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ScienceDirect
Journal of the European Ceramic Society 30 (2010) 963–970
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Microwave dielectric properties and microstructures of Nb_2O_5-$Zn_{0.95}Mg_{0.05}TiO_3 + 0.25TiO_2$ ceramics with Bi_2O_3 addition

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Received 20 May 2009; received in revised form 15 September 2009; accepted 28 September 2009
Available online 24 October 2009

Abstract

The effects of Bi_2O_3 addition on the microwave dielectric properties and the microstructures of Nb_2O_5-$Zn_{0.95}Mg_{0.05}TiO_3 + 0.25TiO_2$ (Nb-ZMT′) ceramics prepared by conventional solid-state routes have been investigated. The results of X-ray diffraction (XRD) indicate the presence of four crystalline phases, $ZnTiO_3$, TiO_2, $Bi_2Ti_2O_7$, and $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ in the sintered ceramics, depending upon the amount of Bi_2O_3 addition. In addition, in order to confirm the existence of $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ phase in the samples, the microstructure of Nb-ZMT′ ceramic with 5 wt.% B_2O_3 addition was analyzed by using a transmission electron micrograph. The dielectric constant of Nb-ZMT′ samples was higher than ZMT′ ceramics. The Nb-ZMT′ ceramic with 5 wt.% Bi_2O_3 addition exhibits the optimum dielectric properties: $Q \times f = 12{,}000$ GHz, $\varepsilon_r = 30$, and $\tau_f = -12$ ppm/°C. Unlike the ZMT′ ceramic sintered at 900 °C, the Nb-ZMT′ ceramics show higher Q value and dielectric constant. Moreover, there is no Zn_2TiO_4 existence at 960 °C sintering. To understand the co-sinterability between silver electrodes and the Nb-ZMT′ dielectrics, the multilayer samples are prepared by multilayer thick film processing. The co-sinterability (900 °C) between silver electrode and Nb-ZMT′ dielectric are well compatible, because there are no cracks, delaminations, and deformations in multilayer specimens.

Keywords: Nb-ZMT′ (Nb_2O_5-$Zn_{0.95}Mg_{0.05}TiO_3 + 0.25TiO_2$); Dielectric resonator; Quality factor; Bi_2O_3; Microwave ceramic; LTCC

1. Introduction

Recently, the development of commercial wireless technologies has made rapid progress because of the improved characteristics of dielectric resonators in microwave ranges. This rapid development of the wireless communication implies to design new ceramics sinterable at low temperature, e.g., at around 900 °C and exhibiting good dielectric properties. This low sintering temperature is of primary importance to produce silver co-sintering devices such as silver based multiplayer ceramic capacitors or hybrid circuits.[1–3] The required specifications in term of dielectrics properties are a high dielectric constant ($\varepsilon_r > 20$), a high quality factor ($Q > 10{,}000$) which corresponds to a low dielectric loss ($\tan\delta = 1/Q$) and a temperature coefficient of the permittivity close to zero ppm/°C. However, the sintering temperature of conventional dielectric ceramics used for microwave resonators, filters, and duplexers of portable phones usually ranges from 1200 to 1500 °C.[2,4] Therefore, these dielectric ceramics are not suitable for use in the conductors that have low melting temperatures such as silver (961 °C) and copper (1064 °C). The development of materials began with the search for a suitable low-firing-temperature dielectric, followed by the modification of the electrical characteristics to meet the above requirements for the specified applications.

There are three compound phases present in the ZnO–TiO_2 phase diagram: Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal), and $Zn_2Ti_3O_8$ (cubic), which is a low-temperature form of $ZnTiO_3$ that exists below 820 °C.[5,6] It has been reported that the zinc titanates ($ZnTiO_3$) can be sintered at 1100 °C without sintering aids.[7] However, if a sintering aid is added, it can be fired at temperatures lower then 900 °C.[7–9] This material has a permittivity (ε_r) of 19, a Q value of 3000 at 10 GHz, and a temperature coefficient (τ_f) of −55 ppm/°C. Kim et al.[9] studied the $ZnTiO_3$–$xTiO_2$ system, where $x = 0$–0.5; the optimum microwave dielectric properties were obtained to be $\tau_f = -20$ ppm/°C, $\varepsilon_r = 27.5$, and $Q \times f = 14{,}000$ GHz for $x = 0.25$ and sintered at 925 °C. Nevertheless, the pure $ZnTiO_3$ phase is not easily obtained because the compound decomposes to

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doi:10.1016/j.jeurceramsoc.2009.09.028

Zn_2TiO_4 and TiO_2 at high temperatures.[10] Kim et al.[8] also studied zinc titanate with a small amount of magnesium addition, and reported that the $(Zn_{1-x}Mg_x)TiO_3$ phase was stable at a much higher temperature, the microwave dielectric properties of which were $\tau_f = -90$ ppm/°C, $\varepsilon_r = 21$, and $Q \times f = 40{,}000$ at $x = 0.05$ sintered at 900 °C.

In the previous study,[11] the microstructure and dielectric properties of the Bi_2O_3 additive in $Zn_{0.95}Mg_{0.05}TiO_3 + 0.25TiO_2$ with 1 wt.% $3ZnO–B_2O_3$ ceramics have been investigated. It was found that 5 wt.% Bi_2O_3 addition can significantly suppress spinel Zn_2TiO_4 phase formation in the ZMT′ ceramics, but the microwave dielectric properties become worse due to low Q value (<600). Although, the permittivity still was kept at ~24. The main purpose of incorporating 0.8 mol.% Nb_2O_5 additive in $Zn_{0.95}Mg_{0.05}TiO_3 + 0.25TiO_2$ ceramics is to improve the microwave dielectric properties of sintered samples at lower temperatures, to obtain a homogeneous microstructure, and to suppress spinel Zn_2TiO_4 phase formation in this study. In addition, the multilayer specimens were fabricated by multilayer thick film processing. The co-sinterability between silver electrodes and the Nb-ZMT′ dielectrics is also studied in this experiment.

