Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 3459–3468
www.elsevier.com/locate/jeurceramsoc

Microwave dielectric properties and microstructures of $Ba_2Ti_9O_{20}$-based ceramics with $3ZnO–B_2O_3$ addition

Ying-Chieh Lee[a,*], Wen-Hsi Leeb, Fuh-Sheng Shieuc

[a] *Electronic Ceramics Research Center, Yageo, Kaohsiung 811, Taiwan*
[b] *Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan*
[c] *Department of Materials Engineering, National Chung Hsing University, Taichung 402, Taiwan*

Received 24 May 2004; received in revised form 16 August 2004; accepted 27 August 2004
Available online 28 October 2004

Abstract

Microwave dielectric properties of the $Ba_2Ti_9O_{20}$-based ceramics with ZnBO addition up to 3 wt.% and containing ZrO_2 were investigated at the sintering temperatures ranging from 900 to 960 °C. Effects of the ZnBO addition on the bulk density, microstructure, and dielectric properties of the $Ba_2Ti_9O_{20}$-based ceramics at microwave frequency were elucidated. X-ray diffraction (XRD) results show the presence of five crystalline phases, $Ba_2Ti_9O_{20}$, $BaZr(BO_3)_2$, $BaTi_4O_9$, $BaZrO_3$ and Zn_2SiO_4 in the sintered ceramics, depending upon the amount of ZnBO addition. Optimum dielectric properties were obtained for the $Ba_2Ti_9O_{20}$-based ceramic with 1 wt.% ZnBO addition and sintered in air at 940 °C for 2 h, having the dielectric properties: $Q = 1137$ ($Q \times f = 8300$), ε_r value = 27.3, and $\tau_f = 2.5$ ppm/°C. In addition, to understand well the effect of the $BaZr(BO_3)_2$ phase on the dielectric properties of $Ba_2Ti_9O_{20}$-based ceramics, the $BaZr(BO_3)_2$ composition was synthesised from individual $BaCO_3$, ZrO_2 and B_2O_3 powders. Plots of dielectric loss versus sintering temperatures show a linearity, and ranges from 0.85 (at 1080 °C) to 0.08 (at 1250 °C). However, the dielectric constant does not increase with increasing sintering temperature, and its value is maintained at 11–13.

Keywords: $Ba_2Ti_9O_{20}$; $BaZr(BO_3)_2$; $ZnO–B_2O_3$; Dielectric constant; Dielectric loss; Temperature coefficient of resonant frequency

1. Introduction

Many researches have been focusing on developing dielectric materials recently with high quality factor ($Q \times f$), high dielectric constant (ε_r) and zero temperature coefficient of resonant frequency (τ_f) for the use of dielectric resonator and microwave device substrate.[1,2] In general, these dielectrics have to be sintered at high temperatures (1300–1650 °C).[3,4,5] However, the sintering temperatures for those microwave dielectrics were too high to apply the low melting point of silver as internal conductors. To reduce the sintering temperature of dielectric materials, glass addition, chemical processing and small particle sizes of the starting materials are generally useful.[6,7] The liquid-phase sintering by adding glass or other low melting point material is generally known to be the most effective and the least expansive way of achieving high density of sintered ceramics. However, the microwave dielectric properties of dielectric resonators were also deeply affected by the liquid sintering temperature due to the development of microstructure at low sintering temperature or the reaction between host material and additive.

A commercially available dielectric powder from Ferro America, which, according to the XRD analysis, is mainly composed of the $Ba_2Ti_9O_{20}$ phase, is used as the host material in this study. It was reported that the TiO_2-rich compounds of the barium titanate-based ceramics with Ti/Ba = 4 and 4.5, i.e. $BaTi_4O_9$, and $Ba_2Ti_9O_{20}$, have superior dielectric properties for microwave resonator applications.[4,6] The dielectric constants and quality factors of the two ceramics are 34.6, 39.8, and 5720, 8000, with temperature coefficients of 14.2 and 2, respectively. Typically microwave dielectric resonators are

* Corresponding author.
E-mail address: y.c.lee@yageo.com (Y.-C. Lee).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.09.007

Table 1
The compositions of host ULF280 ceramic powder

Component	TiO_2	BaO	ZrO_2	ZnO	SrO	HfO_2	B_2O_3	SiO_2
Content (wt.%)	49.9	27.8	12.0	5.0	0.07	0.18	1.5	3.5

required to have a high dielectric constant (ε_r) >35, a low-dielectric loss or high quality factor Q (1/tan δ) >3000, and a near-zero temperature coefficient of resonant frequency (τ_f).[8] According to this powder compositions, 12 wt.% ZrO_2 content was found by XRF analyzing as Table 1 listed. As in the case of pure $BaTiO_3$, three ferroelectric phase transitions can also be observed in $Ba(Ti_{1-y}Zr_y)O_3$ solid solutions for Zr concentrations $y < 0.13$: (1) rhombohedral–orthorhombic, (2) orthorhombic–tetragonal, and (3) tetragona–cubic.[9] It was reported that the increasing of Zr results in reducing the average grain size, decreasing of the dielectric constant (ε_r) and also maintaining low and stable leakage current. This is because Zr^{4+} ion (0.087 nm) has larger ionic size than Ti^{4+} (0.068 nm),[10] and Zr^{4+} is chemically more stable than Ti^{4+}.[11,12]

In this paper, the $Ba_2Ti_9O_{20}$-based ceramics with ZnBO addition is reported. The dielectric properties of $Ba_2Ti_9O_{20}$-based ceramics were characterised. The relation between crystalline phases and microstructures of $Ba_2Ti_9O_{20}$-based ceramics was also investigated. In addition, the dielectric properties of the $BaZr(BO_3)_2$ ceramics also was studied, it was synthesised by conventional solid-state methods from individual $BaCO_3$, ZrO_2 and B_2O_3 powders.

2. Experimental procedures

2.1. The preparation of $Ba_2Ti_9O_{20}$-based ceramic with $3ZnO–B_2O_3$ glass addition

The starting materials contain the ULF280 powder received from the Ferro America and the $3ZnO–B_2O_3$ glass. They are mixed and ball-milled in deionised water with ϕ 2 mm zirconia balls for 10 h. The $3ZnO–B_2O_3$ glass was prepared by weighing the starting materials of ZnO and B_2O_3 (Fluka Chemicals Inc. Germany) as well as mixing them for 1 h in a polyethylene pot mill using agate balls. The mixed powders were calcined in a platinum crucible at 940 °C for 1 h. The calcined powders were pulverised with deionised water in the ball mill for 8 h ($D_{50} \cong 0.6$ μm), dried and screened through a 100 mesh sieve. The melting point of the $3ZnO–B_2O_3$ phase is 957 °C, as given by the phase diagram from Yu and Leonov,[13] and it was added into the ULF280 powder by the amounts of 1 wt.%, 2 wt.%, and 3 wt.%, respectively. After drying, the ball-milled powders were pressed uniaxially into pellets in a steel die. Sintering of the pellets was carried out in air at temperatures ranging from 900 °C to 960 °C for a period of 2 h.

