

## Effect of BaTi<sub>4</sub>O<sub>9</sub> on the sintering and microwave dielectric characteristics of Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics

WEN-CHENG TZOU

*Department of Electrical Engineering, Southern Taiwan University of Technology, YungKang, Tainan, Taiwan, Republic of China*

CHAO-CHIN CHAN

*Department of Chemical Engineering, Kao Yuan Institute of Technology, Lu-Chu, Kaohsiung, Taiwan, Republic of China*

PING-SHOU CHENG

*Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan, Republic of China*

CHENG-FU YANG

*Department of Chemical and Material Engineering, National University of Kaohsiung, Kaohsiung, Taiwan, Republic of China*

In general, dielectric materials for microwave application should satisfy three requirements: high permittivity ( $\epsilon_r$ ), high quality value ( $Q \times f$ ) or low loss, and small temperature coefficient of resonant frequency ( $\tau_f$ ). Most microwave materials with high quality value were focused on the complex perovskite compounds, such as Ba(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> (BMT) [1–3] and Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> (BZT) ceramics [4–8]. The complex perovskite oxide Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramic had been largely studied for its good microwave dielectric properties. This Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramic possessed a suitable  $\epsilon_r \sim 30$ , a relatively high quality value ( $Q \sim 7000$  at 11 GHz), and a stable temperature coefficient of resonant frequency ( $\tau_f \sim 0 \pm 5$  ppm/°C). Unfortunately, the solid-state reaction of BaCO<sub>3</sub>, ZnO, and Ta<sub>2</sub>O<sub>5</sub> was not the most appropriate method, because a high sintering temperature was required to achieve high-density Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> materials (>1500°C), which was too high for industrial applications [9, 10]. Many efforts had been investigated to lower the sintering temperature of Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics by the addition of sintering agent [11]. In this paper, Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> powder calcined at 1200°C for 3 h was used as the precursor and 0.1 mol BaTi<sub>4</sub>O<sub>9</sub> was used to improve the sintering characteristics of Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics. It was found that the addition of BaTi<sub>4</sub>O<sub>9</sub> would lower down the sintering temperatures of Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics. Relationships among the sintering temperatures and the microstructure evolution, the phase formation, and microwave dielectric characteristics of 0.1 mol BaTi<sub>4</sub>O<sub>9</sub>-0.9 mol Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics were developed.

Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> and BaTi<sub>4</sub>O<sub>9</sub> were synthesized by solid state reaction using reagent-grade purity precursors of BaCO<sub>3</sub>, ZnO, Ta<sub>2</sub>O<sub>5</sub>, and TiO<sub>2</sub>. Precursor powders were according to the stoichiometric compound of Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> (BZT) and BaTi<sub>4</sub>O<sub>9</sub> (BT4). The mixed precursors were ball-milled with deionized wa-

ter and agate balls. After mixing, the mixed precursors were dried before being calcined. Then both the Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> and BaTi<sub>4</sub>O<sub>9</sub> powders were calcined at 1150 °C for 2 h. The crystal structure of calcined powders was examined by using an X-ray powder diffractometer. X-ray diffraction (XRD) patterns were taken at  $2\theta = 4^\circ$  per minute using CuK $\alpha$  radiation. The calcined Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> and BaTi<sub>4</sub>O<sub>9</sub> powders were used as precursor and mixed in accordance with 0.1 mol BaTi<sub>4</sub>O<sub>9</sub>-0.9 mol Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> (BT4-BZT) by ball milling with deionized water for 1 h. After drying, the powder was pressed into pellets uniaxially in a steel die. Sintering of these pellets was carried out at the temperatures between 1240 and 1360 °C under ambient conditions for 2 h. The crystalline phases of BT4-BZT ceramics were also investigated using X-ray powder diffractometer. The BT4-BZT densities of sintered specimens as a function of sintering temperature were measured using the Archimedes method. The morphology of the sintered specimens were observed by using the scanning electronic micrograph (SEM). Dielectric characteristics at microwave frequency were measured by Hakki and Coleman's dielectric resonator method [12], which was improved by Courtney [13]. An HP8720ET network analyzer was used for the microwave characteristic measurements. The dielectric constant could be accurately determined by measuring the resonant frequency of the TE<sub>011</sub> mode and verified by the TE<sub>018</sub> resonant modes. The temperature coefficient of the resonant frequency ( $\tau_f$ ) was defined as follows:

$$\tau_f = (f_{85} - f_{20}) / (f_{20} * 65) \quad (1)$$

Where  $f_{20}$  and  $f_{85}$  were the resonant frequency at 20 and 85 °C, respectively.

