

# Study on low temperature sintering and microwave dielectric properties of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics

Ying-Chieh LEE,<sup>†</sup> Ko-Wei WENG,<sup>\*</sup> Wen-Hsi LEE<sup>\*\*</sup> and Yen-Lin HUANG

Department of Material Engineering, National PingTung University of Science & Technology, PingTung 91201, Taiwan

<sup>\*</sup>Institute of Materials and Systems Engineering, MingDao University, ChangHua 52345, Taiwan

<sup>\*\*</sup>Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan

The microwave dielectric properties and microstructures of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics were investigated as a function of B<sub>2</sub>O<sub>3</sub> content and sintered at 940°C for 2 h. Densities of the specimens were enhanced with an increase of B<sub>2</sub>O<sub>3</sub> up to 3 mass% and then decreased. The specimens could be sintered at 940°C without the degradation of the microwave dielectric properties of the specimens. The results of X-ray diffraction (XRD) indicate the presence of five crystalline phases, Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, BaZr(BO<sub>3</sub>)<sub>2</sub>, BaZrO<sub>3</sub>, BaTi<sub>4</sub>O<sub>9</sub>, and Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, in the sintered ceramics, depending upon the amount of B<sub>2</sub>O<sub>3</sub> addition. Moreover, the microstructure of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramic with 3 mass% B<sub>2</sub>O<sub>3</sub> addition was analysed by using a transmission electron micrograph, which the composition of dendrite phase should be BaZr(BO<sub>3</sub>)<sub>2</sub>. The specimens with 3 mass% B<sub>2</sub>O<sub>3</sub> sintered at 940°C for 2 h showed  $\epsilon_r$  of 28.3,  $Q \times f$  value of 10784 ( $Q = 1477$ ), and TCF ( $\tau_f$ ) of -8.2 ppm/°C.

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, Dielectric constant, Quality factor, Temperature coefficient of resonant frequency

[Received October 14, 2008; Accepted January 15, 2009]

## 1. Introduction

With the great increase of interest in the microwave telecommunication system, the development of the dielectric ceramics has accelerated to meet the demand for miniaturization of communication systems. The dielectric resonator has the advantages of the compactness and ease of matching to the microwave integrated circuits. The desired ceramic characteristics for microwave resonators are a high dielectric constant ( $\epsilon_r$ ), low dielectric loss and a near zero temperature coefficient of the resonant frequency (TCF:  $\tau_f$ ). One of the key components in these devices is the multilayer ceramic capacitor (MLCC) that uses Pd as an internal electrode. Since the price of Pd increases and fluctuates over the years, there is a strong drive towards decreasing the use of Pd in the electrodes for microwave multilayer capacitors. At the same time, reducing the size of microwave devices in a communication system has become a new trend, i.e. the dielectric components are miniaturized, which would cut the production cost as well.<sup>1)-4)</sup>

Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> is a classical material for type I MLCC. The high and variable and cost of the noble metals, palladium and silver, classically used to form the inner electrodes is a recurrent economic problem. Using silver or Ag-Pd alloy (for instance 95Ag-5Pd) for these electrodes could be a solution but low sintering temperature is required for firing the capacitors. This solution has in common problem, because classical sintering temperatures of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> in air are around 1300°C. The problem is that this temperature of 1300°C is totally inadequate for the use of 95Ag-5Pd or silver electrodes.<sup>5),6)</sup> It is thus necessary to investigate on the possibility of lowering the sintering temperature of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>. There are several methods commonly used to such as low-melting glass additions, chemical pre-treatment and

processing of ceramic powders, and the usage of small particles for the starting materials.<sup>7)-10)</sup> Among the three methods, liquid-phase sintering using glass addition is known to be the most effective and the least expansive way of achieving high density sintered ceramics, and consequently is widely used in the ceramic industry.

