universal testing machine (Instron-5500, Instron Engineering Corporation, USA) was employed to measure the flexural strength by three point bending, the size of the samples was 3 mm × 4 mm × 36 mm with the span of the 30 mm, the loading speed was 0.5 mm/min, at least 5 specimens for each sample were tested. The fracture surfaces of the samples were examined using FEI Sirion Quanta 200 scanning electron microscopy. The dielectric constants and dielectric loss of the samples were measured by using a Hewlett Packard Impedance Analyzer at 1 MHz at room temperature.

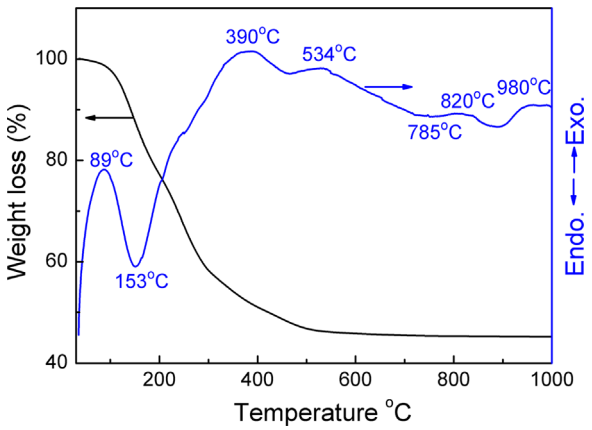

Fig. 1. TG–DTA curves of the dried gels.

3. Result and discussion

3.1. Thermal analysis

The TG–DTA curves of the glass powder made by sol–gel, measured from room temperature to 1000 °C with the hating rate of 10 °C/min, were shown in Fig. 1. The first weight loss and its corresponding endothermic peak at 153 °C indicated that the gel continue to lose the water, alcohols and other organic solvents. The dried gels may absorb the water during the cooling process from 60 °C to room temperature at normal atmosphere. The second weight loss correspond to the endothermic event at 390 °C, was caused by the decomposition of starting materials such as TEOs and nitrate. The last weight loss mainly reflect in DTA carve at 534 °C may attribute to the burning out of the carbon and other organics [1]. The weight of the sample became constant when the calcined temperature was higher than 600 °C which indicated that the pure glass powder can be obtained when the burned temperature of the dried gel was higher than 600 °C. As can be seen from the TG–DTA curves, the glass transition temperature (Tg) was 785 °C, and the endothermic peak at 820 °C and 980 °C correspond to the crystallization of μ-cordierite and α-cordierite, respectively, the result was in good agreement with the literatures [17,18].

The DTA curves of the mixed powder (10–50 wt% AlN) between 400 °C and 1200 °C with the heating rate of 10 °C/min are shown in Fig. 2. The glass transition temperature (Tg) of all the samples was around 800 °C which decreased slightly with the increasing of AlN content. The temperature of the μ-cordierite crystallization decreased with the content of AlN, however, the crystallization temperatures of α-cordierite had converse trend. This result was proved by XRD patterns in next section.

3.2. Phase composition of composites

The XRD patterns of composites with different AlN content sintered at 950 °C for 4 h were shown in Fig. 3. All the