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The effect of sintering temperature and time on microwave properties of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics for resonators

Cheng-Hsing Hsu [a,*], Hong-Tie Soong [b], Cheng-Chi Yu [c], Cheng-Liang Huang [b], Ming-Ta Ku [b]

[a] Department of Electrical Engineering, National United University, No. 1 Lien-Da, Kung-Ching Li, Miao-Li 36003, Taiwan
[b] Department of Electrical Engineering, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan
[c] Department of Communication Engineering, Feng Chia University, No. 100 Wenhwa Road, Seatwen, Taichung 40724, Taiwan

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Abstract

The microwave dielectric properties of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics have been investigated. $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics were prepared by conventional solid-state route with various sintering temperatures and times. The prepared $Sm(Zn_{1/2}Ti_{1/2})O_3$ exhibited a mixture of Zn and Ti showing 1:1 order in the B-site. Higher sintered density of 7.01 g/cm^3 can be produced at 1310 °C for 2 h. The dielectric constant values (ε_r) of 22–31 and the $Q \times f$ values of 4700–37,000 (at 8 GHz) can be obtained when the sintering temperatures are in the range of 1250–1370 °C for 2 h. The temperature coefficient of resonant frequency τ_f was a function of sintering temperature. The ε_r value of 31, $Q \times f$ value of 37,000 (at 8 GHz) and τ_f value of −19 ppm/°C were obtained for $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1310 °C for 2 h. For applications of high selective microwave ceramic resonator, filter and antenna, $Sm(Zn_{1/2}Ti_{1/2})O_3$ is proposed as a suitable material candidate.

Keywords: $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramic; Microwave dielectric properties

1. Introduction

Microwave dielectric ceramics with attractive dielectric properties are being evaluated extensively for substrates and microwave component such as microwave resonators, patch antennas and filters. The advantage of using dielectric resonators is that it makes the size reduction of microwave devices possible [1,2]. Requirements for these dielectric resonators must be the combined dielectric properties of a high dielectric constant ($\varepsilon_r > 25$), a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$) and a near-zero temperature coefficient of resonant frequency (τ_f) [3]. In general, high dielectric constant materials exhibit high dielectric loss (low $Q \times f$ value), while low loss ceramics are always accompanied by low ε_r value. Several complex perovskites ceramics $A(B'_{1/2}B''_{1/2})O_3$ ($A = Me^{2+}$, Me^{3+}; $B' = Me^{2+}$, Me^{3+}; $B'' = Me^{4+}$, Me^{5+}, Me^{6+}) have been reported due to their excellent microwave dielectric properties [4–6]. The $A(B'_{1/2}B''_{1/2})O_3$ compounds can be combined with the materials having positive temperature coefficient of the resonant frequency (τ_f) to form the solid solution with zero τ_f [7,8].

Recently, attempts have been made to satisfy microwave needs by using $Ln(Mg_{1/2}Ti_{1/2})O_3$ (Ln = La, Sm, Nd, Dy, Y) ceramics which have low dielectric loss and reasonable dielectric constant [9–11]. $Ln(Mg_{1/2}Ti_{1/2})O_3$ compositions which were measured quality factor ($Q \times f$) of the ceramic specimens was larger than 30,000 (10 GHz) and dielectric constant revealed between 22 and 27 have noncubic symmetry and the $GdFeO_3$-type structure [9]. Since $Sm(Mg_{1/2}Ti_{1/2})O_3$ has a dielectric constant (ε_r) of 25, a quality factor ($Q \times f$) of 65,500 (GHz) and a temperature coefficient of resonant frequency (τ_f) of −26 (ppm/°C), it is one of $Ln(Mg_{1/2}Ti_{1/2})O_3$ compositions produced to be suitable substrates for YBCO thin film and resonator used in microwave applications.

As mentioned above, because of the ion radius of Zn^{2+} (0.083 nm) is similar for that of Mg^{2+} (0.078 nm), the ion of Mg^{2+} can be substituted with the ion of Zn^{2+} to form $Sm(Zn_{1/2}Ti_{1/2})O_3$ compositions. In this paper, $Sm(Zn_{1/2}Ti_{1/2})O_3$

* Corresponding author. Tel.: +886 37 381401; fax: +886 37 327 887.
E-mail address: hsuch@nuu.edu.tw (C.-H. Hsu).