Generally, it is not easy to find materials which simultaneously satisfy the three required characteristics for microwave dielectric applications because the materials with high dielectric constant have a high dielectric loss and large TCF. A commercially available dielectric powder from Ferro America, which, according to the X-ray diffraction (XRD) analysis, is mainly composed of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phase, is used as the host material in this study. It was reported that the TiO<sub>2</sub>-rich compounds of the barium titanate-based ceramics with Ti/Ba = 4 and 4.5, i.e., BaTi<sub>4</sub>O<sub>9</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, have superior dielectric properties suitable for microwave resonator applications.<sup>11),12)</sup> 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.<sup>8),13)</sup> In general microwave dielectric resonators are required to have a high dielectric constant ( $\epsilon_r$ ) > 35, a low dielectric loss or high quality factor  $Q$  (= 1/tanδ) > 3000, and a near-zero temperature coefficient of resonant frequency ( $\tau_f$ ).<sup>12)</sup>

In this paper, ULF280 commercial powder was used as host materials, which was made by Ferro Corporation. Main composition in this powder was Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phase after sintering at ~1000°C. Author attempts to lower the sintering temperature below 940°C based on ULF280 powder (Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics) with B<sub>2</sub>O<sub>3</sub> addition. Therefore, Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics with B<sub>2</sub>O<sub>3</sub> addition is reported, and the dielectric properties of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics were characterized. The relation between crystalline phases and microstructures of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics was also investigated.

<sup>†</sup> Corresponding author: Y.-C. Lee; E-mail: YCLee@mail.npust.edu.tw

## 2. Experimental

### 2.1 The preparation of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ -based ceramic with $3\text{ZnO-B}_2\text{O}_3$ glass addition

The starting materials contain the ULF280 powder received from the Ferro America and the  $\text{B}_2\text{O}_3$  glass. They are mixed and ball-milled in deionised water with  $\varphi 2$  mm zirconia balls for 10 h. The mixed powders were calcined in a platinum crucible at  $940^\circ\text{C}$  for 1 h. The calcined powders were pulverized with deionised water in the ball mill for 8 h ( $D_{50} \sim 0.6 \mu\text{m}$ ), dried and screened through a 100 mesh sieve.  $\text{B}_2\text{O}_3$  was added into the ULF280 powder by the amounts of 1, 3 and 5 mass%, 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 to  $960^\circ\text{C}$  for a period of 2 h. Composition of the host ULF280 ceramic powder was analysed by X-ray fluorescence and the result is given in **Table 1**.

**Table 1.** Chemical Composition of the Host ULF280 Ceramic

Constituent	$\text{TiO}_2$	$\text{BaO}$	$\text{ZrO}_2$	$\text{ZnO}$	$\text{SrO}$	$\text{HfO}_2$	$\text{B}_2\text{O}_3$	$\text{SiO}_2$
Content (mass%)	49.9	27.8	12.0	5.0	0.07	0.18	1.5	3.5

### 2.2 Characteristics analysis

The crystalline phases of the sintered ceramics were identified by X-ray diffraction pattern analysis (XRD, Bluker D8A) using  $\text{Cu K}\alpha$  radiation for  $2\theta$  from  $10^\circ$  to  $60^\circ$ . The diffraction spectra were collected at a scan rate of  $2.5^\circ/\text{min}$ . Microstructural observation of the sintered ceramics was performed by scanning electron microscopy (SEM; JEOL Ltd., JEL-6400 Japan) equipped with energy-dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) was carried out by a JEOL JEM-4000EX electron microscope operated at an acceleration voltage of 400 kV. The instrument has a spherical aberration coefficient of 1 mm, leading to a point-to-point resolution of  $d = 0.17 \text{ nm}$  at Schertz defocus ( $\Delta z = -48 \text{ nm}$ ). 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 dielectric characteristics at microwave frequencies ( $7.25\text{--}9.31 \text{ GHz}$ ) were measured by the Hakki-Coleman dielectric resonator method, where a cylindrically shaped specimen is positioned between two plates. An HP8719C network analyzer was used for the microwave measuring system. The dielectric properties were calculated from the frequency of the  $\text{TE}_{011}$  resonant mode. For convenience, the  $Q \times f$  factor was used for evaluating the loss quality, where  $f$  is the resonant frequency.

