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Effect of ZnO ratio on sintering behavior and microwave dielectric properties of $BaO–ZnO–TiO_2$ ceramics

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ABSTRACT

Effect of ZnO ratio on the phase formation, the microstructure and microwave dielectric properties of $BaO–ZnO–TiO_2$ ceramics with compositions varying from 1:0.5:3 to 1:0.8:3 ($BaO:ZnO:TiO_2$) were investigated. XRD patterns show that the main crystal phase of the ceramics sintered at 1160 °C to 1220 °C for 2 h was $Ba_4ZnTi_{11}O_{27}$, accompanied by a small number of additional phases: $BaZn_{2.03}Ti_{3.93}O_{10.89}$ and $Ba_2ZnTi_5O_{13}$, but note that all the ceramics with different ZnO ratio sintered at 1180 °C had pure $Ba_4ZnTi_{11}O_{27}$ phase. SEM photographs suggest that ZnO working as sintering aids promoting the densification and grain growth, so when the proportion of ZnO was increased, the dielectric constant increased monotonically, τ_f values decreased continuously and $Q \times f$ values increased first and then declined. Ceramics with composition $BaO–0.6ZnO–3TiO_2$ sintered at 1180 °C had compact and homogeneous microstructure and possessed excellent microwave dielectric properties: relative dielectric constant $\varepsilon_r = 35.77$, $Q \times f = 21{,}288$ GHz and the temperature coefficient of resonant frequency $\tau_f = 1.25$ ppm/°C.

1. Introduction

In the past decades, we have been impressed by the miniaturization of wireless communication devices, which have brought us much comfort and convenience. Developing high performance ceramic dielectric resonators offers an effective approach to realize the miniaturization that is very important for the high-quality and low-cost devices. Microwave dielectric ceramics with high dielectric constant for miniaturization (physical length of a dielectric resonator $\approx 1/\sqrt{\varepsilon_\gamma}$), low-loss for microwave selectivity and a near zero temperature coefficient of resonant frequency for stability have become a hot research topic [1,2]. Compounds such as $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ [3] based on the $BaO–TiO_2$ system have superior microwave dielectric properties: high dielectric constant and large quality factor Q and have been extensively researched and widely used in producing various microwave devices: resonators, filters, oscillators and so on.

Moreover, in order to improve the microwave dielectric properties, appropriate amount of ZnO [4,5], Ta_2O_5 [6], CeO_2 [7] and Ln_2O_3 (Ln = La, Sm, Nd, etc.) [8–11] were added to the $BaO–TiO_2$ system during the raw material stage for the purpose of synthesizing complex phase ceramics and optimizing microwave dielectric properties. These ternary systems have shown the potential application value in microwave devices because of their microwave dielectric properties shown in Table 1. In the $BaO–Nd_2O_3–TiO_2$ ceramics, the main crystal phase was $BaNd_2Ti_5O_{14}$ and the secondary phases $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ were present. And for the $BaO–CeO_2–TiO_2$ ceramics, the main crystalline phase could not be indexed based on any available standard JCPDS patterns. Ceramics of $BaO–Ln_2O_3–TiO_2$ contained the major phase that could be either $BaLn_2Ti_5O_{14}$ or $BaLn_2Ti_4O_{12}$ and additional phases like $BaTi_4O_9$, TiO_2, $Ln_2Ti_2O_7$, etc. [7].

In order to lower the sintering temperature and adjust dielectric properties, there has been an intense interest in adding ZnO into $BaO–TiO_2$ system [12]. Now the commercial microwave dielectric materials based on $BaTi_4O_9/Ba_2Ti_9O_{20}$ doped with ZnO have appeared. And the ternary system $BaO–ZnO–TiO_2$ has been found to contain four ternary phases: $BaZn_2Ti_4O_{11}$, $Ba_4ZnTi_{11}O_{27}$, $Ba_2ZnTi_5O_{13}$ and $Ba_xZn_xTi_{8-x}O_{16}$-hollandite [13]. Belous et al. [4] synthesized ceramics with composition close to $BaZn_2Ti_4O_{11}$ for the purpose of studying the homogeneity range and the microwave dielectric properties of $BaZn_2Ti_4O_{11}$, but ignoring to discuss the effect of ZnO ratio on the microwave dielectric properties of $BaO–ZnO–TiO_2$ ceramics. In this paper, we made the efforts on studying effect of ZnO ratio on the sintering behavior and microwave dielectric properties of $BaO–ZnO–TiO_2$ ceramics.

