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Phase transitions and microwave dielectric properties of Bi_3NbO_7 ceramics with $Bi_4B_2O_9$ addition

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Abstract

The effects of $Bi_4B_2O_9$ on the phase transitions, sinterability and microwave dielectric properties of Bi_3NbO_7 ceramics were investigated. Densities around 96% theoretical could be achieved at 900 °C for samples with up to 20 wt% $Bi_4B_2O_9$ addition. Phase transitions of cubic → tetragonal → cubic with the increase of sintering temperature were observed for the samples with $Bi_4B_2O_9$ addition. Moreover, the $Bi_4B_2O_9$ addition effectively accelerated the phase transition from cubic Bi_3NbO_7 to tetragonal Bi_3NbO_7. $Bi_4B_2O_9$ addition and the sintering temperature significantly affected the microwave dielectric properties mainly due to the phase transitions. When 20 wt% $Bi_4B_2O_9$ was added, a dense ceramic could be sintered at 900 °C with relative permittivity $\varepsilon_r = 79$, microwave quality factor $Qf_0 = 1010$ GHz, and temperature coefficient of resonance frequency $\tau_f = +8$ ppm/°C, which makes it a promising candidate for LTCC applications.

Keywords: Phase transitions; LTCC; $Bi_4B_2O_9$; Microwave dielectric properties

1. Introduction

With the rapid development of miniaturized devices in wireless communication technology, low-temperature cofired ceramics (LTCC) have become more and more important for high-frequency components such as filters, capacitors and transmission lines which can be integrated into multi-chip modules [1–3]. Commercial LTCC materials usually incorporate highly conducting internal electrode metals such as silver (the melting point 961 °C) or copper (the melting point 1080 °C), which are essential for high-*Q* microwave (MW) components. For LTCC applications, dielectric ceramics need to fulfil the requirement of sinterability below the melting point of the electrodes while maintaining good dielectric properties [4].

Recently, several bismuth-based dielectric ceramics were investigated as promising dielectric candidates for LTCC application because of their relatively low sintering temperature and good MW dielectric properties. Valant and Suvorov [5] and Pang et al. [6] have reported the phase formations and MW dielectric properties of several Bi-based binary compounds such as Bi_2O_3–Nb_2O_5 and Bi_2O_3–Sb_2O_3 binary systems. Particularly, $BiNbO_4$ is a typical example of a Bi-based MW dielectric ceramic with a relative permittivity $\varepsilon_r = 43$, a quality factor $Qf_0 = 17{,}000$ GHz, and a temperature coefficient of resonance frequency $\tau_f = +38$ ppm/°C. [7]. Although $BiNbO_4$ ceramics exhibit attractive MW dielectric properties, they have poor chemical compatibility with the most common electrode metal, Ag, which limits their application to LTCC technology [8]. Compared with $BiNbO_4$, Bi_3NbO_7 (BN) ceramics have good chemical compatibility with Ag electrode [9]. Valant and Suvorov [5] have reported the MW dielectric properties of $(1-x)Bi_2O_3 - xNb_2O_5$ compositions in the range of $0.10 < x < 0.29$. The BN ceramics were obtained at $x = 0.25$, where with increasing temperature from 850 to 940 °C, ε_r increased from 91 to 99, Qf_0 decreased from 725 to 300 GHz, and τ_f value decreased from $+100$ to -200 ppm/°C. An interesting phase transition was found wherein a single cubic phase of BN formed below 800 °C and above 930 °C, a single tetragonal phase

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formed in 850–880 °C, and cubic and tetragonal phases coexisted in 800–850 °C and 880–930 °C. However, the τ_f values of both the cubic BN (-200 ppm/°C) and tetragonal BN ($+100$ ppm/ °C) were too high for most passive devices.

$Bi_4B_2O_9$ (BB) ceramics have been used as a sintering aid due to the low sintering temperature (~660 °C) and favourable MW dielectric properties ($\varepsilon_r=39$, $Qf_0=2600$ GHz, and $\tau_f=-203$ ppm/°C) [10]. In our previous work, we have investigated the effects of BB on $BaO-Nd_2O_3-4TiO_2$ (BNT) and reported that a small amount of BB could decrease the sintering temperature of the BNT by up to around 200 °C without a significant degradation of the MW dielectric properties. Meanwhile, the τ_f of the ceramics could be tuned to a near-zero value [10]. Here, BB ceramics were chosen as the additive to modify dielectric properties of BN ceramics and the effects on the phase transitions, sinterability, and MW dielectric properties have been investigated.