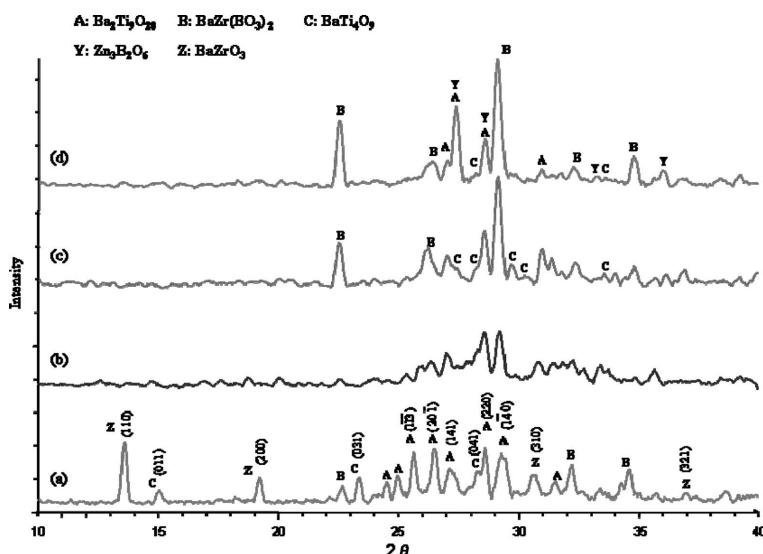
## 3. Results and discussion

In a previous study,<sup>14)</sup> we have investigated the microwave dielectric properties of the  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramics with different addition amounts of  $3\text{ZnO-B}_2\text{O}_3$  (ZnBO). The results indicate that the addition of ZnBO in the  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ -based ceramics can effectively lower the sintering temperature to  $\sim 940^\circ\text{C}$ , and increases the apparent density and dielectric constant of the sintered ceramics. The XRD results show that the sintered ceramics with additives contain the five crystalline phases,  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ,  $\text{BaZr}(\text{BO}_3)_2$ ,  $\text{BaTi}_4\text{O}_9$  and  $\text{Zn}_2\text{SiO}_4$ .

### 3.1 Microstructural evolution in the sintered ceramics

In the  $\text{BaO-TiO}_2$  binary system, many intermediate phases,  $\text{BaTi}_3\text{O}_7$ ,  $\text{BaTi}_5\text{O}_{11}$ ,  $\text{BaTi}_4\text{O}_9$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ , exist in the  $\text{TiO}_2$ -rich side of the phase diagram as reported by Rase and Roy.<sup>15)</sup> The X-ray diffraction spectra from the as-sintered host ceramics and those with different amounts of  $\text{B}_2\text{O}_3$  addition are given in **Fig. 1**. For the host  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ -based ceramics sintered at  $940^\circ\text{C}$  shown in Fig. 1(a), it is obtained that the major crystalline phase is  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ , and minor crystalline phases include  $\text{BaTi}_4\text{O}_9$ ,  $\text{BaZrO}_3$  and  $\text{BaZr}(\text{BO}_3)_2$ .

The XRD spectra for the  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ -based ceramics with 1 mass%, 3 mass% and 5 mass%  $\text{B}_2\text{O}_3$  additions sintered at  $940^\circ\text{C}$  are shown in Fig. 1(b), (c) and (d), respectively. Compared with the spectrum of the host material shown in Fig. 1(a), it can be seen that the peak intensities of the  $\text{BaTi}_4\text{O}_9$  and  $\text{BaZrO}_3$  phases in the 1 mass%  $\text{B}_2\text{O}_3$ -added specimen in Fig. 1(b) are decreased considerably. This result indicates that the  $\text{BaZrO}_3$  phase is easily reacted with  $\text{B}_2\text{O}_3$  to form  $\text{BaZr}(\text{BO}_3)_2$ . The formation of  $\text{BaZr}(\text{BO}_3)_2$  was assumed follow reaction:



**Fig. 1.** X-ray diffraction spectra of (a) the host  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ -based ceramics, and the ceramics with (b) 1 mass%, (c) 3 mass% and (d) 5 mass%  $\text{B}_2\text{O}_3$  additions and sintered at  $940^\circ\text{C}$  for 2 h.

