Available online at www.sciencedirect.com
SciVerse ScienceDirect
Journal of the European Ceramic Society 32 (2012) 883–890
www.elsevier.com/locate/jeurceramsoc

Low-temperature sintered $MgWO_4$–$CaTiO_3$ ceramics with near-zero temperature coefficient of resonant frequency

Mei Guo, Gang Dou, Shuping Gong, Dongxiang Zhou *

Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, PR China

Received 3 October 2011; received in revised form 26 October 2011; accepted 27 October 2011
Available online 21 November 2011

Abstract

The phases, microstructure, composition analysis and microwave dielectric properties of $(1-x)MgWO_4$–$xCaTiO_3$ ceramics with Li_2CO_3–$4H_3BO_3$ additions prepared by solid-state reaction method have been investigated by using X-ray diffraction, scanning electron microscopy, energy-dispersive spectroscopy and advantest network analyzer. The τ_f of $(1-x)MgWO_4$–$xCaTiO_3$ were dependent on phase constitutions. The microwave dielectric properties of $0.91MgWO_4$–$0.09CaTiO_3$ ceramics with Li_2CO_3–$4H_3BO_3$ were characterized, the results indicated that the ε_r and $Q \times f$ were associated with the sintering temperature and amount of Li_2CO_3–$4H_3BO_3$. The sintering temperature of ceramics was reduced to 950 °C from 1150 °C and τ_f was modified to 0 ppm/°C with good $Q \times f$. Addition of 5.0 wt% Li_2CO_3–$4H_3BO_3$ in $0.91MgWO_4$–$0.09 CaTiO_3$ ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r = 15.5$, $Q \times f = 20{,}780$ GHz ($f = 7.1$ GHz) and $\tau_f \sim 0$ ppm/°C. The material has a chemical compatibility with silver, making it a very promising candidate materials for LTCC applications.

Keywords: Powders-solid state reaction; X-ray methods; Traditional ceramics; Dielectric properties; LTCC

1. Introduction

The various modules in electronic packaging, especially in wireless and microwave applications, is developing rapidly, which has resulted in an increasing demand for microwave dielectric materials. With the explosive growth of high frequency wireless communication technology, the dielectric components are greatly in need of realizing miniaturization and integration. Low-temperature co-fired ceramics (LTCC) have been widely investigated as a means of miniaturizing microwave devices.[1] For dielectric materials that are used in LTCC technology, the key characteristic properties required are: (i) low sintering temperature ($T \leq 950$ °C), to use cheaper and highly conductive internal electrode metals, (ii) high dielectric permittivity ($\varepsilon_r > 10$), to reduce the size of microwave devices, (iii) high quality factor ($Q \times f > 10{,}000$ GHz), to minimize dielectric losses and (iv)low-temperature coefficient of resonant frequency (-6 ppm/°C $\leq \tau_f \leq +6$ ppm/°C). From the practical application, dielectric materials should possess a near-zero temperature coefficient of resonant frequency ($\tau_f \sim 0$) for thermally stable electronic devices.[2,3] Thus, the search for microwave dielectric materials with both stable temperature coefficient of resonant frequency and higher quality factor is essential in ceramic material research.[4] $MgWO_4$ ceramics are proposed as good candidates for microwave dielectric materials because of their suitable ε_r of 13.5, a high $Q \times f$ value of 69,000 GHz and a τ_f of -58 ppm/°C.[5] However, the large negative τ_f of -58 ppm/°C could put constraints on their application in LTCC. Consequently, the near-zero τ_f ($\tau_f \sim 0$) is expected to prevent the disturbance from temperature variation. Since the $MgWO_4$ ceramics have negative τ_f values, temperature compensated dopants with large positive τ_f values should be added. $CaTiO_3$ has a τ_f of +859 ppm/°C, $\varepsilon_r = 162$ and $Q \times f = 1290$ GHz,[6,7] therefore it is logical to speculate that the $(1-x)MgWO_4$–$xCaTiO_3$ composite ceramics have adjustable τ_f values. However, the sintering temperatures of $MgWO_4$ and $CaTiO_3$ are 1050 °C and 1400 °C respectively, which are too high to LTCC.[5–7]

Generally, three methods are used to reduce the sintering temperature of dielectric ceramics: low melting-temperature oxides or glass addition, chemical processes and the usage of small particle sized starting materials.[8–11] Chemical synthesis

---

* Corresponding author. Tel.: +86 27 8754 5167; fax: +86 27 8754 5167.
E-mail address: dxzhou@mail.hust.edu.cn (D. Zhou).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.10.042

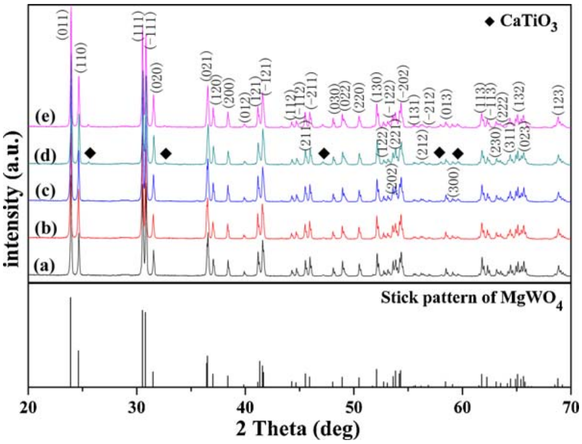

Fig. 1. XRD patterns of (1−x)MgWO$_4$−xCaTiO$_3$ ceramics (a) $x = 0.06$, (b) $x = 0.07$, (c) $x = 0.08$, (d) $x = 0.09$ and (e) $x = 0.10$ sintered at 1,150 °C for 3 h in air.