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ceramics were synthesized by solid-state method and the microwave dielectric properties and the microstructures of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics were also investigated.

2. Experimental procedures

Samples of $Sm(Zn_{1/2}Ti_{1/2})O_3$ were synthesized by conventional solid-state methods from individual high-purity oxide powders (>99.9%): Sm_2O_3, ZnO and TiO_2. The starting materials were mixed according to the desired stoichiometry of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics. The powders were ground in distilled water for 12 h in a ball mill with agate balls. All mixtures were dried and forced through a 100-mesh sieve and calcined at 1100 °C for 2 h. The calcined powder was then remilled for 24 h with 2 wt.% of a 10% solution of PVA as binder. The milled powders were pressed into disk 11 mm in diameter and 5 mm in thickness. A pressing pressure of 2000 kg/cm^2 was used for all samples. These pellets were sintered at temperatures of 1250–1370 °C for 2–10 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The crystalline phases of the sintered ceramics were identified using an X-ray diffraction pattern (XRD). The microstructural observations and analysis of sintered surface were showed by a scanning electron microscopy (SEM). The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method as modified and improved by Courtney [12,13]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25 to +80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at different calcined temperatures and calcined times. The existing phases at each calcined temperatures and calcined times were observed as illustrated in the figure. With increasing calcined temperature, the mixed powders reacted more and the intensity of major $Sm(Zn_{1/2}Ti_{1/2})O_3$ phase was enhanced. However, the disorder phases coexist with the major phase and perhaps seriously affect the microwave dielectric properties of $Sm(Zn_{1/2}Ti_{1/2})O_3$

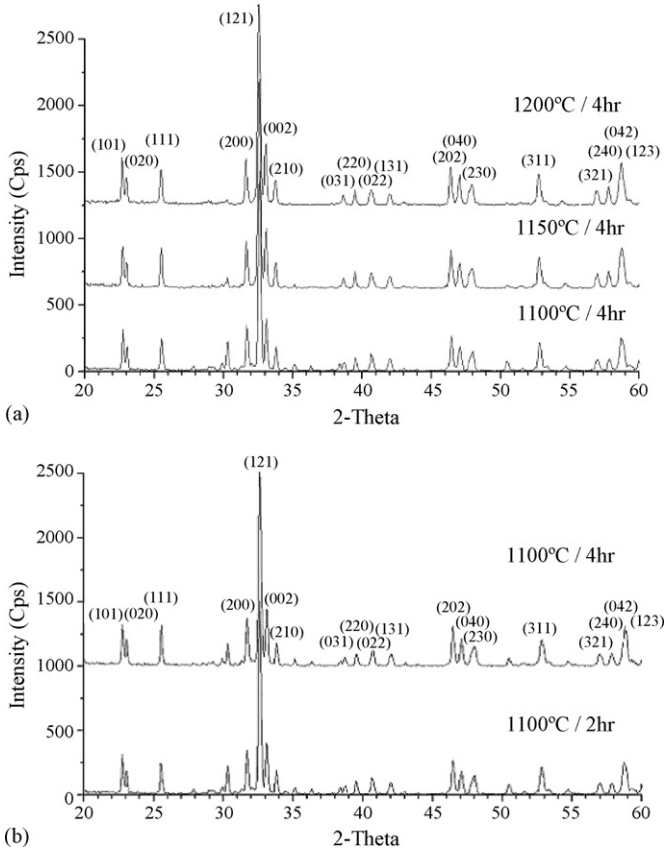

Fig. 1. X-ray diffraction patterns of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at different calcining temperatures and times.