SEM micrographs of BT4-BZT ceramics are investigated under the sintering temperature of

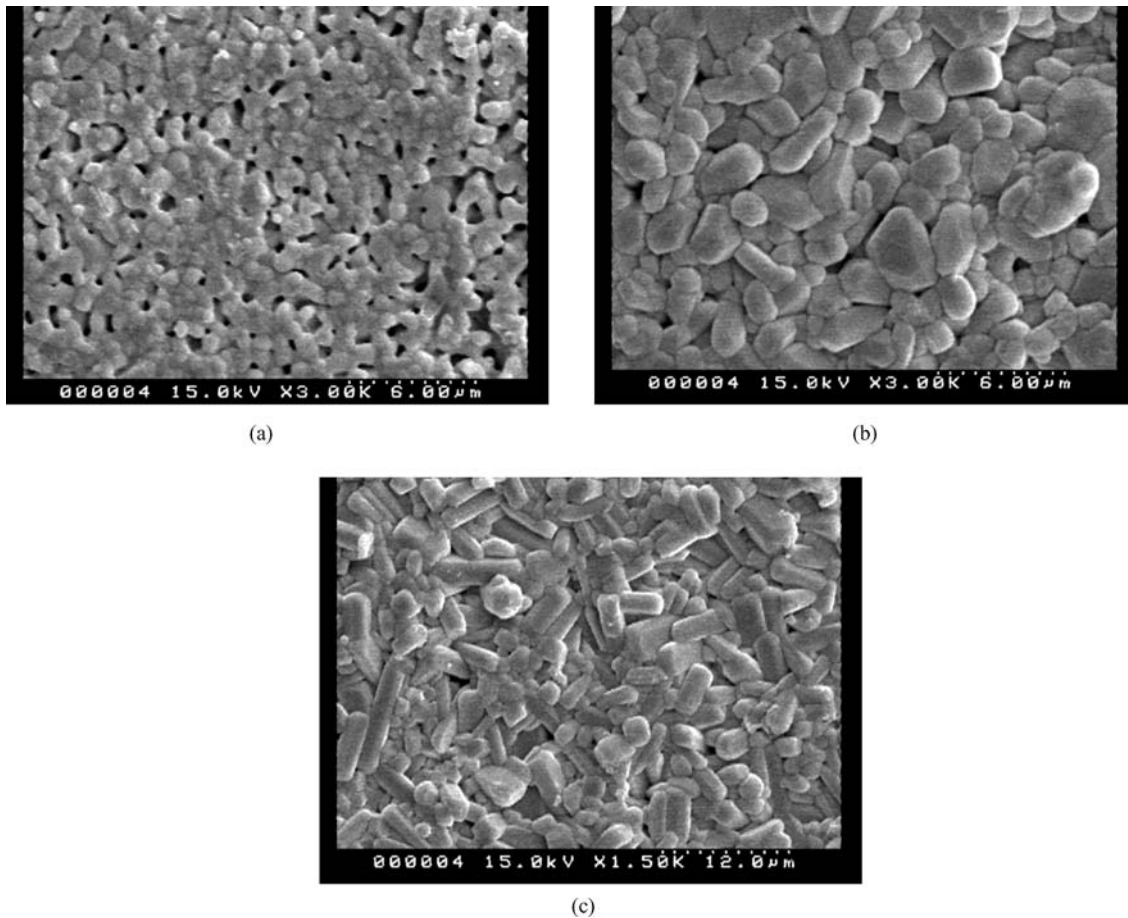


Figure 1 Sintered morphologies of BT4-BZT ceramics, sintered at (a) 1240 °C, (b) 1280 °C, and (c) 1320 °C.

