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Low-temperature sintered Zn_2SiO_4–$CaTiO_3$ ceramics with near-zero temperature coefficient of resonant frequency

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ABSTRACT

The microwave dielectric properties and the microstructures of $(1-x)Zn_2SiO_4-xCaTiO_3$ composite ceramics with Li_2CO_3–H_3BO_3 additives prepared by solid-state reaction method have been investigated. The crystalline phases were studied systematically by using the X-ray diffraction (XRD), microstructures by the scanning electron microscopy (SEM) and composition analysis by energy-dispersive spectroscopy (EDS). The τ_f of $(1-x)Zn_2SiO_4-xCaTiO_3$ was found to be dependent on phase constitution, which is related to the amount of $CaTiO_3$. When $x=0.05$, the τ_f of $(1-x)Zn_2SiO_4-xCaTiO_3$ was near 0 ppm/°C. The microwave dielectric properties of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics samples with Li_2CO_3–H_3BO_3 additives sintered at 900–1000 °C were characterized, and the results indicated that the permittivity and $Q\times f$ were associated with the amount of Li_2CO_3–H_3BO_3 and the sintering temperature. The sintering temperature of ceramics was effectively reduced to 950 °C from about 1250 °C and the temperature coefficient of resonant frequency (τ_f) was modified to −4.5 ppm/°C with good $Q\times f$. The addition of 4.0 wt% Li_2CO_3–H_3BO_3 in $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r=7.1$, $Q\times f=26{,}300$ GHz ($f=7.1$ GHz) and $\tau_f=-4.5$ ppm/°C. Moreover, this material has a chemical compatibility with silver, making it a very promising candidate material for LTCC applications.

1. Introduction

The rapid progress in microwave telecommunication and satellite broadcasting has resulted in an increasing demand for microwave dielectric materials. Low-temperature co-fired ceramics (LTCC) have been widely investigated as a means of miniaturizing microwave devices. For practical application in microwave dielectric materials as substrates or patch antennas in LTCC, the materials must display low permittivity, high quality factor ($Q\times f$), a near zero temperature coefficient of resonant frequency ($\tau_f\sim 0$ ppm/°C) and a low-firing temperature (<961 °C, the melting temperature of Ag electrode) [1–8]. Most commercial LTCC materials have relative permittivity less than 10 and the lowest loss tangent values close to 0.0002 at microwave frequencies. A new-glass-ceramics (NGC) that consists of $MgAl_2O_4$ crystals (spinel) and highly crystallized Li–Mg–Zn–B–Si–O glass has been developed by Murata Manufacturing for microwave or millimeter-wave frequency applications [9]. The KAI Multilayer Division of Kyocera America, Inc. utilizes both the Ferro A6 and DuPont LTCC materials for use in these demanding Multi-Chip Modules.

Willemite (Zn_2SiO_4) ceramics as silicates are proposed as good candidates for millimeter-wave dielectrics because of their low ε_r of 6.6 and high $Q\times f$ value of 219,000 GHz [10]. But the large negative τ_f of −61 ppm/°C and high sintering temperatures (>1300 °C) could put constraints on their application as substrate materials. In order to adjust the τ_f value to zero, TiO_2 ($\tau_f\sim$ +450 ppm/°C) was added. A near zero τ_f value ($\tau_f=1.0$ ppm/°C) can be obtained by adding 11 wt% TiO_2 [10]. However, it required a sintering temperatures as high as 1250 °C. For practical application in LTCC, it is necessary to lower the sintering temperature of the ceramics.

There are three methods to reduce the sintering temperature of microwave dielectric ceramics: first, low melting oxide, mixture oxide or glass addition; second, chemical processing; and finally the use of smaller particles as the starting materials [11–21]. The chemical method is time-consuming and expensive. Pamu et al. found that B_2O_3 could effectively decrease the sintering temperature of $(Zr_{0.8}Sn_{0.2})TiO_4$ to 1150 °C from 1650 °C [22]. In our previous work, it was found that the addition of $BaCu(B_2O_5)$ lowered the sintering temperature of $ZnTiNb_2O_8$ ceramics from above 1250 °C to 950 °C [23]. Li et al. could successfully reduce the sintering temperature of $(Zn_{0.65}Mg_{0.35})TiO_3$–$CaTiO_3$ ceramics from 1150 °C to 950 °C by using CaO–B_2O_3–SiO_2 additive, and adjust τ_f by dopping $CaTiO_3$ [24]. Generally, the addition of low melting point materials such as B_2O_3, CuO, Bi_2O_3, V_2O_5 and Li_2CO_3 is known to be the most effective

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and cheap way to achieve dense sintered ceramics at low sintering temperature.

In this paper, attempts were made to achieve a near-zero τ_f of Zn_2SiO_4, and to lower the sintering temperature below 950 °C. Since Zn_2SiO_4 ceramics have negative τ_f values and $CaTiO_3$ has a τ_f of +859 ppm/°C, ε_r of 162 and $Q\times f$ value of 12,960 GHz [25,26], the $(1-x)Zn_2SiO_4-xCaTiO_3$ composite ceramics should have adjustable τ_f values. In $(1-x)Zn_2SiO_4-xCaTiO_3$ composite ceramics ($x=0.05$), the sintering temperature was lowered below 950 °C by adding Li_2CO_3–H_3BO_3 as a sintering aid. The effects of densification, crystalline phases and microstructure on the microwave dielectric properties of Zn_2SiO_4 ceramics were explored.

