Effects of $BaCu(B_2O_5)$ addition on sintering temperature and microwave dielectric properties of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics*

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The effects of $BaCu(B_2O_5)$ (BCB) addition on the microstructure, phase formation, and microwave dielectric properties of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic are investigated. As a sintering aid, $BaCu(B_2O_5)$ ceramic could effectively lower the sintering temperature of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic from 1100 °C to 950 °C due to the liquid-phase effect. Meanwhile, $BaCu(B_2O_5)$ addition effectively improves the densification of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic and significantly influences the microwave dielectric properties. X-ray diffraction analysis reveals that $Ba_5Nb_4O_{15}$ and $BaWO_4$ coexist with no crystal phase of $BaCu(B_2O_5)$ in the sintered ceramics. The $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics with 1.0 wt% $BaCu(B_2O_5)$ sintered at 950 °C for 2 h presents good microwave dielectric properties of $\varepsilon_r = 19.0$, high $Q \times f$ of 33802 GHz and low τ_f of 2.5 ppm/°C.

Keywords: low-temperature co-fired ceramics, composite ceramics, $BaCu(B_2O_5)$ (BCB)

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1. Introduction

In the past decades, with the development of wireless communication, many microwave dielectric materials have been studied. Up to now, materials with high values of relative permittivity (ε_r), high quality factor values ($Q \times f$), and stable temperature coefficients of the resonant frequency ($\tau_f \leq \pm 10$ ppm/°C) were reported.[1,2] However, most of the sintering temperatures of the ceramic materials are relatively high, which is the reason why the materials cannot be co-fired with Ag or Cu nor applied to the low-temperature co-fired ceramic (LTCC) technology.[3–5] As a result, the lowering of the sintering temperatures of dielectric ceramics is critical in order to apply LTCC technology to the fabrication of dielectric devices, such as resonators and filters.[6–10]

$Ba_5Nb_4O_{15}$, a hexagonal perovskite compound, is one of the most promising dielectric ceramics due to its good microwave dielectric properties of $\varepsilon_r = 39.2$, $Q \times f = 26337$ GHz, and $\tau_f = 79.1$ ppm/°C.[11–13] However, the sintering temperature and the temperature coefficient of the resonant frequency of $Ba_5Nb_4O_{15}$ ceramic are too high to be used in the LTCC for commercial production. Kim *et al.*[14] used B_2O_3 to lower the sintering temperature and the τ_f value of $Ba_5Nb_4O_{15}$. According to the reports, tungstates have low sintering temperatures and excellent microwave dielectric properties.[15,16] Among them, $BaWO_4$ has dielectric properties of $\varepsilon_r = 8$, $Q \times f = 5.75 \times 10^4$ GHz, and $\tau_f = -78$ ppm/°C.[16] Zhang *et al.*[17] combined $(1-x)Ba_5Nb_4O_{15}$ with $xBaWO_4$ ($x = 0.54$ wt%) sintered at 1100 °C, and obtained a superior performance of microwave dielectric properties of $\varepsilon_r = 21$, $Q \times f = 4.95 \times 10^4$ GHz, and $\tau_f = 8.9$ ppm/ °C. However, the sintering temperature of $Ba_5Nb_4O_{15}$–$BaWO_4$ is a little high for LTCC.

$BaCu(B_2O_5)$ (BCB) ceramic is one of the most widely used in LTCC material research due to its low melting point (~850 °C) and superior microwave dielectric properties ($\varepsilon_r = 7.4$, $Q \times f = 5 \times 10^4$ GHz, and $\tau_f = -32$ ppm/°C).[18] Many studies about $BaCu(B_2O_5)$ ceramics have been reported. Many materials, such as $Ba(Zn_{1/3}Nb_{2/3})O_3$, $BaNd_2Ti_5O_{14}$, and $BaTi_4O_9$, with BCB could be sintered below 950 °C without a significant degradation of the microwave dielectric properties.[19,20] For example, BCB-added $Ba_4Sm_{9.33}Ti_{18}O_{54}$ possesses microwave dielectric properties of $\varepsilon_r = 52$, $Q \times f = 4 \times 10^3$ GHz, and $\tau_f = 12$ ppm/ °C at 950 °C.[21]

In this article, BCB is selected as a sintering aid to lower the sintering temperature of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic. The influences of BCB addition on the microstructure, densification, the X-ray diffraction patterns, and the microwave dielectric properties of $Ba_5Nb_4O_{15}$–$BaWO_4$ are investigated.