1240—1320°C, and the results are shown in Fig. 1. With the addition of BaTi<sub>4</sub>O<sub>9</sub>, a much easier densification of Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> ceramics is evidenced in Fig. 1. Using calcined Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> powder as the precursor and sintered at 1450°C, isolated Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> particles and pores are easily observed (not shown here). Sintered at 1240°C, the BT4-BZT ceramic shows a porous structure and the isolated particles are observed (Fig. 1a). Sintered at 1280°C, the pores of BT4-BZT ceramic decrease apparently but still exist in the sintered ceramics and grain growth has been observed (Fig. 1b). As 1320°C is used as sintering temperature, the size of pores can be easily eliminated and the microstructures of BT4-BZT ceramics illustrate a homogeneous bar-typed grains (Fig. 1c).

For BaTi<sub>4</sub>O<sub>9</sub> composition (Fig. 2a), the calcination process leads to form BaTi<sub>4</sub>O<sub>9</sub> phase only. The Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> composition has hexagonal perovskite-typed structure with Zn and Ta showing 1:2 order in B site. If the Zn and Ta are in disorder, the compound has a cubic perovskite-typed structure. For Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> composition (Fig. 2b), the only the disordering phase is revealed in the calcining Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> powder. The initial phases of ZnO and Ta<sub>2</sub>O<sub>5</sub>, the satellite secondary phases, and the ordering Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> phase are not detected in the calcined powder. The X-ray patterns of BT4-BZT ceramics are also shown in Fig. 2 for comparison. The X-ray patterns of 1240°C- (Fig. 2c), 1280°C- (Fig. 2d), and 1320°C-sintered (Fig. 2e)

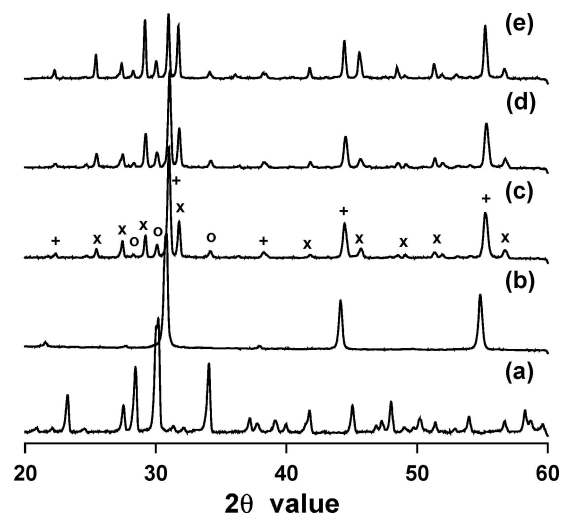


Figure 2 The X-ray patterns for (a) 1150°C-calcined BaTi<sub>4</sub>O<sub>9</sub> powder, (b) 1150°C-calcined Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> powder, and BT4-BZT ceramic sintered at (c) 1240°C, (d) 1280°C, and (e) 1320°C. (+: disordering Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub>, x: ordering Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub>, o: BaTi<sub>4</sub>O<sub>9</sub>).

BT4-BZT ceramics show that the disordering and ordering Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> phases and BaTi<sub>4</sub>O<sub>9</sub> phase coexist. As the sintering temperatures increase, the crystal intensity of ordering Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> phase increases and the crystal intensity of disordering Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> phase decreases. Compared the crystal phases of calcined Ba(Zn<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> powder with those of sintered BT4-BZT ceramics, the 2θ values of