2. Experimental procedures

Both Zn_2SiO_4 and $CaTiO_3$ compounds were individually synthesized by conventional solid-state reaction method using reagent-grade powders: ZnO (99.6%), SiO_2 (99.7%), $CaCO_3$ (99.5%) and TiO_2 (99.6%). For the preparation of Zn_2SiO_4 and $CaTiO_3$ compounds, the high-purity raw materials were weighed according to the desired stoichiometry and ball-milled in a polyethylene jar containing zirconia balls with ethanol for 4 h. After drying at 80 °C, the mixed powders were individually ground and then calcined at 1200 °C for 3 h and 1100 °C for 2 h in air. The compounds were individually re-milled for 4 h to obtain the desired composition: $(1-x)Zn_2SiO_4-xCaTiO_3$ ($x=0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07) and $0.95Zn_2SiO_4$–$0.05CaTiO_3$ doped with 2.0, 3.0, 4.0, 5.0 and 6.0 wt% Li_2CO_3–H_3BO_3. Then the mixed powders were dried, granulated and pressed into several disk-type pellets (25 mm in diameter and 15 mm in thickness). The $(1-x)Zn_2SiO_4-xCaTiO_3$ ($x=0$–0.07) pellets were sintered at 1200–1300 °C for 3 h and the $0.95Zn_2SiO_4$–$0.05CaTiO_3$ pellets containing 2.0–6.0 wt% Li_2CO_3–H_3BO_3 were sintered at 900–1000 °C for 3 h in air.

Crystalline phases of the sintered samples were identified by X-ray diffraction (XRD: PANalytical B.V., X'Pert PRO) using Cu Kα radiation, the microstructures were studied using scanning electron microscope (SEM: Philip, XL30TM) and composition analysis was performed using energy-dispersive spectroscopy (EDS: EDAX, PHOENIX). The bulk densities of the sintered ceramics were measured using the Archimedes method. The microwave dielectric properties were measured by an Advantest network analyzer (E5071C). The ε_r and Q values were measured by using the Hakki–Coleman dielectric resonator method [27,28]. The temperature coefficient of resonant frequency (τ_f) was also measured by the same method using Eq. (1)

$$\tau_f\ (\text{ppm}/^\circ\text{C}) = \frac{(f_{80}-f_{25})\times 10^6}{55 f_{25}} \quad (1)$$

where f_{80} and f_{25} are the resonant frequencies at 80 °C and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction (XRD) patterns of $(1-x)Zn_2SiO_4-xCaTiO_3$ ($x=0.03$–0.07) ceramic samples at the fixed sintering temperature of 1250 °C for 3 h in air. All the

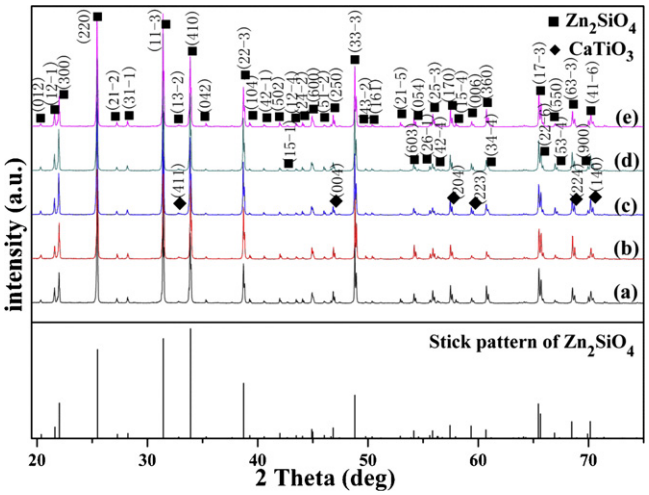

Fig. 1. XRD patterns of $(1-x)Zn_2SiO_4-xCaTiO_3$ ceramics (a) $x=0.03$, (b) $x=0.04$, (c) $x=0.05$, (d) $x=0.06$ and (e) $x=0.07$ sintered at 1250 °C for 3 h in air.

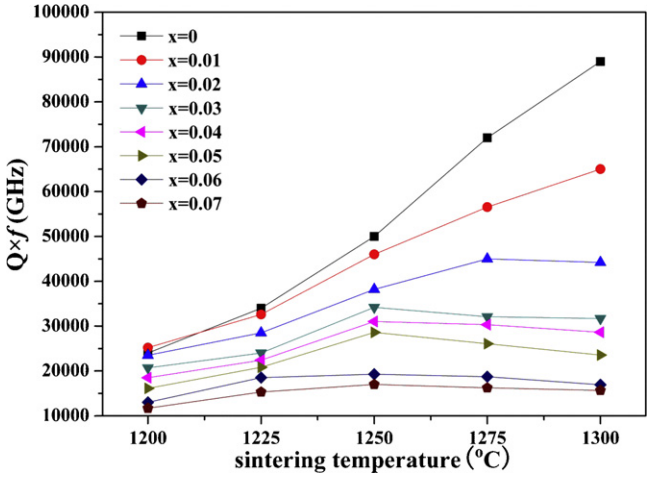

Fig. 2. The $Q\times f$ of $(1-x)Zn_2SiO_4-xCaTiO_3$ ($x=0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07) ceramics sintered at 1200 °C, 1225 °C, 1250 °C, 1275 °C and 1300 °C for 3 h in air.

compounds exhibit the mixture of Zn_2SiO_4 (JCPDS #72-1856) and $CaTiO_3$ (JCPDS #82-0231). The peaks indicated the presence of Zn_2SiO_4 as the main crystalline phase, and $CaTiO_3$ as the minor crystalline phase. Zn_2SiO_4 belongs to the rhombohedral crystal system (space group R-3 (no. 148)), and the lattice parameters are $a=b=13.9720$ Å, $c=9.3340$ Å. $CaTiO_3$ belongs to the orthorhombic crystal system (space group *Pbnm* (no. 62)), and the lattice parameters are $a=5.4642$ Å, $b=5.4804$ Å, $c=7.7452$ Å.