2. Experimental procedures

2.1. Preparation of ZMT' and Nb-ZMT′ ceramics

Samples of ZMT′ were synthesized by conventional solid-state methods from individual high-purity oxide powders: ZnO (Hayashi Chemical Industry, Japan, >99.9%), TiO_2 (Janssen Chemica, Japan, >99.9%), MgO (Showa Chemicals Inc., Japan, >99.9%). The starting materials were ZnO, MgO and TiO_2 powders. They were mixed and ground in deionized water with 2 mm zirconia beads for 24 h, until the mean particle size (D50) was approximately 0.35 μm. The optimum composition of ZMT′ determined in previous studies is $Zn_{0.95}Mg_{0.05}TiO_2 + 0.25TiO_2$ (ZMT′),[8,9] which is adopted as the reference composition. The powders were calcined in air at 900 °C for 5 h after ball milling. Nb_2O_5 was added and fixed at 0.8 mol.%. Bi_2O_3 glass was chosen as sintering aids, and it was added in the amounts of 1, 3, 5 and 10 wt.%, respectively. Then the calcined powders were milled again for 6 h. After grinding, the mean particle size was measured to be about 0.5 μm. After drying, the powders were pressed uniaxially into pellets in a steel die. Sintering of these pellets were carried out at 900, 920 and 940 °C, respectively.

2.2. Fabrication of multilayered Nb-ZMT′ capacitors

In this experiment, MLCC consists of 10 active layers with an overall size of 2.0 mm × 1.25 mm × 0.6 mm and a distance of 17 μm between the internal electrodes. The dielectric in the MLCC is a ceramic material based on the Nb-ZMT′ compound. The Nb-ZMT′ powders were mixed with a resin (polyvinyl butyral), a plasticizer (butyl benzyl phthalate) and a solvent (toluene and ethanol). The resultant slurry was tape casted to a green sheet with 30 μm thickness using the doctor-blade method. Ag pastes were printed as an inner electrode onto the green sheet. These printed sheets were stacked, pressed at 60 °C under a pressure of 5.2×10^7 Pa, and cut into chips. The laminated green chip was sintered from 860 to 920 °C for 2 h after binder burnout (320 °C), and then heat treated at 760 °C for Ag end-termination.

2.3. Characteristics analysis

The crystalline phases of the sintered ceramics were identified by X-ray diffraction pattern analysis (XRD, Bruker D8A) using Cu-K_α radiation for 2θ from 20 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 was measured by the Archimedes method. The particle size was measured using a particle size analyzer (Malvern, Mastersizer 2000, UK). 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 was positioned between two plates.[12] An HP8719C network analyzer was used to measure the microwave property. The dielectric properties were calculated from the frequency of the TE_{011} resonant mode. For convenience, the $Q \times f$ factor was used to evaluate the loss quality, where f is the resonant frequency.

3. Results and discussion

3.1. Effect of Bi_2O_3 addition on phase evolution and microstructure of the ceramics

The hexagonal $ZnTiO_3$ phase remains stable at temperatures below 945 °C and then decomposes to the cubic Zn_2TiO_4 and TiO_2 phases at 945 °C, as indicated in the phase diagram of ZnO–TiO_2.[5] The $Zn_2Ti_3O_8$ phase, known as the low-temperature form of the $ZnTiO_3$ phase, exists at temperatures between 900 and 925 °C. In fact, the decomposition of $ZnTiO_3$ and $Zn_2Ti_3O_8$ phases starts at ~900 °C and completes at ~950 °C. The decomposition reactions of the two compounds at ~950 °C can be describe as follows.

$$2ZnTiO_3(\text{hexagonal}) \rightarrow Zn_2TiO_4(\text{cubic}) + TiO_2(\text{rutile})$$

$$Zn_2Ti_3O_8(\text{cubic}) \rightarrow Zn_2TiO_4 + 2TiO_2$$

In reality, small amounts of the Zn_2TiO_4 phase were also detected at 900 °C as a counterpart of $Zn_2Ti_3O_8$ to satisfy the stoichiometry. Therefore, the formation and transformation reactions of $ZnTiO_3$ can be summarized as follows.

$$ZnO + TiO_2 \xrightarrow{\sim 700\,^\circ C} ZnTiO_3 \xrightarrow{700–900\,^\circ C} ZnTiO_3 + Zn_2Ti_3O_8 + Zn_2TiO_4$$
$$\xrightarrow{900–950\,^\circ C} ZnTiO_3 + Zn_2Ti_3O_8 + Zn_2TiO_4 + TiO_2$$
$$\xrightarrow{\geq 950\,^\circ C} Zn_2TiO_4 + TiO_2$$

These results indicate that the cubic $Zn_2Ti_3O_8$ phase is an intermediate phase of the ZnO–TiO_2 system that exists at

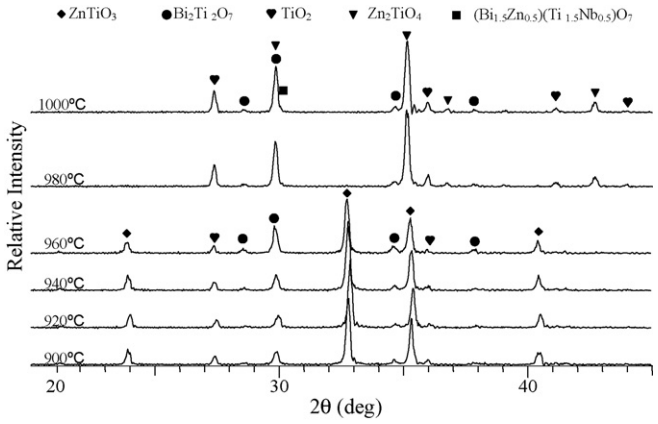


Fig. 1. X-ray diffraction (XRD) spectra of Nb-ZMT′ ceramics with 5 wt.% Bi_2O_3 sintered at (a) 900 °C, (b) 920 °C, (c) 940 °C, (d) 960 °C, (e) 980 °C, and (f) 1000 °C.