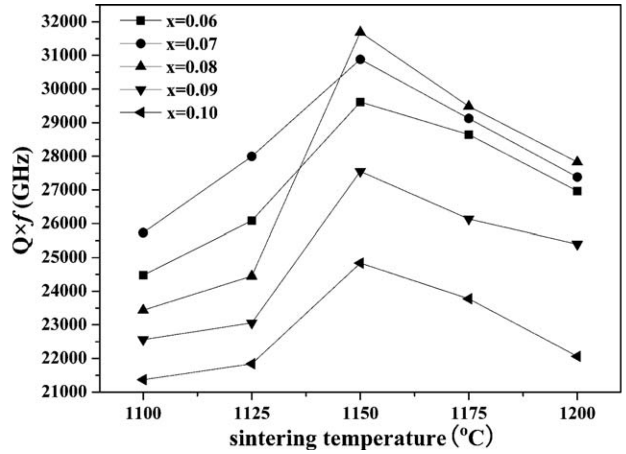

Fig. 2. The Q×f of (1−x)MgWO$_4$−xCaTiO$_3$ ($x = 0.06$, 0.07, 0.08, 0.09 and 0.10) ceramics sintered at 1,100 °C, 1,125 °C, 1,150 °C, 1,175 °C and 1,200 °C for 3 h in air.

complicates the manufacturing procedures and increases the production cost. However, the addition of low melting point materials or glass for liquid-phase sintering has been known to be the most effective and inexpensive way to achieve dense sintered ceramics at low sintering temperature.

In this work, attempts were made to achieve a near-zero τ_f of MgWO$_4$ by doping CaTiO$_3$, and to lower the sintering temperature below 950 °C by doping Li$_2$CO$_3$–4H$_3$BO$_3$. The $(1 - x)$MgWO$_4$–xCaTiO$_3$ composite ceramics should have adjustable τ_f values. In $(1 - x)$MgWO$_4$–xCaTiO$_3$ composite ceramics ($x = 0.09$), the sintering temperature was lowered below 950 °C by adding Li$_2$CO$_3$–4H$_3$BO$_3$ as the sintering aids. The effects of densification, crystalline phases and microstructure on the microwave dielectric properties of MgWO$_4$ ceramics were investigated. The excellent microwave dielectric properties of $\varepsilon_r = 15.5$, $Q \times f = 20{,}780$ GHz ($f = 7.1$ GHz) and $\tau_f \sim 0$ ppm/°C were obtained by adding 5.0 wt% Li$_2$CO$_3$–4H$_3$BO$_3$ in 0.91MgWO$_4$–0.09CaTiO$_3$ ceramics sintered at 950 °C for 4 h in air.

Table 1
The theoretical and the measured permittivity ε_r and τ_f of $(1 - x)$MgWO$_4$–xCaTiO$_3$ ($x = 0.06$, 0.07, 0.08, 0.09, and 0.10) ceramics sintered at 1150 °C for 3 h in air. ε_r (theo.): theoretical permittivity; ε_r (meas.): measured permittivity. τ_f (theo.): theoretical τ_f value; τ_f (meas.): measured τ_f value.

Compounds	ε_r (theo.)	ε_r (meas.)	τ_f (theo.) (ppm/°C)	τ_f (meas.) (ppm/°C)
$x = 0.06$	15.4	14.4	−9.0	−13.5
$x = 0.07$	15.8	14.5	−0.7	−6.2
$x = 0.08$	16.1	14.7	+7.5	0
$x = 0.09$	16.5	14.9	+15.8	+9.0
$x = 0.10$	16.9	15.0	+24.1	+15.2

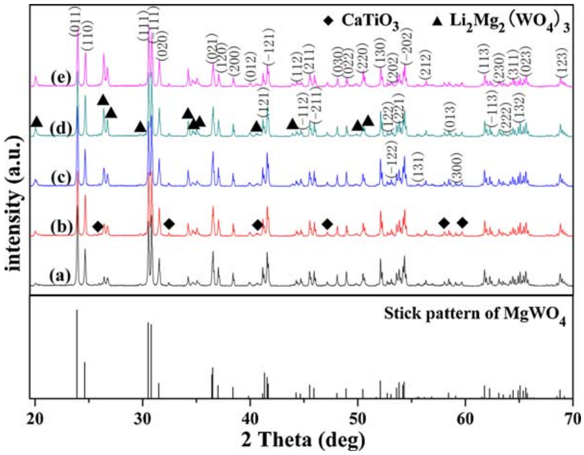

Fig. 3. XRD patterns of 0.91MgWO$_4$−0.09CaTiO$_3$ ceramics with (a) 3.0 wt%, (b) 4.0 wt%, (c) 5.0 wt%, (d) 6.0 wt% and (e) 7.0 wt% Li$_2$CO$_3$-4H$_3$BO$_3$ addition sintered at 950 °C for 4 h in air.

2. Experimental procedure

MgWO$_4$ and CaTiO$_3$ compounds were individually synthesized by conventional solid-state reaction method using reagent-grade powders: MgO (99.0%), WO$_3$ (99.6%), CaCO$_3$

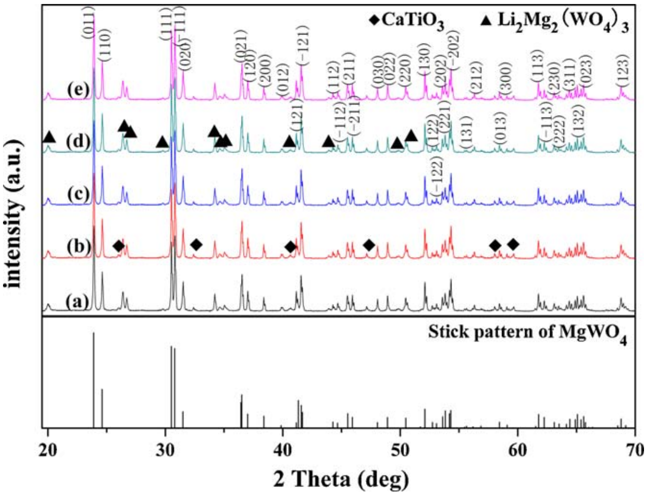

Fig. 4. XRD patterns of 0.91MgWO$_4$−0.09CaTiO$_3$ ceramics with 5.0 wt% Li$_2$CO$_3$−4H$_3$BO$_3$ addition sintered at (a) 900 °C, (b) 925 °C, (c) 950 °C, (d) 975 °C and (e) 1,000 °C for 4 h in air.