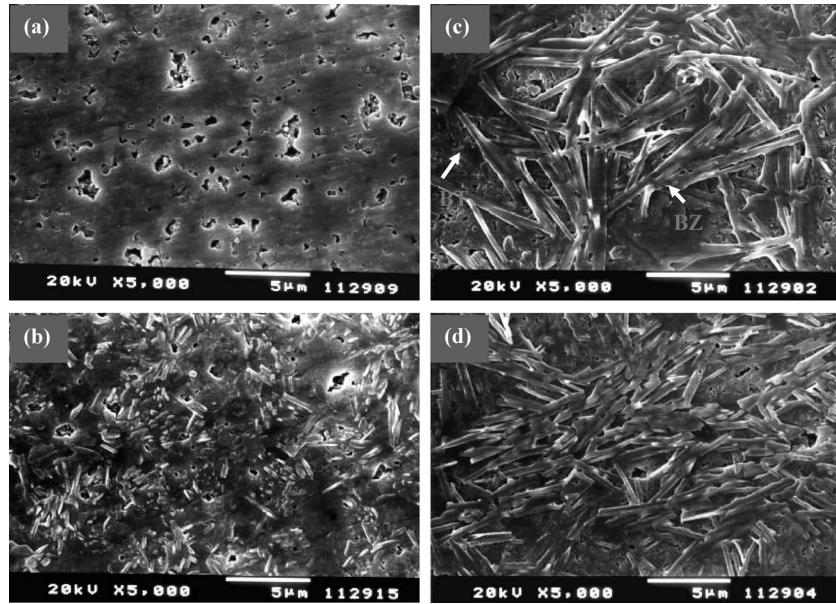
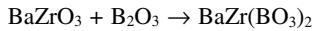


Fig. 2. SEM micrographs of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics with (a) 0 mass%, (b) 1 mass% (c) 3 mass% and (d) 5 mass% B<sub>2</sub>O<sub>3</sub> additions and sintered at 940°C for 2 h, upon thermally etched at 820°C/30 min. BT: Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, BZ: BaZr(BO<sub>3</sub>)<sub>2</sub>.



In addition, it is noted that some of the diffraction peaks of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phase disappear, but other peaks appear, suggesting a change of crystalline orientation or texture in the sintered specimen. By adding 3 mass% B<sub>2</sub>O<sub>3</sub> into the host Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based material results in the formation of a new phase, Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, among others, in the sintered ceramic as shown in Fig. 1(c). Furthermore, from the 104 peak of the BaZr(BO<sub>3</sub>)<sub>2</sub> phase at 29.2°, which overlaps with the 220 peak of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, it is obtained that the content of the BaZr(BO<sub>3</sub>)<sub>2</sub> phase in the 3 mass% B<sub>2</sub>O<sub>3</sub> -added specimen is increased significantly. On the other hand, the X-ray diffraction spectrum of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics with 5 mass% B<sub>2</sub>O<sub>3</sub> addition shown in Fig. 1(d) is similar to that with 3 mass% B<sub>2</sub>O<sub>3</sub> addition, Fig. 1(c), except that the peak of the Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phase at 27.3° and 36° is increased noticeably in the later case. In summary, the XRD result indicates that additions of the B<sub>2</sub>O<sub>3</sub> phase in the host ceramics have enhanced the formation of the BaZr(BO<sub>3</sub>)<sub>2</sub> phases in the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based materials. In addition, the peak intensity of Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> was increased significantly at 5 mass% B<sub>2</sub>O<sub>3</sub> addition.

SEM micrographs of the B<sub>2</sub>O<sub>3</sub> -added specimens sintered at 940°C are shown in Figs. 2(a)–(d), for the amounts of 0, 1, 3, and 5 mass% B<sub>2</sub>O<sub>3</sub> addition, respectively. The microstructure of the sintered ceramics shows a lot of change, in which a dendrite phase was increased with B<sub>2</sub>O<sub>3</sub> increasing. According to the XRD spectra of Fig. 1, the composition of dendrite phase should be BaZr(BO<sub>3</sub>)<sub>2</sub> since the intensity of BaZr(BO<sub>3</sub>)<sub>2</sub> peak was increased significantly with B<sub>2</sub>O<sub>3</sub> increasing. Moreover, it is found that the dendrite phase was increased with B<sub>2</sub>O<sub>3</sub> increasing, and this phase with huge amount in the sintered ceramic was observed for 3 mass% and 5 mass%. However, the amount of dendrite phase of the samples with 5 mass% B<sub>2</sub>O<sub>3</sub> addition is larger than 3 mass% B<sub>2</sub>O<sub>3</sub> addition. The dendrite phase was further analysed by transmission electron micrograph (TEM).