700–950 °C, rather than a low-temperature form of $ZnTiO_3$.[6,8]

Fig. 1 shows the XRD results for Nb-ZMT′ with 5 wt.% Bi_2O_3 addition sintered at temperatures ranging from 900 to 1000 °C. It is interesting to note that no cubic Zn_2TiO_4 phase is present in the Nb-ZMT′ ceramic with 5 wt.% Bi_2O_3 addition, even at a temperature as high as 960 °C. This is contradicted by the phase diagram, which indicates that the $ZnTiO_3$ ceramic would decompose at 945 °C. This result is the same as previous study,[11] Bi_2O_3 addition can be inhibited Zn_2TiO_4 formation in ZMT′ ceramics at sintered temperatures of up to 960 °C. Also from our previous study,[13] it is known that the Zn_2TiO_4 phase was formed in ZMT′ ceramics with 1 wt.% 3ZnO–B_2O_3 addition sintered at 920 °C. In other words, it can be concluded that the addition of Bi_2O_3 can suppress the formation of the Zn_2TiO_4 phase in the Nb-ZMT′ ceramics. Fig. 2 shows the XRD results for Nb-ZMT′ ceramics sintered at 900 °C with different amounts of Bi_2O_3. For the undoped Nb-ZMT′ ceramics sintered at 900 °C, as shown in Fig. 2(a), it can be observed that the ceramic contains two well-characterized phases, namely TiO_2 and $ZnTiO_3$.[14] For Nb-ZMT′ ceramics with 3, 5 and 10 wt.% Bi_2O_3 additions sintered at 900 °C, as shown in Fig. 2(c)–(e), respectively, it is found that the major crystalline phases are the same as those of the undoped Nb-ZMT′ ceramics, along with two extra-phases identified to be $Bi_2Ti_2O_7$ and $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$. When Bi_2O_3 and Nb_2O_5 are doped into ZMT′ ceramics, Nb^{5+} obviously exhibit a preference for the Ti-sites, since the ionic radius of Ti^{4+} ($r = 0.605$ Å) is close to that of Nb^{5+} ($r = 0.64$ Å), and Bi^{3+} substitute a preference for the Zn-sites, because the ionic radius of Zn^{2+} ($r = 0.74$ Å) is close to that of Bi^{3+} ($r = 0.81$ Å). It can be assumed that small amount of $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ is formed based on element ionic radius, because the XRD analysis revealed that the phase structures of substituted sample has a $Bi_2Ti_2O_7$ phase (Fig. 2). That means Nb^{5+} partly substituting for Ti^{4+} at B site and Bi^{3+} partly substituting for Zn^{2+} at A site result a relatively stable substitutional solid solution $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$. It is not easy to identify the phases between $Bi_2Ti_2O_7$ and $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ compounds, since the angles and intensities of peak are almost the same between them from XRD data. However, the amount of $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ phase formed in ZMT′ ceramics is less then $Bi_2Ti_2O_7$ phase due to Nb_2O_5 doped is only 0.8 mol.% and the Nb has solubility limit. The $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ phase was further analyzed by transmission electron micrograph (TEM).

Fig. 3 shows the XRD results of the sintered ceramics having the composition of Nb-ZMT′ with different amounts of Bi_2O_3. We separated two groups for discussion, one is Nb-ZMT′ with different amounts of Bi_2O_3 sintered at 920 °C (Fig. 3(a)–(c)), the other one is Nb-ZMT′ with different amounts of Bi_2O_3 sintered at 940 °C (Fig. 3(d)–(f)). For the composition of Nb-ZMT′ ceramics with 1 wt.% Bi_2O_3 addition sintered at 920 °C, as shown in Fig. 3(a), it can be observed that the ceramic contains TiO_2, $ZnTiO_3$ and $Bi_2Ti_2O_7$ phases. For the composition of Nb-ZMT′ ceramics with 3 and 5 wt.% Bi_2O_3 additions, as shown in Fig. 3(b) and (c), respectively, it is found that the major crystalline phases are the same as those of the Nb-ZMT′ ceramics with 1 wt.% Bi_2O_3 additions, without extra-phases are identified. When the sintering temperature rises from 920 to 940 °C, the microstructure of the ceramics is change a lot. For the composition of Nb-ZMT′ ceramics with 1 wt.% Bi_2O_3 addi-

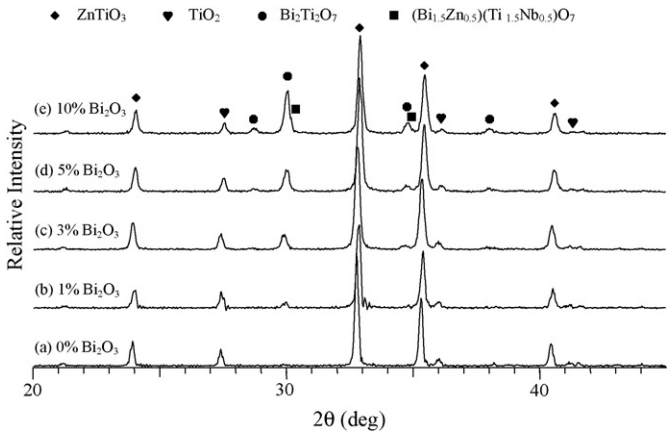


Fig. 2. X-ray diffraction (XRD) spectra of Nb-ZMT′ ceramics sintered at 900 °C with dopant (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.% and (e) 10 wt.% Bi_2O_3.