2.2. The preparation of $BaZr(BO_3)_2$ ceramic

Samples of $BaZr(BO_3)_2$ were prepared by conventional solid-state methods from individual high-purity oxide powder (>99.9%): $BaCO_3$ (Hayashi Chemical Industries, Japan), ZrO_2 (Janssen Chemica, Japan), and B_2O_3 (Fluka Chemicals Inc., Germany). The starting materials were mixed according to the desired stoichiometry and ground in deionised water for 6 h in a ball-mill with ϕ 2 mm zirconia balls, and the mean particle size (D_{50}) is 0.5 μm. The powders were calcined in air at 900 °C for 3 h after milling. Then the calcined powders were milled again for 6 h. The mean particle size is about 0.4 μm. After drying, the powders were pressed uniaxially into pellets in a steel die. Sintering of these pellets were carried out at temperatures between 1080 °C and 1250 °C for a period of 2 h.

2.3. Characteristics analysis

The crystalline phases of the sintered ceramics were identified by X-ray diffraction pattern analysis (XRD, Philips X'Pert-MPD) using Cu Kα radiation for 2θ from 10° to 60°. The diffraction spectra were collected at a scan rate of 2.5°/min. Microstructural observation of the sintered ceramics was performed by scanning electron microscopy (SEM, Jeol. JEL-6400 Japan) equipped with energy-dispersive spectroscopy (EDS). The bulk density of the sintered pellets were measured by the Archimedes method. The particle size was measured by particle size analyzer (Malvern, Mastersizer 2000, UK). The sintering shrinkage of these samples was measured at a heating rate of 5 °C/min in air by a thermo-mechanical analyzer (TMA, Netzsch DIL 402C, Germany). The dielectric characteristics at microwave frequencies (7.25–9.31 GHz) were measured by the Hakki–Coleman dielectric resonator method, where a cylindrically shaped specimen is positioned between two plates.[14] An HP8719C network analyzer was used for the microwave measuring system. The dielectric properties were calculated from the frequency of the TE_{011} resonant mode. For convenience, the $Q \times f$ factor was used for evaluating the loss quality, where f is the resonant frequency. Composition of the host ULF280 ceramic powder was analysed by X-ray fluorescence and the result is given in Table 1.

3. Results and discussion

3.1. Phase evolution in the sintered $Ba_2Ti_9O_{20}$-based ceramics

In the $BaO–TiO_2$ binary system, many intermediate phases, $BaTi_3O_7$, $BaTi_5O_{11}$, $BaTi_4O_9$, and $Ba_2Ti_9O_{20}$, are present in the TiO_2-rich side of the phase diagram, as reported by Rase and Roy.[15] The X-ray diffraction spectra from the as-sintered host ULF280 ceramic and those with different

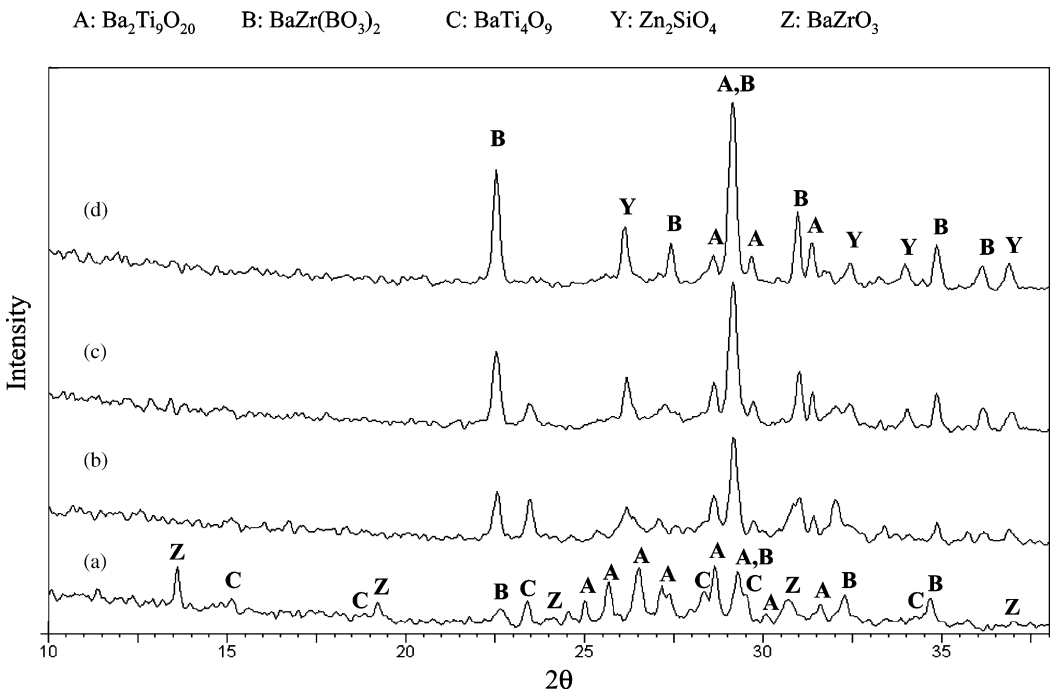

Fig. 1. X-ray diffraction spectra of (a) the host ULF280 ceramic and the ceramics with (b) 1 wt.%, (c) 2 wt.%, and (d) 3 wt.% additions and sintered at 940 °C for 2 h.

amounts of ZnBO addition are given in Fig. 1. For the host ceramic sintered at 940 °C shown in Fig. 1(a), it is obtained that there are three crystalline phases, $Ba_2Ti_9O_{20}$, $BaTi_4O_9$, $BaZrO_3$ present in the specimen. Among them, it has been reported that the $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ phases have high dielectric constants, low-dielectric losses, and low-temperature coefficients of resonant frequency,[4,8,16] and are considered to be the potential ceramic materials suitable for dielectric resonators at microwave frequency.