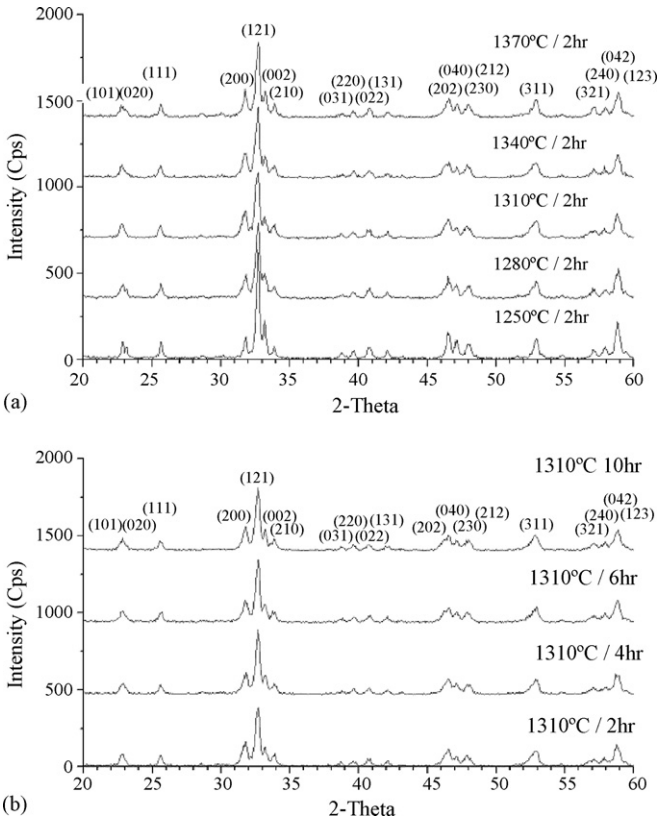

Fig. 2. X-ray diffraction patterns of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures and times.

ceramics. Homogeneous $Sm(Zn_{1/2}Ti_{1/2})O_3$ phase with a orthorhombic structure belong to Pnm_{21} space group could be obtained and the less disorder phases were also detected at 1100 °C for 2 h. This was reason for choosing 1100 °C for 2 h as the calcined temperature.

Fig. 2 shows the XRD patterns of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures. Same spectral angle of X-ray diffraction peaks were observed at sintering temperatures 1250–1370 °C. Second phase was not observed at different sintering temperature, due to fact that detection of a minor phase by XRD is extremely difficult. On the other hand, the XRD patterns of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at 1310 °C with different sintering time were also demonstrated. It is observed that no significant change was detected in the XRD patterns of the $Sm(Zn_{1/2}Ti_{1/2})O_3$, and it also exhibits an orthorhombic-type crystal structure.