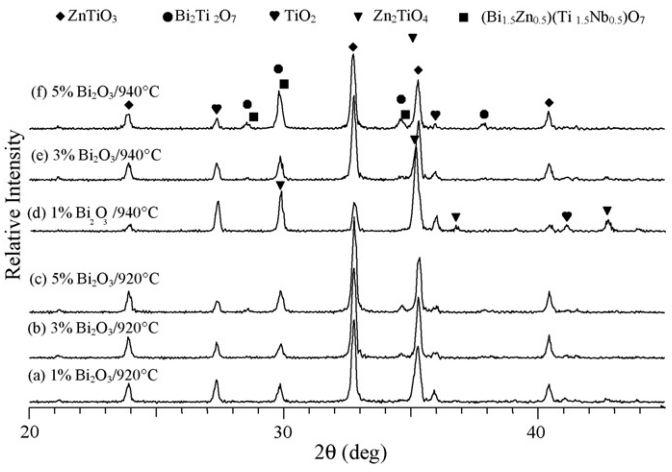


Fig. 3. X-ray diffraction (XRD) spectra of Nb-ZMT′ ceramics with different Bi_2O_3 contents/sintering temperature: (a) 1%/920 °C, (b) 1%/940 °C, (c) 3%/920 °C, (d) 3%/940 °C, (e) 5%/920 °C, and (f) 5%/940 °C.