The XRD spectra for the ULF280 ceramics with 1 wt.%, 2 wt.% and 3 wt.% ZnBO additions sintered at 940 °C are shown in Fig. 1(b)–(d), respectively. Compared with the host material, it is noted that the intensity of the $Ba_2Ti_9O_{20}$ phase decreases, and the $BaTi_4O_9$ and $BaZrO_3$ phases are nearly disappeared in the sintered ceramic with 1 wt.% ZnBO addition. On the contrary, the $BaZr(BO_3)_2$ phase increases and a new phase, Zn_2SiO_4, is observed in the specimen. As the amounts of ZnBO addition increase above 2 wt.%, the con-

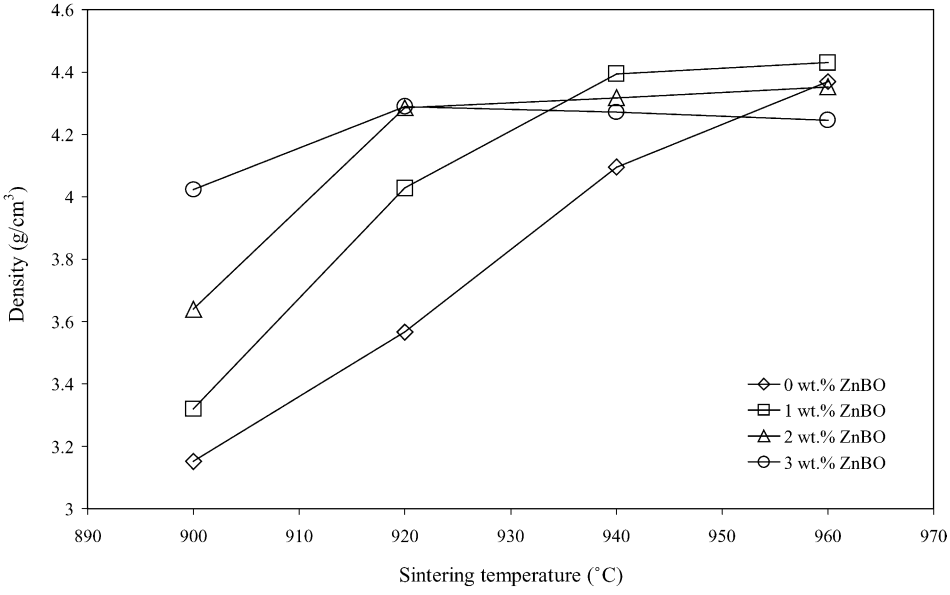

Fig. 2. Bulk density vs. sintering temperature of the ULF280 ceramics with ZnBO additions.

tent of the two crystalline phases, $BaZr(BO_3)_2$ and Zn_2SiO_4, is increased noticeably. As indicated in the XRD spectra of Fig. 1, the (1 0 4) peak of the $BaZr(BO_3)_2$ phase at 28.5° is very strong for the ceramics with 3 wt.% ZnBO addition. The results suggest that the addition of ZnBO glass phase has enhanced the formation of $BaZr(BO_3)_2$ and Zn_2SiO_4 phases in the $Ba_2Ti_9O_{20}$-based ceramics.

3.2. Physical properties of the sintered $Ba_2Ti_9O_{20}$-based ceramics

As described in the experimental, the ULF280 ceramics with different amounts of ZnBO addition were sintered in air at temperatures ranging from 900 °C to 960 °C for 2 h, and the particle size of the starting powder was controlled at 0.5 ± 0.1 μm. Fig. 2 shows the bulk density of the ULF280 ceramic pellets as a function of the sintering temperature. It can be seen that in general the density of the sintered ceramics increases with the sintering temperature. The extent of the increasing rate, however, depends on the amount of the ZnBO additions. Theoretical density of the $Ba_2Ti_9O_{20}$ ceramic is reported to be 4.61 g/cm^3.[17] The ULF280 ceramics with 1 wt.% ZnBO addition can be sintered to over 96% of the theoretical density, i.e. 4.43 g/cm^3, at 940 °C for 2 h in air. The bulk density remains much the same as the sintering temperature is further increased, e.g. 960 °C.

The influence of the sintering temperature on the bulk density of the ULF280 ceramics is, however, dependent upon the amounts of the ZnBO addition. For example, the saturation temperature, at which the bulk density of the sintered ceramics reaches 93% of the theoretical value, for the 2 wt.% and 3 wt.% ZnBO added ceramics is lowered to 920 °C. Similar results are reported by other investigators[18] that the ZnBO glass phase assists in the densification of the $Ba_2Ti_9O_{20}$ dielectrics through liquid-phase sintering. It is also interesting to note that the sintered ceramic with highest bulk density is not associated with the ceramic having highest ZnBO addition. In fact, the addition of 1 wt.% ZnBO to the ULF280 ceramics that were sintered at 940 °C and 960 °C has resulted in the highest density among the sintered specimens.

SEM micrographs of the ZnBO added specimens sintered at 940 °C are shown in Fig. 3(a)–(c), for the amount of 1 wt.%, 2 wt.%, and 3 wt.% ZnBO addition, respectively. The microstructure of the sintered ceramics shows a lot of change, in which a dendrite phase was increased with ZnBO increasing. According to the XRD spectra of Fig. 1, the composition of dendrite phase should be $BaZr(BO_3)_2$ since the intensity of $BaZr(BO_3)_2$ peak was increased significantly with ZnBO increasing. The dendrite phase was further analysed by energy-dispersive spectroscopy (EDS) and the result is given in Fig. 4. Compared with the matrix phase, it is obtained that the dendrite phase has higher signal intensities in Zr, Ba, and Ti, along with Si and Zn, in which the X-ray energies of the Ba *L* lines and Ti *K* lines are superimposed. The X-ray diffraction analysis in the previous section has clearly shown that higher ZnBO addition has enhanced the formation of the $BaZr(BO_3)_2$ phase. It is therefore believed that the dendrites are composed of $BaZr(BO_3)_2$ phase, in which it may surrounded by the Zn_2SiO_4 phase. Further study of the microstructure using transmission electron microscopy would be useful to figure out the issue.