2. Experimental procedure

Specimens of the BB ceramics were prepared by a conventional mixed route from the dried, reagent-grade Bi_2O_3 (99.9%, Acros Organics) and B_2O_3 (99.9%, Sigma Aldrich). Stoichiometric proportions of the above raw materials were ball-milled for 8 h in iso-propanol medium, then dried, and calcined at 580 °C for 2 h. Compositions of BN were fabricated using Bi_2O_3 (99.9%, Acros Organics) and Nb_2O_3 (99.9%, Sigma Aldrich) as the starting reagents. The appropriate amounts of dry raw materials were weighed and attrition milled for 1 h with yttria stabilised zirconia media in iso-propanol. Mixed powders of BN were calcined at 700 °C for 2 h. The reacted powders were sieved through a 355 μm sieve and then attrition milled as above. After remilling with BB, the powders were dried and pressed into pellets of 8 mm diameter and ~3 mm thickness by uniaxial pressing at an applied load of ~0.6 t for 1 min. Pellets were then sintered 4 h in air at sintering temperatures ranging from 800 to 950 °C. Bulk densities of the sintered samples were measured using the Archimedes method with distilled water.

X-ray diffraction (XRD) was performed at a step size of 0.02° with a scan rate and range of 1°/min, using an X-ray diffractometer (D500, Siemens, Munich, Germany) equipped with CuKα ($\lambda=1.5405$ Å) radiation operating at 40 kV and 30 mA. The microstructures of the sintered samples were examined by scanning electron microscopy (SEM;JSM-6400, JEOL Corporation, Tokyo, Japan). The JSM 6400 was equipped with Link systems energy dispersive (EDS) X-ray detectors. A MW vector network analyser (R3767CH, Advantest Corporation, Tokyo, Japan) was used to measure the dielectric properties at MW frequencies. ε_r and Qf_0 were measured by the transmission resonant cavity technique in an Au-coated brass cavity and fused silica support. A Peltier device was used to heat up the cavity in order to measure the resonant frequency, f_0, between 25 and 80 °C. A linear fit to the data was used to calculate τ_f.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms which reveal the phase assemblage of the BN ceramics with BB addition