TEM micrograph and the electron diffraction patterns of 3 mass% B<sub>2</sub>O<sub>3</sub>-added samples sintered at 940°C were performed, as shown in Fig. 3. From Fig. 3(a), it can be seen that two different

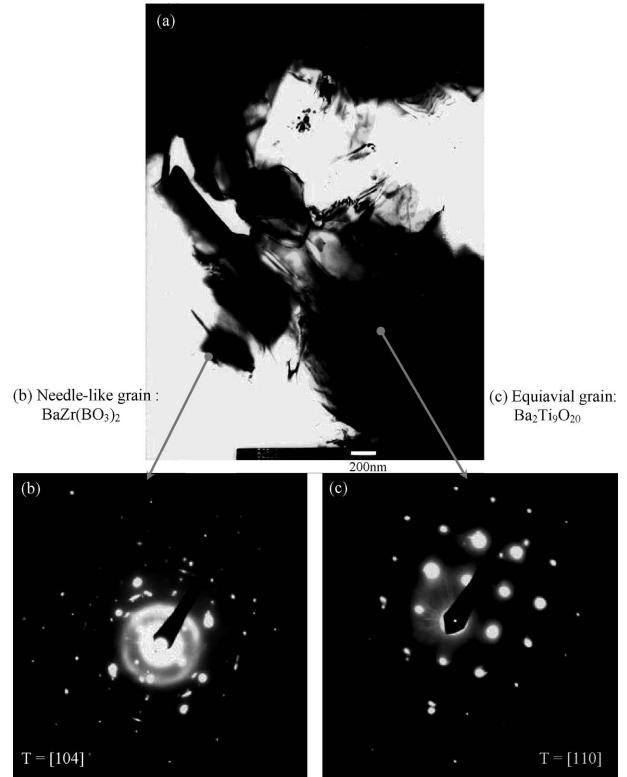


Fig. 3. TEM micrographs and selected-area diffraction patterns of grain in Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramic with the addition of 3 mass% B<sub>2</sub>O<sub>3</sub> sintered at 940°C (a) TEM micrographs (b) SAD of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> and (c) SAD of BaZr(BO<sub>3</sub>)<sub>2</sub>.

grains existed in the sample: the equiaxial grains were symbolized as (A), and the dendrite grains were symbolized as (B). Four phases, Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, BaZrO<sub>3</sub> and BaZr(BO<sub>3</sub>)<sub>2</sub>, coexisted in the samples from XRD patterns, and the major phase is

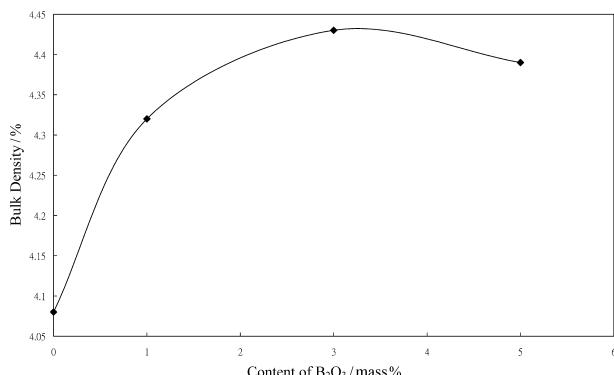


Fig. 4. Bulk density vs  $B_2O_3$  content of the  $Ba_2Ti_9O_{20}$ -based ceramics sintered at 940°C.

$Ba_2Ti_9O_{20}$ . According to the electron diffraction patterns, the equiaxial grain symbolized as (A) in Fig. 4(b) was constituted by  $Ba_2Ti_9O_{20}$  phase. The dendrite grain (B) was considered to be  $BaZr(BO_3)_2$  according to the electron diffraction patterns, as shown in Fig. 3(c). This result indicates that  $BaO$ ,  $ZrO_2$  and  $B_2O_3$  form a liquid phase acting as a secondary phase at low sintering temperature. When the  $B_2O_3$  melt, the formed liquid reacts with  $BaO$ ,  $ZrO_2$ , which works as a  $BaZr(BO_3)_2$  grain growth and precipitation from  $Ba_2Ti_9O_{20}$  grain. When a liquid shows good wetting of a grain, it is because the formation of the liquid phase results in the reduced interface energy. The driving force for growth is thus lowered.<sup>16)</sup>

