Journal of Alloys and Compounds 509 (2011) 5988–5995

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

A new temperature stable microwave dielectric ceramics: $ZnTiNb_2O_8$ sintered at low temperatures

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ARTICLE INFO

Article history:
Received 25 August 2010
Received in revised form 13 January 2011
Accepted 15 January 2011
Available online 22 January 2011

Keywords:
LTCC
$\tau_f = 0$ ppm/°C
Microwave dielectric properties
$ZnTiNb_2O_8$–$x$$TiO_2$
$BaCu(B_2O_5)$

ABSTRACT

The phases, microstructure and microwave dielectric properties of $ZnTiNb_2O_8$–$xTiO_2$ composite ceramics with different weight percentages of $BaCu(B_2O_5)$ additive prepared by solid-state reaction method have been investigated using the X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The results showed that the microwave dielectric properties were strongly dependent on densification, grain sizes and crystalline phases. The sintering temperature of $ZnTiNb_2O_8$ ceramics was reduced from 1250 °C to 950 °C by doping $BaCu(B_2O_5)$ additive and the temperature coefficient of resonant frequency (τ_f) was adjusted from negative value of −52 ppm/°C to 0 ppm/°C by incorporating TiO_2. Addition of 2 wt% $BaCu(B_2O_5)$ in $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.8$) ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r = 38.89$, $Q \times f = 14{,}500$ GHz ($f = 4.715$ GHz) and $\tau_f = 0$ ppm/°C, which represented very promising candidates as LTCC dielectrics for LTCC applications.

1. Introduction

Microwave dielectric materials have attracted increasing research interest because they are promising in applications of mobile and satellite communication. With the rapid growth of the wireless communication systems, the dielectric component must be miniaturized in order to reduce the size of microwave devices in communication systems. Thus, low-temperature-cofired ceramics (LTCC) have been widely investigated [1]. For dielectric materials that are used in LTCC technology, the key characteristic properties required are: (i) low sintering temperature ($T \le 950$ °C, to use cheaper and highly conductive internal electrode metals), (ii) high dielectric permittivity ($\varepsilon_r > 20$, 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 $\le \tau_f \le +6$ ppm/°C). From 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].

Up to now, many materials with good microwave dielectric properties have been reported, however, most of them have high sintering temperatures (above 1200 °C) [3]. For example, $ZnTiNb_2O_8$ microwave dielectric ceramics have good microwave dielectric properties with a dielectric permittivity of 34, a $Q \times f$ of 42,500 GHz and a τ_f of −52 ppm/°C, but the sintering temperature of $ZnTiNb_2O_8$ ceramics was above 1200 °C, which is too high to be applicable to LTCC [4,5]. And many researchers have developed several approaches to reduce the sintering temperature of the ceramics: (i) the usage of small particle sized starting materials synthesized by wet chemical methods such as the sol–gel and coprecipitation methods and (ii) the addition of low-melting glasses, oxide or mixed-oxide additives, such as ZnO–B_2O_3–SiO_2 (ZBS), Li_2O–B_2O_3–SiO_2 (LBS), Li_2O–ZnO–B_2O_3 (LZB), V_2O_5, CuO, B_2O_3 and $BaCu(B_2O_5)$ (BCB) [6–22]. For the first approach, chemical synthesis complicates the manufacturing and increases the production cost. However, for the second approach, glass or mixed-oxide addition for liquid-phase sintering has been known to be the most popular and cheapest method for achieving densified ceramics. For example, the addition of 2 wt% Li_2O–ZnO–B_2O_3 (LZB) glass to the $ZnTiNb_2O_8$ ceramics sintered at low temperatures showed promising microwave dielectric properties ($\varepsilon_r = 31.8$, $Q \times f = 25{,}013$ GHz and $\tau_f = -62$ ppm/°C) [5]. However, the large negative temperature coefficient of resonant frequency ($\tau_f = -62$ ppm/°C) could limit its practical application in LTCC. Consequently, the near-zero τ_f ($\tau_f \sim 0$) is expected to prevent the disturbance from temperature variation. Since the $ZnTiNb_2O_8$ ceramics have negative τ_f values, temperature compensated dopants with large positive τ_f values should be added. TiO_2 (rutile) has $\tau_f = +400$ ppm/°C, $\varepsilon_r = 100$ and $Q \times f = 10{,}000$ GHz [23], therefore it is logical to speculate that the $ZnTiNb_2O_8$–TiO_2 composite ceramics have adjustable τ_f values.

As far as we know, there have been few papers studied on the adjustment of the temperature coefficient of resonant frequency (τ_f) of $ZnTiNb_2O_8$ ceramics sintered at low temperatures. It is well known that $BaCu(B_2O_5)$ (BCB) decreases the sintering temperature

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0925-8388/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2011.01.095

of many materials, such as $Li_2CoTi_3O_8$, $Ba_3Ti_5Nb_6O_{28}$, $Ba_4LiTa_3O_{12}$, $Ba_4LiNb_3O_{12}$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$. These materials showed good microwave dielectric properties [24–28].