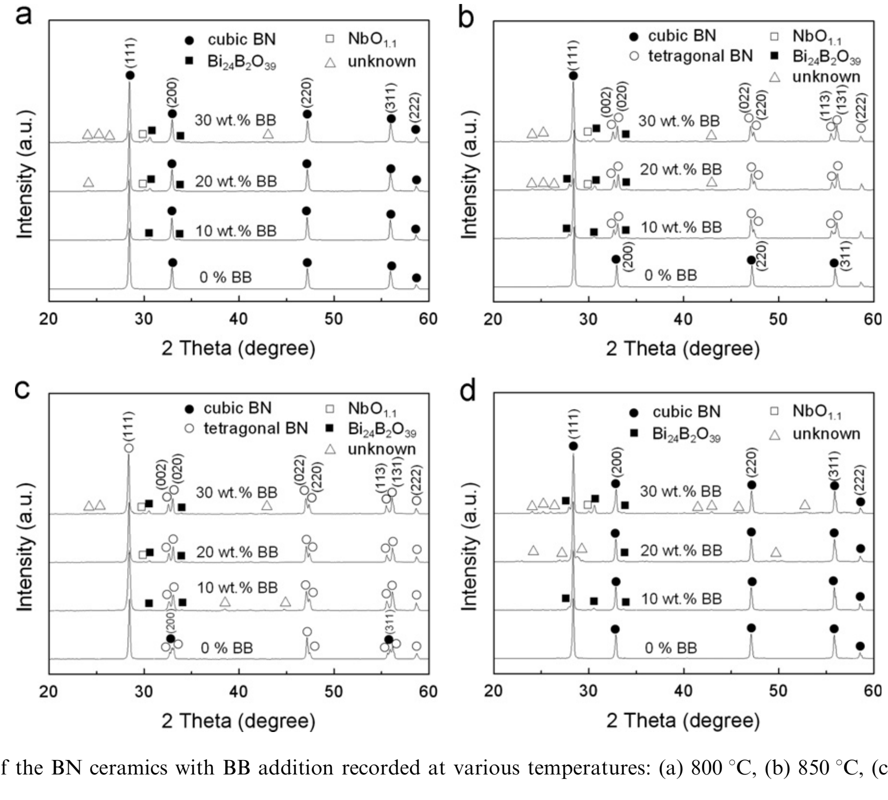

Fig. 1. XRD patterns of the BN ceramics with BB addition recorded at various temperatures: (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C.

sintered at 800–950 °C and 50 °C intervals. The XRD traces of BN powders sintered at 800 °C, shown in Fig. 1(a), did not reveal the presence of any secondary phases and all peaks could be indexed to a single phase cubic structure (space group: $Fm3^{-}m$). The lattice parameters were calculated to be $a = 5.451(3)$ Å. Similar to the results of the undoped BN, the main phase of cubic-BN was revealed for the samples with various amounts of BB addition, as shown in Fig. 1(a). Additionally, several additional peaks were observed and indexed t $Bi_{24}B_2O_{39}$ and $NbO_{1.1}$ phases, but attempts to identify the extra peaks at low angles have been unsuccessful so far. The formation of bismuth-rich phase ($Bi_{24}B_2O_{39}$) caused the consumption of niobium in BN ceramics, and the niobium-rich phase ($NbO_{1.1}$) therefore was formed as a secondary phase. Meanwhile, the remnant boron and bismuth related compound might interact and form a $B_2O_3-Bi_2O_3$ related liquid phase and/or the crystalline phase(s), which could improve the sinterability of BN ceramics.

The lattice parameters of the cubic phase for the sample without BB addition sintered at 850 °C were calculated to be $a = 5.453(6)$ Å (Fig. 1(b)). Compared with the sample sintered at 800 °C, the lattice parameters did not change significantly with the sintering temperature. However, the XRD patterns of the BB-doped samples sintered at 850 °C, as shown in Fig. 1(b), showed new peaks corresponding to the tetragonal phase with a new set of diffraction lines, which appeared at the same 2θ angles approximately as those of the cubic phase. The result implies that the addition of BB effectively accelerated the phase transition from cubic BN to tetragonal BN. It is noteworthy that the BB addition also resulted in the appearance of secondary phases, while the intensity of the secondary phases increased with the increase in the amount of BB addition.

With an increase in the sintering temperature to 900 °C, the XRD patterns of the undoped BN showed a two-phase composition with split tetragonal diffraction lines of (002,020), (022,220), and (113,131), indicating the occurrence of phase transitions from cubic BN to tetragonal BN, as shown in Fig. 1(c). However, for BB-doped samples, the cubic phase disappeared and only the tetragonal phase was detected. It seems that BB addition could restrain the occurrence of the cubic phase. The real reason for the observed phase variation was that the BB addition could effectively decrease the temperature of phase transition.

When the sintering temperature increased to 950 °C, the main phase of all the samples was cubic phase, indicating that the phase transition of tetragonal → cubic occurred, as shown in Fig. 1(d). It is interesting to note that all the samples underwent a cubic → tetragonal → cubic BN phase transition with an increase in temperature (Fig. 1). Furthermore, it can be concluded that both the cubic to tetragonal and tetragonal to cubic phase transition temperatures of BB-doped samples are shifted to lower temperature compared with that of undoped BN ceramics.

Fig. 2 shows the bulk densities of the BB-doped BN ceramics as a function of sintering temperature from 800 to 950 °C. The theoretical density for full densification is difficult to determine because of the complicated phase transitions and material reactions in the samples. It can be seen from Fig. 2 that sintering at 850 °C was sufficient to accomplish the appropriate densification for all the BB-doped samples. The density for the sample sintered at 800 °C was comparatively low, but increased with the increasing sintering temperature to a maximum at 900 °C and then slightly declined thereafter. For example, the 10 wt% BB-doped sample sintered at 900 °C reached a bulk density of ~8.03 g/cm^3, which was equivalent to a relative density of ~95.9% assuming no phase transitions and no material reactions occurred. The density variation can be attributed to a small amount of trapped porosity and the volatile species in the samples, such as bismuth and boron. It is worth pointing out that the serious volatilization of bismuth and/or boron (the melting points of Bi_2O_3 and B_2O_3 are 825 °C and 450 °C, respectively) at high temperature would result in nonstoichiometry in the samples.