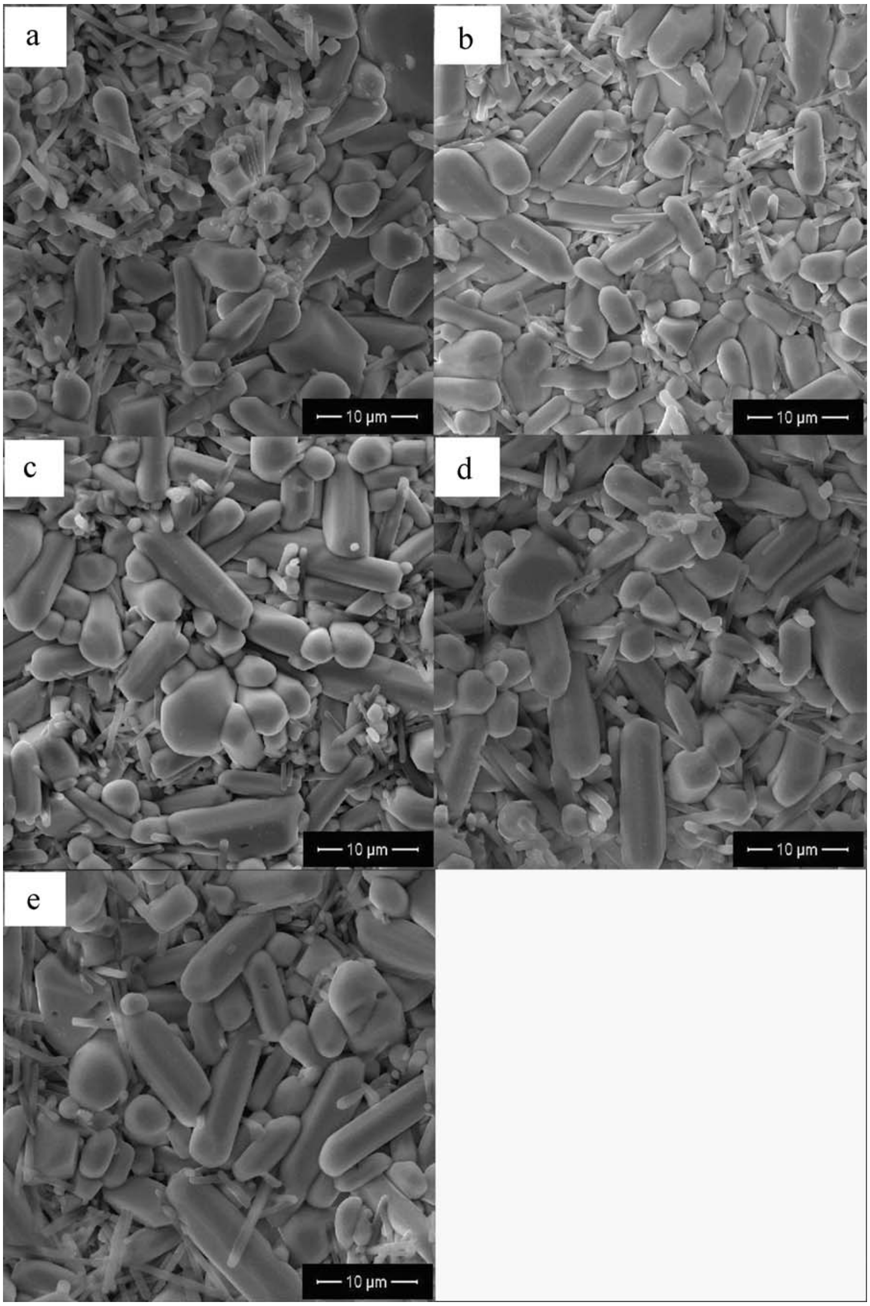

Fig. 5. SEM micrographs of $0.91MgWO_4-0.09CaTiO_3$ ceramics with (a) 3.0 wt%, (b) 4.0 wt%, (c) 5.0 wt%, (d) 6.0 wt% and (e) 7.0 wt% $Li_2CO_3-4H_3BO_3$ addition sintered at 950 °C for 4 h in air.

(99.5%) and TiO_2 (99.6%). For the preparation of $MgWO_4$ and $CaTiO_3$ compounds, the high-purity raw materials were weighed according to the desired stoichiometry, 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 1000 °C for 4 h and 1100 °C for 2 h in air. The compounds were individually re-milled for 4 h according to the desired composition: $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$, 0.07, 0.08, 0.09 and 0.10) and $0.91MgWO_4$–$0.09CaTiO_3$ doped with 3.0, 4.0, 5.0, 6.0, and 7.0 wt% Li_2CO_3–$4H_3BO_3$. Then the mixed powders were dried, granulated and pressed into several disk-type pellets (25 mm in diameter and 15 mm in thickness). The $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$–0.10) pellets were sintered at 1100–1200 °C for 3 h and the $0.91MgWO_4$–$0.09CaTiO_3$ pellets containing 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ were sintered at 900–1000 °C for 4 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