At present, attempts have been made to achieve the near-zero τ_f of the $ZnTiNb_2O_8$ ceramics by adding TiO_2 (rutile), and to lower the sintering temperature below 950 °C ($T \leq 950$ °C) by adding BCB as the sintering aid. Meanwhile, high $Q \times f$ and ε_r values are needed. This paper has investigated the effect of densification, microstructure and crystalline phases on the microwave dielectric properties of the $ZnTiNb_2O_8$ ceramics, and densification, microstructure and crystalline phases are influenced by the amount of BCB, the sintering temperature and the amount of TiO_2. The excellent microwave dielectric properties ($\tau_f = 0$ ppm/°C, $Q \times f = 14{,}500$ GHz ($f = 4.715$ GHz) and $\varepsilon_r = 38.89$) were obtained by the addition of 2 wt% BCB to the $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.8$) compounds sintered at 950 °C.

2. Experimental procedures

Both $ZnTiNb_2O_8$ (ZTN) and $BaCu(B_2O_5)$ (BCB) compounds were synthesized independently using a conventional solid-state reaction method. For the preparation of $ZnTiNb_2O_8$ compound, high-purity oxide ZnO (99.6%), TiO_2 (99.6%) and Nb_2O_5 (99.5%) were first weighed, then ball-milled in a polyethylene jar containing zirconia balls with ethanol as the solvent, and finally calcined at 1100 °C for 2 h. The BCB mixed-oxide additive was synthesized by mixing $BaCO_3$ (99.7%), CuO (97.5%) and H_3BO_3 (99.5%) with a molar ratio of 1:1:2; the compounds were then ball-milled in a polyethylene jar containing zirconia balls with ethanol as the solvent, and calcined at 800 °C for 2 h. Then, different weight percentages (1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%) of BCB mixed-oxide additive were added to $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$, 0.70, 0.75, 0.80 and 0.85) compounds. After ball-milling for 4 h using an ethanol solvent, the powders were dried, granulated, and pressed into several disk-type pellets with 15 mm diameter and 7 mm thickness. Next, the pellets were sintered at 950 °C for 2 h in air. We have observed that the $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) compounds have favorable $Q \times f$ values and dielectric permittivity when 2 wt% of BCB were added. Therefore 2 wt% of BCB was added to the $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) compounds and the pellets with 2 wt% of BCB were sintered at different sintering temperatures of 900 °C, 925 °C, 950 °C, 975 °C and 1000 °C respectively in order to investigate the effects of different sintering temperatures on microwave dielectric properties.

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 characterized by 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 at a frequency range of 4–6 GHz by Advantest network analyzer (R3767C). The ε_r and Q values at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method [29,30]. The temperature coefficient of resonant frequency (τ_f) was measured by the Eq. (1) given below:

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

where f_{80} and f_{25} are the resonant frequencies at 80 °C and 25 °C respectively and they were also measured by the Hakki–Coleman dielectric resonator method.

3. Results and discussion

3.1. Microstructure evolution of compounds

The XRD patterns of $ZnTiNb_2O_8$–$0.8TiO_2$ ceramic samples with different BCB contents (1–5 wt%) that were sintered at 950 °C are shown in Fig. 1(a). Fig. 1(b) shows the XRD patterns of the $ZnTiNb_2O_8$–$0.8TiO_2$ ceramic samples with 2 wt% of BCB sintered at different temperatures (900–1000 °C). And Fig. 1(c) depicts the XRD patterns of $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) with 2 wt% of BCB sintered at 950 °C for 2 h. It should be noted that the $ZnTiNb_2O_8$–$0.8TiO_2$ sample with 2 wt% of BCB showed a zero τ_f, but this will be discussed later.

In Fig. 1(a)–(c), it was found that all the samples contained two phases: $ZnTiNb_2O_8$ (JCPDS #48-0323) and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (JCPDS #39-0291) with peaks indicating the presence of $ZnTiNb_2O_8$ as the main crystalline phase, and with $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ as the