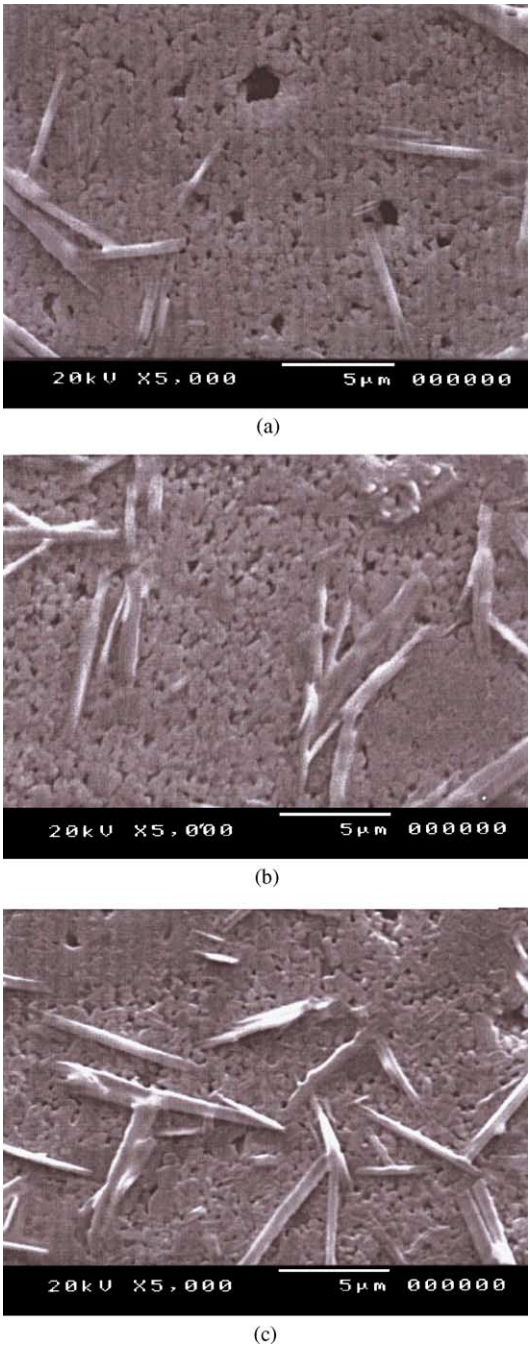

Fig. 3. SEM micrographs of the ULF280 ceramics with (a) 1 wt.%, (b) 2 wt.%, and (c) 3 wt.% ZnBO additions and sintered at 940 °C for 2 h.

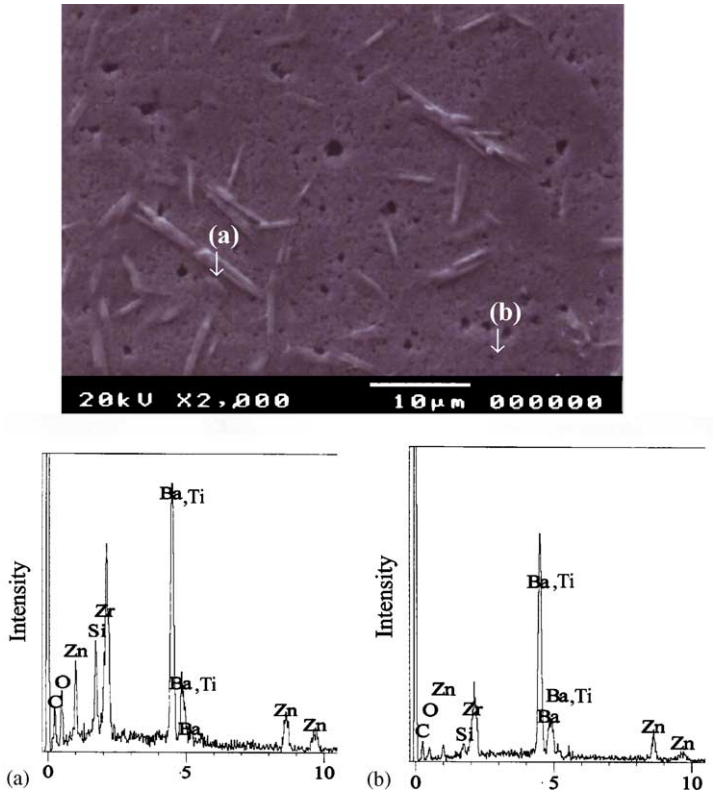

Fig. 4. Microstructure of the ULF280 ceramic with 3 wt.% ZnBO addition and sintered at 940 °C for 2 h, in which the compositions of (a) dendrites and (b) the matrix were analysed by energy-dispersive spectroscopy.

Fig. 5 shows the linear dimension change of the sintered ceramic pellets during the firing process using dilatometric measurement. Additions of a small amount of the ZnBO glass result in the dilatational curves that have a lower sintering temperature and shrinkage rate, as displayed in Fig. 5(b)–(d). The undoped sample shrinks from 926.8 °C as Fig. 5(a) shows, whereas the ZnBO-doped samples shrunk at a lower temperature. The 3 wt.% ZnBO-doped sample reached the onset point of shrinkage at 846.9 °C. Apparently, the ZnBO formed a liquid phase at low temperature, which promoted sintering.

3.3. Dielectric properties of the sintered $Ba_2Ti_9O_{20}$-based ceramics

The dielectric constant of the ULF280 ceramics was measured at 1 MHz, and the result is shown in Fig. 6. Similar to the bulk density versus sintering temperature curves in Fig. 2,

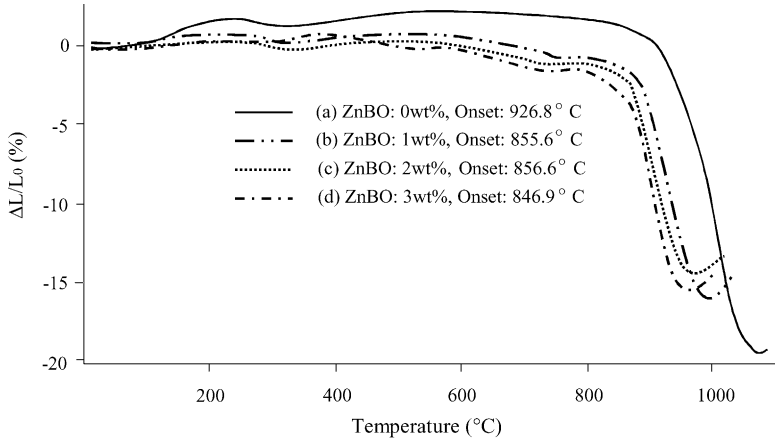

Fig. 5. Dilatometric curves of the ULF280 ceramics with different amounts of the ZnBO addition.