2. Experiment procedures

2.1. Sample preparation

The samples used in this study were prepared by conventional solid-state reaction technique. The starting materials were reagent grade $BaCO_3$, ZnO and TiO_2. The

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Table 1
Phase composition and microwave dielectric properties of BaO–TiO_2–ZnO/Ta_2O_5/CeO_2/rare earth oxides.

Ceramics	Main phases	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Remarks
BaO–nZnO–4TiO_2, n = 2–2.1.	$BaZn_2Ti_4O_{11}$	30	68,000–83,000	−30	[4]
BaO–0.6ZnO–3TiO_2	$Ba_4ZnTi_{11}O_{27}$	36	21,288	1.5	This work
BaO–0.5Ta_2O_5–0.375TiO_2	$Ba_8Ta_4Ti_3O_{24}$	34	23,000	75	[6]
BaO–2CeO_2–$n$$TiO_2$, n = 3, 4 and 5.	Unknown phase	27–38	7,200–19,100	9–159	[7]
BaO–10La_2O_3–16TiO_2	$La_4Ti_3O_{12}$	42	8,600	−17	[8]
BaO–Sm_2O_3–4TiO_2	$BaSm_2Ti_4O_{12}$	70	7,000	−15	[9]
BaO–Nd_2O_3–$n$$TiO_2$, n = 4 and 5.	$BaNd_2Ti_5O_{14}$	80–83	5,700–11,560	62–151	[10]

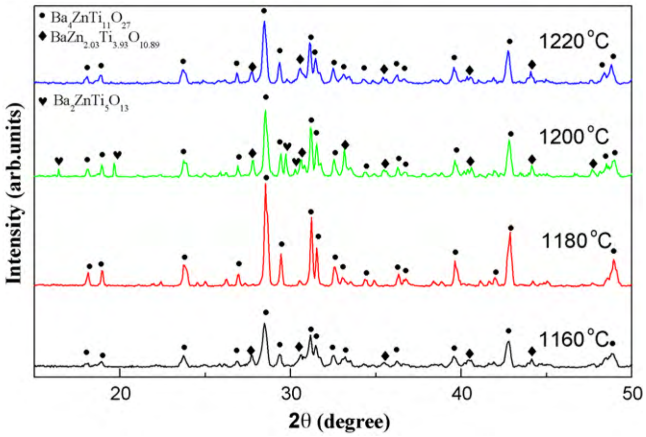

Fig. 1. XRD patterns of BaO–0.6ZnO–3TiO_2 ceramics at various sintering temperatures for 2 h.

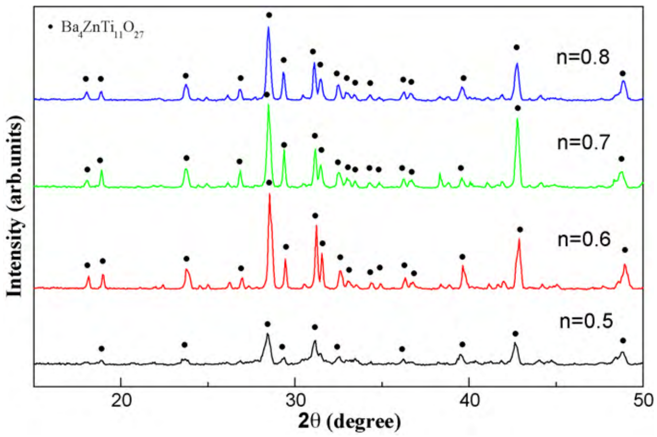

Fig. 2. XRD patterns of BaO–nZnO–TiO_2ceramics sintered at 1180 °C for 2 h.