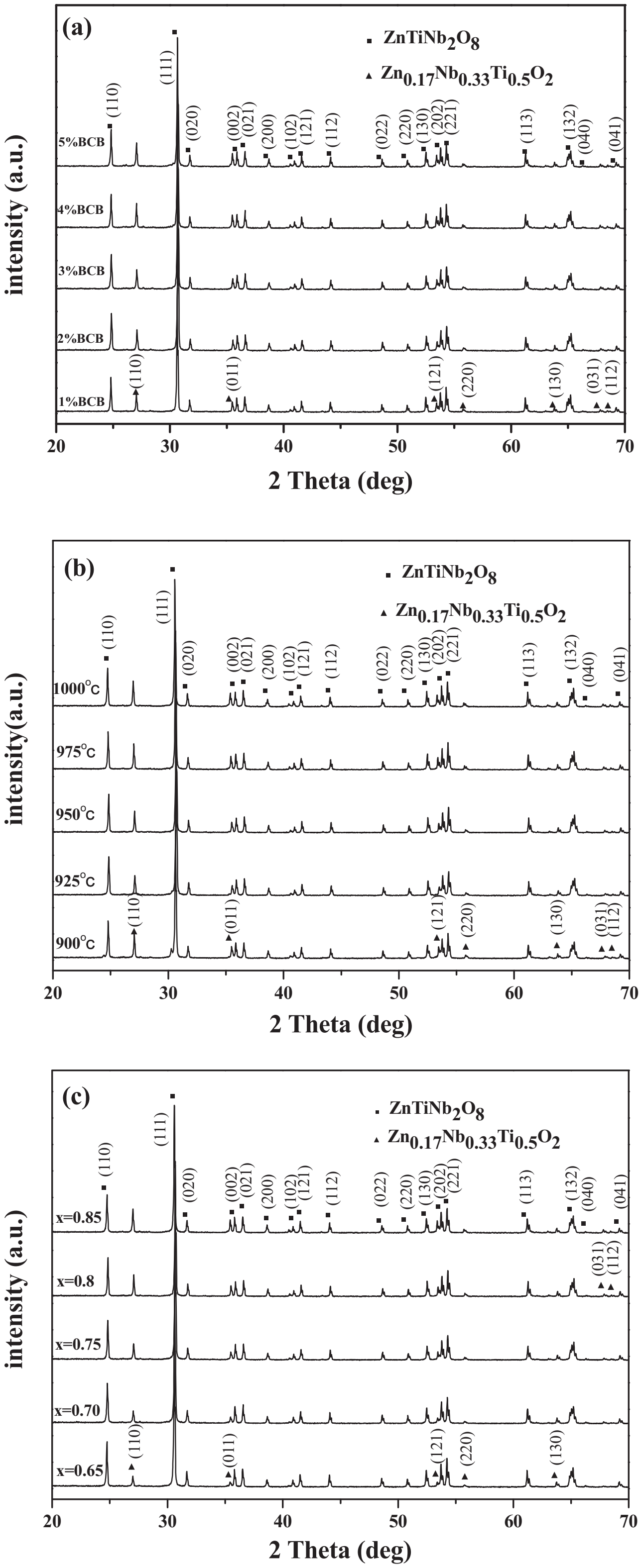
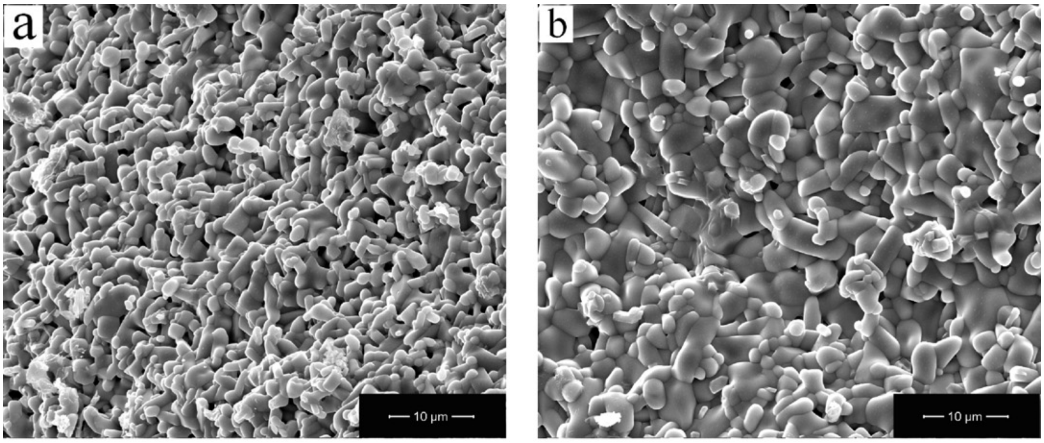
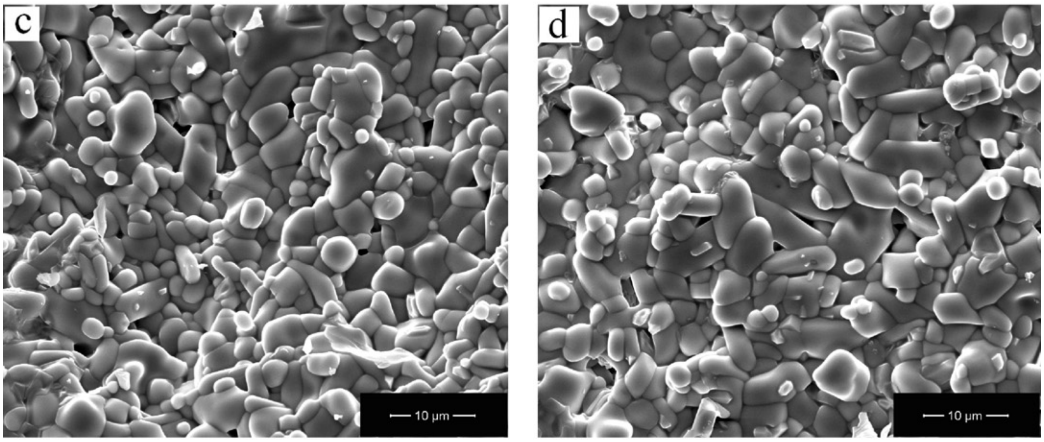


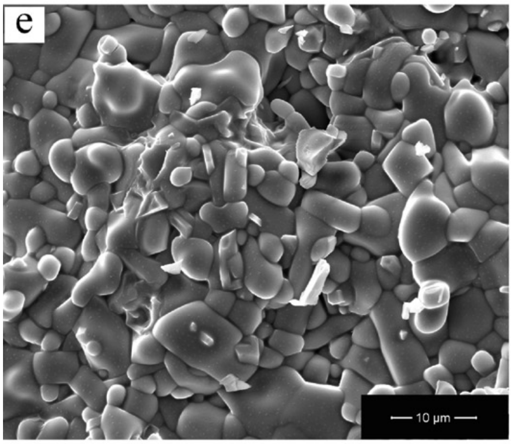
Fig. 1. (a) XRD patterns for $ZnTiNb_2O_8$–0.8 TiO_2 samples sintered at 950 °C and doped with 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% of BCB, (b) XRD patterns for $ZnTiNb_2O_8$–$0.8TiO_2$ samples with 2 wt% of BCB sintered at various temperatures of 900 °C, 925 °C, 950 °C, 975 °C and 1000 °C, (c) XRD patterns for $ZnTiNb_2O_8$–$xTiO_2$ with 2 wt% of BCB sintered at 950 °C, where $x = 0.65$, 0.7, 0.75, 0.8, 0.85.