Fig. 2 shows the $Q\times f$ values of $(1-x)Zn_2SiO_4-xCaTiO_3$ ($x=0$–0.07) ceramics sintered at 1200–1300 °C for 3 h in air. The $Q\times f$ value of samples decreased gradually with increasing $CaTiO_3$ content. Zn_2SiO_4 has a higher $Q\times f$ value of 219,000 GHz, and $CaTiO_3$ has a lower $Q\times f$ of 12,960 GHz [9,16]. Consequently, when the $CaTiO_3$ content increased, the $Q\times f$ values of the compounds decreased gradually due to its relatively lower $Q\times f$ value. However, when $x=0$, 0.01 or 0.02, the $Q\times f$ value of $(1-x)Zn_2SiO_4-xCaTiO_3$ ceramic samples increased with increasing sintering temperature. The ceramics may not have been sintering enough at 1200–1300 °C, because of the high sintering temperatures of Zn_2SiO_4 (more than 1350 °C). When $x=0.03$–0.07, the $Q\times f$ value of $(1-x)Zn_2SiO_4-xCaTiO_3$ ceramic samples first increased with the sintering temperature to a maximum value at 1250 °C and then decreased at higher temperature. The decrease in $Q\times f$ at temperature higher than 1250 °C may have been as a result of oversintering. These also proved that the addition of $CaTiO_3$ can decrease the sintering temperature of Zn_2SiO_4 ceramics.

Table 1 shows that the theoretical and the measured permittivity ε_r and τ_f values of $(1-x)Zn_2SiO_4-xCaTiO_3$ ($x=0$–0.07) ceramics sintered at 1250 °C for 3 h. The theoretical permittivities of the composite ceramic were obtained from the well-known Lichtenecker empirical rule [29].

$$\log\varepsilon = V_1\log\varepsilon_1 + V_2\log\varepsilon_2 \quad (2)$$

where V_1 and V_2 are the volume fractions; ε_1 and ε_2 are the permittivities of the Zn_2SiO_4 ceramic and the $CaTiO_3$ ceramic, respectively. The measured permittivity of the $(1-x)Zn_2SiO_4-xCaTiO_3$ composite ceramic agreed well with the theoretical value (Table 1). It increased from 6.6 to 9.9 as the x value increased from 0 to 0.07.

The temperature coefficient of resonant frequency (τ_f) can be obtained from the thermal expansion coefficient α_L and the temperature coefficient of permittivity τ_ε as follows:

$$\tau_f = -\alpha_L - \frac{1}{2\tau_\varepsilon} \quad (3)$$

Table 1
Permittivity ε_r and τ_f of $(1-x)Zn_2SiO_4 - xCaTiO_3$ (x = 0–0.07) composite ceramics sintered at 1250 °C for 3 h in air.

Compounds	ε_r (theo.)	ε_r (meas.)	τ_f (theo.) (ppm/°C)	τ_f (meas.) (ppm/°C)
x = 0 [9]		6.6		−61.0
x = 0.01	6.7	6.7	−54.9	−52.0
x = 0.02	6.9	6.8	−48.8	−43.5
x = 0.03	7.0	7.1	−42.6	−31.5
x = 0.04	7.2	7.2	−36.3	−17.7
x = 0.05	7.4	8.2	−30.0	+0.8
x = 0.06	7.5	9.1	−23.7	+15.8
x = 0.07	7.7	9.9	−17.3	+28.6

ε_r (theo.): theoretical permittivity; ε_r (meas.): measured permittivity.
τ_f (theo.): theoretical τ_f value; τ_f (meas.): measured τ_f value.

The τ_ε is defined as the following:

$$\tau_\varepsilon = V_1\tau_{\varepsilon 1} + V_2\tau_{\varepsilon 2} \quad (4)$$

where V_1 and V_2 are the volume fraction of $ZnSiO_4$ and $CaTiO_3$. According to the Lichtenecker empirical rule, the mixing rule of τ_f can be described like this:

$$\tau_f = V_1\,\tau_{f1} + V_1\,\tau_{f2} \quad (5)$$

where τ_{f1} and τ_{f2} are the τ_f values of the $ZnSiO_4$ and $CaTiO_3$ phase, respectively. The theoretical τ_f values of the $(1-x)Zn_2SiO_4 - xCaTiO_3$ composite ceramics were calculated using the function (5). The τ_f values results were listed in Table 1. The measured τ_f was somewhat positive compared to the theoretical value. This might result from the element diffusion in the $(1-x)Zn_2SiO_4 - xCaTiO_3$ compounds. When the $CaTiO_3$ increased from 0 mol% to 7.0 mol%, the τ_f value of the sample increased from −61.0 ppm/°C to +28.6 ppm/°C. Zn_2SiO_4 has a lower τ_f of −61.0 ppm/°C, and $CaTiO_3$ has a higher τ_f of +859 ppm/°C [10,25]. Consequently, when the $CaTiO_3$ content increased, the τ_f value of the sample increased gradually. A near zero τ_f value (τ_f = 0.8 ppm/°C) can be obtained in $0.95Zn_2SiO_4$–$0.05CaTiO_3$ compounds sintering at 1250 °C for 3 h in air.

The XRD patterns of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramic samples with 2.0–6.0 wt% Li_2CO_3–H_3BO_3 additives sintered at 950 °C for 3 h are shown in Fig. 3. Fig. 4 shows the XRD patterns of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramic samples with 4.0 wt% Li_2CO_3–H_3BO_3 additives sintered at different temperatures (900–1000 °C) for 3 h in air. The XRD patterns showed that the samples contained three phases: the first is Zn_2SiO_4 (JCPDS #72-1856), the second is $CaTiO_3$ (JCPDS #82-0231) and the third phase. Unfortunately, the third phase has not been identified. The XRD patterns of the $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramic did not change markedly with the sintering temperatures in the range of 900–1000 °C or the increasing Li_2CO_3–H_3BO_3 content from 2.0 wt% to 6.0 wt%.

The SEM micrographs of the $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with different wt% of Li_2CO_3–H_3BO_3 additive (2.0–6.0 wt%) sintered at 950 °C for 3 h are shown in Fig. 5(a)–(e). The grains got more and more dense with the increasing Li_2CO_3–H_3BO_3 content. However, when the Li_2CO_3–H_3BO_3 content was more than 4.0 wt%, abnormal grain growth was observed. The SEM micrographs of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ samples with 4.0 wt% Li_2CO_3–H_3BO_3 sintered at different temperature (900–1000 °C) are presented in Fig. 6(a)–(e). It can be seen that the grains became larger and denser with increasing sintering temperature.