powders were weighed according to non-stoichiometric ratio of BaO–nZnO–3TiO_2 with n = 0.5, 0.6, 0.7 and 0.8. Initially, the mixtures of the powders were milled in plastic jars using deionized water and zirconia balls for 20 h. Then the milled mixtures were dried and calcined at 1000 °C for 2.5 h. Subsequently, with 5 wt% PVA solution as a binder, the calcined powders without grinding were pressed into cylindrical samples with 18 mm in diameter and 9 mm in thickness under a pressure of 250 kg/cm^2. At last, these samples were sintered at 1160–1220 °C for 2 h.

2.2. *Characterization*

The bulk densities of the sintered samples were measured by the Archimedes method. The phase compositions were identified by X-ray diffraction (XRD) using Cu Kα radiation (DX-1000 CSC). Microstructure observation was conducted by using scanning electron microscopy (SEM, FEI Inspect F). The dielectric characteristics at microwave frequencies (4.726–4.953 GHz) were measured by the Hakki–Coleman dielectric resonator method in the TE_{011} mode using a network analyzer(HP83752A) [14]. The sintered samples used for this measurement had the ratio: diameter:height = 1.9–2.3. The τ_f values were determined from the difference between the resonant frequencies obtained at 25 °C and 80 °C.

3. Results and discussion

X-ray diffraction patterns of BaO–0.6ZnO–3TiO_2 ceramics sintered at different temperatures are shown in Fig. 1. From the XRD patterns, the diffraction peaks indexed to $Ba_4ZnTi_{11}O_{27}$ as the main crystalline phase, which is identified to be a monoclinic crystal structure with $C2/m$ space group, and the diffraction peaks of the secondary phases $BaZn_{2.03}Ti_{3.93}O_{10.89}$ and $Ba_2ZnTi_5O_{13}$ also appeared. The holding temperature had a great influence on the phase compositions. As the sintering temperature was increased from 1160 °C to 1220 °C, $BaZn_{2.03}Ti_{3.93}O_{10.89}$ disappeared at 1180 °C and appeared again at the higher sintering temperature and $Ba_2ZnTi_5O_{13}$ only appeared at 1200 °C, which was seemingly in contradiction with that these two phases were stable at 1250 °C [13]. The explanation for this contradiction could be that in our composition the stability of $BaZn_{2.03}Ti_{3.93}O_{10.89}$ and $Ba_2ZnTi_5O_{13}$ was weakened by the solid solution effect of excessive ZnO and the formation of the other phases. When samples were sintered at 1180 °C, the diffraction peaks of $Ba_4ZnTi_{11}O_{27}$ enhanced and no secondary phases were detected. Fig. 2 shows the XRD patterns of BaO–nZnO–TiO_2 ceramics sintered at 1180 °C for 2 h. While compositions changed from 1:0.5:3 to 1:0.8:3, the patterns indicated that the main crystalline phase was also $Ba_4ZnTi_{11}O_{27}$ without other phases. Moreover, the diffraction intensity changed with different ZnO content and the ceramics with composition BaO–0.6ZnO–3TiO_2 had the strongest diffraction peaks, which illustrated that the crystallization was relatively perfect.

Fig. 3(a) shows the bulk densities of BaO–nZnO–3TiO_2 ceramics sintered at various temperatures for 2 h. The densities of BaO–0.5ZnO–3TiO_2 ceramics in a low ZnO content were remarkably increased with increasing sintering temperature, and for n = 0.6–0.8, there were a maximum values for bulk densities at 1180 °C, therefore, associating Fig. 2 we can draw a conclusion that samples with compositions BaO–0.6–0.8ZnO–3TiO_2 could be