(a) 1.0 wt % BCB (b) 2.0 wt % BCB



(c) 3.0 wt % BCB (d) 4.0 wt % BCB

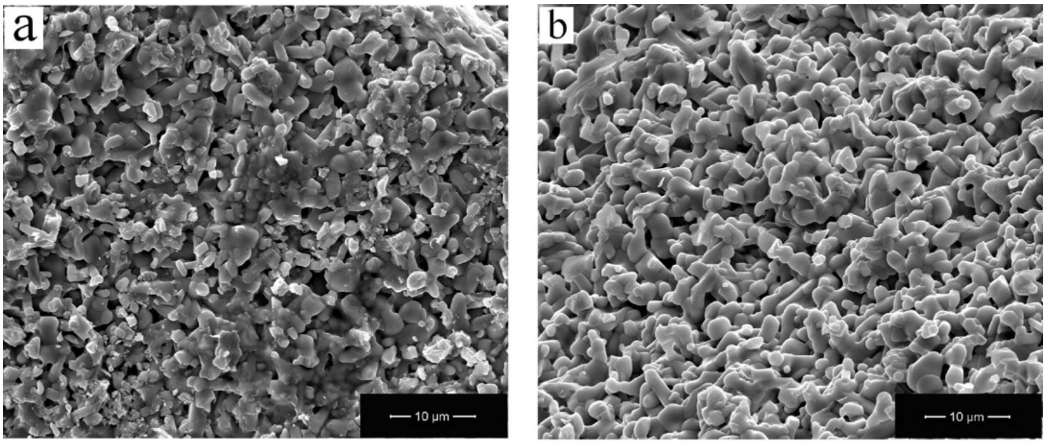


(e) 5.0 wt % BCB

Fig. 2. SEM micrographs of $ZnTiNb_2O_8$–$0.8TiO_2$ samples sintered at 950 °C and doped with different amount of BCB: (a) 1.0 wt%, (b) 2.0 wt%, (c) 3.0 wt%, (d) 4.0 wt% and (e) 5.0 wt% of BCB.

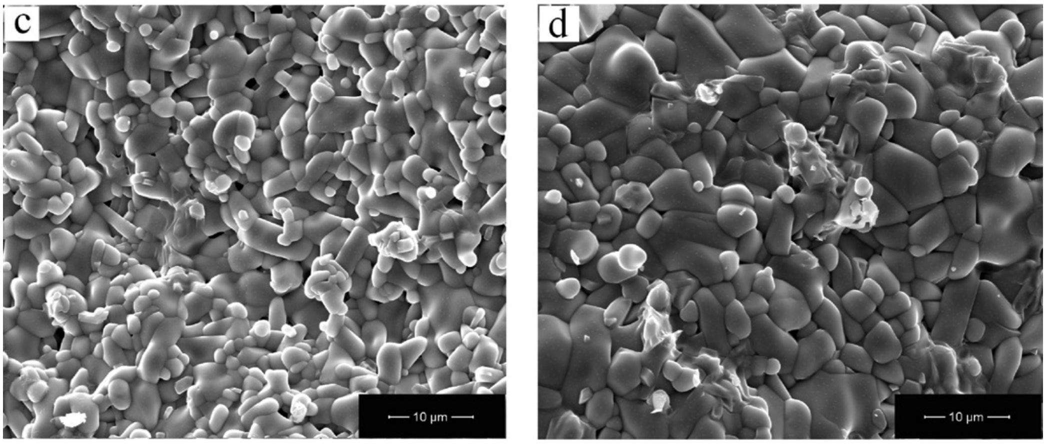
minor crystalline phase. Fig. 1(a) and (b) show that the phases and peak intensity remained almost unchanged with the addition of BCB up to 5 wt% and sintering temperature up to 1000 °C. A special phenomenon was observed in Fig. 1(c), the intensities of diffraction peaks related to the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase increased gradually with increasing TiO_2 content. $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ belongs to the tetragonal crystal system (space group $P42/mnm$ (no. 136)), and the lattice parameters are $a = b = 4.6739$ Å, $c = 3.0214$ Å [31,32]. $ZnTiNb_2O_8$ belongs to the Orthorhombic crystal system (space group *Pbcn* (no. 60)), and the lattice parameters are $a = 4.6746(5)$ Å, $b = 5.6621(5)$ Å, $c = 5.0137(4)$ Å [33,34].