### 3.2 Physical properties of the sintered ceramics

As described in the experimental procedure, the  $Ba_2Ti_9O_{20}$ -based ceramics with different amounts of  $B_2O_3$  addition were sintered in air at 940°C for 2 h, and the particle size of the starting material was controlled at  $0.5 \pm 0.1 \mu m$ . Figure 4 shows the apparent density of the  $Ba_2Ti_9O_{20}$ -based ceramics pellets as a function of  $B_2O_3$  content. It can be seen that the apparent density of the sintered ceramics increases with  $B_2O_3$  additions, and then slight decrease after reaching  $4.43 \text{ g/cm}^3$ , i.e., 96% of the theoretical density. Theoretical density of the  $Ba_2Ti_9O_{20}$  ceramic was reported to be  $4.61 \text{ g/cm}^3$ .<sup>17)</sup> This result is similar to other reports that the  $B_2O_3$  phase could assist in the densification of the  $Ba_2Ti_9O_{20}$  dielectrics through liquid-phase sintering.<sup>6,10)</sup>

### 3.3 Dielectric properties of the sintered ceramics

The dielectric constant of the  $Ba_2Ti_9O_{20}$ -based ceramics with different the addition of  $B_2O_3$  was shown in Fig. 5(a). Similar to the relative density vs  $B_2O_3$  content curves in Fig. 5, the dielectric constant of the  $Ba_2Ti_9O_{20}$ -based ceramics increases with increasing of  $B_2O_3$  content. The  $\epsilon_r$  value of the  $Ba_2Ti_9O_{20}$ -based ceramics without addition of  $B_2O_3$  is 25.5, where sintering was carried out at 940°C, the sample exhibits inferior microwave properties due to low densification. The maximum  $\epsilon_r$  value is about 28.3 for the specimens with the addition of 3 mass%  $B_2O_3$ . In other words, the result suggests that the  $B_2O_3$  phase is very effective in increasing the dielectric constant of the ceramics, in particular at low sintering temperatures. Because, the addition of  $B_2O_3$  effectively led to promote densification of  $Ba_2Ti_9O_{20}$ -based ceramics as compared without  $B_2O_3$  doped sample. It must be pointed out, however, that second phases such as  $BaZr(BO_3)_2$  and  $Zn_3B_2O_6$ , and the grain size of the sintered ceramics may have essential effects on the dielectric constant of the ceramics as reported by Kanai et al.<sup>18)</sup>

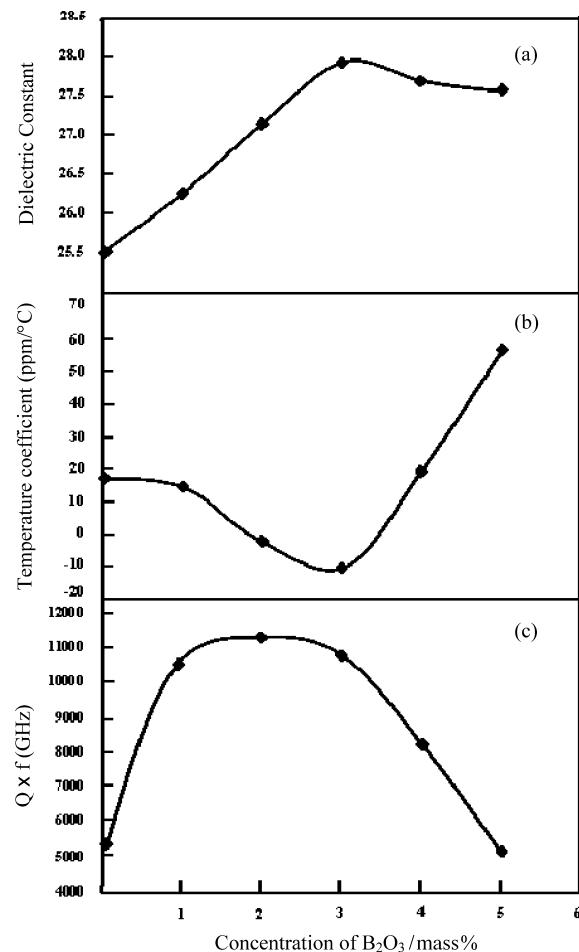


Fig. 5. Electrical properties of the  $Ba_2Ti_9O_{20}$ -based ceramics with different amounts of  $B_2O_3$  addition sintered at 940°C (a) dielectric constants, (b) temperature coefficient of resonant frequency, and (c)  $Q \times f$  values.