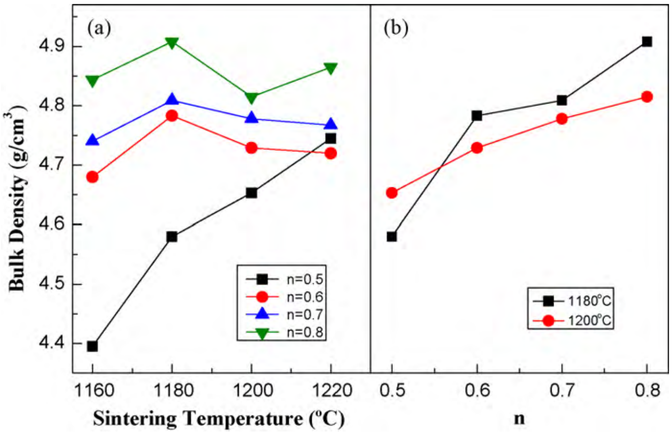

Fig. 3. Bulk densities of BaO–nZnO–3TiO_2 ceramics sintered at various temperatures (a) and with different compositions (b).

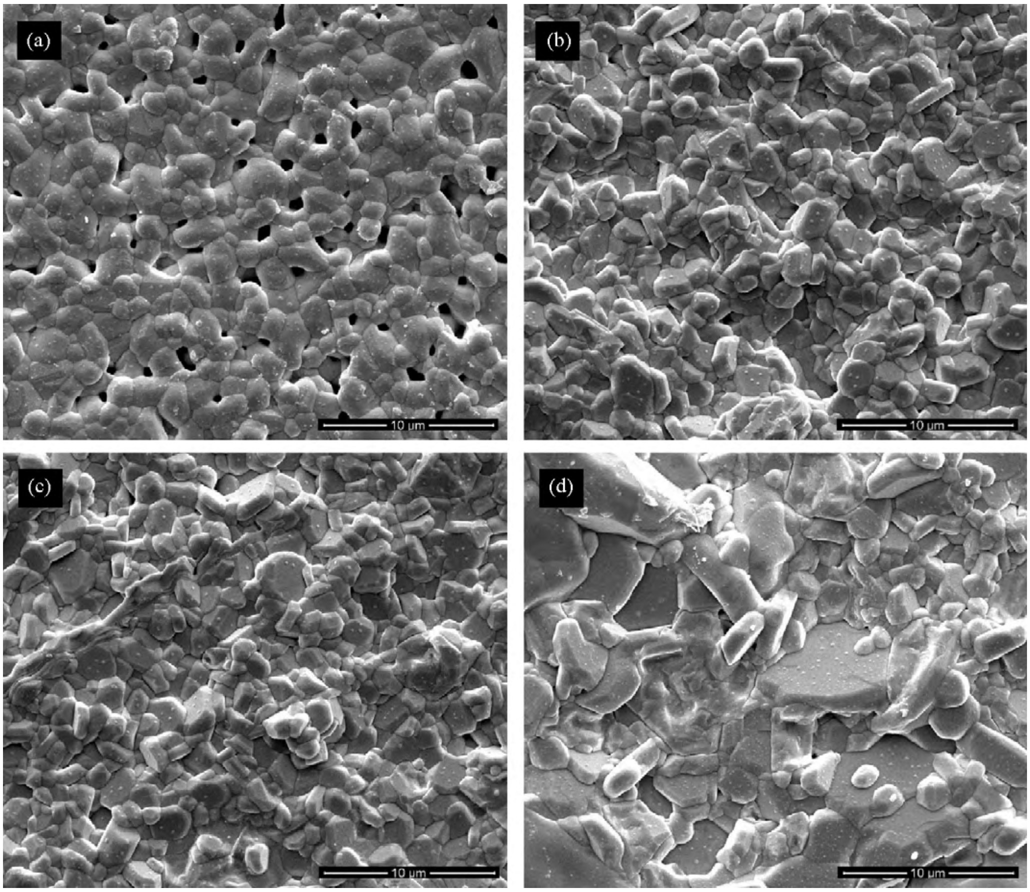

Fig. 4. SEM photographs of BaO–nZnO–3TiO$_2$ ceramics sintered at 1180 °C for 2 h: (a) $n = 0.5$, (b) $n = 0.6$, (c) $n = 0.7$ and (d) $n = 0.8$.

well sintered at 1180 °C with compact structure and no secondary phases. From Fig. 3(b), the variation tendency of the bulk densities for samples sintered at 1180 °C and 1200 °C is that the bulk densities increased with a higher proportion of ZnO in compositions BaO–nZnO–3TiO$_2$, which could be attributed to ZnO's flux effect in sintering process. During sintering the intermediate products with low melting point formed liquid phase, in which ions transferred easily, so the densification was improved [12,15]. The above results implied that densities of BaO–nZnO–3TiO$_2$ ceramics were closely related to their sintering temperature and the proportion of ZnO.