SEM micrographs of the $ZnTiNb_2O_8$–$0.8TiO_2$ ceramics with different BCB contents (1–5 wt%) sintered at 950 °C are shown in Fig. 2(a)–(e). Obviously, in Fig. 2(a), the grains of the sample with 1 wt% BCB were not dense, and this may directly decrease the microwave dielectric properties of the $ZnTiNb_2O_8$–$xTiO_2$



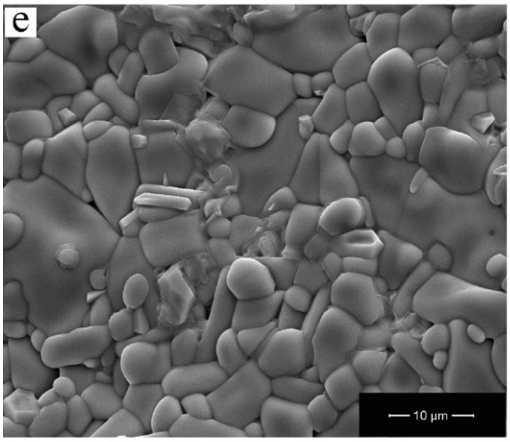
(a) 900 °C

(b) 925 °C



(c) 950 °C

(d) 975 °C

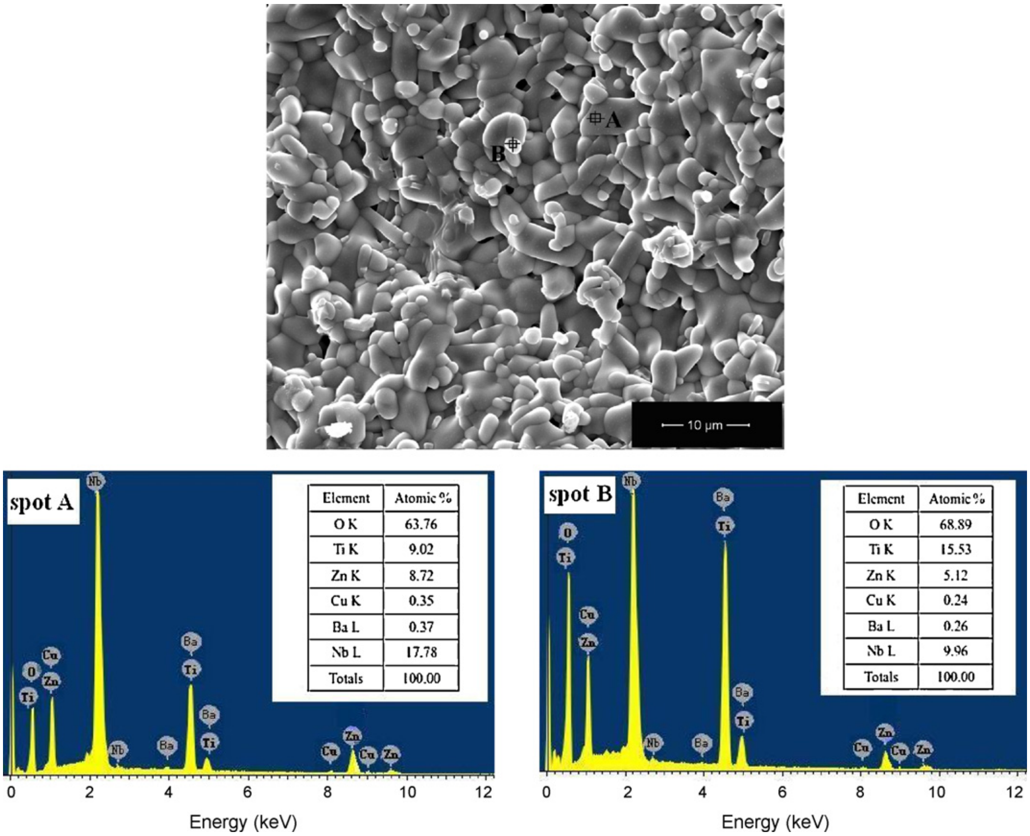


(e) 1000 °C

Fig. 3. SEM micrographs of $ZnTiNb_2O_8$–$0.8TiO_2$ samples with 2 wt% of BCB sintered at different temperatures: (a) 900 °C, (b) 925 °C, (c) 950 °C, (d) 975 °C and (e) 1000 °C.

compounds. However, the grains were very dense with the BCB content of 2–5 wt%. SEM micrographs of 2 wt% BCB doped $ZnTiNb_2O_8$–0.8 TiO_2 samples sintered at different temperature (900–1000 °C) are presented in Fig. 3(a)–(e). It can be seen that the $ZnTiNb_2O_8$–$0.8TiO_2$ ceramics was not dense and the grain did not grow at 900 °C, shown in Fig. 3(a). However, rapid grain growth was observed at 925 °C in Fig. 3(b) and the pores were almost eliminated for the specimen sintered at 950 °C as shown in Fig. 3(c). Therefore, it can be deduced that the low relative density of the compounds resulted from the porous specimens sintered at 900 °C or 925 °C. However, the grain size increased with increasing BCB content as shown in Fig. 2(a)–(e) and with increasing sintering temperature as shown in Fig. 3(a)–(e) due to the liquid-phase effect. Two kinds of grains were found, the bigger and smaller ones were present in the specimens of BCB-doped $ZnTiNb_2O_8$–$xTiO_2$ ceramics.

Fig. 4 shows the EDS analysis of the $ZnTiNb_2O_8$–$0.8TiO_2$ samples with 2.0 wt% of BCB sintered at 950 °C. The results indicate that the ratio of Zn:Ti:Nb:O of spot A (bigger grains) is about



Element	Atomic %
O K	63.76
Ti K	9.02
Zn K	8.72
Cu K	0.35
Ba L	0.37
Nb L	17.78
Totals	100.00

Element	Atomic %
O K	68.89
Ti K	15.53
Zn K	5.12
Cu K	0.24
Ba L	0.26
Nb L	9.96
Totals	100.00

Fig. 4. EDS analysis of $ZnTiNb_2O_8$–$0.8TiO_2$ samples with 2 wt% of BCB sintered at 950 °C.