In order to analyze the composition, the EDS of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ samples with 4.0 wt% Li_2CO_3–H_3BO_3 sintered at 950 °C for 3 h is shown in Fig. 7. The results indicated the ratio of Zn:Si:O of spot A is about 2:1:4, which is consistent with the composition of Zn_2SiO_4. And the ratio of Ca:Ti:O of spot B is about 1:1:3, which is also consistent with the composition of $CaTiO_3$. These supported the results of XRD which showed that the samples contained two separate phases of Zn_2SiO_4 and $CaTiO_3$. It seems impossible to detect lithium and boron ions using an EDS detector, meaning that the Li_2CO_3–H_3BO_3 could not be detected. However, the Li_2CO_3–H_3BO_3 has been successfully applied as a sintering aid to enhance the sintering properties of the $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics, as shown in Figs. 5 and 9(a).

The XRD pattern and BSEM micrograph of the $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 4.0 wt% Li_2CO_3–H_3BO_3

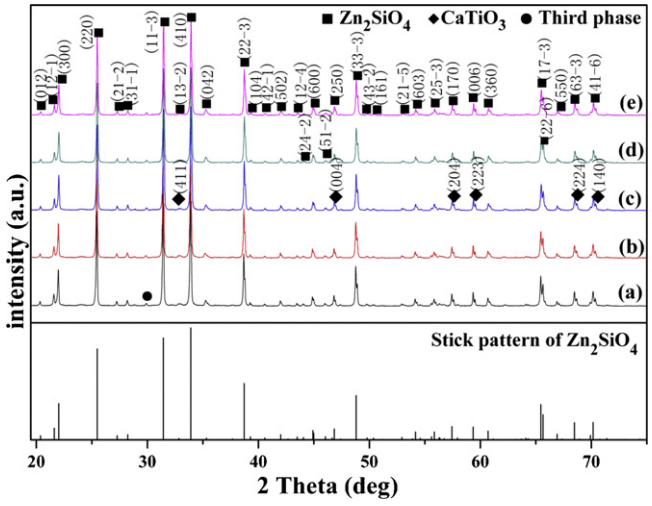

Fig. 3. XRD patterns of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with (a) 2.0 wt%, (b) 3.0 wt%, (c) 4.0 wt%, (d) 5.0 wt% and (e) 6.0 wt% Li_2CO_3–H_3BO_3 additives sintered at 950 °C for 3 h in air.

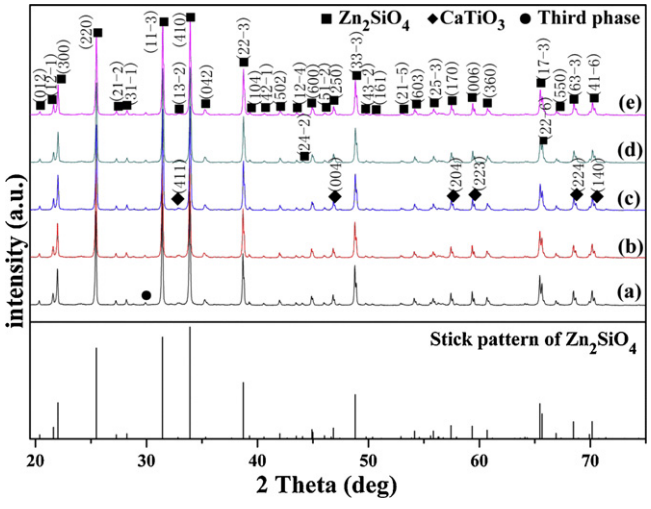

Fig. 4. XRD patterns of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 4.0 wt% Li_2CO_3–H_3BO_3 additives sintered at (a) 900 °C, (b) 925 °C, (c) 950 °C, (d) 975 °C and (e) 1000 °C for 3 h in air.