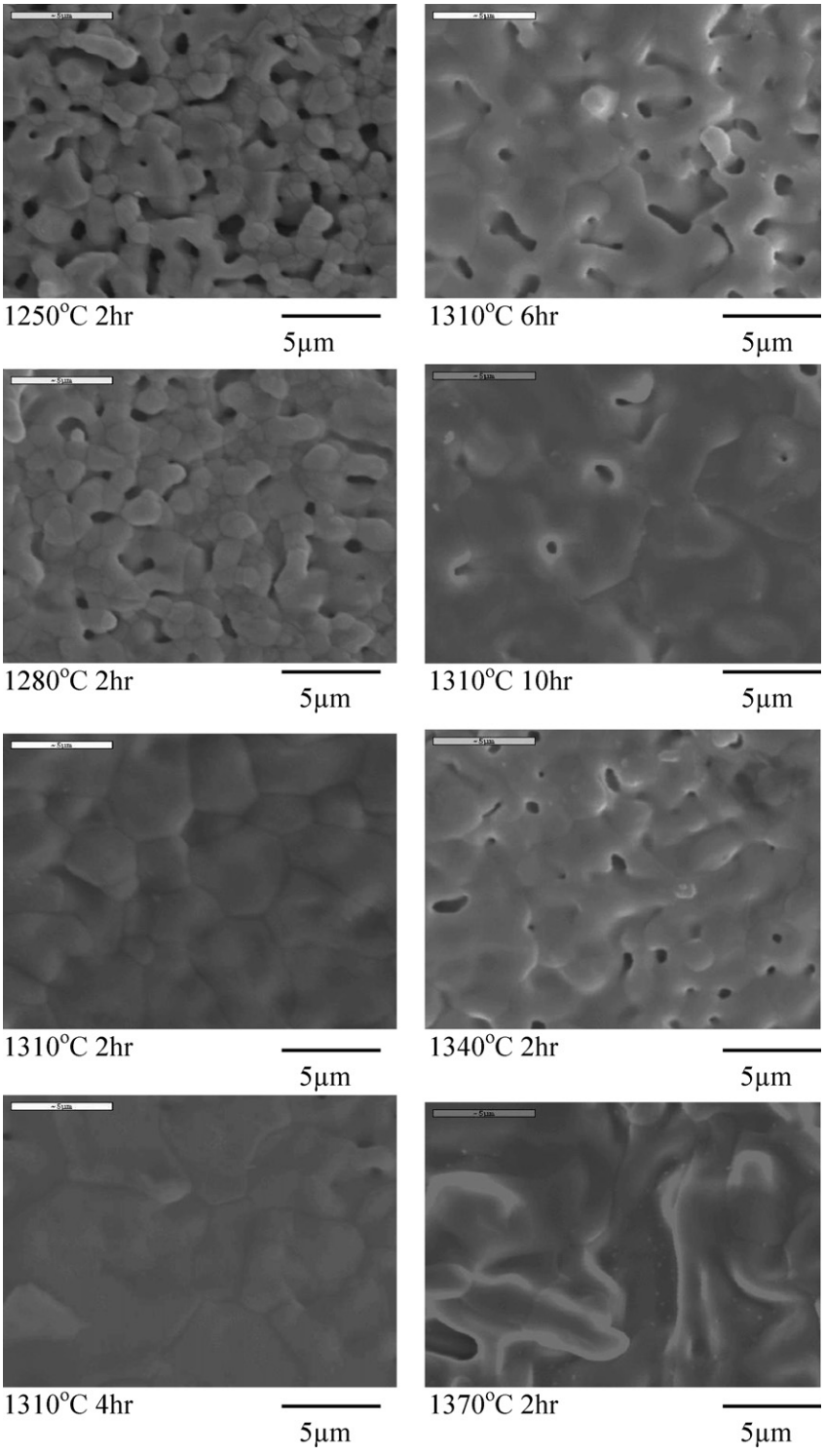

Fig. 3. SEM micrographs of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at different sintering temperatures and times.

The surface microstructural photographs of $Sm(Zn_{1/2}Ti_{1/2})O_3$ sintering at different sintering temperature and sintering time are showed in Fig. 3. The porosity decreased with increasing sintering temperature and dense morphology was observed 1310 °C owing to grain growth. An uniform grain morphology was also achieved at 1310 °C. However, abnormal grain growth appeared for $Sm(Zn_{1/2}Ti_{1/2})O_3$ specimen at sintering temperatures higher then 1340 °C, which could affect its microwave dielectric properties. Moreover, grain growth was still undergoing when prolonging the sintering time of the specimen. Increase in the abnormal grain was observed for $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics at 1310 °C with sintering time increased from 2 to 10 h. These may directly affect the microwave dielectric properties of $Sm(Zn_{1/2}Ti_{1/2})O_3$ samples.

The plot of bulk density of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics versus the sintering temperature and sintering time is illustrated in Fig. 4. The density increased with increasing sintering temperature to a maximum at 1310 °C and thereafter it decreased. The increase of density was due to decrease in the porosity of the sample and enhanced the grain size as shown in Fig. 3. Moreover, higher sintering temperature would cause abnormal grain growth resulted in a decrease in density. On the other hand, increase in the sintering time would produce the abnormal grain growth resulting in a decrease in the density. The decrease in density may also directly affect the microwave dielectric properties of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics.

