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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 $\varepsilon_r$ value of 6.6, a quality factor $Q \times f$ value of 219,000 GHz and a temperature coefficient of resonant frequency $\tau_f$ value of −61 ppm/°C. By adding $TiO_2$ with large positive $\tau_f$ value (450 ppm/°C), near zero $\tau_f$ value can be achieved in a wide sintering temperature range. With 11 wt% of $TiO_2$, an $\varepsilon_r$ value of 9.3, a $Q \times f$ value of 113,000 GHz, and a $\tau_f$ 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 $\varepsilon_r$ 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 $\varepsilon_r$, a very low loss and a near zero temperature coefficient of resonant frequency $\tau_f$. 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 $\tau_f$ (−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 $\varepsilon_r$.[5] In this work, we first found that willemite ceramic is a good millimeter-wave dielectric which possesses low $\varepsilon_r$, very high $Q \times f$, but relatively large negative $\tau_f$ value (−61 ppm/°C). In order to adjust the $\tau_f$ value near to zero, $TiO_2$ with high positive $\tau_f$ 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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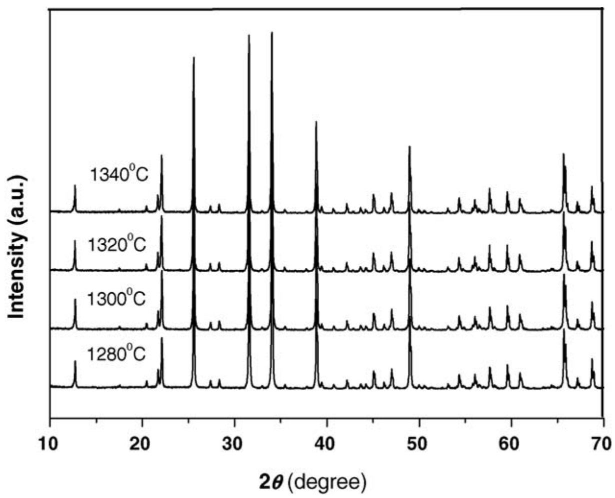


Fig. 1. XRPD patterns of willemite ceramics sintered in the temperature range from 1280 to 1340 °C.

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 ($\tau_f$) 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, $\varepsilon_r$, $Q \times f$ and $\tau_f$ 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 $\varepsilon_r$ and sintering temperature showed almost the same trend as that between density and sintering temperature. The $\varepsilon_r$ value increased from 6.0 to 6.6 with increasing the sintering temperature from 1280 to 1340 °C. It implies that the increase for $\varepsilon_r$ 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