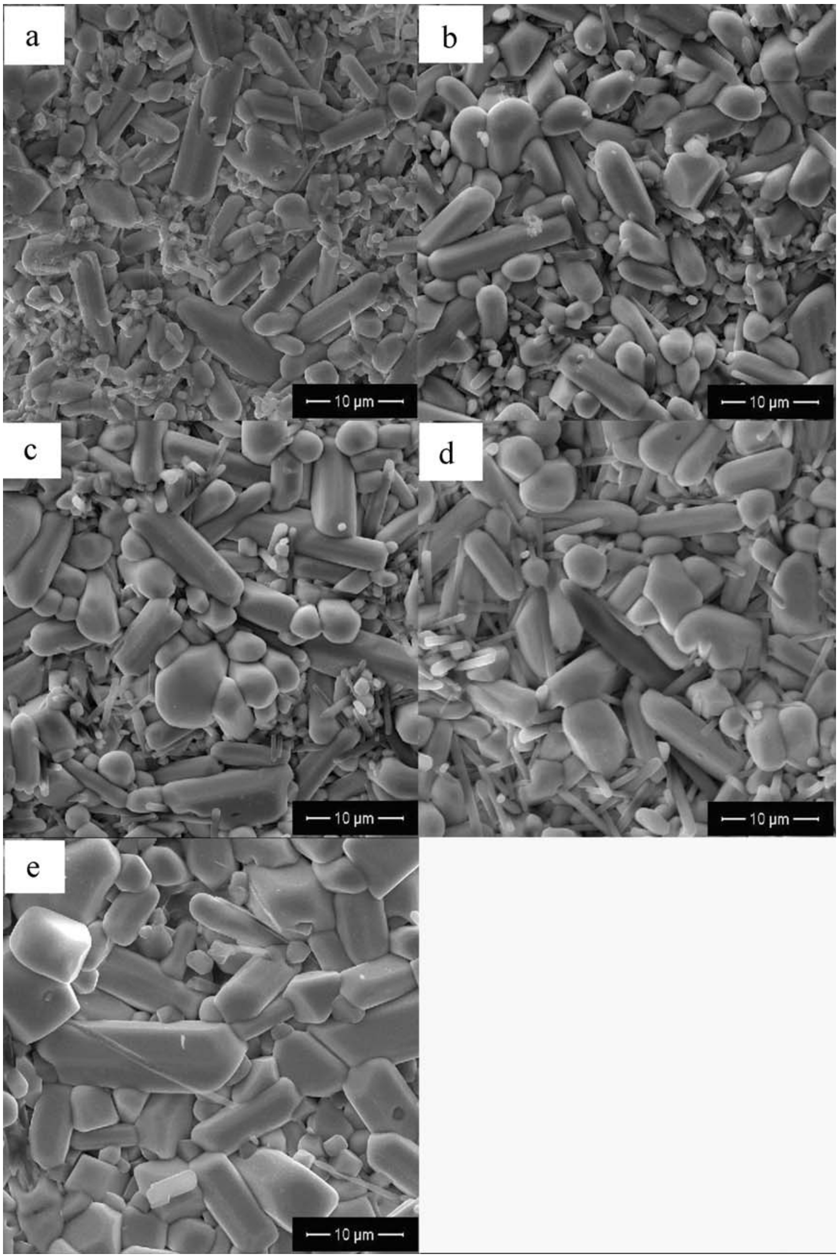

Fig. 6. SEM micrographs of $0.91MgWO_4-0.09CaTiO_3$ ceramics with 5.0 wt% $Li_2CO_3-4H_3BO_3$ addition sintered at (a) 900 °C, (b) 925 °C, (c) 950 °C, (d) 975 °C and (e) 1,000 °C for 4 h in air.

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.[12,13] The temperature coefficient of resonant frequency (τ_f) was also measured by the same method using Eq. (1)

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

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 $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$–0.10) ceramic samples at the fixed temperature of 1150 °C for 3 h in air. All the compounds exhibit the mixture of $MgWO_4$ (JCPDS #73-0562) and $CaTiO_3$ (JCPDS #22-0153). It is speculated that in the $(1-x)MgWO_4$–$xCaTiO_3$ system, the $CaTiO_3$ phase could coexist with $MgWO_4$ phase. $MgWO_4$ belongs to the monoclinic crystal system (space group R2/c (no. 13)), and the lattice parameters are $a = 4.6864$ Å, $b = 5.6755$ Å, $c = 4.9284$ Å.[14] $CaTiO_3$ belongs to the orthorhombic crystal system (space group Pnma (no. 62)), and the lattice parameters are $a = 5.4405$ Å, $b = 7.6436$ Å, $c = 5.3812$ Å.[15] And, it was observed that the intensities of diffraction peaks of the $CaTiO_3$ phase increased gradually with the increase in proportion of $CaTiO_3$ in the compounds.

Fig. 2 shows the $Q \times f$ values of $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$–0.10) ceramics sintered at 1100–1200 °C for 3 h in air. The $Q \times f$ values of the $(1-x)MgWO_4$–$xCaTiO_3$ compounds were in the range between 21,000 and 32,000 GHz. The $Q \times f$ values of the samples neither increased nor decreased with the increasing $CaTiO_3$ content, they showed a sharp increase followed by a pattern of decrease. In other words, in the $(1-x)MgWO_4$–$xCaTiO_3$ composite ceramics, Fig. 2 shows that there was no direct relation between the $Q \times f$ value and the composition. It is a fact that, many factors are thought to affect the microwave dielectric loss, and the loss include the intrinsic and the extrinsic losses. The intrinsic losses are dependent on the crystal structure and mainly caused by lattice vibration modes,[16] while the extrinsic losses are associated with many factors, such as impurities, microstructural defects, densification or porosity, grain size, second phase, presence of liquid-phase or grain boundaries.[17] Therefore, our results may happen because of influence from the intrinsic factors could be shielded by the extrinsic ones. However, when the sintering temperature increased, the $Q \times f$ value of ceramic samples first increased to a maximum value at 1150 °C and then decreased at higher temperature.

Table 1 shows that the theoretical and the measured permittivity ε_r and τ_f values of $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$–0.10) ceramics sample sintered at 1150 °C for 3 h. The theoretical permittivities of the composite ceramic were obtained from the well-known Lichtenecker empirical rule:[18]

$$lg\varepsilon = V_1\, lg\ \varepsilon_1 + V_2\, lg\, \varepsilon_2 \tag{2}$$

where V_1 and V_2 are the volume fractions of $MgWO_4$ and $CaTiO_3$; ε_1 and ε_2 are the permittivity of the $MgWO_4$ and $CaTiO_3$ ceramic respectively. The measured permittivity ε of the $(1-x)MgWO_4$–$xCaTiO_3$ composite ceramic were consistent with the theoretical value (Table 1). It increased from 14.4 to 15.0 as the x value increased from 0.06 to 0.1.

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

$$\tau_f = -\alpha_L - \frac{1}{2\tau_e} \tag{3}$$

The τ_ε is defined as the following:

$$\tau_\varepsilon = V_1\, \tau_{\varepsilon 1} + V_2\, \tau_{\varepsilon 2} \tag{4}$$

Therefore, according to the Lichtenecker empirical rule, the mixing rule of τ_f value could be described as:

$$\tau_f = V_1\, \tau_{f1} + V_2\, \tau_{f2} \tag{5}$$

where V_1 and V_2 are the volume fraction of $MgWO_4$ and $CaTiO_3$, τ_{f1} and τ_{f2} are the τ_f values of the $MgWO_4$ and $CaTiO_3$ phase, respectively. The theoretical τ_f values of the $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$–0.10) composite ceramics