1:1:2:7.3, which is approximately consistent with the composition of $ZnTiNb_2O_8$. The ratio of Zn:Nb:Ti:O of spot B (smaller grains) is about 1:2:3:13, which is also approximately consistent with the composition of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$. This may suggest that the EDS analysis of both spot A and spot B corroborated the XRD results of the samples consisting of the two phases $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$. However, EDS analysis has confirmed that small Cu and Ba ions were detected at a ratio of approximately 1:1. It is impossible to detect boron ions using an EDS detector, and this may indicate that the BCB has been incorporated into the matrix $ZnTiNb_2O_8$–$xTiO_2$ compounds and the BCB has been successfully applied as a sintering aid for liquid-phase sintering to enhance the sintering properties of the $ZnTiNb_2O_8$–$xTiO_2$ ceramics.

Fig. 5 shows the relative density of $ZnTiNb_2O_8$–$xTiO_2$ samples doped with 2 wt% of BCB with the different sintering temperature of 900–1000 °C. Obviously, the relative density of the samples increased with the increasing sintering temperature due to the decrease in the porosity and the enlargement of the grain size. However, when the sintering temperature was above 950 °C ($T \geq 950$ °C), they reached above 96% of the theoretical density and the density of samples mostly has not changed indicating that the samples sintered above 950 °C ($T \geq 950$ °C) were very dense as shown in Fig. 3(c)–(e). All the parameters shown above including densification, grain sizes and crystalline phases that may directly affect the microwave dielectric properties of the $ZnTiNb_2O_8$–$xTiO_2$ compounds.

3.2. Microwave dielectric property of compounds

In many cases, although the sintering aids could reduce the sintering temperature, they may also induce a significant deterioration in dielectric properties, so appropriate weight percentage of BCB should be chosen as a sintering aid to lower the sintering temperature of the $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) ceramics in order to give a high $Q \times f$ and a high ε_r. The effect of BCB content (1–5 wt%) on microwave dielectric properties with the sintering temperature of 950 °C will be discussed.

Fig. 6 shows the $Q \times f$ values and dielectric constant ε_r of $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) compounds with different BCB content (1–5 wt%) sintered at 950 °C. When 1 wt% of BCB were added to $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) compounds, the $Q \times f$ value and dielectric constant ε_r were both very low, because the sample with 1 wt% of BCB was not dense, shown in Fig. 2(a). However, it can be seen that the $Q \times f$ value and dielectric constant ε_r

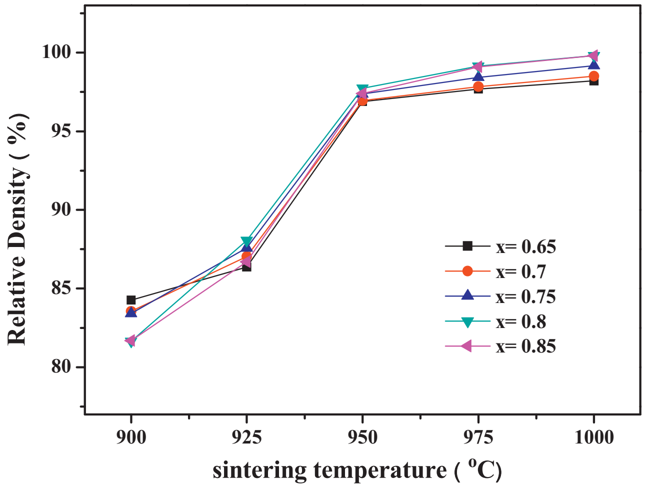


Fig. 5. The relative density of $ZnTiNb_2O_8$–$xTiO_2$ samples with 2 wt% of BCB sintered at different temperatures of 900 °C, 925 °C, 950 °C, 975 °C and 1000 °C.

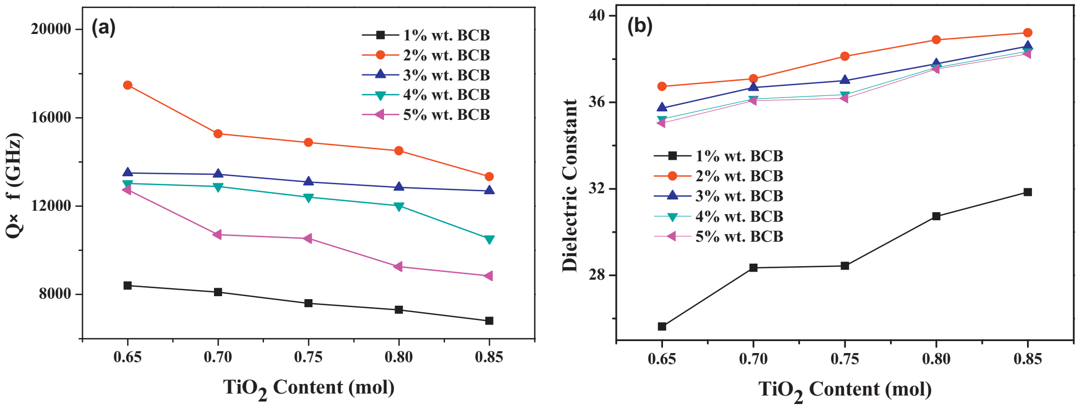


Fig. 6. (a) The $Q \times f$ and (b) dielectric constant of $ZnTiNb_2O_8$–$xTiO_2$ samples sintered at 950 °C and doped with 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% of BCB.