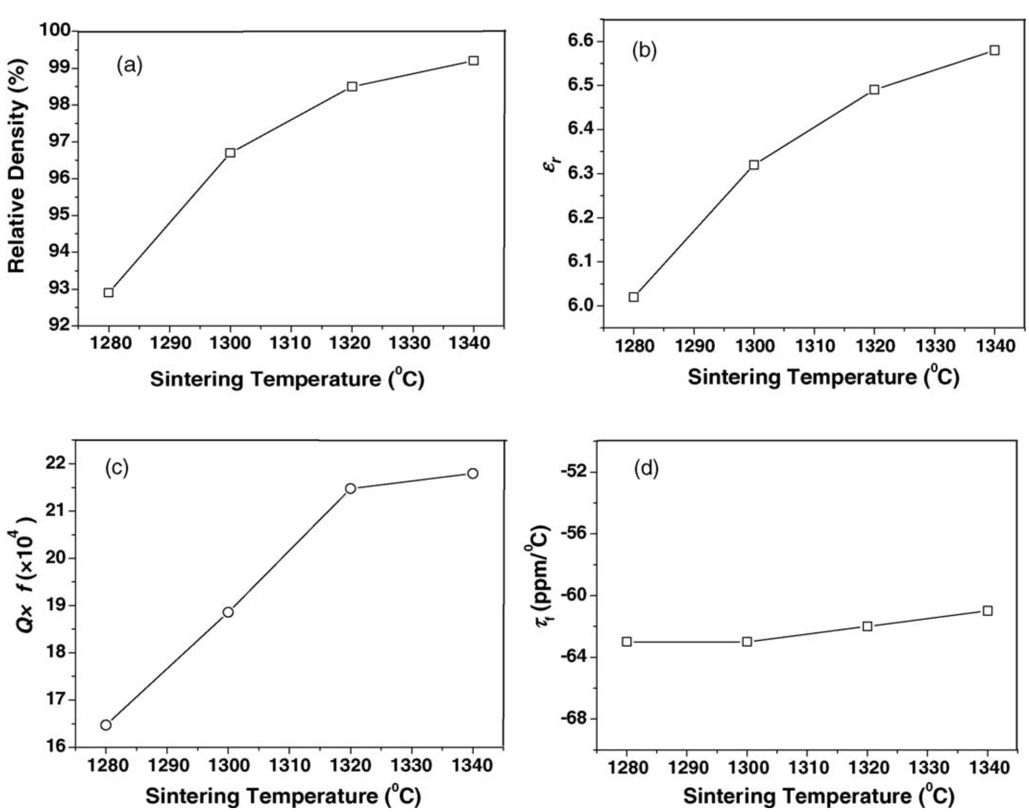


Fig. 2. The variations of relative density, $\varepsilon_r$, $Q \times f$, and $\tau_f$ with sintering temperature for willemite ceramics.

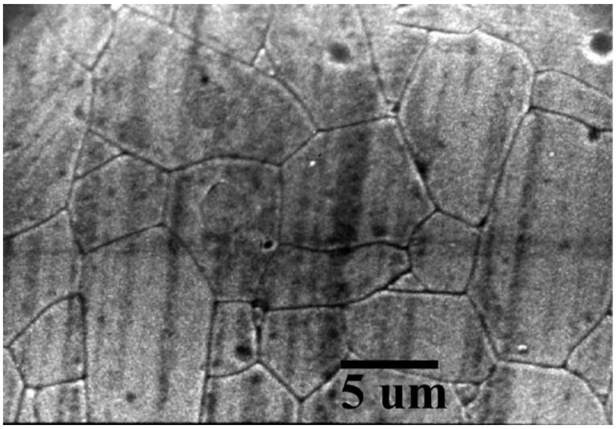


Fig. 3. SEM micrograph of willemite ceramic sintered at 1340 °C for 2 h.

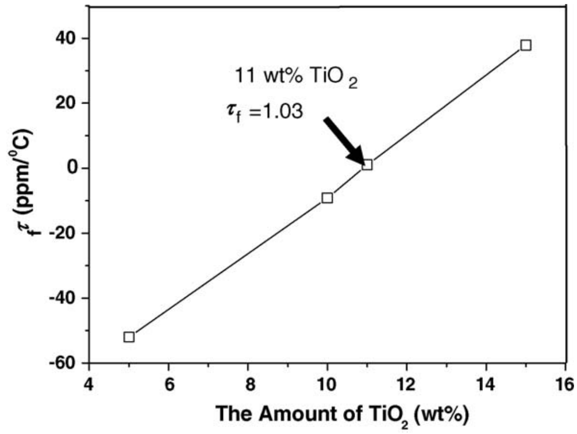


Fig. 4. The variation of $\tau_f$ with $TiO_2$ content for samples sintered at 1250 °C.

lattice vibrational modes and ion occupation; extrinsic contribution: such as pores and secondary phases. Relative density also plays an important role in affecting the dielectric loss. And in general, the large grain size of well-sintered ceramics resulted in low dielectric loss. The $Q \times f$ value of the sample sintered at 1340 °C reached up to 219,000. There are no significant changes in the $\tau_f$ of the samples sintered at different temperatures, and also hardly any relationship between $\tau_f$ and sintering temperatures is found. The $\tau_f$ values vary from −61 to −63 ppm/°C on sintering in the temperature range from 1280 to 1340 °C. Typical SEM micrographs of thermally etched pellets prepared at 1340 °C are shown in Fig. 3. Microstructures show the absence of pores and the average grain size is about 7 μm.