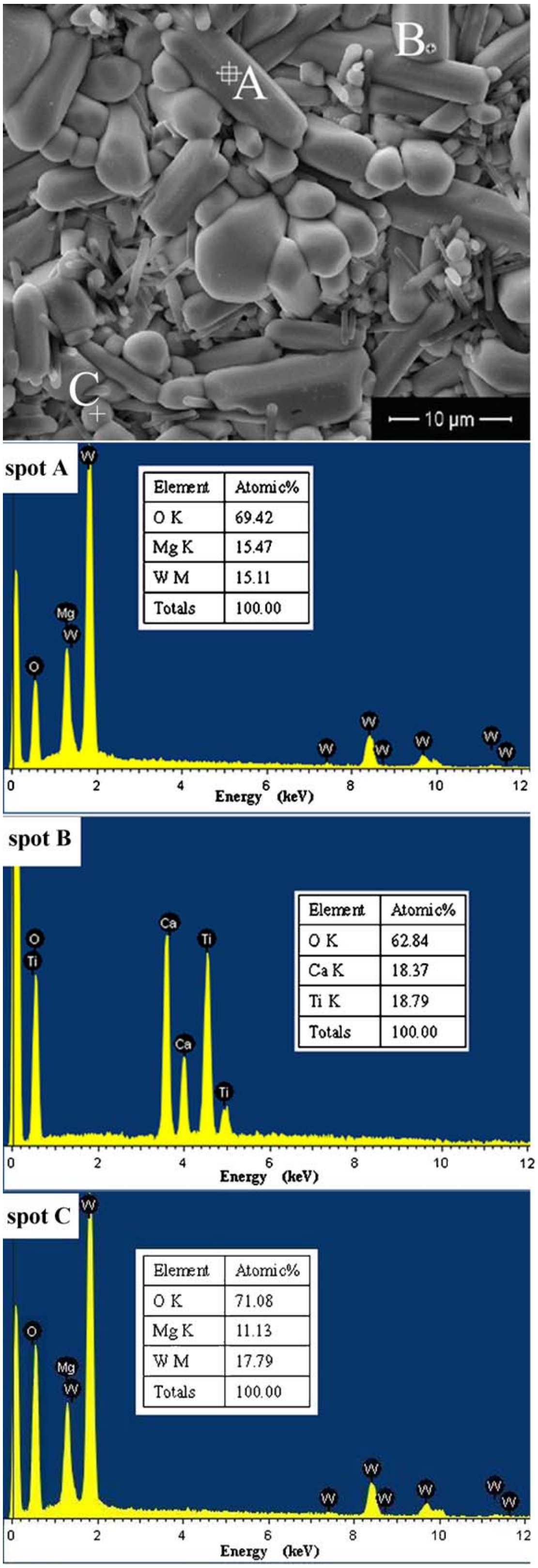

Fig. 7. EDS analysis of $0.91MgWO_4-0.09CaTiO_3$ samples with 5.0 wt% $Li_2CO_3-4H_3BO_3$ addition sintered at 950 °C for 4h in air.

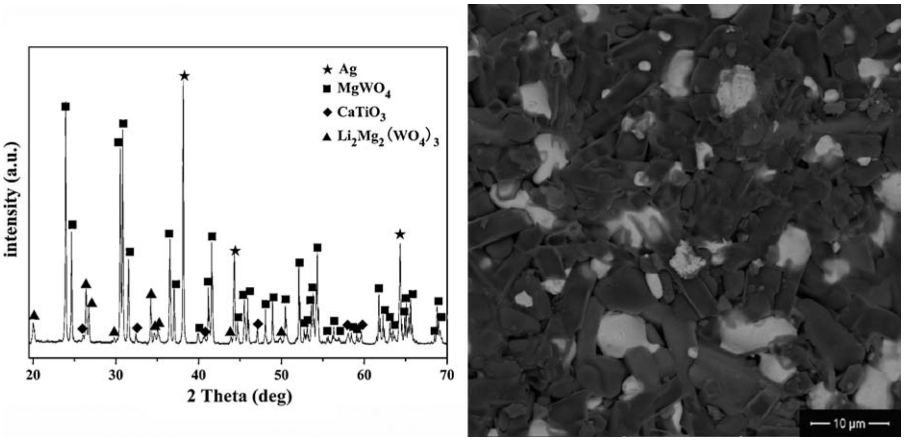

Fig. 8. XRD pattern and BSEM micrograph of $0.91MgWO_4-0.09CaTiO_3$ ceramics with 5.0 wt% $Li_2CO_3-4H_3BO_3$ and 20.0 wt% Ag addition sintered at 950 °C for 4 h in air.

were calculated by using the Eq. (5) and the results were also listed in Table 1. $CaTiO_3$ has a higher τ_f of +859 ppm/°C, while $MgWO_4$ has a lower τ_f of −58 ppm/°C. The theoretical τ_f value of the sample increased with the increasing $CaTiO_3$ content. Similarly, the measured τ_f value of the sample also increased with increasing $CaTiO_3$ content, and the change of the theoretical and measured τ_f value displayed similar behavior. When the $CaTiO_3$ increased from 6.0 mol% to 10.0 mol%, the measured τ_f value of the sample increased from −13.5 ppm/°C to 15.2 ppm/°C. A zero τ_f value ($\tau_f = 0$ ppm/°C) could be obtained in $0.92MgWO_4$–$0.08CaTiO_3$ compounds at 1150 °C for 3 h in air. To further decrease the sintering temperature of the microwave dielectric ceramic $(1-x)MgWO_4$–$xCaTiO_3$, small contents of Li_2CO_3–$4H_3BO_3$ were doped into the ceramics samples. In general, low melting-temperature addition or glass has a negative τ_f.[3,15] For the $(1-x)MgWO_4$–$xCaTiO_3$ ceramic system doped with Li_2CO_3–$4H_3BO_3$, hence, in order to obtain a closer zero τ_f, a slight higher x than 0.08, $x = 0.09$ mol may be suitable.

Fig. 3 depicts XRD patterns of $0.91MgWO_4$–$0.09CaTiO_3$ ceramics sample with 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 950 °C for 4 h. Fig. 4 shows XRD patterns of $0.91MgWO_4$–$0.09CaTiO_3$ ceramics with 5.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 900–1000 °C for 4 h in air. For the $0.91MgWO_4$–$0.09CaTiO_3$ ceramics sample doped with Li_2CO_3–$4H_3BO_3$ addition, $MgWO_4$ (JCPDS #73-0562) and $CaTiO_3$ (JCPDS #22-0153) remained noticeable. A new phase of $Li_2Mg_2(WO_4)_3$ (JCPDS #44-0665) appeared compared to the pure $(1-x)MgWO_4$–$xCaTiO_3$ ($x = 0.06$–0.10) ceramic samples. Moreover, according to the intensity of the peaks in Fig. 3, it can be observed that the content of $Li_2Mg_2(WO_4)_3$ increased with the increasing Li_2CO_3–$4H_3BO_3$ addition. However, the XRD patterns of the $0.91MgWO_4$–$0.09CaTiO_3$ ceramic did not show significant change with the sintering temperatures in the range of 900–1000 °C.