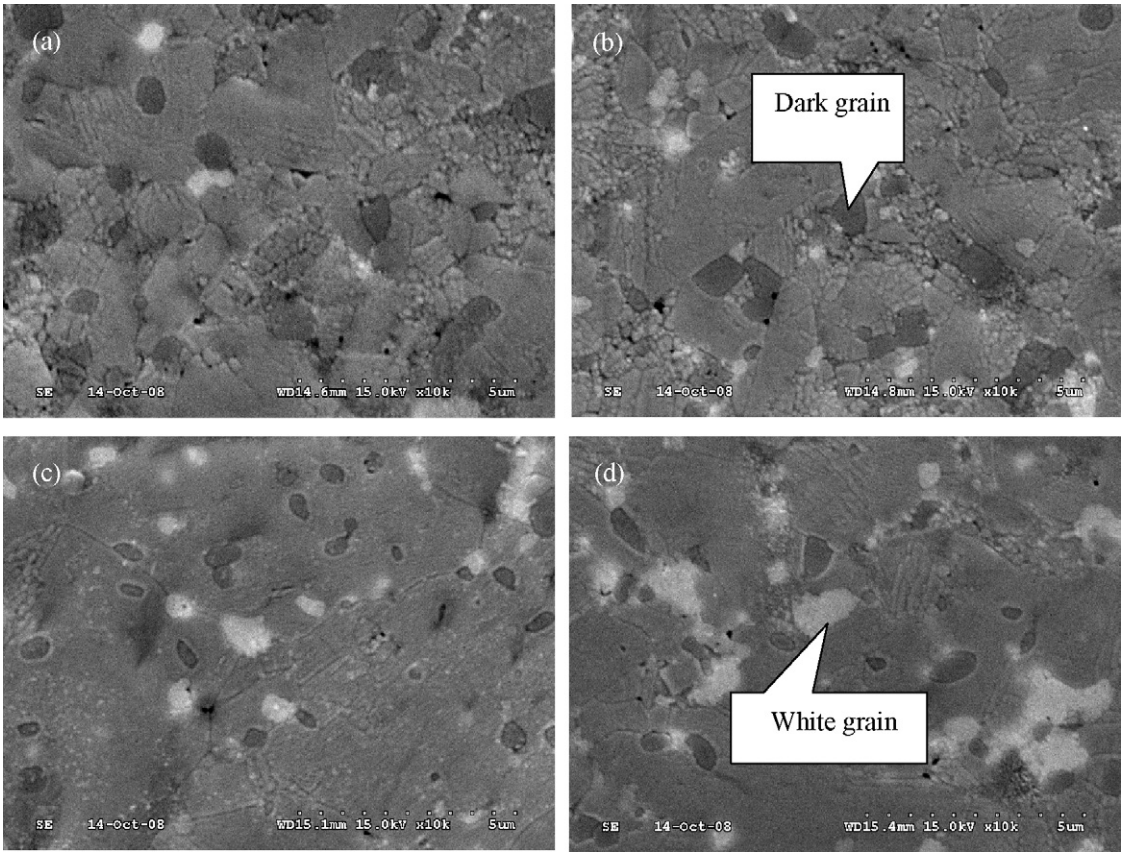


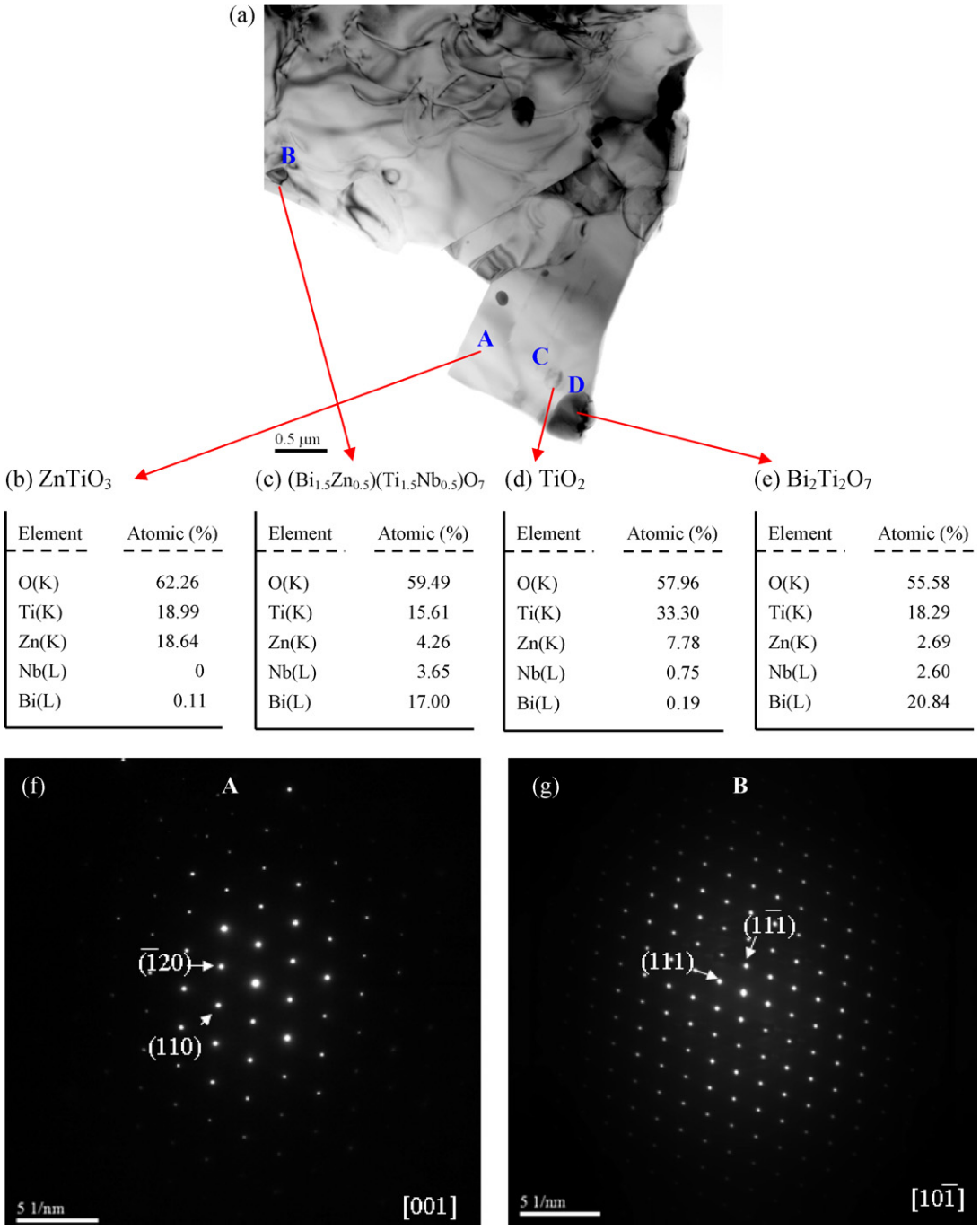
Fig. 4. SEM micrographs of the Nb-ZMT′ ceramics sintered at 900 °C with (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.% and (d) 10 wt.% Bi_2O_3.

tion sintered at 940 °C, as shown in Fig. 3(d), there are contained three phases in the sample, namely TiO_2, $ZnTiO_3$ and Zn_2TiO_4. When the same heat treatments were applied in Nb-ZMT′ ceramics with 5 wt.% Bi_2O_3 addition (Fig. 3(f)), the microstructure of the ceramics mainly consisted of TiO_2, $ZnTiO_3$ and $Bi_2Ti_2O_7$. This result indicates that the Bi_2O_3 dopant content and sintering temperature play an important role, which suppress the formation of the Zn_2TiO_4 phase in the Nb-ZMT′ ceramics.

Fig. 4 shows SEM micrographs of the Nb-ZMT′ ceramics sintered at 900 °C with 1, 3, 5, and 10 wt.% Bi_2O_3 addition. It seems that the microstructures are closely correlated to the Bi_2O_3 content. The gray, similar rectangular grains are $ZnTiO_3$ phases, the dark grains are rutile phases (TiO_2) [9], and the white grains are second phases ($Bi_2Ti_2O_7$). However, the microstructure of the sintered ceramics shows a slight change, that is, a new second phase is increased significantly with the increasing of Bi_2O_3 content, as shown in Fig. 3(c) and (d), for those samples which contain 5 and 10 wt.% Bi_2O_3, respectively. The volume of second phase grain is ∼6% and ∼15% for sample with 5 and 10 wt.% Bi_2O_3 addition, respectively. The second phase was further analyzed by TEM energy-dispersive-spectroscopy, and the results for Nb-ZMT′ ceramics with 5 wt.% Bi_2O_3 addition sintered at 900 °C for 2 h are shown in Fig. 5. TEM-EDX and TEM-electron diffraction were used to provide more detailed information on these intergranular phases in the samples. However, according to XRD identification, there are four phases in the BST with 5 wt.% Bi_2O_3 addition, these phases are included $ZnTiO_3$, $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$, $Bi_2Ti_2O_7$, and TiO_2. The EDX results of part A (Fig. 5(b)), showed only Zn, Ti and O in the matrix; no Nb and Bi were detected. For this matrix phase A, an electron diffraction pattern was done as shown in Fig. 5(f), the result indicates this matrix phase should be a $ZnTiO_3$. The EDX results of part B, it did provide an indication of Nb in phase B (Fig. 5(c)). Therefore, phase B, which XRD data had suggested to be $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$. This result can be supported by electron diffraction pattern analyzing as shown in Fig. 5(g). For the EDX data of part C and D (Fig. 5(d)–(e)), the results indicate that the compounds should be TiO_2, and $Bi_2Ti_2O_7$, respectively. The phase D analyzed by EDX contained Bi, Ti and O with low levels of Nb and Zn, Fig. 5(e). Therefore, this phase was the Nb and Zn-containing phase D, suggested by XRD to be $Bi_2Ti_2O_7$. TEM-EDX, as with phase D, indicated a low level of Nb substituted to Ti and Zn replaced to Bi.