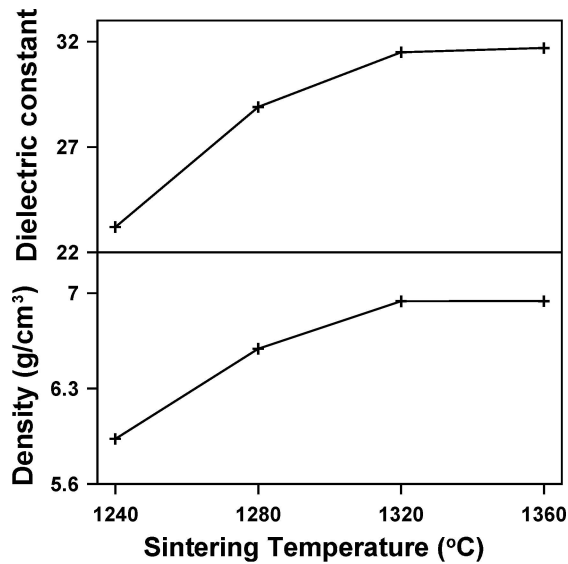


Figure 3 The bulk densities and the dielectric constants of BT4-BZT ceramics, as a function of sintering temperature.

sintered BT4-BZT ceramics are shifted to higher  $2\theta$  values. The appearance of ordering  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  phase is thought as the reason. As the sintering temperatures are higher than  $1360^\circ\text{C}$ , the BT4-BZT ceramics will be melted. This result suggests that some types of eutectic phases may exist between  $\text{BaTi}_4\text{O}_9$  and  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ , and the eutectic phases will improve the elimination of sinterability of  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ceramics.

Fig. 3 plots the densities of BT4-BZT ceramics as a function of sintering temperature. As Fig. 3 shows, the  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  and  $\text{BaTi}_4\text{O}_9$  will crystal as independent phases. The theoretical densities of BT4-BZT ceramics are calculated from the values of  $\text{BaTi}_4\text{O}_9$  ceramics of  $4.525 \text{ g/cm}^3$  [14] and  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ceramics of  $7.675 \text{ g/cm}^3$  [4]. The theoretical densities are calculated using following equation:

$$D = (W_1 + W_2)/(W_1/D_1 + W_2/D_2) \quad (2)$$

where  $W_1$  and  $W_2$  are the weight percent of the  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ceramics and  $\text{BaTi}_4\text{O}_9$  ceramics in the mixtures, and  $D_1$  and  $D_2$  are the densities of the  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  and  $\text{BaTi}_4\text{O}_9$  ceramics, respectively. The calculated theoretical densities of BT4-BZT ceramics are  $6.975 \text{ g/cm}^3$ . BT4-BZT ceramics with a bulk density higher than 99.5% theoretical density is obtained with ease at a sintering temperature of  $1320^\circ\text{C}$ . As the sintering temperatures are higher than  $1320^\circ\text{C}$ , the densities of BT4-BZT ceramics increase slightly. The dielectric constants ( $\epsilon_r$  values) of BT4-BZT ceramics are also shown in Fig. 3. As the sintering temperatures increase from 1240 to  $1320^\circ\text{C}$ , the  $\epsilon_r$  values critically increase. The decrease in pores and the increase in grain growth are thought as the reason. For BT4-BZT ceramics sintered at  $1320^\circ\text{C}$ , the  $\epsilon_r$  value is saturated at 31.5, which is higher than the those of  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ceramics reported, and the higher  $\epsilon_r$  values are thought to be related to the crystal phases. From Fig. 2, the  $\text{BaTi}_4\text{O}_9$  ( $\epsilon_r \sim 38.0$ ) and  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ( $\epsilon_r$

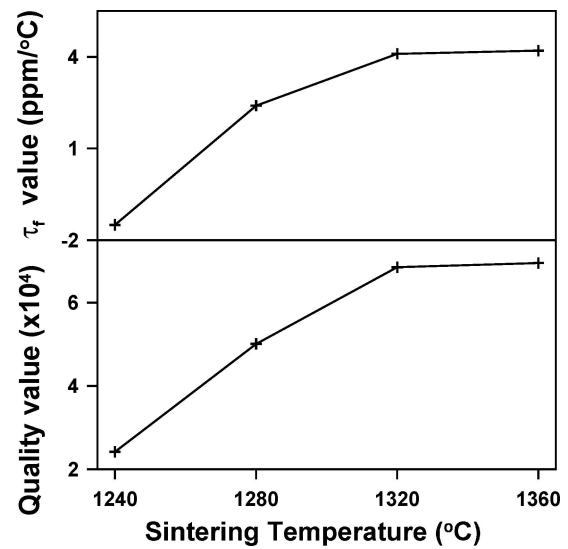


Figure 4 The quality values and temperature coefficients of resonant frequency of BT4-BZT ceramics, as a function of sintering temperature.

