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Characterization and dielectric behavior of willemite and TiO_2-doped willemite ceramics at millimeter-wave frequency

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Abstract

Willemite ceramics (Zn_2SiO_4) have been successfully prepared in the temperature range from 1280 to 1340 °C. It is found that willemite ceramics possess excellent millimeter-wave dielectric properties: a dielectric constant ε_r value of 6.6, a quality factor $Q \times f$ value of 219,000 GHz and a temperature coefficient of resonant frequency τ_f value of −61 ppm/°C. By adding TiO_2 with large positive τ_f value (450 ppm/°C), near zero τ_f value can be achieved in a wide sintering temperature range. With 11 wt% of TiO_2, an ε_r value of 9.3, a $Q \times f$ value of 113,000 GHz, and a τ_f value of 1.0 ppm/°C are obtained at 1250 °C. The relationships between microstructure and properties are also studied. Our results show that willemite with appropriate TiO_2 is an ideal temperature stable, low ε_r and high $Q \times f$ dielectric for millimeter-wave application.

Keywords: Willemite; Microstructure final; Dielectric properties; Substrates

1. Introduction

Recent developments in microelectronics technologies have created a great demand for substrate materials with a very low dielectric constant ε_r, a very low loss and a near zero temperature coefficient of resonant frequency τ_f. They will play a crucial role in the future generation of microwave integrated circuit (MIC). As a result, considerable efforts have been made to develop new low as well as high dielectric constant materials for applications in electronics industries. For substrate application, low dielectric constant is very important because it yields higher signal propagation velocity through a dielectric medium which is given by:

$$v_p = \frac{c}{\sqrt{\varepsilon_r}} \quad (1)$$

Low dielectric constant will also reduce inductive crosstalk and noise generation in the MIC. Low loss is another critical requirement for lightweight portable devices for long battery life. This property is characterized by quality factor $Q \times f$ which is a system property relating to the efficiency of use of power supplied to the device. It is defined as the ratio of energy stored to energy lost per cycle. Al_2O_3, forsterite (Mg_2SiO_4) and $ZnAl_2O_4$ are three candidates for substrate application.[1–4] However, their large negative τ_f (−60 to −79 ppm/°C) and high sintering temperatures (>1400 °C) put constraints on their application as substrate materials. In search of new high performance materials for millimeter-wave device, silicates are proposed to be good candidates for millimeter-wave dielectrics because of their low ε_r.[5] In this work, we first found that willemite ceramic is a good millimeter-wave dielectric which possesses low ε_r, very high $Q \times f$, but relatively large negative τ_f value (−61 ppm/°C). In order to adjust the τ_f value near to zero, TiO_2 with high positive τ_f value (450 ppm/°C) was added to willemite. The chemical reaction between TiO_2 and willemite is also studied.

2. Experimental

High-purity powders ZnO (99.99%) and SiO_2 (99.9%) were used as the raw materials. The weighed powders were ball-milled in a polyethylene bottle with ZrO_2 balls for 24 h using ethanol as medium. After drying at 100 °C, the mixed powders were ground and then calcined at 1150 °C for 2 h. The pure calcined powders or calcined powders with 5–15 wt% TiO_2 (99.8%) were ball-milled again for 24 h and dried. The powders were then mixed with poly vinyl alcohol (PVA) as a binder and powdered and granulated. The granulated powders were sub-

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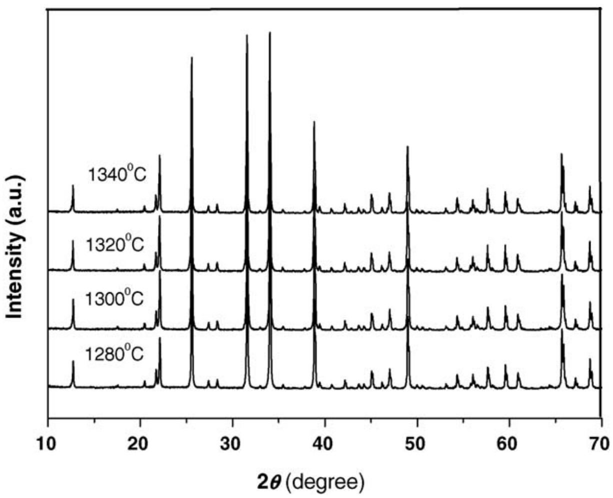

Fig. 1. XRPD patterns of willemite ceramics sintered in the temperature range from 1280 to 1340 °C.

sequently pressed into disks of 12 mm diameter under 98 MPa, followed by cold-isostatic-pressing (CIP) under 200 MPa. These powder compacts were fired in air at selected temperatures.