3.2. Effect of Bi_2O_3 addition on microwave dielectric properties of the ceramics

The dielectric constant of the ceramics was measured, and the results are shown in Fig. 6(a). The ε_r value of Nb-ZMT′ ceramics is significantly related to the Bi_2O_3 content, e.g., the dielectric constants of the ceramic are 25.1, 27.8, 30.2 and 31.6 for Bi_2O_3 content at 1, 3, 5 and 10 wt.%, respectively. In addition, the dielectric constants of the ZMT′ ceramics (undoped Nb_2O_5) with different amounts of Bi_2O_3 addition are kept at ∼24. Unlike



Element	Atomic (%)
O(K)	62.26
Ti(K)	18.99
Zn(K)	18.64
Nb(L)	0
Bi(L)	0.11

Element	Atomic (%)
O(K)	59.49
Ti(K)	15.61
Zn(K)	4.26
Nb(L)	3.65
Bi(L)	17.00

Element	Atomic (%)
O(K)	57.96
Ti(K)	33.30
Zn(K)	7.78
Nb(L)	0.75
Bi(L)	0.19

Element	Atomic (%)
O(K)	55.58
Ti(K)	18.29
Zn(K)	2.69
Nb(L)	2.60
Bi(L)	20.84

Fig. 5. TEM analysis for the specimen with 5 wt.% Bi_2O_3 addition sintered at 900 °C (a) micrograph, (b) EDX data of A part, (c) EDX data of B part, (d) EDX data of C part, (e) EDX data of D part, (f) diffraction pattern of A part and (g) diffraction pattern of B part.

the Nb-ZMT′ ceramics with Bi_2O_3 addition, the ZMT′ ceramics with increasing amounts of Bi_2O_3 show slightly variation of dielectric constant. In a previous study,[11] we have investigated the microwave dielectric properties of the ZMT′ ceramics with different amounts of Bi_2O_3 addition. A comparison between the ceramics with and without Nb_2O_5 dopant on the microstructure of the ceramics will be described briefly below. The XRD results show that both of the sintered ceramics with Bi_2O_3 addition contain the three crystalline phases, $ZnTiO_3$, TiO_2, and $Bi_2Ti_2O_7$. Nevertheless, dopant of Nb_2O_5 in the ZMT′ ceramics also produces the $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ phase, this is $A_2B_2O_7$ cubic pyrochlores phase. As we known,[15] pyrochlore-type oxides with the general formula $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ (BZTN) have been attracting a lot of attention because of their excellent dielectric constant and low firing temperature. BZTN ceramic is one of the most promising materials due to its stability and excellent dielectric properties ($\varepsilon_r = \sim 200$ and $\tan\delta = 0.01\%$ at 1 MHz). Therefore, the existence of a small amount of cubic pyrochlores phase can increase the dielectric constant of the ceramic because the dielectric constant of BZTN is much higher than that of the hexagonal $ZnTiO_3$ phase, $\varepsilon_r = 19$.[9] It is therefore believed that the higher dielectric constant is related to the

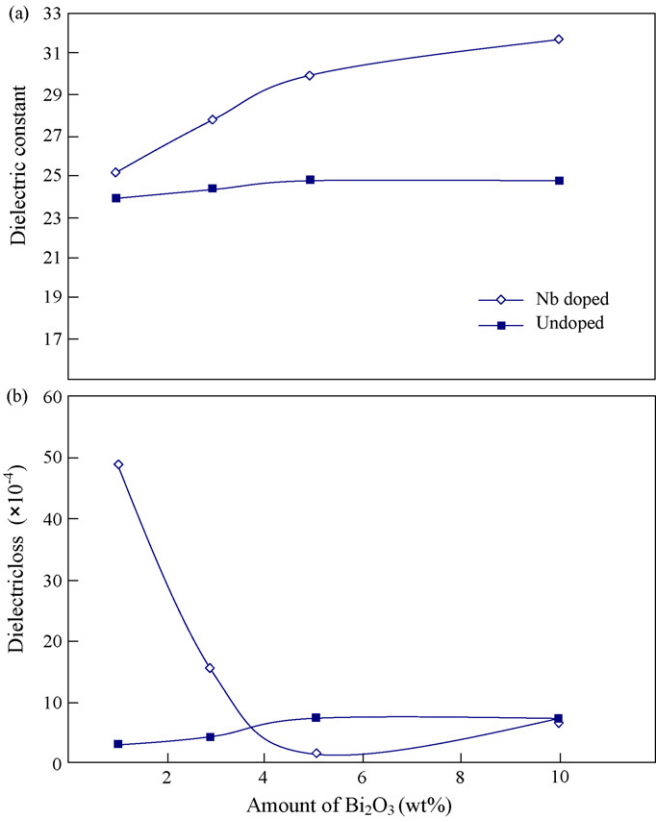


Fig. 6. The dielectric properties of the Nb-ZMT′ ceramics sintered at 900 °C as a function of the amount of Bi_2O_3 addition, (a) dielectric constants and (b) dielectric loss.