reached a maximum when $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) were added with 2 wt% of BCB. Fig. 6(a) shows that the $Q \times f$ value decreased when the BCB content exceeded 2 wt%. Many factors are thought to affect the microwave dielectric loss, which can be divided into the intrinsic and the extrinsic losses. The intrinsic losses are dependent on the crystal structure and mainly caused by lattice vibration modes [35], while the extrinsic losses are associated with imperfections in the crystal structure such as impurities, microstructural defects, densification or porosity, grain size and grain boundaries [36]. The addition of sintering aids has an influence on the physical properties of ceramics. However, the concentration of the sintering aid is small and in many cases it is entirely incorporated into the crystal lattice of the matrix [37], which is proved by the EDS results mentioned above. Thus, according to the liquid-phase sintering mechanism reported by Valant et al. [37], the liquid-phase sintering process in the present work might be as follows: (i) the formation of a low-temperature BCB liquid-phase, (ii) a reaction with the matrix $ZnTiNb_2O_8$–$xTiO_2$ compounds, which is accelerated by the liquid-phase and (iii) the consequent enhancement of elementary sintering mechanisms. The incorporation of the BCB into the crystal lattice of the $ZnTiNb_2O_8$–$xTiO_2$ compounds may increase with an increase of the BCB addition, resulting in the increase of imperfections in the crystal structure. This led to the decrease of $Q \times f$ value. Therefore, by adding appropriate weight percentage of BCB, we can reduce the influence of sintering aid on the particular physical properties of ceramics. Fig. 6(a) shows that the addition of 2 wt% BCB should be suitable. Furthermore, from XRD results (Fig. 1(a)) and SEM observations (Fig. 2(a)–(e)), it is shown that $Q \times f$ values of the samples with different wt% of BCB were also affected by the grain size. This is because only grain size increased with increasing BCB content as shown in Fig. 2(a)–(e), while phases and peak intensity remained almost unchanged as shown in Fig. 1(a). The liquid-phase sintering also played an important role in the increase of grain size and decrease in $Q \times f$ values. From Fig. 6(b), the dielectric constant of $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) compounds decreased with the increase of BCB content from 2 to 5 wt%, which may be as a result of BCB with a low dielectric constant. It was also found that the addition of 2 wt% of BCB was the optimum way to enhance the microwave dielectric properties.

As the sintering temperature has a significant influence on the microwave dielectric properties of ceramics, the effect of different sintering temperatures (900–1000 °C) on microwave dielectric properties was then investigated.

Fig. 7 shows the $Q \times f$ value and dielectric constant ε_r of $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.65$–0.85) compounds with 2 wt% of BCB sintered at 900–1000 °C. The $Q \times f$ values first increased and then decreased with the increasing sintering temperature, and the $Q \times f$ values reached the maximum value at 950 °C, shown in Fig. 7(a). From XRD results in Fig. 1(b) and SEM observations in Fig. 3(a)–(e), it can be seen that the $Q \times f$ values of the ceramics sintered at different temperatures were mainly affected by densification (or porosity) and grain size, because phases and peak intensity also remained almost unchanged for the compounds with 2 wt% of BCB sintered at different temperatures, but densification and grain size increased with the increasing sintering temperature. According to the classical dielectric theory, it is expected that as the grain size increases, the Q value would increase because a reduction in the number of grain boundaries per unit volume would result in a material with a lower loss [36]. In fact, the samples have the highest $Q \times f$ value when the average grain size of the samples is about 2–5 μm, while $Q \times f$ values decrease with the increase of the average grain size

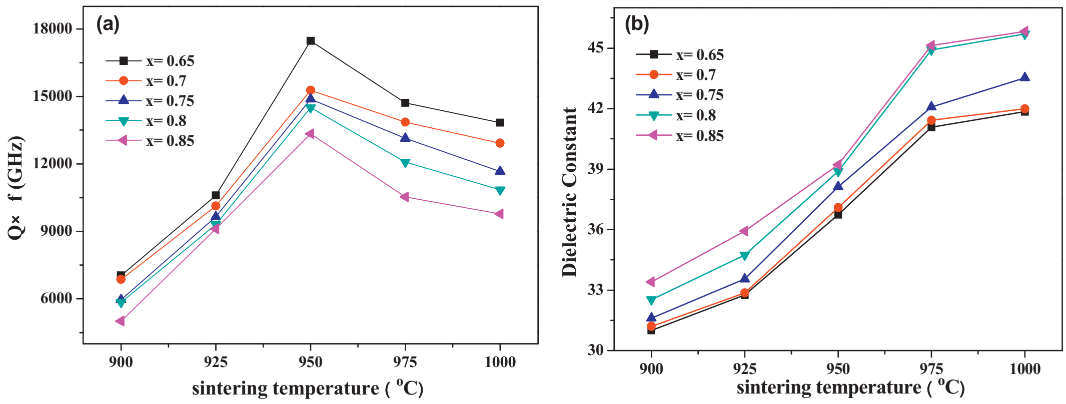


Fig. 7. (a) The $Q \times f$ (b) dielectric constant of $ZnTiNb_2O_8$–$xTiO_2$ samples with 2 wt% of BCB sintered at different temperatures of 900 °C, 925 °C, 950 °C, 975 °C and 1000 °C.