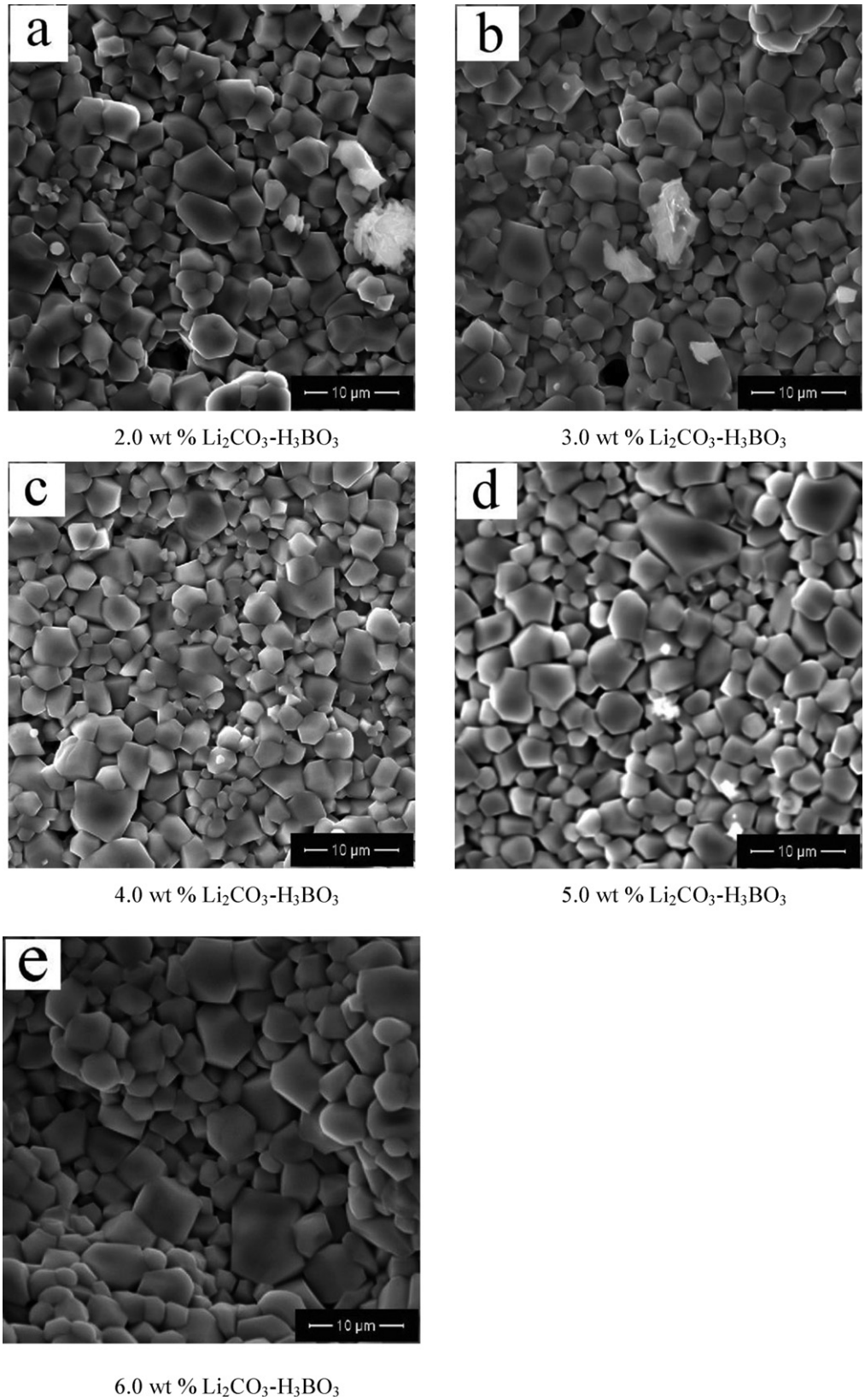

Fig. 5. SEM micrographs of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with (a) 2.0 wt%, (b) 3.0 wt%, (c) 4.0 wt%, (d) 5.0 wt% and (e) 6.0 wt% Li_2CO_3–H_3BO_3 additives sintered at 950 °C for 3 h in air.

and 20.0 wt% Ag addition sintered at 950 °C for 3 h are shown in Fig. 8. All the major peaks of Ag are observed in the XRD pattern and no phase containing silver compounds was present. In the BSEM micrograph, pale Ag particles have a uniform distribution in the ceramic and do not react with it. Therefore the composite exhibits chemical compatibility with Ag electrodes and the co-firing of Ag electrodes with the $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics is possible.