Fig. 5 demonstrates the dielectric constant of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics as a function of its sintering temperature and sintering time. Due to higher porosity, the sample could be filled with air into the pores, dielectric constant of the sample would be affected and reduced by pore. The relationships between dielectric constant and sintering temperature reveal the same trend as that for density and sintering temperature since higher density represents lower porosity. The dielectric constants were increased with the increase of sintering temperature, and distinctly decreased at temperatures above 1310 °C with sintering 2 h. The increased of dielectric constant could be demonstrated owing to higher densities. On the other hand, non-uniform grain would be produced with the longer

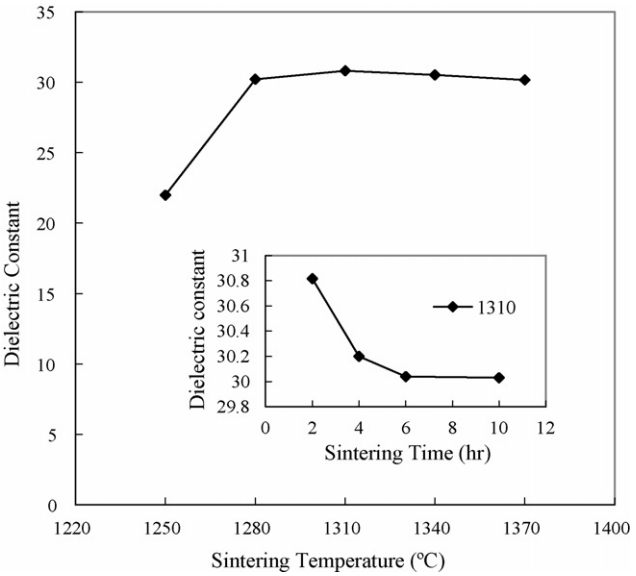

Fig. 5. Dependence of sintering temperature and time of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics on dielectric constant.

sintering time owing to much more energy provided by increasing sintering times. It may degrade the dielectric constant at the longer sintering time. The dielectric constant of the well-sintered $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics ranged from 22 to 31 at 1250–1370 °C. A maximum dielectric constant of 31 was obtained for $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics sintered at 1310°C for 2 h. The variation of the ε_r value was mainly a result from the density of the specimen.

The $Q \times f$ value of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics as a function of it sintering temperature and sintering time is illustrated in Fig. 6. It also revealed the same trend with the density. The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores and the second phases [14]. The $Q \times f$ value increased with increased sintering temperature to a maximum at 1310 °C and thereafter it decreased for 2 and 10 h. It may due to the porous specimens were observed at the lower sintering temperature, and this is the reason causing $Q \times f$ value to be diminished.

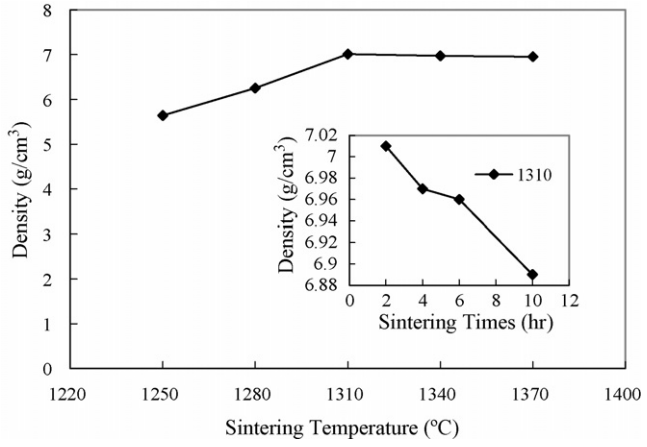

Fig. 4. Dependence of sintering temperature and time of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics on relative density.

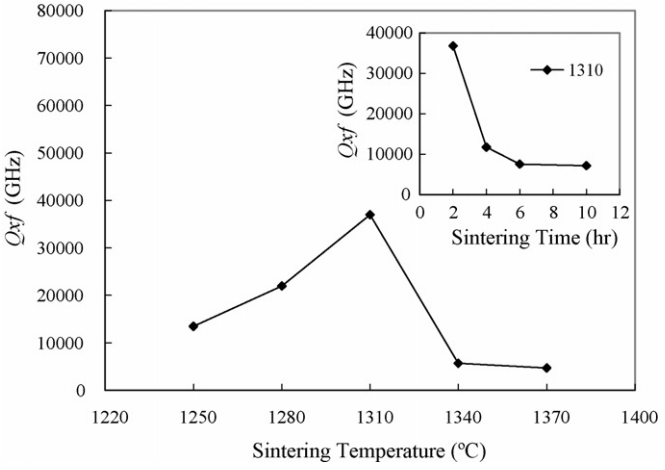

Fig. 6. Dependence of sintering temperature and time of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics on quality factor ($Q \times f$) value.