2. Experimental procedure

High-purity powders of $BaCO_3$ (99%), Nb_2O_5 (99.9%), and WO_3 (99%) were used as starting materials. Raw materials for $Ba_5Nb_4O_{15}$ and $BaWO_4$ were separately weighed and milled using zirconia balls. Then $Ba_5Nb_4O_{15}$ and $BaWO_4$ powders were obtained by calcining the powders at

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1000 °C and 750 °C respectively. To synthesize BCB powder, high-purity powders of $BaCO_3$(99%), CuO(99%), and H_3BO_3(99.5%) were weighed and mixed in a nylon jar with zirconia balls, then dried and calcined at 800 °C. Then, BCB-doped $(1-x)Ba_5Nb_4O_{15}$–$xBaWO_4$ ($x = 0.55$ wt%) mixtures were prepared by pure $Ba_5Nb_4O_{15}$, $BaWO_4$, and 0.6–1.4 wt% of BCB by weight ratio. The composite powders were ball milled with zirconia balls, then dried and mixed with an appropriate amount of PVA. The screened powders were pressed into disks with 12-mm diameter and 5 mm–7 mm height by uniaxially pressing under a pressure of 150 MPa. These samples were heated to 600 °C and held at this temperature for 4 h to remove the organic binder and then sintered at 875 °C–1000 °C for 2 h.

The Archimedes method was used to measure the bulk densities of the samples. The relative densities were obtained from the bulk densities and the theoretical densities. The theoretical densities were calculated according to the following formula:

$$\rho = \frac{w_1 + w_2}{w_1/\rho_1 + w_2/\rho_2}, \tag{1}$$

where ρ_1 and ρ_2 are the theoretical densities of $Ba_5Nb_4O_{15}$ and $BaWO_4$, and w_1 and w_2 are the weight fractions of $Ba_5Nb_4O_{15}$ and $BaWO_4$ respectively.[22]

The phase compositions of sintered samples were analyzed using an X-ray diffractometer (XRD) (XRD: DX-2700). The surface micrographs of the samples were analyzed using scanning electron microscopy (SEM) (SEM: INCA penta FETX3 oxford). Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method using a network analyzer (N5230A, Agilent) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA). The temperature coefficients of resonant frequency (τ_f) were obtained in a temperature range from 20 °C to 80 °C. The values were calculated from the following formula:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)}, \tag{2}$$

where f_T and f_0 are the resonant frequencies at T and T_0, respectively.

3. Results and discussion

Figure 1 shows the XRD patterns of $Ba_5Nb_4O_{15}$–$BaWO_4$ with different amounts of the BCB sintered at 950 °C for 2 h. It is clearly seen that all of the peaks could be indexed in terms of the $Ba_5Nb_4O_{15}$ (•) and $BaWO_4$(♦). It is reported that the different crystallized structures of two phases and the different coordination numbers (CN) of Nb and W in their crystal structures might be the reason for the coexistence of $Ba_5Nb_4O_{15}$ and $BaWO_4$.[17] Figure 1 shows that there is no clue that a crystal phase of BCB exists in the BCB-added $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics, in contrast to the XRD patterns of undoped samples in Zhang *et al.*'s work.[17] This result might be explained by the studies about BCB-added $BaSm_2Ti_4O_{12}$ (BST) and $BaNd_2Ti_4O_{12}$ (BNT).[23] There are no peaks of a second phase, though BST and BNT were added with a lot of BCB (up to 20 mol%). This is because BCB liquid phase cannot crystallize in the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics when cooling and remains as the amorphous phase.

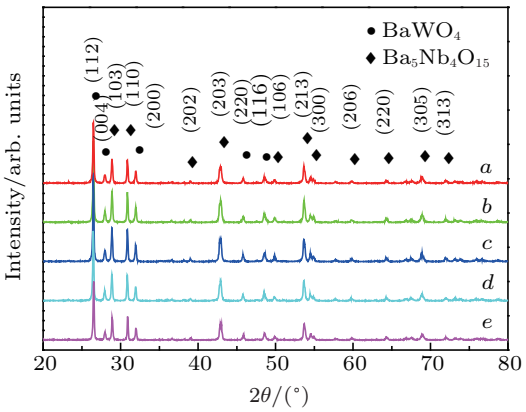


Fig. 1. (color online) X-ray diffraction (XRD) patterns of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics with different amounts of BCB additive at 950 °C for 2 h. Curve *a*: 0.6 wt% BCB; curve *b*: 0.8 wt% BCB; curve *c*: 1.0 wt% BCB; curve *d*: 1.2 wt% BCB; and curve *e* 1.4 wt% BCB.

The SEM micrographs of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics added with different amounts of BCB are illustrated in Fig. 2. As can be seen, there are two types of grains in the samples. The surface of the specimen is covered by the liquid phase. Grains of $Ba_5Nb_4O_{15}$ and $BaWO_4$ would be affected differently by BCB. So, we can speculate that BCB has different effects on $Ba_5Nb_4O_{15}$ and $BaWO_4$ as a sintering aid. BCB has a stronger effect on one of $Ba_5Nb_4O_{15}$ and $BaWO_4$, which makes some grains melt sintered at 950 °C. From Fig. 2(a), many small pores are observed in the sample; these pores may be attributed to the poor sinterability with low BCB content (0.6 wt%). With the increase of the BCB content, the pores are slowly getting smaller. A dense microstructure is formed when the amount of BCB is 1.0 wt% as shown in Fig. 2(c) and less pores are seen. However, a further increase of BCB results in the thawing of most grains in the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic in Fig. 2(d), which may lead to the increase of the loss.