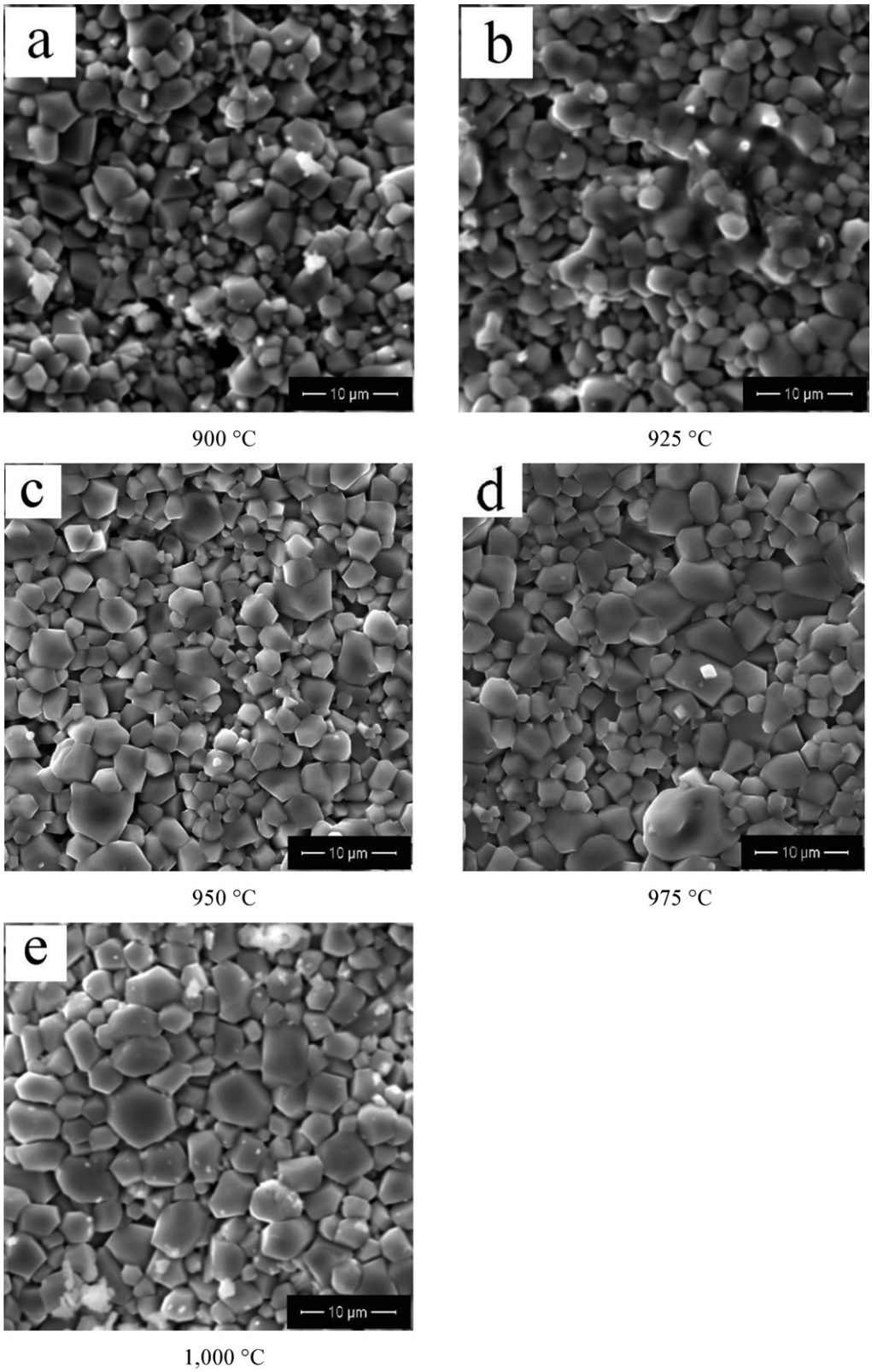

Fig. 6. SEM micrographs of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 4.0 wt% Li_2CO_3–H_3BO_3 additives sintered at (a) 900 °C, (b) 925 °C, (c) 950 °C, (d) 975 °C and (e) 1000 °C for 3 h in air.

Fig. 9(a) shows the relative density of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramic samples with 2.0–6.0 wt% Li_2CO_3–H_3BO_3 sintered at 900–1000 °C for 3 h in air. The relative density of the samples increased with the increasing sintering temperature due to the decrease in the porosity and the increase of the grain sizes. However, when the sintering temperature was above 950 °C, the relative densities of samples of more than 4.0 wt% Li_2CO_3–H_3BO_3 were almost invariable and at over 94% of the theoretical density, which

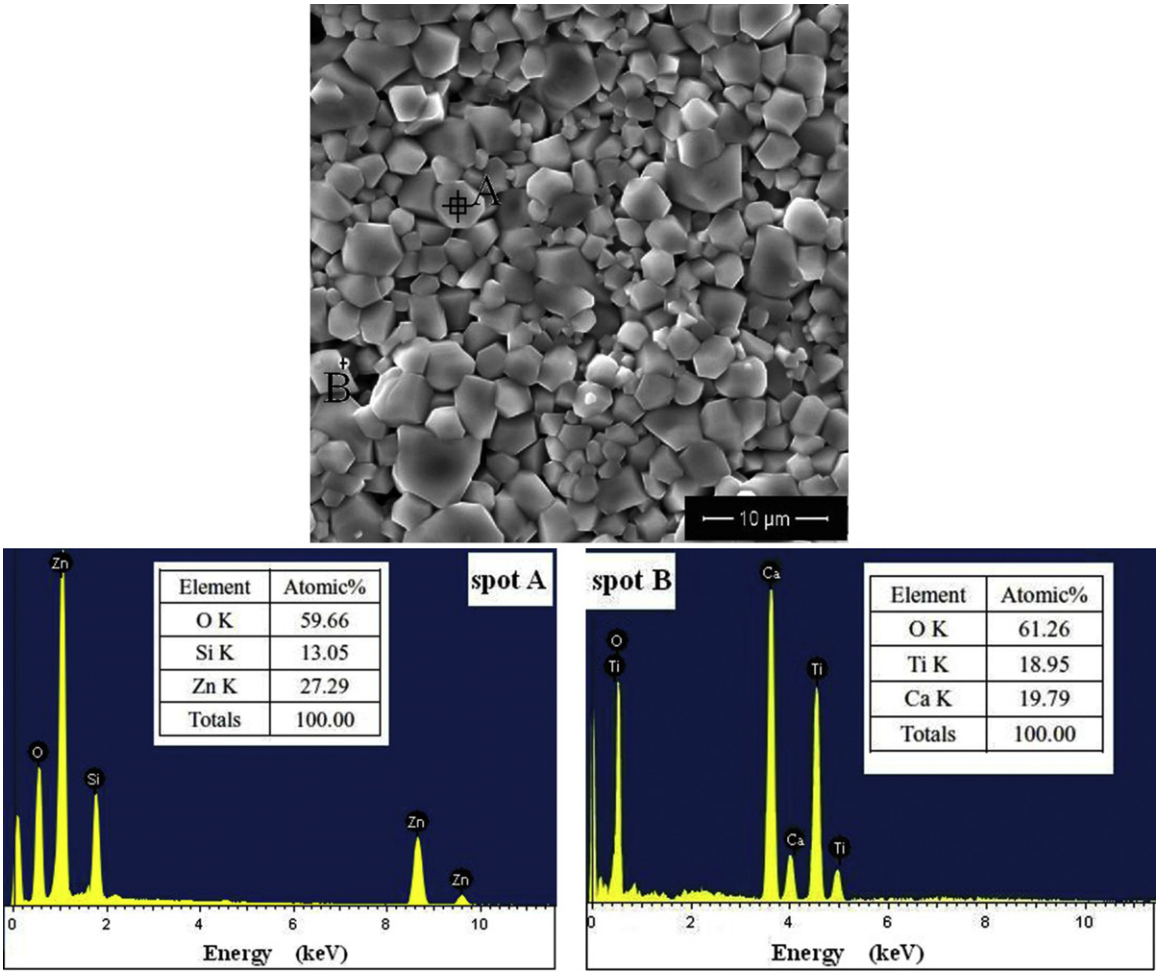

Fig. 7. EDS analysis of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ samples with 4.0 wt% Li_2CO_3–H_3BO_3 additives sintered at 950 °C for 3 h in air.

indicated that the samples with 4.0 wt% Li_2CO_3–H_3BO_3 which were sintered above 950 °C were very dense as shown in Fig. 6(c)–(e).