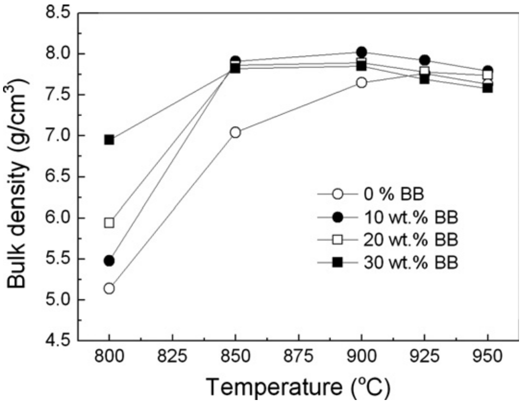

Fig. 2. Bulk densities of BN ceramics with various BB additions for various sintering temperatures.

Fig. 3(a)–(d) shows the SEM micrographs of the BN ceramics doped with different amounts of BB additions. The changes in the density and grain size can be seen in the SEM micrographs of selected BB-doped ceramics. For the ceramics without BB addition, a porous microstructure was developed with a large number of pores and a small grain size (~1 μm), as shown in Fig. 3(a), which showed agreement with the relatively low bulk densities of the ceramics. However, in the sample doped with BB addition, the pores were eliminated and homogeneous distributions of grains were developed, probably due to the formation of the $Bi_2O_3-B_2O_3$ related liquid phase during the sintering process, which could assist the densification of the BN ceramics. Actually, it is believed that the BB addition melted during the sintering due to the low melting point (~700 °C). It can be seen that the grain sizes of samples with different amounts of BB additions sintered at 850 °C are similar and the values are ~3 μm, which is much larger than that of undoped BN ceramics (~1 μm). This result means that the BB addition worked as a grain growth accelerant. The grain growth that occurred in the BB-doped samples could be explained by the liquid phase assisted grain