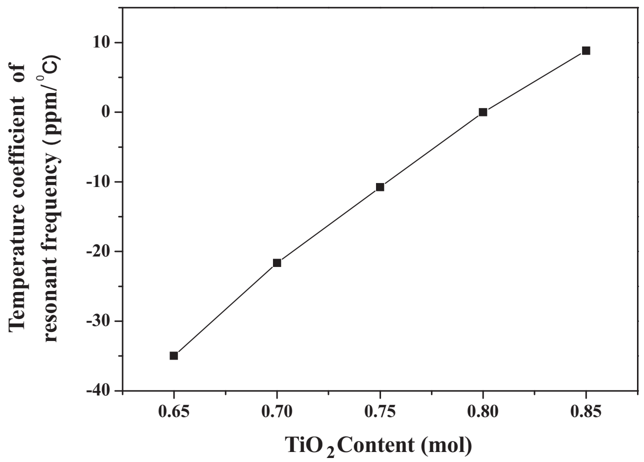


Fig. 8. The τ_f of $ZnTiNb_2O_8$–$xTiO_2$ samples with 2 wt% of BCB sintered at 950 °C.

larger than 5 μm. Alford and co-workers [36] also observed similar results for alumina, which is in contrast to the classical theory. In such complex systems, the contradiction between our experiment results and the classical theory may be a result of the interaction of many parameters such as grain size, porosity or the presence of liquid-phase, which have made it difficult to give definitive remarks on grain size-loss relationships [36]. Consequently we cannot utilize mechanically the grain size-loss relationships theory that the Q value would increase as the grain size increases. Fig. 7(b) shows that the relative dielectric constant ε_r increased with an increased sintering temperature because this variation of dielectric constant was associated with the bulk densification.

Besides the addition of BCB and the sintering temperature, the content of TiO_2 also effects to the microwave dielectric properties of compounds. Figs. 6(a) and 7(a) show that the $Q \times f$ values of the compounds decreased with the increasing TiO_2 content. Figs. 6(b) and 7(b) show that the relative dielectric constant ε_r increased with the increasing TiO_2 content. Referring to XRD patterns in Fig. 1(c), we observed that peak intensity of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase increased gradually with increasing TiO_2 content. $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ has a higher dielectric constant of 95, a $Q \times f$ of 15,000 GHz and $\tau_f = +237$ ppm/°C, in contrast, $ZnTiNb_2O_8$ has a lower dielectric constant of 34, a higher $Q \times f$ of 42,500 GHz and $\tau_f = -52$ ppm/°C [4,38]. Consequently, when TiO_2 content increased, the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ content increased, so the $Q \times f$ values of the compounds decreased gradually due to the relatively lower $Q \times f$ value of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ ceramics as 15,000 GHz and the dielectric constants ε_r increased gradually due to its higher dielectric constant of 95.

In order to achieve the zero τ_f $ZnTiNb_2O_8$ sintered at the low temperature, the effect of TiO_2 content ($x = 0.65$–0.85) on the temperature coefficient of the resonant frequency (τ_f) was studied. Fig. 8 shows the relation between τ_f and TiO_2 content for samples with 2 wt% BCB sintered at 950 °C. It can be seen the τ_f increased gradually with the increase of TiO_2 content and the τ_f value increased from −34.96 ppm/°C to +8.84 ppm/°C as the x value increased from 0.65 to 0.85. Moreover, when $x = 0.8$, the temperature coefficient of the resonant frequency was zero ($\tau_f = 0$ ppm/°C) for the $ZnTiNb_2O_8$–$xTiO_2$ compounds with 2 wt% of BCB. XRD patterns in Fig. 1(c) have shown that peak intensity of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase increased gradually with increasing TiO_2 content and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ has a high τ_f of +237 ppm/°C [38], so the τ_f of the samples increased with the increasing TiO_2 content. Kim et al. have reported that for the $ZnTiNb_2O_8$ ceramics, good dielectric properties were achieved at the sintering temperature of 1250 °C, while in our work, a much lower sintering temperature of 950 °C was shown to exhibit excellent dielectric properties with BCB as the sintering aid. It is well known 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. We have successfully achieved $\tau_f = 0$ ppm/°C when $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.8$) compounds were doped with 2 wt% of BCB.

4. Conclusions

The phases, microstructure and microwave dielectric properties of $ZnTiNb_2O_8$–$xTiO_2$ composite ceramics with different wt% of $BaCu(B_2O_5)$ additive have been investigated using the X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The results showed that the microwave dielectric properties were strongly dependent on densification, grain sizes and crystalline phases, which were both influenced by the amount of BCB, the sintering temperature and the amount of TiO_2. The sintering temperature of ceramics was effectively reduced from 1250 °C to 950 °C and the temperature coefficient of resonant frequency (τ_f) was successfully modified to 0 ppm/°C with reasonably good $Q \times f$ and ε_r. Addition of 2 wt% BCB to $ZnTiNb_2O_8$–$xTiO_2$ ($x = 0.8$) ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r = 38.89$, $Q \times f = 14{,}500$ GHz ($f = 4.715$ GHz) and $\tau_f = 0$ ppm/°C, which represented very promising candidates as LTCC dielectric materials for LTCC applications.

Acknowledgements

We acknowledge the helpful discussion with Prof. G.H. Chen and we also acknowledge PHD John Albaya and X. Jiang who help us correct English language.

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