Fig. 9(b) and (c) shows the permittivity ε_r and $Q \times f$ values of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramic samples with 2.0–6.0 wt% Li_2CO_3–H_3BO_3 sintered at 900–1000 °C for 3 h in air. It can be seen that the permittivity ε_r and density showed a similar trend with the increasing temperature and Li_2CO_3–H_3BO_3 content, because densification of the ceramics plays an important role in influencing the permittivity ε_r [30]. Fig. 9(c) shows that the $Q \times f$ values first increased and then decreased with the increase of the Li_2CO_3–H_3BO_3 content and sintering temperature, and the $Q \times f$ values of the ceramic samples reached a maximum value at 950 °C

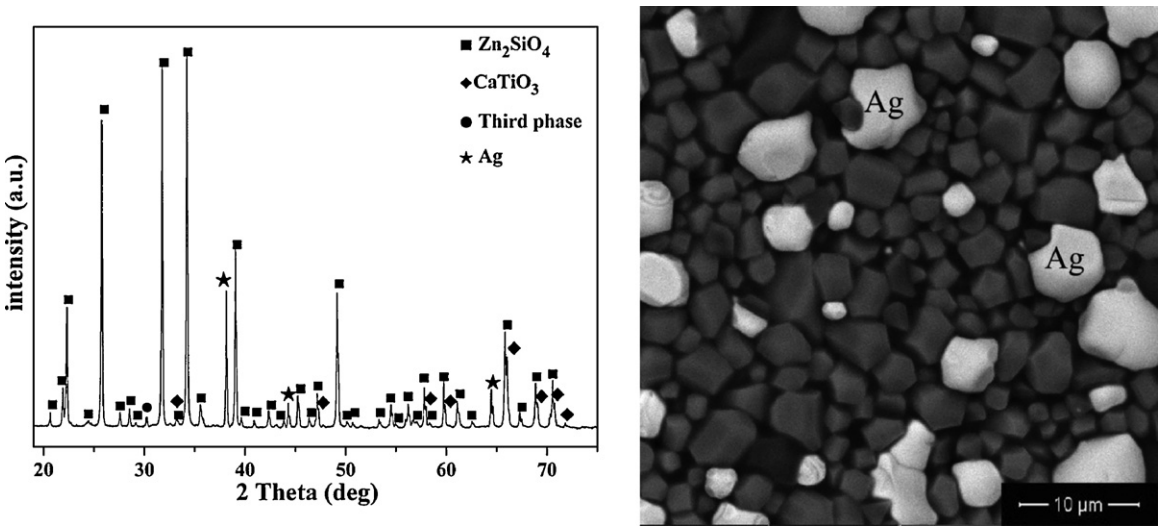

Fig. 8. XRD pattern and BSEM micrograph of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 4.0 wt% Li_2CO_3–H_3BO_3 and 20.0 wt% Ag addition sintered at 950 °C for 3 h in air.

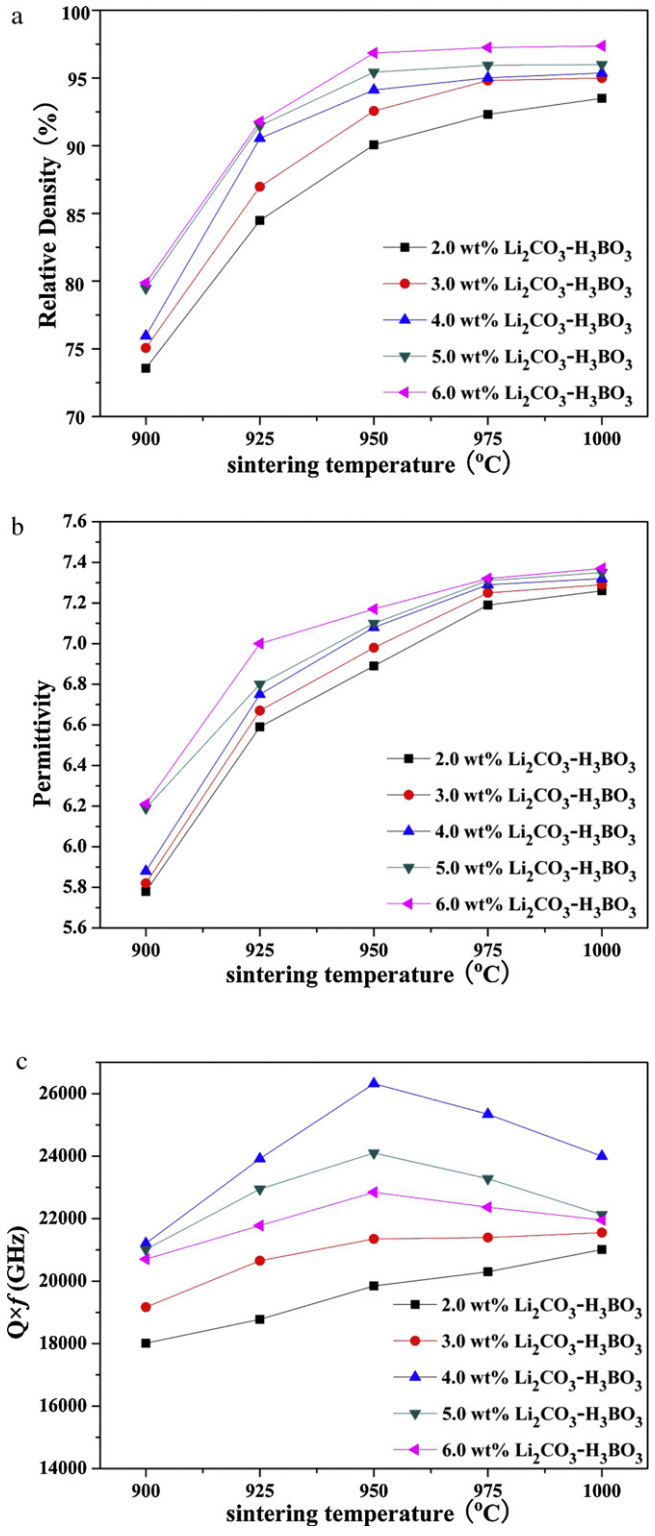

Fig. 9. (a) The relative density, (b) the permittivity and (c) the $Q \times f$ of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 2.0, 3.0, 4.0, 5.0 and 6.0 wt% of Li_2CO_3–H_3BO_3 additives sintered at 900 °C, 925 °C, 950 °C, 975 °C and 1000 °C for 3 h in air.