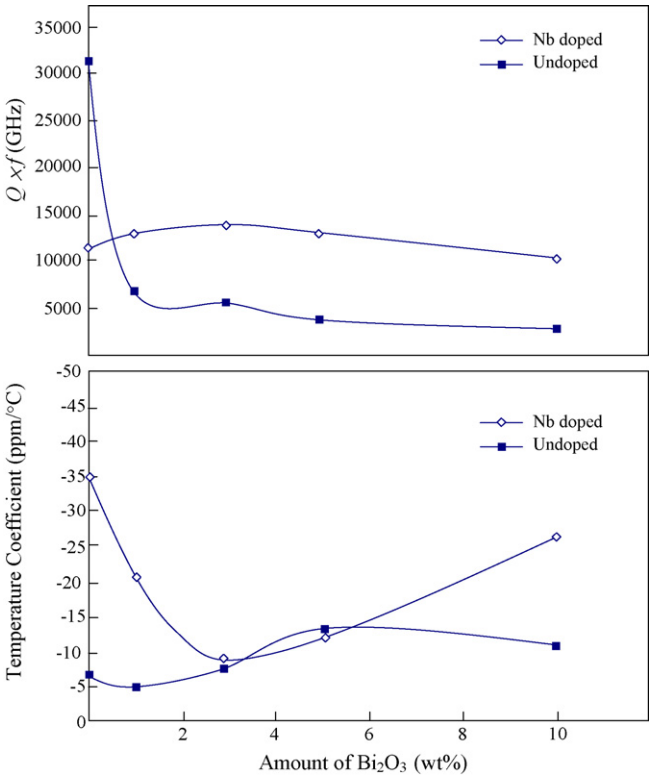


Fig. 7. The $Q \times f$ values and temperature coefficients of resonant frequency of the Nb-ZMT′ ceramics sintered at 900 °C as a function of the amount of added Bi_2O_3 addition.

pyrochlores phase evolution when the Bi_2O_3 is added in Nb-ZMT′ ceramics. The dielectric loss of the ceramics as a function of Bi_2O_3 amount is shown in Fig. 6(b). The $\tan\delta$ value of Nb-ZMT′ ceramics is also deeply related to the Bi_2O_3 content, and minimum $\tan\delta$ (0.02%) is obtained at 5 wt.% Bi_2O_3 addition. On the other hand, the dielectric loss of the ZMT′ ceramics is below 0.1% for the samples with different amounts of Bi_2O_3. However, this result suggests that the Nb-ZMT′ ceramics with Bi_2O_3 addition can have good dielectric properties, which would be accompanied by an increase in the dielectric constant.

The $ZnTiO_3$ ceramic is an interesting material with a negative τ_f of −55 ppm/°C, ε_r of 19 and a Q value of 3000 at 10 GHz.[13] Fig. 7 shows the $Q \times f$ value of the ceramics as a function of the amount of Bi_2O_3. The $Q \times f$ values of the ZMT′ ceramics without Bi_2O_3 addition are higher than that in the case of the Nb-ZMT′ ceramics. In contrast, the $Q \times f$ values of the Nb-ZMT′ ceramics with Bi_2O_3 addition are higher than that in the case of the ZMT′ ceramics. The reason for this is attributed to a formation of $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$ when the Bi_2O_3 is added into Nb-ZMT′ ceramics. This cubic pyrochlores phase has excellent dielectric properties as we mentioned above. For ZMT′ ceramics, when the 1 wt.% Bi_2O_3 was added to the ceramics, the $Q \times f$ value decreased rapidly from 32,000 to 7000. This result is probably due to the formation of the second phase $Bi_2Ti_2O_7$ from the low-loss hexagonal ilmenite structure and rutile phase, as illustrated in Fig. 2. It is known that the microwave dielectric loss is mainly controlled by the second phases formed or the crystal defects and grain boundaries.[16,17] Nevertheless, from the point of view of practical application, ceramics with a low $Q \times f$ value are not suitable for high-frequency applications. Moreover, the $Q \times f$ values of Nb-ZMT′ ceramics are slightly increased with Bi_2O_3 increasing then slightly decreased at 5 and 10 wt.% Bi_2O_3. Fig. 7 also shows the temperature coefficient of the resonant frequency, τ_f, at the maximum Q value as a function of the amount of Bi_2O_3 for samples. The Nb-ZMT′ ceramics with 3 wt.% Bi_2O_3 addition has a τ_f closer to zero than those of other compositions, which is a condition required for microwave device applications. The ZMT′ ceramic is known for its temperature-stable characteristic. The τ_f values did not change much when Bi_2O_3 was added to the ZMT′ ceramic. However, the τ_f value of the Nb-ZMT′ ceramic with 3 wt.% Bi_2O_3 addition exhibited the smallest negative value of −10 ppm/°C.