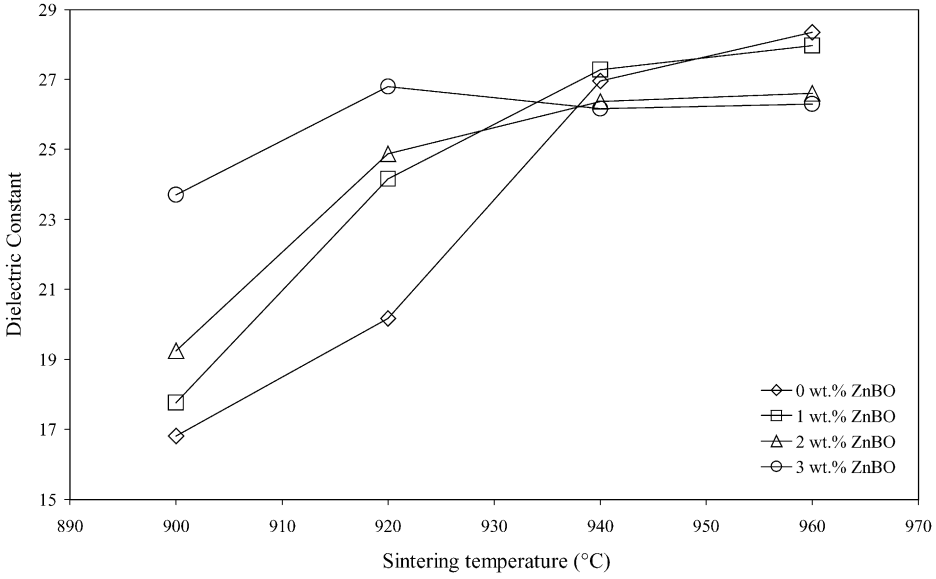

Fig. 6. Dielectric constant versus sintering temperature of the ULF280 ceramics with ZnBO additions.

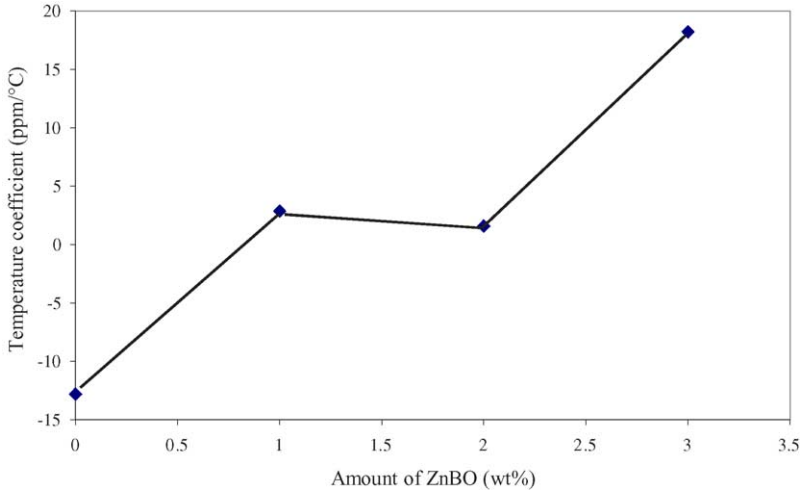

Fig. 7. The temperature coefficients of resonant frequency, τ_f, of the ULF280 ceramics as a function of the ZnBO addition.

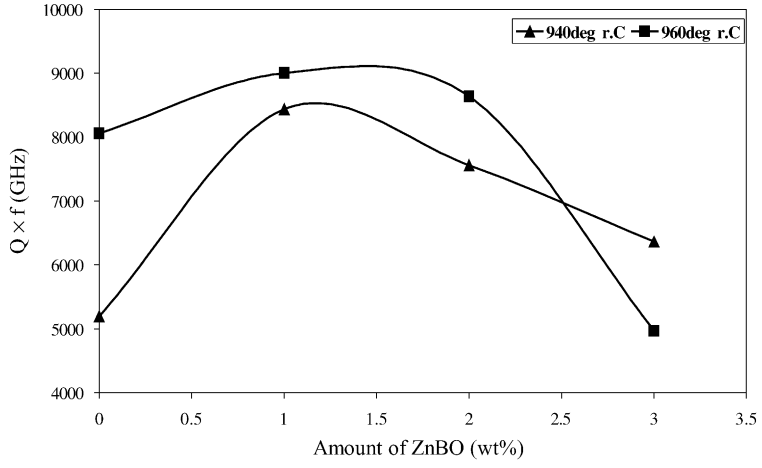

Fig. 8. The $Q \times f$ values of the ULF280 ceramics as a function of the ZnBO addition.

the dielectric constant of the ULF280 ceramics increases with the sintering temperature. The ε_r value of the ULF280 ceramic without ZnBO addition spans from 16.1 (900 °C) to 28.3 (960 °C). For this class of ceramics, it is possible to obtain high dielectric constant, e.g. $\varepsilon_r > 24$, only by raising the sintering temperature above 940 °C. The sintering temperature can be lowered down to 920 °C by an addition of 1 wt.% or 2 wt.% of ZnBO glass to the ceramics. Further increase of the ZnBO content up to 3 wt.%, high ε_r value can be achieved at 900 °C. Therefore, it can be concluded that the ZnBO glass phase is very effective in lowering the sintering temperature of the ULF280 ceramics having high dielectric constant.

A close look of the dielectric constant of the ULF280 ceramics with 3 wt.% ZnBO addition reveals that the value slightly decreases with the sintering temperature at above 920 °C, a result very similar to the the bulk density versus sintering temperature curves in Fig. 2. This observation suggests that the bulk density of the sintered ceramics determine, to a large extent, the dielectric constant of the sintered ceramics. Kanai et al.[7] has suggested that second phases such as $BaZr(BO_3)_2$ and Zn_2SiO_4, and the grain size of the sintered ceramics could have strong effects on the dielectric constant of the sintered ceramics. Nevertheless, the experimental results of this study seem to suggest that the dielectric constant of the ULF280 ceramics is mainly controlled by the bulk density of the sintered ceramics.

Fig. 7 shows the temperature coefficient of resonant frequency, τ_f, at maximum Q value as a function of the ZnBO addition. It can be easily seen that the ULF280 ceramics with 1 wt.% and 2 wt.% ZnBO additions have τ_f close to zero, i.e. 2.5 and 1.5, which satisfies the requirement for microwave device applications.

Fig. 8 shows the $Q \times f$ values of the ULF280 ceramics sintered at 940 °C and 960 °C as a function of the ZnBO addition. In contrast to those with 3 wt.% ZnBO addition, the $Q \times f$ values of the ULF280 ceramics with less than 2 wt.% ZnBO additions and sintered at 960 °C are higher than the corresponding ceramics and sintered at 940 °C. In practice, sintering at 940 °C is preferred although the $Q \times f$ value (8300) of the ceramic is slightly lower than that (9000) of the ceramic sintered at 960 °C.