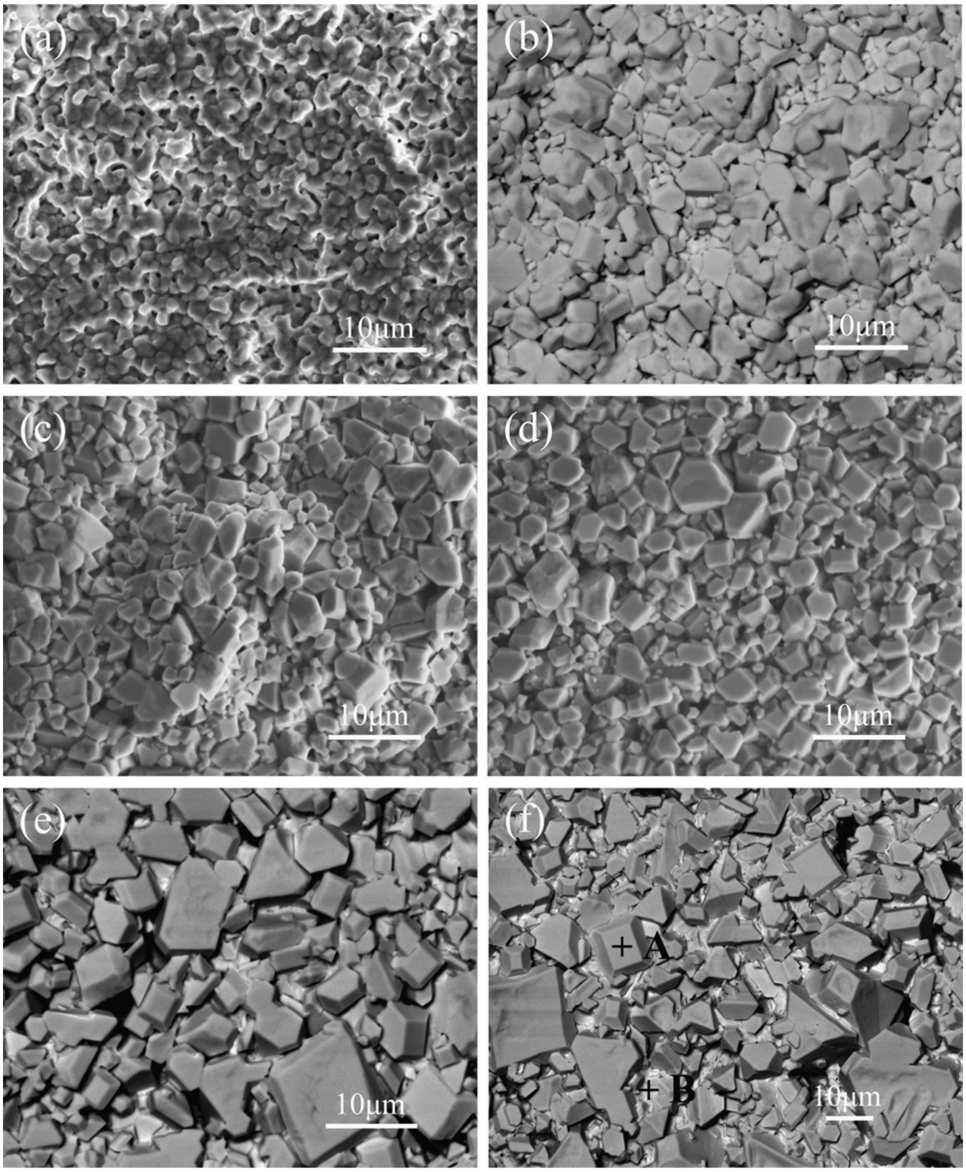

Fig. 3. Secondary electron images of the BN ceramic doped with (a) 0 wt% BB, (b) 10 wt% BB, (c) 20 wt% BB, and (d) 30 wt% BB sintered at 850 °C; backscattered electron images of the BN ceramics doped with (e) 30 wt% BB sintered at 900 °C, and (f) 30 wt% BB sintered at 950 °C.

growth. Moreover, the grain size of the samples increased evidently with the increase of sintering temperature. As shown in Fig. 3(e), when the sintering temperature increased to 900 °C, the grain growth of 30 wt% BB-doped sample occurred with the average grain size of 4.5 μm. It is noteworthy that a further increase in the sintering temperature (950 °C) does not seem to promote the grain growth clearly compared with the samples sintered at 900 °C, which may be attributed to the presence of a large amount of the liquid phase, as shown in Fig. 3(f).

To identify the composition of the secondary phases, EDS analysis was performed on the 30 wt% BB-doped sample sintered at 950 °C, which is shown in Fig. 3(f). The results of quantitative analysis are given in Table 1. For the matrix, Bi and Nb elements were detected at a ratio of approximately 3:1, which confirms the matrix as the BN phase. However, a large amount of Bi element was detected in the secondary phases, indicating that the secondary phases could consist of a Bi-rich phase. Even though the B element cannot be detected due to the detection limit of the EDS detector, the B element is believed to exist in the samples because B was added as a composition element of BB

Table 1
Chemical compositions of 30 wt% BB-doped BN ceramic sintered at 950 °C.

Element	Atomic %	
	Matrix (A)	Secondary phase (B)
Bi	74.37	93.63
Nb	25.63	6.37

addition. Hence, the composition of the secondary phases was considered to be a $Bi_2O_3-B_2O_3$ related phase and these secondary phases might be $Bi_{24}B_2O_{39}$ and $Bi_2O_3-B_2O_3$ liquid phases. In addition, the $NbO_{1.1}$ phase was confirmed in XRD patterns (Fig. 1), but was not observed in the backscatter images (Fig. 3(e) and (f)) probably due to the small amount of this phase.