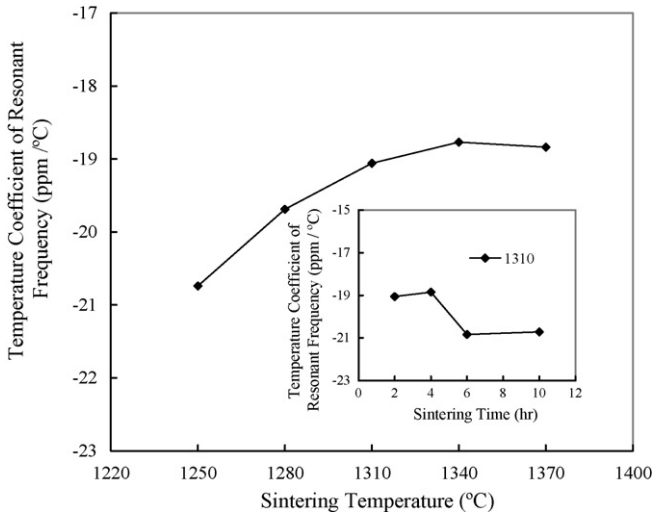

Fig. 7. Dependence of sintering temperature and time of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics on τ_f value.

Moreover, the decrease in $Q \times f$ value at the higher sintering temperature was due to the rapid grain growth as observed in Fig. 2. On the other hand, the $Q \times f$ value of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics would degrade when the sintering time exceeded 2 h. That degrade was also due to the abnormal grains were pronounced product at longer sintering times as also observed in Fig. 2. Density also plays an important role in controlling the dielectric loss and this has been shown for other microwave dielectric materials. Since the variation of the $Q \times f$ value was consistent with that of the density, it implies that the $Q \times f$ value was dominated by the change of density. Moreover, uniform grain morphology resulted in less dielectric loss also benefit to the $Q \times f$ value of the ceramics. A maximum $Q \times f$ value 37,000 was obtained for specimen sintered at 1310 °C for 2 h. The low dielectric loss would make $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics very promising in practical microwave applications.

Fig. 7 shows the temperature coefficient of resonant frequency (τ_f) of the $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics as a function of its sintering temperature. The temperature coefficient of resonant frequency (τ_f) is well known related to the composition and the second phase of a material. Since the composition remained unchanged and no second phase was detected, the τ_f values which was detected was not significant changed by various sintering temperatures as expected. The τ_f value varied from −18.7 to −20.7 ppm/°C as the sintering temperature increased from 1250 to 1370 °C. On the other hand, τ_f values were slightly changed from −18.8 to −21 ppm/°C by various sintering times. At 1310 °C, a τ_f value of −19 ppm/°C was measured for $Sm(Zn_{1/2}Ti_{1/2})O_3$ sintered for 2 h.

4. Conclusion

The effect of sintering temperature and time on microwave properties of $Sm(Zn_{1/2}Ti_{1/2})O_3$ ceramics for resonators were discovered. The ceramics exhibited an orthorhombic structure belong to Pnm_{21} space group at 1250–1370 °C. Since the variation of the microwave dielectric properties was consistent with that of the density, it implies that the microwave dielectric properties were dominated by the change of density. Excellent microwave dielectric properties ($\varepsilon_r \sim 31$, $Q \times f$ value ~37,000 (at 8 GHz) and τ_f value ~ −19 ppm/°C) can be obtained for $Sm(Zn_{1/2}Ti_{1/2})O_3$ sintered at 1310 °C for 2 h. For the search of excellent ε_r and $Q \times f$ dielectric material for applications in wireless communication system, $Sm(Zn_{1/2}Ti_{1/2})O_3$ would be a suitable candidate.

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