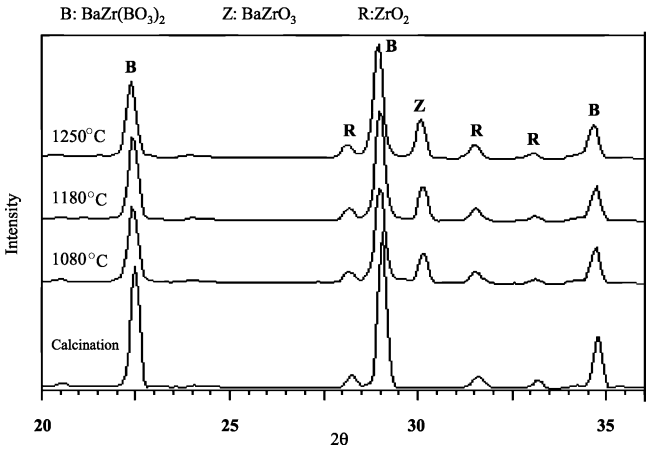

Fig. 9. X-ray diffraction spectra of the $BaZr(BO_3)_2$ ceramics sintered at (a) 1080 °C, (b) 1180 °C and (c) 1250 °C for 2 h.

3.4. Phase evolution in the sintered $BaZr(BO_3)_2$ ceramics

The X-ray diffraction spectra of the calcined powder and as-sintered ceramic are given in Fig. 9. The XRD spectrum of the calcined powder at 1100 °C reveals that the $BaZr(BO_3)_2$ phase is the main crystalline phase with ZrO_2 as a minor

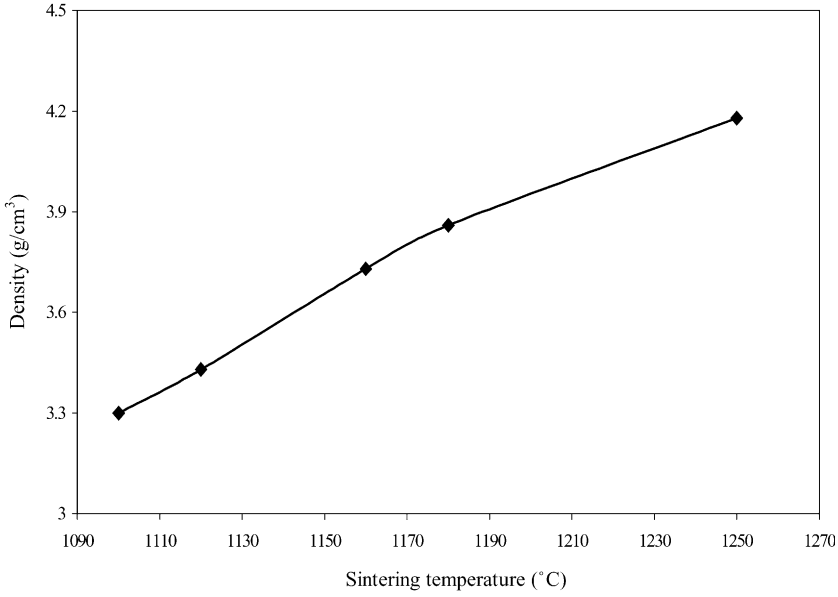

Fig. 10. Bulk density vs. sintering temperature of the $BaZr(BO_3)_2$ ceramics.

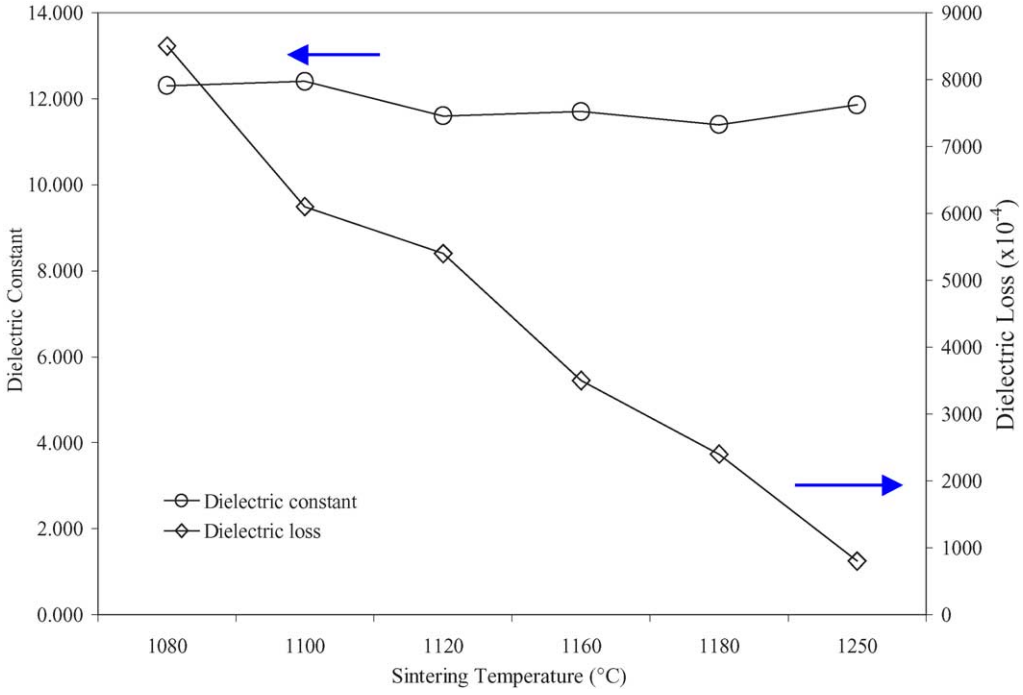

Fig. 11. Dielectric constant and dielectric loss of the $BaZr(BO_3)_2$ ceramics as a function of the sintering temperature.

phase. On the other hand, the XRD pattern of the sintered sample consists of mainly the $BaZr(BO_3)_2$ crystalline phase with $BaZrO_3$ and ZrO_2 as minor phases. The diffraction peaks of the $BaZrO_3$ phase increase slightly with increasing sintering temperature.

3.5. Physical and dielectric properties of the sintered $BaZr(BO_3)_2$ ceramics

The bulk density of the $BaZr(BO_3)_2$ ceramics as a function of sintering temperatures is shown in Fig. 10.