The scanning electron micrographs recorded from surface of samples sintered at 1180 °C for 2 h are displayed in Fig. 4(a)–(d), for the composition BaO–nZnO–3TiO$_2$: $n = 0.5$, $n = 0.6$, $n = 0.7$, $n = 0.8$, respectively. It is observed in Fig. 4(a) that there were a considerable number of pores, which caused a low bulk density $\rho = 4.580\ \mathrm{g/cm^3}$. From pictures Fig. 4(b)–(d), we can find that the crystal grains were in close contact and there were few pores, thus the highest bulk density $\rho = 4.908\ \mathrm{g/cm^3}$ in this research appeared for the sample BaO–0.8ZnO–3TiO$_2$. But it is noteworthy that the grain size distribution was different. For samples with $n = 0.5$, 0.6 and 0.7, the grain size distribution was about 1–3 μm, but for $n = 0.8$, there was a non-uniform grain morphology and some crystal grains grew quickly with grain size up to 9 μm. Let us make a conclusion that increasing the proportion of ZnO in BaO–nZnO–3TiO$_2$ compositions from $n = 0.5$ to $n = 0.8$, the densification and grain growth could be promoted simultaneously.

Fig. 5 illustrates the energy dispersive X-ray spectrometer (EDS) spectra of surface for BaO–0.6ZnO–3TiO$_2$ ceramics sintered at 1180 °C (a) and 1220 °C (b). The peaks for Zn became weak when sintering temperature increased. The results shown Ba:Zn:Ti mol ratio was 1:0.57:2.97 (1180 °C)and 1:0.51:2.98 (1220 °C). This indicated there was evaporation of ZnO due to the high sintering temperature. Similar results have been reported by Cho et al. [16], who confirmed the occurrence of Zn evaporation in La(Zn$_{1/2}$Ti$_{1/2}$)O$_3$. Therefore, besides affecting phase compositions directly, the sintering temperature could affect the phase compositions indirectly by causing the Zn evaporation. Fortunately, when the samples were sintered at 1180 °C, the phase composition was irrelevant to the ZnO ratio since there was excessive ZnO in our compositions. But the evaporation should influence the densification process.

The dielectric constant of BaO–nZnO–3TiO$_2$ ceramics is shown in Fig. 6 as a function of ZnO ratio. It was obvious that the dielectric constant increased monotonically with a higher proportion of ZnO. The variation tendency of dielectric constant was in accord with the trend between bulk densities and the proportion of ZnO. In these compositions the high dielectric constant came from high bulk density. Fig. 7 shows the $Q \times f$ and τ_f values of BaO–nZnO–3TiO$_2$ ceramics sintered at 1180 °C for 2 h. Let us first pay attention to the τ_f values, which are mainly determined by the phase composition of ceramics and the degree of densification. The τ_f values declined as the proportion of ZnO increased, which was strongly attributed to the increase of densification. This might suggest that the τ_f value could be adjusted by adding different proportion of ZnO, but the practicability was weak, because the proportion of ZnO also had significant influences on microstructure and other microwave properties. Then associating Fig. 4 and Fig. 7, there was a substantial connection between microstructure and $Q \times f$ values. As we know, besides that the lattice vibration modes mainly cause the microwave dielectric loss, the additional phases, the porosity, the crystal defects and the average grain size contribute to the microwave dielectric loss. The composition providing the best