In order to adjust the $\tau_f$ value to zero, $TiO_2$ with high positive $\tau_f$ value (450 ppm/°C) was added. Fig. 4 shows the relationship between the $\tau_f$ and $TiO_2$ content of willemite ceramics sintered at 1250 °C. The $\tau_f$ of willemite ceramics increases almost linearly with increasing $TiO_2$ content. The values change from −52 to 37 between 5 and 15 wt% of $TiO_2$ addition. A near zero $\tau_f$ value can be obtained in the composite of willemite with 11 wt% $TiO_2$. Fig. 5(a)–(d) show the variation of density, $\varepsilon_r$, $Q \times f$ and $\tau_f$ with sintering temperature for willemite ceramics containing 11 wt% of $TiO_2$. Apparent density, $\varepsilon_r$ and $Q \times f$ all increase with increasing the sintering temperature from 1200 to 1250 °C, and further increases in sintering temperature show hardly any change in properties. This implies that high dense bodies can be

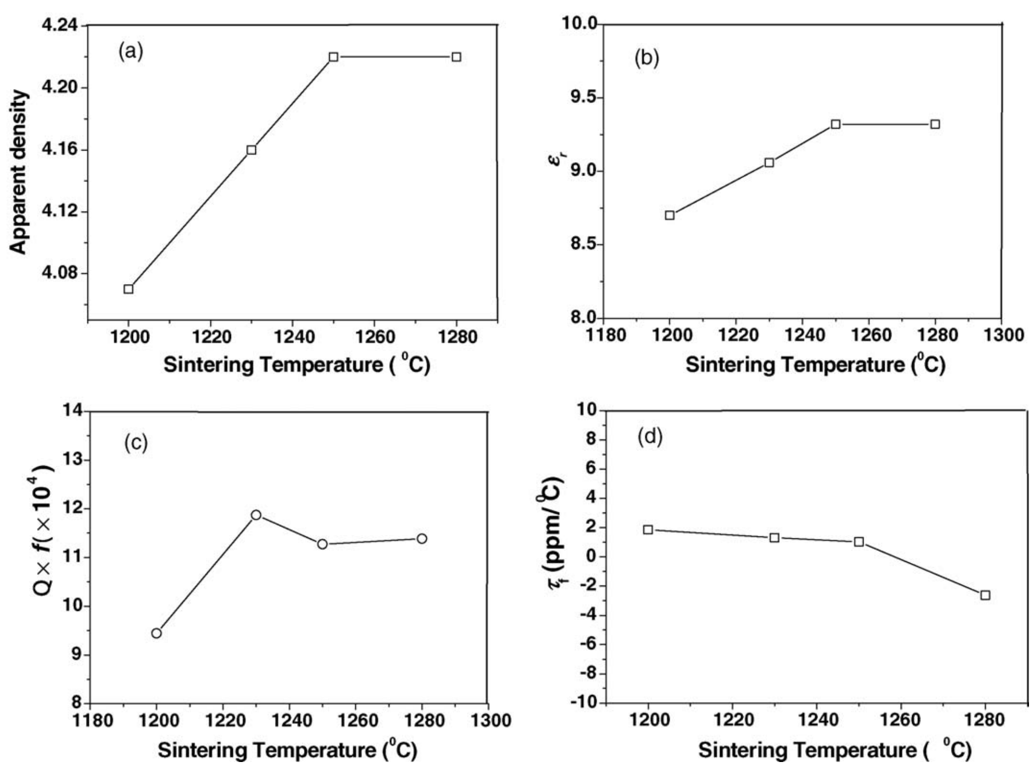


Fig. 5. The variations of apparent density, $\varepsilon_r$, $Q \times f$, and $\tau_f$ with sintering temperature for willemite ceramics added with 11 wt% $TiO_2$.

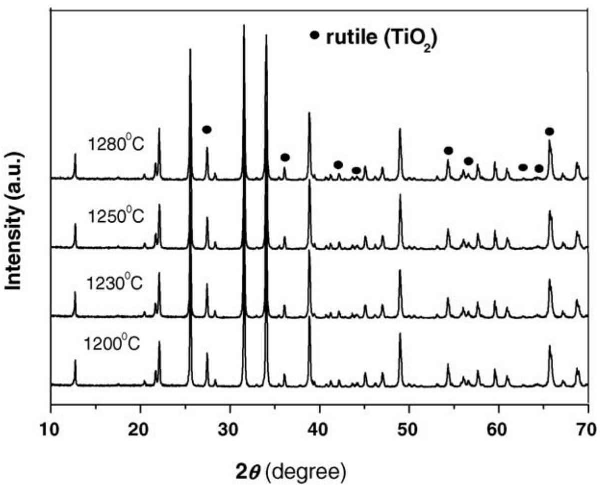


Fig. 6. XRPD patterns of willemite ceramics added with 11 wt% $TiO_2$ sintered in the temperature range from 1200 to 1280 °C.