The SEM micrographs of the $0.91MgWO_4$–$0.09CaTiO_3$ ceramics with 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 950 °C for 4 h in air are shown in Fig. 5(a)–(e). The SEM micrographs of $0.91MgWO_4$–$0.09CaTiO_3$ samples with 5.0 wt% Li_2CO_3–$4H_3BO_3$ sintered at 900–1000 °C for 4 h are presented in Fig. 6(a)–(e). Fig. 5 shows that the grains became enlarged with the increasing Li_2CO_3–$4H_3BO_3$ additive. However, the grains first gradually became denser with the increase of Li_2CO_3–$4H_3BO_3$ additive from 3.0 wt% to 5.0 wt%, and then the densification slightly decreased with the Li_2CO_3–$4H_3BO_3$ additive of more than 6.0 wt%. Fig. 6 shows that the grains became enlarged and denser with the increasing sintering temperature. These might affect the density of the samples, and the discussion of sample density will be discussed later. Three types of grains were present in the specimens of Li_2CO_3–$4H_3BO_3$ doped $(1-x)MgWO_4$–$xCaTiO_3$ ceramics.

In order to analyze the composition, the EDS of $0.91MgWO_4$–$0.09CaTiO_3$ samples with 5.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 950 °C for 4 h is shown in Fig. 7. The results indicated the ratio of Mg:W:O of rod-shaped grain (spot A) is about 1:1:4, which was consistent with the composition of $MgWO_4$. Robert pullar and co-workers also observed $MgWO_4$ with similar shape.[19] The ratio of Ca:Ti:O of spot B is about 1:1:3, which was also consistent with the composition of $CaTiO_3$. It seems impossible to detect lithium and boron ions using an EDS detector, resulting in restricted detection of Li_2CO_3–$4H_3BO_3$. The ratio of Mg:W:O of spot C is approximate 2:3:12, which was consistent with the composition of the $Li_2Mg_2(WO_4)_3$. These corroborated the results of XRD that the samples contained phases of $MgWO_4$, $CaTiO_3$ and $Li_2Mg_2(WO_4)_3$.

The XRD pattern and BSEM micrograph of $0.91MgWO_4$–$0.09CaTiO_3$ samples with 5.0 wt% Li_2CO_3–$4H_3BO_3$ addition and 20.0 wt% Ag addition sintered at 950 °C for 4 h are shown in Fig. 8. All the major peaks of Ag were observed in the XRD pattern and no phase of silver compounds present. In the BSEM micrograph, pale Ag particles had a uniform distribution in the ceramic and did not react with it. Therefore, the composite exhibits chemical compatibility with Ag electrodes and the co-firing of Ag electrodes with the $0.91MgWO_4$–$0.09CaTiO_3$ ceramics is possible.

Fig. 9(a) shows the relative density of $0.91MgWO_4$–$0.09CaTiO_3$ ceramic samples with 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 900–1000 °C for 4 h in air. The relative density of the samples increased with

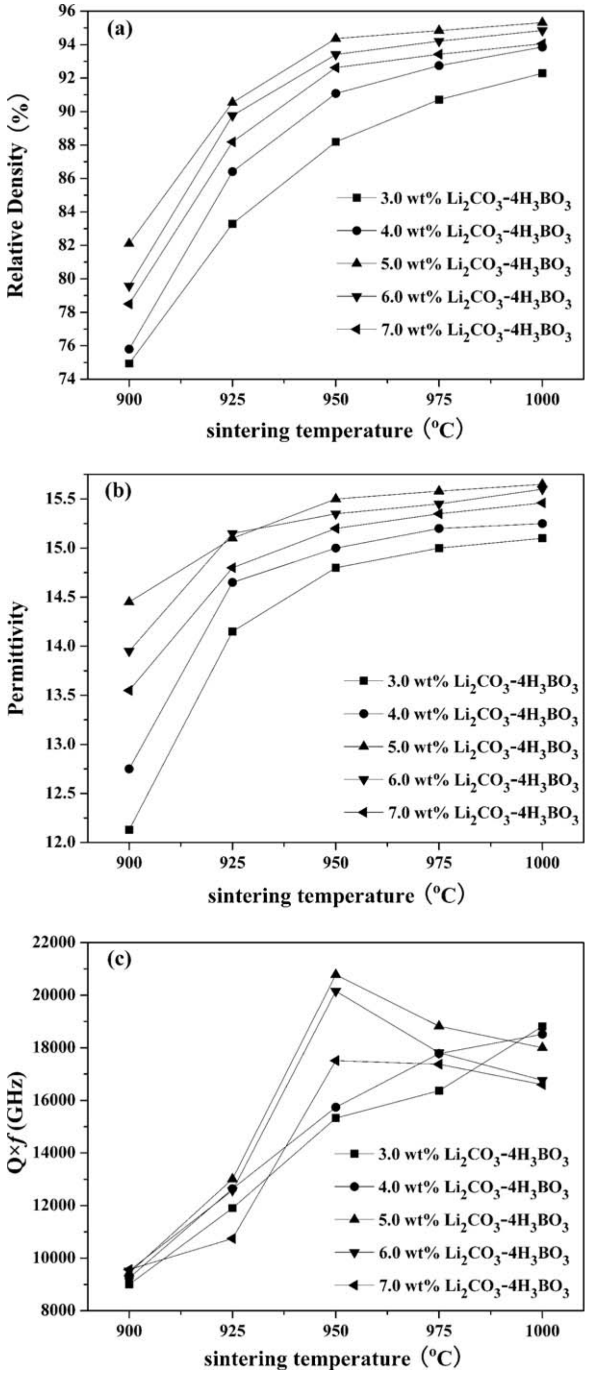

Fig. 9. (a) The relative density, (b) the permittivity and (c) the Q×f of $0.91MgWO_4-0.09CaTiO_3$ ceramics with 3.0, 4.0, 5.0, 6.0 and 7.0 wt% $Li_2CO_3-4H_3BO_3$ addition sintered at 900 °C, 925 °C, 950 °C, 975 °C and 1,000 °C for 4 h in air.