If ~25 vol%  $BaZr(BO_3)_2$  dendrite phase is occupied and is rather than dispersed in host ceramic for sample with 3 mass%  $B_2O_3$  addition (Fig. 2(c)), the dielectric constant of  $Ba_2Ti_9O_{20}$ -based ceramic is calculated using Maxwell's equation (1),<sup>19)</sup>

$$\epsilon_m = \epsilon_2 \left( 1 + \frac{3V_f(\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\epsilon_2 - V_f(\epsilon_1 - \epsilon_2)} \right) \quad (1)$$

where  $V_f$  is the volume fraction occupied by the dispersed phases,  $\epsilon_1$  and  $\epsilon_2$  are the permittivity of  $BaZr(BO_3)_2$  and  $Ba_2Ti_9O_{20}$  ceramic, respectively;  $\epsilon_m$  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 mass%  $B_2O_3$  addition is 31.4. The experimentally obtained results give values smaller than the estimated values. This is due to another phases existed in the sample such as  $Zn_3B_2O_6$ .

Figure 5(b) shows the temperature coefficient of resonant frequency,  $\tau_f$ , at maximum  $Q$  value as a function of the addition of  $B_2O_3$ . The  $\tau_f$  value of the samples decreases gradually from 17.5 ppm/ $^{\circ}\text{C}$  (0 mass%  $B_2O_3$ ) to -8.2 ppm/ $^{\circ}\text{C}$  (3 mass%  $B_2O_3$ ), and then increases rapidly to 58.2 ppm/ $^{\circ}\text{C}$  for the sample with 5 mass%  $B_2O_3$  addition. The temperature coefficient of resonant frequency is known to be related to the composition and the sec-

ondary phase of the material. Since a large  $\tau_f$  value is not suitable for application at microwave frequency, the result suggests that the addition of 5 mass% B<sub>2</sub>O<sub>3</sub> in the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics is too much. In addition, the XRD result in Fig. 1 shows that 5 mass% B<sub>2</sub>O<sub>3</sub> addition enhances the formation of the Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phase and BaZr(BO<sub>3</sub>)<sub>2</sub> in the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics. It is believed that the high  $\tau_f$  value is related to the presence of the second phase, Zn<sub>3</sub>B<sub>2</sub>O<sub>6</sub> in the sintered ceramics.

The  $Q \times f$  values of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics sintered at 940°C for 2 h as a function of the B<sub>2</sub>O<sub>3</sub> addition is shown in Fig. 5(c). It can be seen that the  $Q \times f$  value of the sintered ceramics increases rapidly with the addition of B<sub>2</sub>O<sub>3</sub>, and then reaches a saturation value for the ceramics with 1 mass% and 3 mass% B<sub>2</sub>O<sub>3</sub> additions; subsequently, it drops down to the value close to the host Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics for the specimen with 5 mass% B<sub>2</sub>O<sub>3</sub> addition. In a previous study,<sup>20)</sup> we have investigated the dielectric properties of the BaZr(BO<sub>3</sub>)<sub>2</sub> ceramics. The results indicate that the dielectric properties of BaZr(BO<sub>3</sub>)<sub>2</sub> ceramics is: (1)  $K$  values is kept on ~12 from sintering temperature 1080°C to 1250°C, (2) loss tangent is significantly reduced with sintering temperatures increased from 8500 at 1080°C to 801 at 1250°C. As we known,  $Q$  value depends on dielectric loss, it is therefore shown poor performance in high frequency when BaZr(BO<sub>3</sub>)<sub>2</sub> phase was formed a lot of in microwave ceramics. The maximum  $Q \times f$  value, 10784 GHz, was obtained for the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics with 3 mass% B<sub>2</sub>O<sub>3</sub> addition.