3.3. Dielectric properties and microstructures of the Nb-ZMT′ MLCCs

The multilayer specimens were fabricated by tape casting, screen printing, and laminating. A green sheet with 30 μm thickness was obtained by a caster with a doctor blade. Conductor pastes of pure Ag were then printed on it to form the internal electrode. The multilayer specimens were sintered in the range 860–920 °C, and then heat treated at 760 °C for Ag end-termination. Fig. 8 shows scanning electron microscopic pictures for Nb-ZMT′ multilayer ceramic capacitors (MLCC) with pure silver electrodes sintered at 900 °C. It is found there are no flaws at the interface. It means that a good physical match

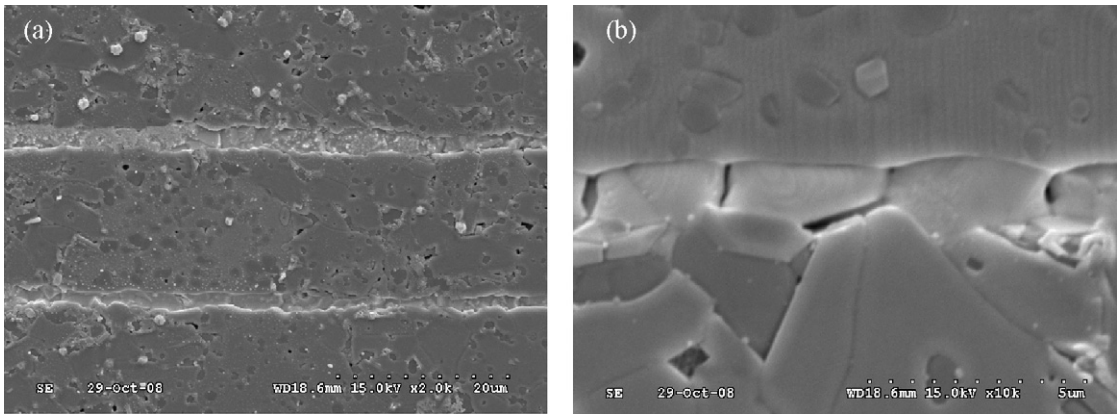


Fig. 8. Scanning electron microscope pictures for Nb-ZMT′ multilayer ceramic capacitors with pure silver electrodes sintered at 900 °C, (a) magnification 2000×, (b) magnification 10,000×.

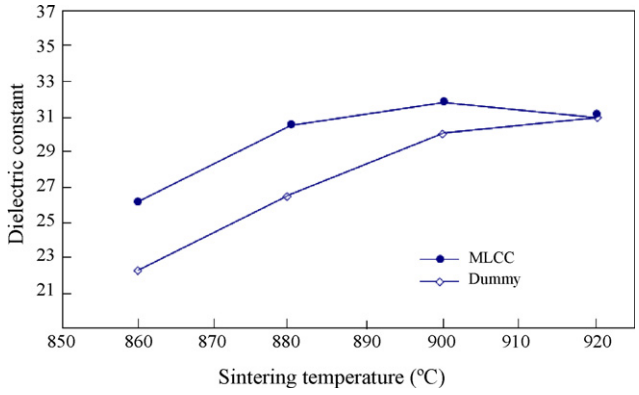


Fig. 9. Dielectric constant of the Nb-ZMT′ ceramic and Nb-ZMT′ multilayer ceramic capacitors as a function of the sintering temperature.

silver electrode and Nb-ZMT′ dielectric. Several papers have pointed out that the cracking, delamination, and deformation of the MLCCs resulting from physical mismatch and sintering shrinkage.[18–20] It is therefore that the Nb-ZMT′ ceramic could be compatible for LTCC application. The dielectric constant of the Nb-ZMT′ MLCCs as a function of the sintering temperature is shown in Fig. 9. It can be seen that, in general, the dielectric constant of the sintered Nb-ZMT′ MLCC increases with the sintering temperature. The decrease of ε_r can be explained by a reduction of density and the effect of liquid-phase sintering of the Nb-ZMT′ MLCCs.[21,22] This trend is the same as Nb-ZMT′ ceramic. The multilayer samples have lower ε_r value after reaching a maximum value at 900 °C. This can be attributed to the low melting point of Ag electrodes with strong shrinkage during sintering at 920 °C. Moreover, it was observed that the dielectric constant of capacitors in the multilayer form is higher than that in the disk form. Two reasons can be given: one is some form of interactions between the thin dielectrics and Ag electrodes are responsible for the higher ε_r,[23,24] and the other one is that the low melting point of Ag leads to transient liquid sintering when Ag is transferred to the dielectric layer.[25]

4. Conclusions

The microwave properties and microstructures were affected by the addition of Nb_2O_5 and Bi_2O_3 for ZMT′ ceramics. Two kinds of new secondary phases were found in this study; it is believed to be related to Bi_2O_3, since it also appeared in specimens that contained ≥3 wt.% Bi_2O_3. A transmission electron microscopy was used to analyze the secondary phases for Nb-ZMT′ ceramic with 5 wt.% B_2O_3 addition, both of secondary phases were identified to be $Bi_2Ti_2O_7$ and $(Bi_{1.5}Zn_{0.5})(Ti_{1.5}Nb_{0.5})O_7$. In addition, Bi_2O_3 addition can be inhibited Zn_2TiO_4 formation in Nb-ZMT′ ceramics at sintered temperatures of up to 960 °C. In this study, Nb-ZMT′ ceramics with 5 wt.% Bi_2O_3 were sintered at 900 °C for 2 h, the dielectric properties were $Q \times f = 12{,}000$ GHz, $\varepsilon_r = 30$, and $\tau_f = -12$ ppm/°C. On the other hand, the co-sinterability between silver and the Nb-ZMT′ dielectric seem to be well compatible, because there are no cracks, delaminations, and deformations in multilayer specimens. It is therefore that the Nb-ZMT′ ceramic could be suitable for LTCC application.

Acknowledgements

The authors would like to acknowledge the financial support of this study by the National Science Council of Taiwan under Contract No. NSC97-2221-E-020-003.

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