Fig. 4 presents the relative permittivity for BN ceramics with different weight percents of BB addition as a function of sintering temperature. Generally, the ε_r depends on the bulk density and phase constituents. From Fig. 4, the ε_r of BB-doped samples increased to a maximum and thereafter it decreased, which is similar to that of undoped samples. The increase of the ε_r for BB-doped samples can be attributed to the enhanced densification due to liquid-phase sintering, whereas the decrease in ε_r as the sintering temperature exceeded 900 °C can be ascribed to the overheating which caused the decline of density [11]. Additionally, the ε_r decreased with the addition of a higher amount of BB due to the lower ε_r of the BB (~ 39) compared with pure BN. The low relative permittivity of additional phases, such as $Bi_{24}B_2O_{39}$, $NbO_{1.1}$ and $B_2O_3-Bi_2O_3$ related phases (labelled as unknown phase in the X-ray patterns), formed due to the addition of BB might be attributed to the decrease in permittivity as well.

The Qf_0 values of the BB-doped BN ceramics sintered at various temperatures are demonstrated in Fig. 5. For the undoped samples, the Qf_0 values first increased with the increase of temperature and a maximum value of 650 GHz was obtained; thereafter, the Qf_0 values decreased, attributable to the cubic → tetragonal → cubic phase transitions, as shown in Fig. 1. Note that the cubic BN ceramics (300 GHz) have a smaller Qf_0 value in the MW region than that of the tetragonal BN ceramics (725 GHz) [5]. Hence, the samples sintered at 900 °C consisting of the cubic phase and the tetragonal phase exhibited a larger Qf_0 value. The Qf_0 values of BB-doped samples showed a similar trend as that of the undoped BN ceramics, as shown in Fig. 5. With an increase in sintering temperature from 800 to 900 °C, the Qf_0 values of 10 wt% and 20 wt% BB-doped samples increased to a maximum value because a cubic → tetragonal phase transition occurred. A further increase in the sintering temperature caused a decrease in Qf_0 values, the main reason for which is due to the tetragonal → cubic phase transition. However, for the 30 wt% BB-doped samples, the maximum value of Qf_0 was obtained at 850 °C and beyond this temperature it decreased. In addition, the relatively low densities and the appearance of secondary phases of the BB-doped samples sintered at elevated temperature are also considered to be other reason for the decline of Qf_0 values. Furthermore, the emergence of $NbO_{1.1}$ phase implies that the migration of Nb from BN matrix occurred. The result may cause the presence of lattice defects in a non-stoichiometric BN matrix, which may also affect the Qf_0 [12]. In general, the dielectric loss can be attributed to both the intrinsic and extrinsic losses. The intrinsic losses are due to the anharmonic forces that mediate the interaction between crystal and phonons [13], which might have effects on the Qf_0 values of BN ceramics; however, it needs further investigation. Nevertheless, extrinsic losses associated with extended dislocations, as discussed above, such as porosity and secondary phases, might dominate the dielectric losses in BN ceramics.

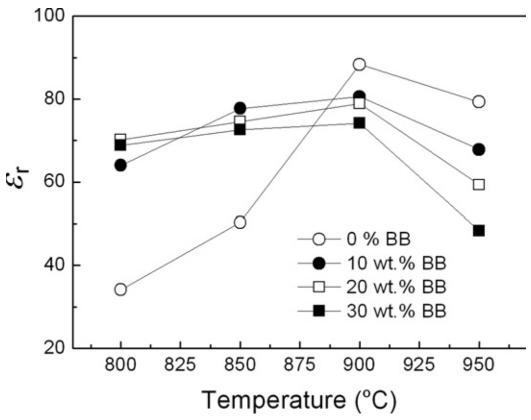

Fig. 4. Relative permittivity of BN ceramics with different BB additions as a function of sintering temperature.

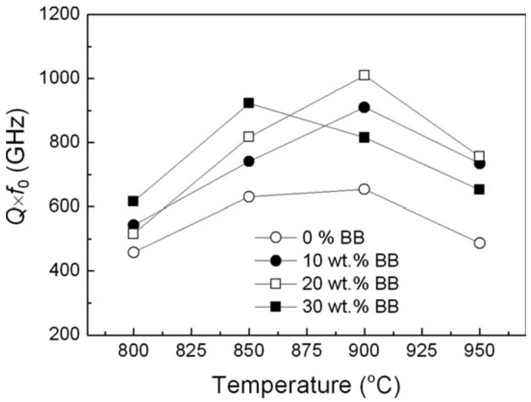

Fig. 5. Qf_0 values of BN ceramics with different BB additions as a function of sintering temperature.