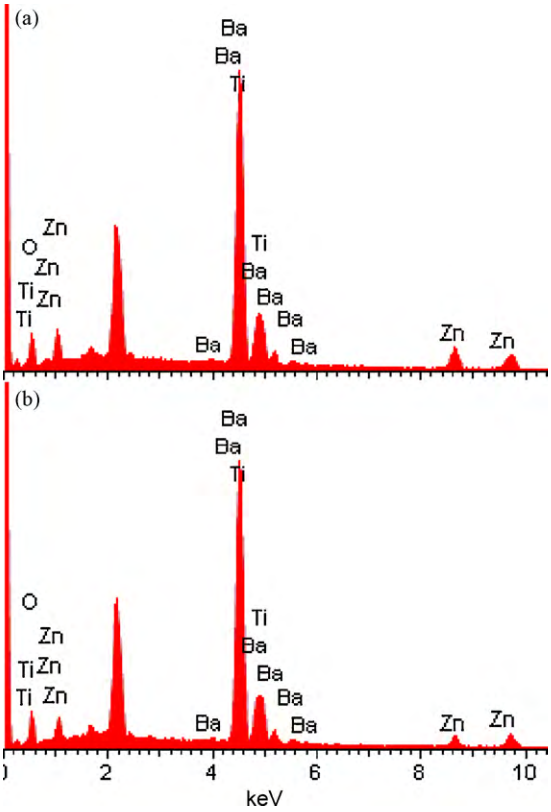

Fig. 5. The energy dispersive X-ray spectrometer (EDS) spectra of surface for BaO–0.6ZnO–3TiO_2 ceramics sintered at 1180 °C (a) and 1220 °C (b).

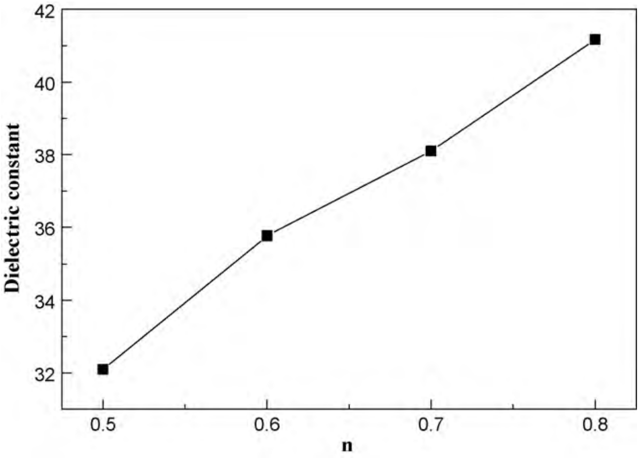

Fig. 6. Dielectric constant of BaO–*n*ZnO–3TiO_2 ceramics with various ZnO content sintered at 1180 °C for 2 h.

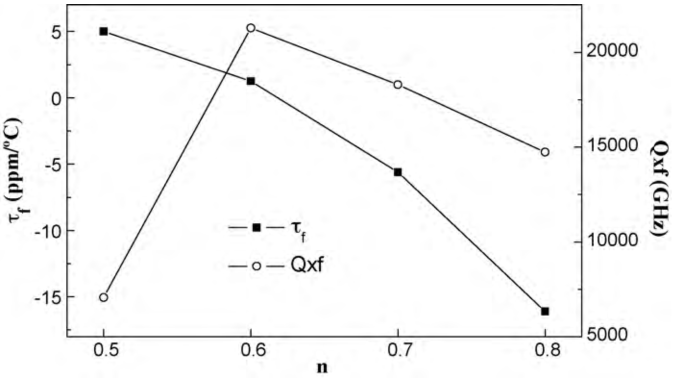

Fig. 7. $Q \times f$ and τ_f values of BaO–*n*ZnO–3TiO_2 ceramics sintered at 1180 °C for 2 h.

microstructure such as few pores, concentrated grain size distribution, pure phase composition and well crystallization can possess a high $Q \times f$ value. The elimination of pores cased the $Q \times f$ values increased strongly from 7072 to 21,288 GHz. Then $Q \times f$ values decreased due to the inhomogeneous grain growth, because the inhomogeneous grain growth caused more defects in the crystal boundary and these defects increased the extrinsic losses. Thus the ceramics with ratio 1:0.6:3 had excellent microwave dielectric properties: $\varepsilon_r = 35.77$, $Q \times f = 21{,}288$ GHz, and the temperature coefficient of resonant frequency τ_f was 1.25 ppm/°C.