Figure 3 shows the relative densities of the $Ba_5Nb_4O_{15}$–$BaWO_4$ samples with the addition of 0.6–1.4 wt% BCB each as a function of sintering temperature from 875 °C to 1000 °C. It is obvious that the relative densities of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics with small amounts of BCB increase with the sintering temperature below 950 °C. Because the melting temperature of BCB is below 850 °C, it can effectively reduce the sintering temperature of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic and thus assist in the densification of the ceramics (see

Figs. 2(a) and 2(b)). However, when the sintering temperature is above 950 °C, the relative densities of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics (1 wt%–1.4 wt%) slightly decrease, which should be attributed to the volatilization of BCB. Therefore, 950 °C is regarded as the optimum sintering temperature because of the higher relatively density.

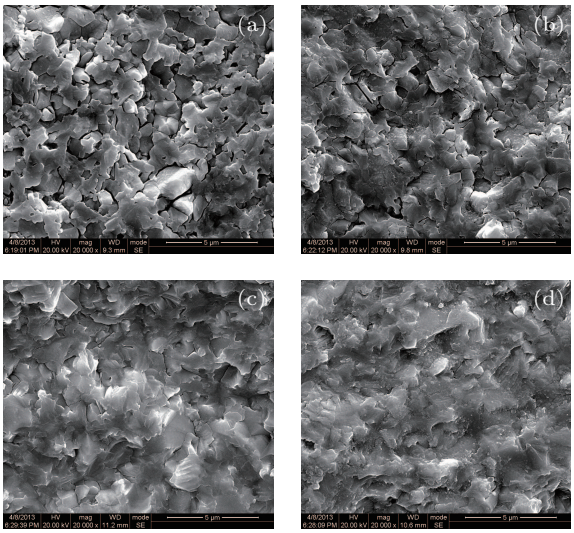


Fig. 2. (color online) Scanning electron micrographs of the $Ba_5Nb_4O_{15}$–$BaWO_4$ samples doped with different amounts of BCB additive sintered at 950 °C: (a) 0.6 wt%, (b) 0.8 wt%, (c) 1.0 wt%, and (d) 1.2 wt%.

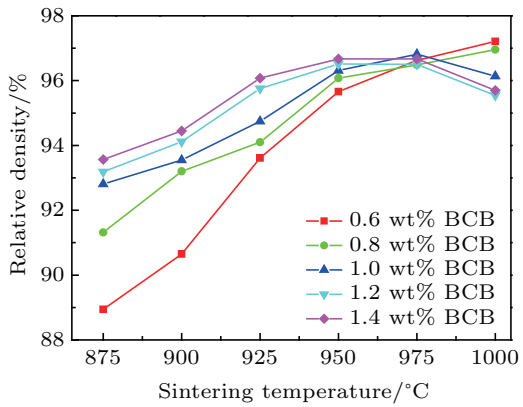


Fig. 3. (color online) Plots of relative densities of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics with various amounts of BCB additive versus sintering temperature (in a range from 875 °C to 1000 °C for 2 h).

Figure 4 shows the relative permittivity (ε_r) curves of $Ba_5Nb_4O_{15}$–$BaWO_4$ samples doped with different amounts of BCB, each as a function of sintering temperature. The value of the relative permittivity increases with the increase of sintering temperature. The relative permittivity curves of $Ba_5Nb_4O_{15}$–$BaWO_4$ samples sintered below 925 °C have relatively large changes due to the changes of the relative density in Fig. 3. With an increase of the BCB content, the value of relative permittivity increases. This is because, within a certain range, more content of sintering agent results in higher densities of the ceramic as can be seen from Fig. 3. A change of the relative permittivity of the ceramic tends to be flat when being sintered above 925 °C. Meanwhile, the relative permittivity is affected by the content of BCB. As the relative permittivity of the BCB ceramic is low ($\varepsilon_r = 7.4$), the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic with a larger amount of BCB has a relatively low value of the relative permittivity above 950 °C. This phenomenon is consistent with the one reported by Santha and Sebastian.[21]

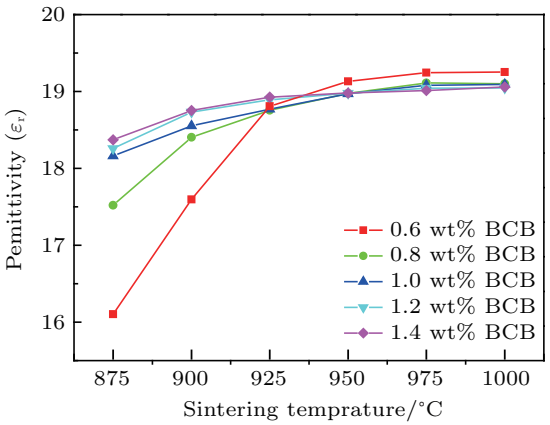


Fig. 4. (color online) Plots of relative permittivity versus sintering temperature of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics doped with different amounts of BCB addition (sintering temperature from 875 °C to 1000 °C for 2 h).