Fig. 6 shows τ_f for all compositions as a function of sintering temperature. In general, the ratio of the different phases somewhat determine the value of τ_f, and the total τ_f can be calculated by a logarithmic mixture rule, if the τ_f of each of the phases in a dielectric is known [14]. As shown in Fig. 6, the BB-doped samples showed an initial increase in τ_f with increasing sintering temperature,which is mainly attributed to the different τ_f values for the cubic BN and the tetragonal BN phases (-200 ppm/°C for the former and $+100$ ppm/°C for the latter), [5], and therefore the τ_f values increased due to the formation of the tetragonal phase as the sintering temperature increased. However, when the sintering temperature increased to 950 °C, the cubic BN phase with negative τ_f value was formed again (Fig. 1(d)), which decreased the τ_f value. It is noted that the undoped BN sintered at 850 °C showed a larger negative τ_f value (-160 ppm/°C) compared with that of BB-doped

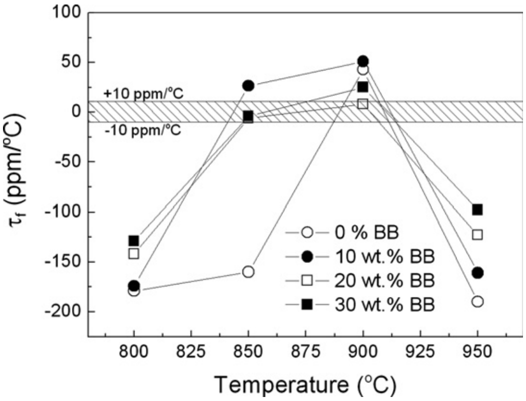

Fig. 6. τ_f values of BN ceramics with different BB additions as a function of sintering temperature.

samples, mainly because the undoped BN showed a cubic BN phase at this sintering temperature (Fig. 1(b)). Near-zero τ_f (+8 ppm/°C) was achieved for 20% BB doped BN at 900 °C, at which composition $\varepsilon_r \sim 79$ and $Qf_0 \sim 1010$ GHz. This indicates that the BB addition effectively improves the τ_f values and therefore the BN ceramics with BB addition are much more closes to practical applications. In addition, the variation of τ_f in the BN ceramics is strongly related to the phase transitions, which implied that the τ_f value was sensitive to the sintering temperature as well. Hence, near-zero τ_f may be readily achieved for this material by controlling the amount of BB addition and sintering temperature more precisely than has been reported in the literature [9,15].

The possible applications of BB doped BN ceramics in LTCC modules and modern MW circuitry are worthy of consideration due to their low sintering temperature (~900 °C), high permittivity (~79), and near zero τ_f value, although the dielectric losses of this materials do not look so attractive. Nevertheless, our study shows that the BB added BN ceramics exhibit much lower dielectric losses ($Qf_0 \sim 1010$ GHz), in contrast to both the cubic BN ($Qf_0 \sim 725$ GHz) and tetragonal BN ($Qf_0 \sim 300$ GHz) [5]. Additionally, the BN composition is chemically compatible with the silver electrode (the compounds richer in bismuth than $Bi_5Nb_3O_5$ are considered to be cofireable with silver electrodes) [16]. This coupled with the MW dielectric properties therefore opens up the possibility of using BB-doped BN ceramics in LTCC technology.

4. Conclusions

The phase transitions and MW dielectric properties of BB-doped BN ceramics were investigated. BB addition was used to improve the sinterability and modify the τ_f value to near zero of BN ceramics. Phase-transition sequence cubic → tetragonal → cubic with the increase of sintering temperature was observed for the samples with BB addition. Moreover, the addition of BB could effectively accelerate the phase transition from cubic to tetragonal. The addition of BB and sintering temperature produced significant alteration in the MW dielectric properties of BN ceramics. The relative permittivity was strongly dependent on the amount of BB addition, while the Qf_0 value and the τ_f of the samples with BB addition increased with the increasing sintering temperature to a maximum and then declined thereafter, which are related to the phase transitions. The BN ceramic sintered with 20 wt% BB addition at 900 °C, exhibited ε_r of 79, Qf_0 of 1010 GHz, and τ_f of +8 ppm/°C, which makes it a promising candidate for LTCC applications.

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