4. Summary

The BaO–*n*ZnO–3TiO_2 ceramics with $n = 0.5$–0.8 have been prepared by the conventional solid-state ceramic route for the purpose of investigating effect of ZnO ratio on the sintering behavior and microwave dielectric properties. As the sintering temperature increased from 1160 °C to 1220 °C, $Ba_4ZnTi_{11}O_{27}$ phase appeared as main crystalline phase accompanied by a small number of secondary phases: $BaZn_{2.03}Ti_{3.93}O_{10.89}$ and $Ba_2ZnTi_5O_{13}$. However, when increasing ZnO ratio, all samples sintered at 1180 °C had $Ba_4ZnTi_{11}O_{27}$ as a major phase without secondary phases. And furthermore, ZnO functioned as sintering aids, which promoted the densification and grain growth and thus, influenced the microwave dielectric properties. Moreover, the evaporation of Zn was also confirmed. When the proportion of ZnO was increased, the dielectric constant increased monotonically, τ_f values decreased continuously and $Q \times f$ values increased first and then decreased. Ceramics with composition BaO–0.6ZnO–3TiO_2 sintered at 1180 °C for 2 h had compact and homogeneous structure and possessed excellent microwave dielectric properties: relative dielectric constant $\varepsilon_r = 35.77$, $Q \times f = 21{,}288$ GHz and the temperature coefficient of resonant frequency $\tau_f = 1.25$ ppm/°C

References

[1] S.J. Fiedziuszko, S. Holmes, IEEE 2 (2001) 50–60.
[2] M.T. Sebastian, Dielectric Materials for Wireless Communication, Elsevier, 2008.
[3] W.-Y. Lin, R.A. Gerhardt, R.F. Speyer, J. Mater. Sci. 34 (1999) 3021–3025.
[4] A.G. Belous, O.V. Ovchar, M.-K. Marjeta, M. Valant, J. Eur. Ceram. Soc. 26 (2006) 3733–3739.
[5] G.-Q. Wang, S.-H. Wu, H. Su, Mater. Lett. 59 (2005) 2229–2231.
[6] Y. Atsushi, O. Hirotaka, K. Akinori, J. Eur. Ceram. Soc. 26 (2007) 2069–2074.
[7] H. Sreemoolanadhan, M.T. Sebastian, R. Ratheesh, R. Blachnik, M. Woehlecke, B. Schneider, M. Neumann, P. Mohanan, J. Solid State Chem. 177 (2004) 3995–4000.
[8] H. Yamada, T. Okawa, Y. Tohdo, H. Ohsato, J. Eur. Ceram. Soc. 26 (2006) 2059–2062.
[9] H. Osato, Jpn. J. Appl. Phys. 31 (1992) 3136–3138.
[10] Y.-P. Fu, C.-W. Liu, C.-H. Lin, C.-K. Hsieh, Ceram. Int. 31 (2005) 667–670.
[11] Y.-C. Wu, S.-F. Wang, Y.-R. Wang, W.-J. Wu, J. Alloys Compd. 468 (2009) 522–527.
[12] S.-H. Wu, G.-Q. Wang, Y.-S. Zhao, H. Su, J. Eur. Ceram. Soc. 23 (2003) 2565–2568.
[13] R.S. Roth, C.J. Rawn, C.G. Lindsay, J. Solid Chem. 104 (1993) 99–118.
[14] B.W. Hakki, P.D. Coleman, IEEE Trans. Microw. Theory Tech. MTT8 (1960) 402–410.
[15] C.-L. Huang, J.-L. Hou, C.-L. Pan, C.-Y. Huang, J. Alloys Compd. 450 (2008) 359–363.
[16] S.-Y. Cho, M.-K. Seo, K.-S. Hong, S.-J. Park, Mater. Res. Bull. 32 (1997) 725–735.