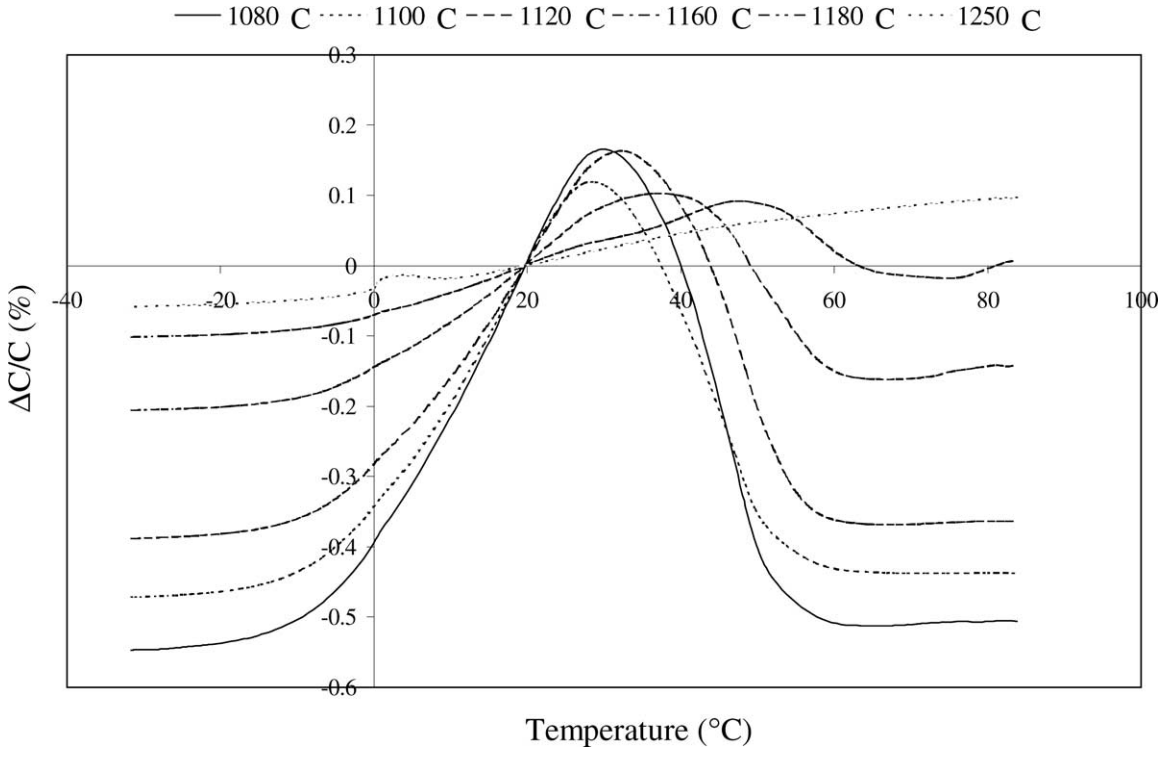

Fig. 12. T_c curve of the $BaZr(BO_3)_2$ ceramics with sintering temperature.

It shows that the density of the sintered ceramics increases approximately linearly with the sintering temperature ranging from 1080 °C to 1250 °C. The bulk density of the $BaZr(BO_3)_2$ ceramic sintered at 1250 °C for 2 h is 4.12 g/cm^3.

The dielectric constant and dielectric loss of the $BaZr(BO_3)_2$ ceramics were measured at 1 MHz, and the results are shown in Fig. 11. The ε_r of the $BaZr(BO_3)_2$ ceramic ranges from 12.3 (1080 °C) to 11.85 (1250 °C) at 1 MHz. In contrast to results of density versus sintering temperature, the dielectric constant of the ceramic does not increase with sintering temperature. The reason could be because the dielectric constant of the $BaZr(BO_3)_2$ ceramic saturates at about 11–13. However, the dielectric constant should increase with increasing sintering temperature which is associated with the density increase. On the other hand, the dielectric loss is also decreased with increasing sintering temperature, which would be accompanied by the decrease in dielectric constant. By combining the two effects of density and dielectric loss, the dielectric constant would be nearly independent of the sintering temperature.

If ~20 vol.% $BaZr(BO_3)_2$ dendrite phase is occupied and is rather than dispersed in host ceramic for sample with 3 wt.% ZnBO addition (Fig. 3(c)), the dielectric constant of $Ba_2Ti_9O_{20}$-based ceramic is calculated using J. C. Maxwell's Eq. (1),[19]

$$\varepsilon_m = \varepsilon_2 \left\{ 1 + \frac{3V_f(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 - V_f(\varepsilon_1 - \varepsilon_2)} \right\} \quad (1)$$

where V_f is the volume fraction occupied by the dispered phases, ε_1 and ε_2 are the permittivity of $BaZr(BO_3)_2$ and $Ba_2Ti_9O_{20}$ ceramic, respectively; ε_m is permittivity of mixtures ($Ba_2Ti_9O_{20}$-based ceramics). The dielectric constant of the $Ba_2Ti_9O_{20}$-based ceramics are estimated from the values of pure $BaZr(BO_3)_2$ ceramics (12.0) and $Ba_2Ti_9O_{20}$ ceramics (39.8). The estimated dielectric constants for $Ba_2Ti_9O_{20}$-based ceramic with 3 wt.% ZnBO addition is 32.9. The experimentally obtained results give values smaller than the estimated values.

Fig. 11 also shows the dielectric loss of the $BaZr(BO_3)_2$ ceramic as a function of sintering temperature It can be seen that the dielectric loss decreases linearly with sintering temperature. Because high-density ceramics can be obtained at higher sintering temperatures (Fig. 10), this means that the pores became less in the high-density ceramics. It was considered that the high dielectric loss was mainly caused by insufficient densification of the $BaZr(BO_3)_2$ ceramic.[6] Nonetheless, the dielectric loss of the $BaZr(BO_3)_2$ ceramic of about 0.08 is still very high, compared with those of $Ba_2Ti_9O_{20}$ or $MgTiO_3$ materials ($\tan\delta < 0.002$).[6,20] In addition, the dielectric loss of the $BaZr(BO_3)_2$ ceramic was also measured at the high-frequency range by the modified Hakki–Coleman dielectric resonator method.[14] For samples sintered at 1250 °C, the dielectric loss of the $BaZr(BO_3)_2$ ceramic is about 0.014 ($Q = 71$) at 11 GHz. This result suggests that the $BaZr(BO_3)_2$ phase formed in $Ba_2Ti_9O_{20}$-based ceramics may have detrimental effects on the high-frequency characteristics of the microwave ceramics.