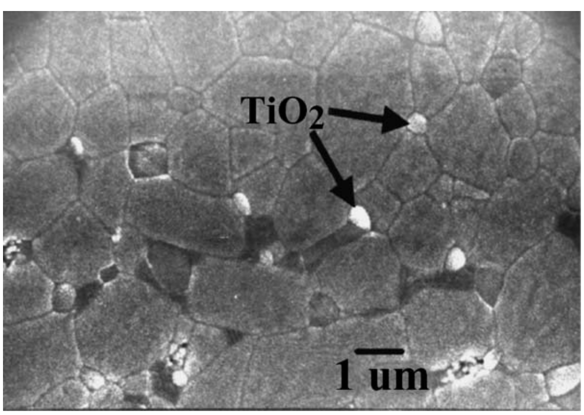


Fig. 7. SEM micrograph of willemite ceramic added with 11 wt% $TiO_2$ sintered at 1250 °C for 2 h.

achieved when sintered at temperatures as low as 1250 °C. It is well known that $TiO_2$ always acts as sintering aid to improve the sinterability of second ceramic materials. So it is evident that the addition of 11 wt% $TiO_2$ reduced the sintering temperature from 1320 °C for pure willemite ceramics to 1250 °C. The $\varepsilon_r$ value increases from 6.5 to 9.3, and $Q \times f$ value decreases from 219,000 to 113,000 GHz by the addition of 11 wt% $TiO_2$. These properties are excellent as compared to other conventional dielectric materials currently in use for ceramic substrate applications. The results clearly indicate that the $TiO_2$-doped willemite ceramic is an ideal temperature stable, low $\varepsilon_r$ and high $Q \times f$ dielectric for substrate application. Most interestingly, unlike $TiO_2$-doped forsterite, in which the $\tau_f$ value easily changes due to the formation of additional phase of $MgTi_2O_5$, [6] in $TiO_2$-doped willemite ceramics, the $\tau_f$ remains almost a constant. Fig. 6 shows the XRPD patterns of the $Zn_2SiO_4$ ceramics containing 11 wt% $TiO_2$ and sintered in the temperature range from 1200 to 1280 °C. For all samples, only the peaks of willemite and $TiO_2$ are detected. This indicates that only a "composite" mixing effect occurs between willemite and $TiO_2$. Fig. 7 shows the micrograph of willemite ceramic containing 11 wt% $TiO_2$ and sintered at 1250 °C for 2 h. A dense body with few pores is obtained. The large grains of about 2 μm with gray color are willemite and the smaller white grains are $TiO_2$. This result is consistent with that of XRPD analysis.

## 4. Conclusions

Millimeter-wave dielectric ceramics of willemite ($Zn_2SiO_4$) were prepared by solid-state reaction method. Excellent millimeter-wave dielectric properties, an $\varepsilon_r$ value of 6.6, a $Q \times f$ value of 219,000 GHz and a $\tau_f$ value of −61 ppm/°C were obtained. In order to adjust $\tau_f$ value to zero, $TiO_2$ with large positive $\tau_f$ value was added. Near zero $\tau_f$ value can be obtained by adding 11 wt% $TiO_2$ and sintering in a wide sintering temperature range. With 11 wt% of $TiO_2$, an $\varepsilon_r$ value of 9.3, a $Q \times f$ value of 113,000 GHz, and a $\tau_f$ value of 1.0 ppm/°C were obtained at 1250 °C. XRPD analysis revealed that only a "composite" mixing effect occurred between willemite and $TiO_2$ which was responsible for keeping the $\tau_f$ as a constant in a wide range of sintering temperatures. Our results show that willemite with appropriate $TiO_2$ is an ideal temperature stable, low $\varepsilon_r$ and high $Q \times f$ dielectric for millimeter-wave application.

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