the increasing sintering temperature due to the decrease in porosity and the enlargement of grain sizes. When the sintering temperature was above 950 °C ($T \geq 950$ °C), the density of samples doped with 3.0 wt% or 4.0 wt% Li_2CO_3–$4H_3BO_3$ had not yet saturated, and had clearly increased. However, when the content of Li_2CO_3–$4H_3BO_3$ was more than 5.0 wt%, the densities of samples were almost invariable and at over 92% of the theoretical density, which indicated that the samples with 5.0 wt% Li_2CO_3–$4H_3BO_3$ sintered above 950 °C ($T \geq 950$ °C) were very dense and reached saturation refer to Fig. 6(c)–(e) above. However, the relative density slightly decreased with the Li_2CO_3–$4H_3BO_3$ content of more than 6.0 wt%. As shown in Fig. 5(c)–(e) above, the SEM showed that densification slightly decreased with the Li_2CO_3–$4H_3BO_3$ additive of more than 6.0 wt%. Moreover, XRD pattern (Fig. 3) showed the content of $Li_2Mg_2(WO_4)_3$ increased with the increasing Li_2CO_3–$4H_3BO_3$ addition. The theoretical density of $Li_2Mg_2(WO_4)_3$ is 5.68 g/cm^3,which was lower than that of $MgWO_4$ with 6.89 g/cm^3. Consequently, excessive Li_2CO_3–$4H_3BO_3$ addition (6.0 wt% or 7.0 wt%) could slightly decrease the relative density. These might directly affect the microwave dielectric properties of the $(1-x)MgWO_4$–$xCaTiO_3$ compounds.

Fig. 9(b) show the permittivity ε_r values of $0.91MgWO_4$–$0.09CaTiO_3$ ceramic samples with 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 900–1000 °C for 4 h in air. It can be seen that the permittivity ε_r of the samples increased with the increasing sintering temperature. However, the permittivity showed a sharp increase followed by a pattern of decrease with the increase of the Li_2CO_3–$4H_3BO_3$, and it reached the maximum when the content of the Li_2CO_3–$4H_3BO_3$ is 5.0 wt%. The change of permittivity and density displayed similar behavior. Hence, the permittivity ε_r was significantly affected by the density.

Fig. 9(c) shows the $Q \times f$ values of $0.91MgWO_4$–$0.09CaTiO_3$ ceramic samples with 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 900–1000 °C for 4 h in air. The $Q \times f$ values of the samples with 3.0 wt% or 4.0 wt% Li_2CO_3–$4H_3BO_3$ increased with the increasing sintering temperature. This might be related to the density of the samples. As shown in Fig. 9(a) and (c), both the density and the $Q \times f$ values of $0.91MgWO_4$–0.09 $CaTiO_3$ samples with 3.0 wt% or 4.0 wt% Li_2CO_3–$4H_3BO_3$ kept increasing and they reached the maximum value at 1000 °C. Furthermore, when the Li_2CO_3–$4H_3BO_3$ content exceeded 5.0 wt%, it was noticed that the $Q \times f$ values first increased and then decreased with the increasing sintering temperature, and reached a maximum at 950 °C , as shown in Fig. 9 (c). When the sintering temperature is below 950 °C ($\leq$950 °C), the increase of $Q \times f$ value of samples doped with 5.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ might be related to the increase of density of the sample, as shown in Fig. 9(a). However, when the sintering temperature exceeded 950 °C, the $Q \times f$ value of $0.91MgWO_4$–$0.09CaTiO_3$ ceramics slightly decreased with increasing sintering temperature. This could be related to the abnormal grain growth due to extremely high sintering temperature. The grain which was sintered at 1000 °C was as larger as 15 μm. Robert pullar and co-workers also found that the poor $Q \times f$ was because of discontinuous grain growth.[19] Moreover, for 5.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ doped samples, the $Q \times f$ value of $0.91MgWO_4$–$0.09CaTiO_3$ ceramics at above 950 °C ($T \geq 950$ °C) decreased with increasing Li_2CO_3–$4H_3BO_3$ content. A maximum $Q \times f$ value of 20,780 GHz was obtained for $0.91MgWO_4$–$0.09CaTiO_3$ ceramics with 5.0 wt% of Li_2CO_3–$4H_3BO_3$ sintered at 950 °C. As mentioned above, the extrinsic losses were associated with many factors: densification or porosity, grain size, as well as

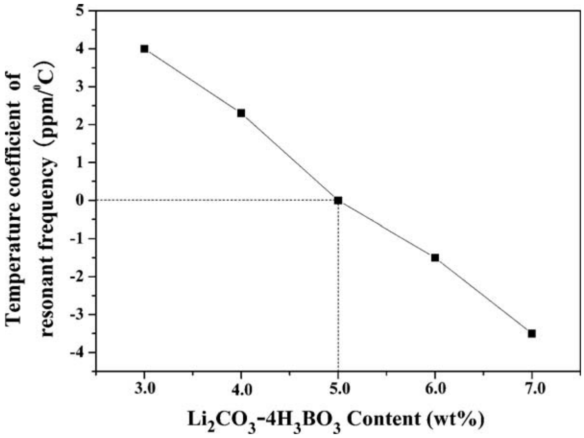

Fig. 10. The τ_f of $0.91MgWO_4-0.09CaTiO_3$ ceramics with 3.0, 4.0, 5.0, 6.0 and 7.0 wt% of $Li_2CO_3-4H_3BO_3$ addition sintered at 950 °C for 4h in air.

imperfections in the crystal structure caused by impurities.[19] When the content of Li_2CO_3–$4H_3BO_3$ increased (more than 5.0 wt%), the incorporation of the Li_2CO_3–$4H_3BO_3$ into the $0.91MgWO_4$–$0.09CaTiO_3$ compounds might increase, resulting in the increase of imperfections in the crystal structure. Moreover, the decrease in $Q \times f$ could be related to the decrease of density as a result of the present of excessive $Li_2Mg_2WO_4$, which may lead to the decrease of $Q \times f$ value.