The $Q \times f$ values of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics with BCB additions, each as a function of sintering temperature are shown in Fig. 5. With the increase of the BCB content, the $Q \times f$ values basically first increase and then decrease. For the 1 wt% BCB, the $Q \times f$ value reaches a maximum. Many factors are believed to affect the microwave dielectric loss, and these factors can be divided into two kinds: the intrinsic loss and the extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes, while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes, and densification or porosity.[13] Comparing Fig. 5 with Fig. 3, it can be seen that the variation of the $Q \times f$ value in BCB-doped $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics is due to the change of the relative density. Meanwhile, the decrease of the $Q \times f$ values might also be influenced by the increase of the liquid phase content, which might lead to trapped porosity. Therefore, the relative density of ceramics has a great influence on the $Q \times f$ value, meanwhile, the liquid phase can also affect the $Q \times f$ value.

Figure 6 shows the temperature coefficients of resonance frequency (τ_f) of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics sintered at 950 °C with different amounts of BCB. The value of the temperature coefficient of resonance frequency decreases with the increasing of BCB content. This phenomenon can be explained by the compositions and the phases of the ceramics. According to the reports, the temperature coefficient of the resonance frequency can be tuned by the formation of a solid solution or mixtures of dielectrics with opposite τ_f

values.[17] According to the previous report, the τ_f value of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics is 8.9 ppm/°C. BCB, which exists as an amorphous state, has a negative τ_f value. Therefore, the temperature coefficient of the resonant frequency of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic can be reduced by adding the BCB.

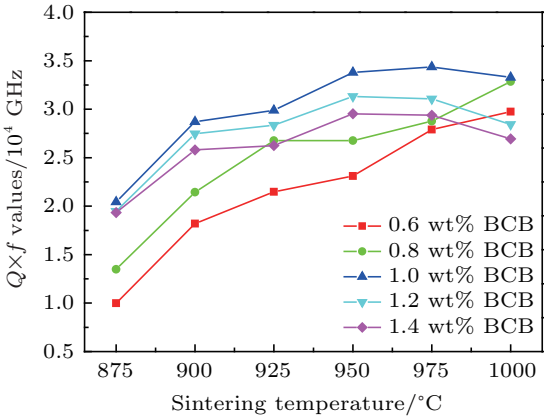


Fig. 5. (color online) Plots of $Q \times f$ values of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics with different amounts of BCB additive versus sintering temperature (in a range from 875 °C to 1000 °C for 2 h).

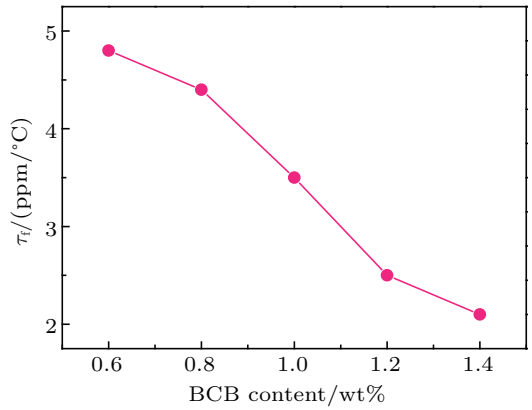


Fig. 6. (color online) Temperature coefficients of resonant frequency (τ_f) of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics varying with BCB content in a range of 0.6 wt%–1.4 wt% BCB at 950 °C for 2 h.

4. Conclusions

The effects of BCB addition on the sintering temperature, density, microstructure, and the microwave dielectric properties of the $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics are investigated. The sintering temperature of $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramic is reduced by BCB to 950 °C without a significant degradation of the microwave dielectric properties. However, the temperature coefficient of resonant frequency (τ_f) could be improved. Typically, the 1 wt% BCB-doped $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics sintered at 950 °C for 2 h has good microwave dielectric properties of $\varepsilon_r = 19.0$, high $Q \times f = 33802$ GHz, and low $\tau_f = 2.5$ ppm/°C. Therefore, $BaCu(B_2O_5)$-added $Ba_5Nb_4O_{15}$–$BaWO_4$ ceramics are promising candidates for the LTCC application.

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