when 4.0 wt% Li_2CO_3–H_3BO_3 was added. As the grains became more and more dense with increasing Li_2CO_3–H_3BO_3 content as shown in Fig. 5(a)–(e), the $Q \times f$ values were expected to increase. However, the $Q \times f$ values decreased when the Li_2CO_3–H_3BO_3 content was more than 4.0 wt%. It might be related to abnormal growth of the grains, as their grain sizes were as large as 10 μm as shown in

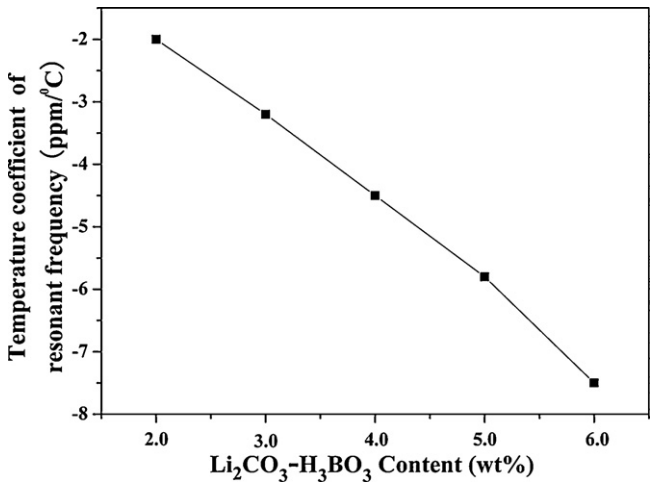

Fig. 10. The τ_f of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 2.0, 3.0, 4.0, 5.0 and 6.0 wt% of Li_2CO_3–H_3BO_3 addition sintered at 950 °C for 3 h in air.

Fig. 5(d) and (e). Therefore, the addition of 4.0 wt% of Li_2CO_3–H_3BO_3 is the optimum way that we found to enhance the microwave dielectric properties of the material. The effectiveness of sintering aids was very much affected by the sintering temperatures [31]. According to Fig. 9(c), the $Q \times f$ values of the sample doped with 4.0 wt% Li_2CO_3–H_3BO_3 reached the maximum when the sintering temperature was as high as 950 °C. It also may be because the samples had high density and homogenous grain size at 950 °C. From XRD results in Fig. 4 and SEM observations in Fig. 6(a)–(e), phases and peak intensity remained almost unchanged for the compounds with 4.0 wt% of Li_2CO_3–H_3BO_3 regardless of sintering temperature, but densification and grain sizes increased with the increasing sintering temperature. According to the classical dielectric theory, the Q value should increase as the grain size increases, because a reduction in the number of grain boundaries per unit volume would result in a material with a lower loss [32]. In fact, the samples had the highest $Q \times f$ value when the average grain sizes of the samples was about 2–5 μm as shown in Figs. 5(c) and 6(c). Alford et al. [32] also observed similar results for alumina, and in our previous work [33], $ZnTiNb_2O_8$ with $BaCu(B_2O_5)$ display similar behavior which is in contrast to classical theory. This may be as a result of the interaction of many factors, such as grain size, porosity or presence of liquid-phase, which made it difficult to give definitive remarks on grainsize-loss relationships [32]. Therefore, we cannot make practical use of the grainsize–loss relationships in this case [33].

Fig. 10 shows the τ_f value of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics with 2.0–6.0 wt% Li_2CO_3–H_3BO_3 additives sintered at 950 °C for 3 h in air. The τ_f decreased slightly with an increase of Li_2CO_3–H_3BO_3 content, changing from −2.0 ppm/°C to −7.5 ppm/°C. The third phase was observed when the Li_2CO_3–H_3BO_3 addition was doped to $(1-x)Zn_2SiO_4 - xCaTiO_3$ ceramic samples, but not observed in pure $(1-x)Zn_2SiO_4 - xCaTiO_3$ samples. The slight decrease in τ_f with the increase of Li_2CO_3–H_3BO_3 content may be related to this third phase. A low temperature coefficient of the resonant frequency ($\tau_f \sim 0$ ppm/°C) is one of the most important properties for microwave dielectric materials in LTCC applications. We have achieved $\tau_f = -4.5$ ppm/°C when $0.95Zn_2SiO_4$–$0.05CaTiO_3$ compounds were doped with 4.0 wt% of Li_2CO_3–H_3BO_3.

4. Conclusions

In this work, the temperature coefficient of resonant frequency (τ_f) of Zn_2SiO_4 was adjusted by doping with $CaTiO_3$ at 1250 °C, and Li_2CO_3–H_3BO_3 additives were used as sintering

aids to effectively lower the sintering temperature of the material. The temperature coefficient of resonant frequency (τ_f) was found to be dependent on phase constitutions, which is in turn related to the amount of $CaTiO_3$ present. When $x = 0.05$, the τ_f of $(1-x)Zn_2SiO_4 - xCaTiO_3$ approached 0 ppm/°C. The dielectric properties of $0.95Zn_2SiO_4$–$0.05CaTiO_3$ samples with Li_2CO_3–H_3BO_3 additives sintered at 900–1000 °C were investigated, and the results indicated that the behaviors of the permittivity and $Q \times f$ were associated with the amount of Li_2CO_3–H_3BO_3 and the sintering temperature. As a result, the sintering temperature of the ceramics was effectively reduced to 950 °C from above 1250 °C and the temperature coefficient of resonant frequency (τ_f) was successfully modified to −4.5 ppm/°C with good $Q \times f$. Addition of 4.0 wt% Li_2CO_3–H_3BO_3 to $0.95Zn_2SiO_4$–$0.05CaTiO_3$ ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r = 7.1$, $Q \times f = 26{,}300$ GHz ($f = 7.1$ GHz) and $\tau_f = -4.5$ ppm/°C. Moreover, the material was compatible with Ag electrodes, making it a very promising candidate material for LTCC applications.

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