Fig. 10 shows the τ_f value of $0.91MgWO_4$–$0.09CaTiO_3$ ceramics with 3.0–7.0 wt% Li_2CO_3–$4H_3BO_3$ addition sintered at 950 °C for 4 h in air. It can be seen the τ_f shifted slightly towards the negative direction with increasing Li_2CO_3–$4H_3BO_3$ content. The τ_f value was tuned from +4.0 ppm/°C to −3.5 ppm/°C. The $Li_2Mg_2(WO_4)_3$ phase was observed when the Li_2CO_3–$4H_3BO_3$ addition was doped to $0.91MgWO_4$–$0.09CaTiO_3$ ceramic samples, but not observed in pure $(1-x)MgWO_4$–$xCaTiO_3$ samples, and the content of $Li_2Mg_2(WO_4)_3$ increased with the increasing Li_2CO_3–$4H_3BO_3$ addition. The slight decrease in τ_f with the increase of Li_2CO_3–$4H_3BO_3$ content could be related to the $Li_2Mg_2(WO_4)_3$ phase. When the Li_2CO_3–$4H_3BO_3$ content was 5.0 wt%, the $\tau_f \sim 0$ was obtained. It is a fact that one of the most important properties is the low temperature coefficient of the resonant frequency ($\tau_f \sim 0$ ppm/°C) when considering dielectric materials for these LTCC applications. When the Li_2CO_3–$4H_3BO_3$ content is 5.0 wt%, the $\tau_f \sim 0$ ppm/°C was successfully obtained for the $0.91MgWO_4$–0.09 $CaTiO_3$ ceramics.

4. Conclusions

In the work, the temperature coefficient of resonant frequency (τ_f) of $MgWO_4$ was adjusted by doping $CaTiO_3$ at 1150 °C, and Li_2CO_3–$4H_3BO_3$ additives were used as sintering aids to effectively lower its sintering temperature. The temperature coefficient of resonant frequency (τ_f) was found to be dependent on phase constitutions, which was related to the amount of $CaTiO_3$. When $x = 0.08$, the τ_f of $(1-x)MgWO_4$–$xCaTiO_3$ was near to 0 ppm/°C. The dielectric properties of $0.91MgWO_4$–$0.09CaTiO_3$ samples with Li_2CO_3–$4H_3BO_3$ additives sintered in 900–1000 °C were investigated, and the results indicated that the behaviors of the permittivity and $Q \times f$ were associated with the sintering temperature and the amount of Li_2CO_3–$4H_3BO_3$. As a result, the sintering temperature of ceramics was effectively reduced to 950 °C from 1150 °C and temperature coefficient of resonant frequency (τ_f) was successfully modified to 0 ppm/°C with good $Q \times f$. Addition of 5.0 wt% Li_2CO_3–$4H_3BO_3$ in $0.91MgWO_4$–$0.09CaTiO_3$ ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r = 15.5$, $Q \times f = 20{,}780$ GHz ($f = 7.1$ GHz) and $\tau_f \sim 0$ ppm/°C. Moreover, the material has a chemical compatibility with silver, making it a promising and an ideal candidate materials for LTCC applications.

References

1. Sasikala TS, Suma MN, Mohanan P, Pavithran C, Sebastian MT. Forsterite-based ceramic-glass composites for substrate applications in microwave and millimeter wave communications. *J Alloys Compd* 2008;**461**:555–9.
2. Wersing W. Microwave ceramics for resonators and filters. *Curr Opin Solid State Mater Sci* 1991;**1**:715–31.
3. Sebastian MT. *Dielectric materials for wireless communication*. Oxford: Elsevier Science; 2008.
4. Surendran KP, Santha N, Mohanan P, Sebastian MT. Temperature stable low loss ceramic dielectrics in $(1-x)$ $ZnAl_2O_4$–$xTiO_2$ system for microwave substrate applications. *Eur Phys J B* 2004;**41**:301–6.
5. Yoon SH, Kim DW, Cho SY, Hong KS. Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds. *J Eur Ceram Soc* 2006;**26**:2051–4.
6. Subramanian V, Murthy VRK, Viswanathnan B. Microwave dielectric properties of certain simple alkaline earth perovskite compounds as a function of tolerance factor. *Jpn J Appl Phys* 1997;**36**:194–7.
7. Wise PL, Reaney IM, Lee WE, Price TJ, Iddles DM, Cannell DS. Structure-microwave property relations in $(Sr_{1-x}Ca_x)_{n+1}Ti_nO_{3n+1}$. *J Eur Ceram Soc* 2001;**1**:1723–6.
8. Huang CL, Chen YB. Microwave properties of B_2O_3-doped $Nd(Mg_{1/2}Ti1_{/2})O_3$–$CaTiO_3$ dielectric resonators at microwave frequency. *Mater Lett* 2006;**60**:198–202.
9. Wu SP, Luo JH, Cao SX. Microwave dielectric properties of B_2O_3-doped $ZnTiO_3$ ceramics made with sol–gel technique. *J Alloys Compd* 2010;**502**:147–52.
10. Lim JB, Jeong YH, Nguyen NH, Nahm S, Paik JH, Kim JH, et al. Low temperature sintering of the $Ba_2Ti_9O_{20}$ ceramics using B_2O_3/CuO and $BaCu(B_2O_5)$ additives. *J Eur Ceram Soc* 2007;**27**:2875–9.
11. Kim MH, Lim JB, Kim JC, Nahm S. Synthesis of $BaCu(B_2O_5)$ ceramics and their effect on the sintering temperature and microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics. *J Am Ceram Soc* 2006;**89**:3124–8.
12. Hakki BW, Coleman PD. *IEEE Trans Micro Theory Tech* 1960;**8**:402–10.
13. Courtney WE. *IEEE Trans Micro Theory Tech* 1970;**18**:476–85.
14. Filipenko OS, Pobedimskaya EA, Ponomarev VI, Belov NV. *Kristallografiya* 1968;**13**:1073–5.
15. Winchell AN. Elements of optical mineralogy. *J Wiley* 1951;**2**:92.
16. Gurevich VL, Tagantsev AK. Intrinsic dielectric loss in crystals. *Adv Phys* 1991;**40**:719–67.
17. Penn SJ, Alford NM, Templeton A, Wang X, Xu M, Reece M, et al. Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. *J Am Ceram Soc* 1997;**80**:1885–8.
18. Wu YG, Zhao XH, Li F, Fan ZG. Evaluation of mixing rules for dielectric constants of composite dielectrics by MC-FEM calculation on 3D cubic lattice. *J Electroceram* 2003;**11**:227–39.
19. Pullar RC, Farrah S, Alford NM. $MgWO_4$, $ZnWO_4$, $NiWO_4$ and $CoWO_4$ microwave dielectric ceramics. *J Eur Ceram Soc* 2007;**27**:1059–63.