$\sim 29.5$ ) phases coexist in the sintered BT4-BZT ceramics, the higher  $\epsilon_r$  values of BT4-BZT ceramics are caused by the higher dielectric constants of  $\text{BaTi}_4\text{O}_9$  ceramics.

The quality values ( $Q \times f$ ) of BT4-BZT ceramics are investigated as a function of sintering temperature, and the results are shown in Fig. 4. As the sintering temperatures increase from 1240 to  $1320^\circ\text{C}$ , the  $Q \times f$  values also increase critically. The  $Q \times f$  values of BT4-BZT ceramics reach a saturation value of 68500 at  $1320^\circ\text{C}$ -sintered ceramics, then the  $Q \times f$  values of BT4-BZT ceramics slightly increase with the further increase of sintering temperature to  $1360^\circ\text{C}$ . The  $\tau_f$  values of BT4-BZT ceramics are also shown in Fig. 4. As the sintering temperatures change from 1240 to  $1320^\circ\text{C}$ , the  $\tau_f$  values of BT4-BZT ceramics linearly change from  $-1.5 \text{ ppm}/^\circ\text{C}$  to  $4.1 \text{ ppm}/^\circ\text{C}$ .

The addition of 0.1 mol  $\text{BaTi}_4\text{O}_9$  into the  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  composition will improve the sinterability of  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ceramics. The needed sintering temperatures of BT4-BZT ceramics are about  $1320^\circ\text{C}$ , the temperature is similar to  $\text{BaTi}_4\text{O}_9$  ceramics but it is much lower than  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  ceramics. The BT4-BZT ceramic sintered at  $1320^\circ\text{C}$  had the microwave dielectric property of  $\epsilon_r = 31.5$ ,  $Q \times f$  value of 68500, and temperature coefficient of resonant frequency  $\tau_f = 4.1 \text{ ppm}/^\circ\text{C}$ .

## Acknowledgements

The authors would like to this opportunity to acknowledge the financial support of the National Science Council (contract no. NSC 93-2216-E-218-008) of Republic of China

## References

1. E. S KIM and K. H. YOON, *Ferroelectrics* **133** (1992) 187.
2. T. TAKADA, S. F. WANG, S. YOSHJKAWA, S. J JANG and R. E. NEWNHAM, *J. Am. Ceram. Soc.* **77** (1994) 1909.
3. *Idem.*, *ibid.* **77** (1994) 2485.
4. S. B DESU and H. M. O`BRYAN, *ibid.* **68** (1985) 546.

5. X. M. CHEN, Y. SUZUKI and N. SATO, *J. Mater. Sci. Mater. Electr.* **5** (1994) 244.
6. I. QAZI, I. M REANEY and W. E. LEE, *J. Eur. Ceram. Soc.* **21** (2001) 2613.
7. O. RENOULT, J. P BOILOLOT and F. CHAPUT, *J. Am. Ceram. Soc.* **75** (1992) 3337.
8. M. ONDA, J. KUWATA, K. KANETA, K. TOYAMA and S. NOMURA, *Jpn. J. Appl. Phys.* **21** (1982) 1707.
9. S. KAWASHIMA, M. NISHIDA, I. UEDA and H. QUCHI, *J. Am. Ceram. Soc.* **66** (1983) 421.
10. P. K DAVIES and *ibid.* **80** (1997) 1727.
11. F. ROULLAND, R. TERRAS and S. MARINEL, *Mater. Sci. Eng. B* **104** (2003) 156.
12. B. W HAKKI and P. D. COLEMAN, *IEEE Trans. on M.T.T.* **8** (1960) 402.
13. W. E. COURTNEY, *IEEE Trans. on M.T.T.* **18** (1970) 476.
14. C. F. YANG, *Jpn. J. Appl. Phys.* **38** (1999) 3576.

*Received 11 August  
and accepted 14 October 2004*