#### 4. Conclusions

Effects of B<sub>2</sub>O<sub>3</sub> addition on the microstructure, physical and dielectric properties of the Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramics have been investigated. It is obtained that addition of the B<sub>2</sub>O<sub>3</sub> phase in the ceramics can effectively enhance the densification of samples, and increases the dielectric constant of the sintered ceramics. The microstructure of the sintered ceramics shows a lot of change, in which a needle-like phase was increased with B<sub>2</sub>O<sub>3</sub> increasing. The composition of dendrite phase should be BaZr(BO<sub>3</sub>)<sub>2</sub> which was confirmed by TEM. The Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>-based ceramic with 3 mass% B<sub>2</sub>O<sub>3</sub> addition and sintered at 940°C in air for 2 h exhibits optimum microwave properties of  $\epsilon_r = 28.3$ ,  $\tau_f = -8.2$  ppm/°C, and  $Q \times f = 10784$ .

**Acknowledgement** The authors would like to acknowledge the

financial support of this research by the National Science Council of Taiwan under contract No. NSC96-2218-E-020-005

#### References

- 1) C. L. Huang and M. H. Weng, *Mater. Lett.*, **43**, 32–35 (2002).
- 2) H. Jantunen, R. Rautioaho, A. Unsimaki and S. Leppavuori, *J. Eur. Ceram. Soc.*, **20**, 2331–2336 (2000).
- 3) T. Hatanoa, T. Yamaguchia, W. Sakamotoa, T. Yogo, K. Kikutaa, H. Yoshidab, N. Tanakab and S. Hiranoa, *J. Eur. Ceram. Soc.*, **24**, 507–510 (2004).
- 4) D. F. K. Hennings, *J. Eur. Ceram. Soc.*, **21**, 1637–1642 (2001).
- 5) Q. Zeng, W. Li, J. L. Shi, J. K. Guo, H. Chen and M. L. Liu, *J. Eur. Ceram. Soc.*, **27**, 261–265 (2007).
- 6) J. A. Lee, J. H. Lee and J. J. Kim, *J. Eur. Ceram. Soc.*, **26**, 2111–2115 (2006).
- 7) C. F. Yang, *Jpn. J. Appl. Phys.*, **38**, 3576–3579 (1999).
- 8) Y. C. Lee, W. H. Lee and F. T. Shiao, *Jpn. J. Appl. Phys.*, **43**, 7596–7599 (2004).
- 9) Q. L. Zhang, H. Yang, J. L. Zou and H. P. Wang, *Mater. Lett.*, **59**, 880–884 (2005).
- 10) S. F. Wang, C. C. Chiang and C. H. Wang, *Mater. Chem. Phys.*, **79**, 256–260 (2003).
- 11) J. K. Plourde, D. F. Linn, H. M. O'Bryan, Jr. and J. Thomson, Jr., *J. Am. Ceram. Soc.*, **58**, 418–420 (1975).
- 12) H. M. O'Bryan, Jr., J. Thomson, Jr. and J. K. Ploured, *J. Am. Ceram. Soc.*, **57**, 450–453 (1974).
- 13) Y. C. Lee, W. H. Lee and F. S. Shieh, *J. Eur. Ceram. Soc.*, **15**, 3459–3468 (2005).
- 14) Y. C. Lee, W. H. Lee and F. S. Shieh, *Jpn. J. Appl. Phys.*, **41**, 6049–6052 (2002).
- 15) D. E. Rase and R. Roy, *J. Am. Ceram. Soc.*, **38**, 102–113 (1955).
- 16) E. R. Nielsen, E. Ringgaard and M. Kosec, *J. Eur. Ceram. Soc.*, **22**, 1847–1855 (2002).
- 17) G. Kniajer, K. Dechant and P. Apte, 1997 International Conference on Multichip Modules, *IEEE*, 121–127 (1997).
- 18) H. Kanai, O. Furukawa and S. I. Nakamura, *J. Mater. Sci.*, **31**, 1609–1614 (1996).
- 19) A. J. Moulson, and J. M. Herbert, *Electroceramics. Materials Properties Applications*, London, 79–82 (1990).
- 20) Y. C. Lee, W. H. Lee, F. S. Shieh and C. L. Hu, *Jpn. J. Appl. Phys.*, **43** [7A] 4306–4039 (2004).