The bulk densities of the fired samples were measured by the Archimedes method using distilled water as a medium. Their crystal structures were determined by X-ray powder diffraction (XRPD) obtained using Cu Kα radiation and filtered through Ni foil (Rigaku; RAD-B system). The micrographs of the thermally etched samples were obtained by scanning electron microscopy (SEM).

The dielectric properties in the millimeter-wave frequency were measured by the Hakki–Coleman dielectric resonator method, [6] where a cylindrically shaped specimen is positioned between two copper plates. An HP8757C network analyzer was used as the measuring system. The dielectric constant was calculated by the resonant frequency of the TE_{011} resonant mode. The temperature coefficient of the resonator frequency (τ_f) was obtained in the temperature range from 25 to 80 °C.

3. Results and discussions

Fig. 1 shows the XRPD patterns of willemite ceramics sintered in the temperature range from 1280 to 1340 °C. Only peaks of willemite are observed, which can be indexed as a trigonal structure. Fig. 2(a)–(d) show the variations of relative density, ε_r, $Q \times f$ and τ_f with sintering temperature for willemite ceramics. A large increase in density was first observed at a temperature between 1280 and 1300 °C, i.e., from a relative density 94.1 to 96.7%, suggesting that rapid densification occurred at a temperature above 1280 °C, and then only a small change occurred with further increase in the sintering temperature. The relationship between ε_r and sintering temperature showed almost the same trend as that between density and sintering temperature. The ε_r value increased from 6.0 to 6.6 with increasing the sintering temperature from 1280 to 1340 °C. It implies that the increase for ε_r of willemite ceramics with sintering temperature is due to the increase of density and reduced porosity. The $Q \times f$ also increases with increasing temperature. The dielectric loss is caused by two reasons, i.e., intrinsic contribution: such as

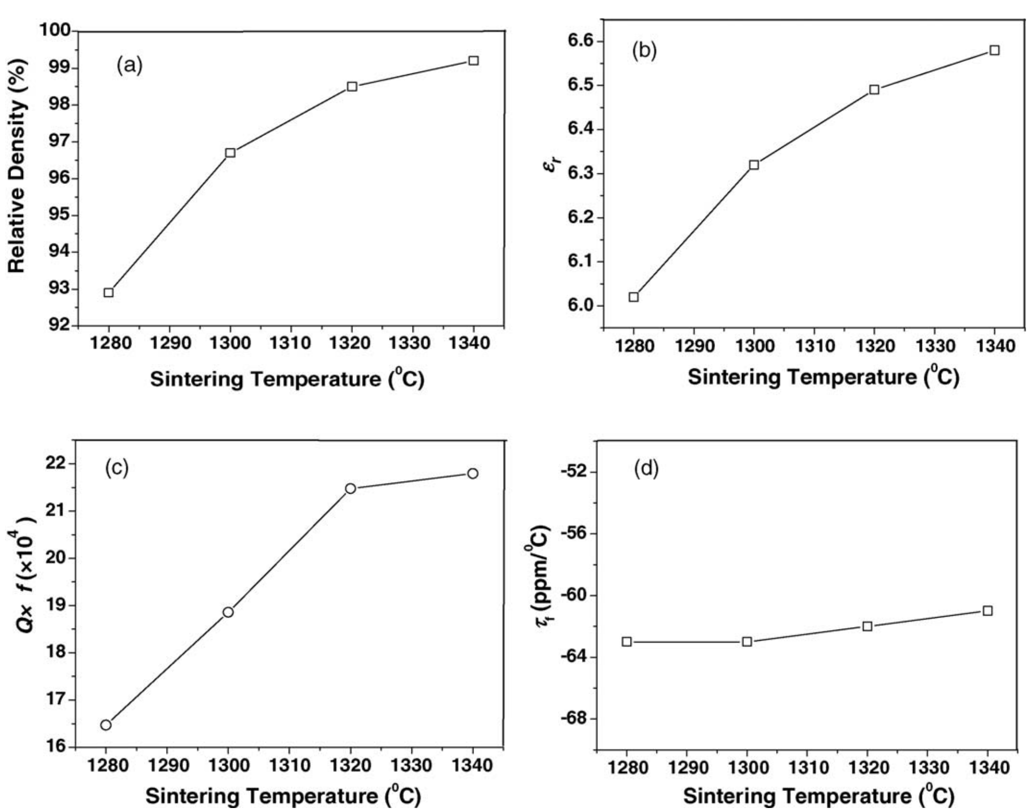

Fig. 2. The variations of relative density, ε_r, $Q \times f$, and τ_f with sintering temperature for willemite ceramics.