Fig. 12 shows the T_c (T_ε) curves of the $BaZr(BO_3)_2$ ceramic at different sintering temperatures ranging from −30 °C to + 80 °C. At lower sintering temperatures such as 1080 °C, the ceramic exhibits poor T_c characteristics, in which the $\Delta C/C$ value changes from ~−0.5% to ~+0.2%. On the other hand, the ceramic sintered at 1250 °C shows very stable T_c behavior (~−0.05% to ~+0.1%). The temperature coefficient of dielectric constant (T_ε) is commonly cited in the literature for capacitor dielectrics. As is well-known, a small temperature coefficient of the resonant frequency (T_f) ensures the stability of the microwave components at different working temperatures. T_f can be correlated to T_ε by

$$T_f = -\frac{1}{2}T_\varepsilon - \alpha$$

where α is the linear thermal expansion coefficient of the dielectric. α is typically in the range of 3–15 ppm/°C for most ceramics. T_ε is clearly the dominant part in T_f. It is easily understood that the adjustment of T_f toward 0 ppm/°C can be achieved by modifying the base composition using materials of opposite T_ε or restraining the unexpected second phase formed in the host materials.[21]

4. Conclusions

The phase evolution, physical and dielectric properties of the $Ba_2Ti_9O_{20}$-based ceramics by the addition of ZnBO glass phase have been investigated. It is obtained that the addition of the ZnBO glass phase in the ceramics can effectively lower the sintering temperature, and increases the bulk density and dielectric constant of the sintered ceramics. The $Ba_2Ti_9O_{20}$-based ceramic with 1 wt.% ZnBO addition and sintered at 940 °C in air for 2 h exhibits optimum microwave properties of ε_r = 27.3, τ_f = 2.5 ppm/°C, and $Q \times f$ = 8300. Moreover, the microstructures and dielectric properties of $BaZr(BO_3)_2$-based ceramics were investigated. The results of X-ray diffraction (XRD) indicate that it consists of mainly the $BaZr(BO_3)_2$ crystalline phase with $BaZrO_3$ and ZrO_2 as minor phases. The following dielectric properties of $BaZr(BO_3)_2$-based ceramics were obtained: (1) K values are maintained at ~12 for sintering temperatures of 1080 °C to 1250 °C; (2) dielectric loss is significantly reduced with increasing sintering temperature from 0.85 at 1080 °C to 0.08 at 1250 °C; and, (3) insulation resistance increases markedly with increasing sintering temperature. As is well-known, the Q factor depends on dielectric loss (Q is given by $1/\tan\delta$); it therefore showed poor performance at high frequency when $BaZr(BO_3)_2$ phase was much formed in the microwave ceramics.

References

1. Huang, C. L. and Weng, M. H., Low-fire $BiTaO_4$ dielectric ceramics for microwave applications. *Mater. Lett.*, 2002, **43**, 32–35.
2. Takada, T., Wang, S. F., Yoshikawa, S., Jang, S. J. and Newnham, R. E., Effects of glass additions on $(Zr,Sn)TiO_4$ for microwave applications. *J. Am. Ceram. Soc.*, 1994, **77**, 2485–2488.
3. Takada, T., Wang, S. F., Yoshikawa, S., Jang, S. J. and Newnham, R. E., Effect of glass additions on BaO-TiO–TiO_2–WO_3 microwave ceramics. *J. Am. Ceram. Soc.*, 1909, **77**, 1916.
4. Yang, C. F., The microwave characteristics of glass-$BaTi_4O_9$ ceramics. *Jpn. J. Appl. Phys.*, 1999, **38**, 3576–3579.
5. Hirano, S. I., Hayashi, T. and Hatto, A., Chemical processing and microwave characteristics of $(Zr,Sn)TiO_4$ microwave dielectrics. *J. Am. Ceram. Soc.*, 1991, **74**, 1320–1324.
6. Cheng, C. M., Yang, C. F. and Lo, S. H., Sintering and dielectric properties of $Ba_2Ti_9O_{20}$ microwave ceramics by glass addition. *Jpn. J. Appl. Phys.*, 1997, **86**, 1604–1607.
7. Kanai, H., Furukawa, O. and Nakamura, S. I., Effect of B_2O_3 and SiO_2 on dielectric properties and reliability of a lead-based relaxor dielectric. *J. Mater. Sci.*, 1996, **31**, 1609–1614.
8. O'Bryan Jr., H. M., Thomson Jr., J. and Ploured, J. K., A new BaO-TiO–TiO_2 compound with temperature-stable high permitivity and low microwave loss. *J. Am. Ceram. Soc.*, 1974, **57**, 450–453.
9. Hennings, D., Schnell, A. and Simon, G., Diffuse ferroelectric phase transitions $Ba(Ti_{1-y}Zr_y)O_3$ ceramics. *J. Am. Ceram. Soc.*, 1982, **65**, 539–544.
10. Choi, W. S., Boo, J. H., Yi, J. and Hong, B., The effect of annealing on the 0.5% Ce-doped $Ba(Zr_xTi_{1-x})O_3$ (BZT) thin film deposited by RF magnetron sputtering system. *Mater. Sci. Semi. Proc.*, 2003, **5**, 211–214.
11. Yu, Z., Ang, C., Guo, R. and Bhalla, A. S., Ferroelectric-relaxor behavior of $Ba(Ti_{0.7}Zr_{0.3})O_3$ ceramics. *J. Appl. Phys.*, 2002, **92**, 2655–2657.
12. Tang, X. G., Wang, J., Wang, X. X. and Chan, H. L. W., Effect of grain size on the dielectric properties and tunabilities of sol-gel derived $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics. *Solid State Commun.*, 2004, **131**, 163–168.
13. Levin, E. M., Robbins, C. R. and Mcmurdie, H. F., *Phase Diagrams for Ceramists*, *Vol 1*. The American Ceramic Society, Columbus, Ohio, 1964, p. 300.
14. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacities in the millimeter range. *IRE Trans. Microwave Theory Tech.*, 1960, **MTT8**, 402–410.
15. Rase, D. E. and Roy, R., Phase equilibria in the system BaO-TiO–TiO_2. *J. Am. Ceram. Soc.*, 1955, **38**, 102–113.
16. Plourde, J. K., Linn, D. F., O'Bryan Jr., H. M. and Thomson Jr., J., $Ba_2Ti_9O_{20}$ as a microwave dielectric resonator. *J. Am. Ceram. Soc.*, 1975, **58**, 418–420.
17. Tillmanns, E., Hofmeister, W. and Baur, W. H., Crystal structure of the microwave dielectric resonator $Ba_2Ti_9O_{20}$. *J. Am. Ceram. Soc.*, 1983, **66**, 268–271.
18. Kniajer, G., Dechant, K. and Apte, P., International conference on multichip modules. *IEEE* 1997, 121–127.
19. Moulson, A. J. and Herbert, J. M., *Electroceramics*. Materials Properties Applications, London, 1990, pp. 79–82.
20. Jantunen, H., Rautioaho, R., Unsimaki, A. and Leppavuori, S., Compositions of $MgTiO_3$–$CaTiO_3$ ceramic with two borosilicate glasses for LTCC technology. *J. Eur. Ceram. Soc.*, 2000, **20**, 2331–2336.
21. Dai, S. X., Huang, R. F. and Wilcox, D. L., Use of titanates to achieve a temperature-stable low-temperature cofired ceramic dielectric for wireless applications. *J. Am. Ceram. Soc.*, 2002, **85**, 828–832.