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Microwave dielectric properties and low-temperature sintering of $Ba_3Ti_4Nb_4O_{21}$ ceramics with B_2O_3 and CuO additions

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Abstract

The low sintering temperature and the good dielectric properties such as high dielectric constant (ε_r), high quality factor ($Q \times f$) and small temperature coefficient of resonant frequency (τ_f) are required for the application of chip passive components in the wireless communication technologies. In the present study, the sintering behaviors and dielectric properties of $Ba_3Ti_4Nb_4O_{21}$ ceramics were investigated as a function of B_2O_3–CuO content. $Ba_3Ti_4Nb_4O_{21}$ ceramics with B_2O_3 or CuO addition could be sintered above 1100 °C. However, the additions of both B_2O_3 and CuO successfully reduced the sintering temperature of $Ba_3Ti_4Nb_4O_{21}$ ceramics from 1350 to 900 °C without detriment to the microwave dielectric properties. From the X-ray diffraction (XRD) studies, the sintering behaviors and the microwave dielectric properties of low-fired $Ba_3Ti_4Nb_4O_{21}$ ceramics were examined and discussed in the formation of the secondary phases. The $Ba_3Ti_4Nb_4O_{21}$ sample with 1 wt% B_2O_3 and 3 wt% CuO addition, sintered at 900 °C for 2 h, had the good dielectric properties: $\varepsilon_r = 65$, $Q \times f = 16{,}000$ GHz and $\tau_f = 101$ ppm/°C.

Keywords: Low-temperature sintering; Dielectric properties; Borides; Carbides; $Ba_3Ti_4Nb_4O_{21}$

1. Introduction

The rapid progress in mobile and satellite communication system has accelerated the development of dielectric materials at microwave frequencies. Moreover, low temperature co-fired ceramics (LTCC) is finding increased usage as an interconnect substrate, especially in microwave applications due to the high conductivity of the conductors and low loss of the LTCC dielectrics. LTCC has the potential to incorporate multilayer structures and buried passive components, with minimal processing steps, thus leading to very compact microwave subsystems.

A survey of commercial LTCC materials shows that the vast majority of them have dielectric constants around 4–5 and 7–9 that provide high signal propagation speeds in an electronic circuit. Many of the materials are based on the mixtures of low-melting glasses with alumina as a filler for the dielectric tape. However, in certain applications low dielectric loss LTCC materials with higher dielectric constants in the range of 15–200 can offer design and functional benefits for electronic packaging without speed deterioration.[1,2]

In the past, the several microwave dielectric compositions including (Zr,Sn)TiO_4,[3] $SrTiO_3$–$NdAlO_3$,[4] BaO–TiO_2–WO_3,[5] $Ba_5Nb_4O_{15}$[6] and BaO–Ln_2O_3–TiO_2 (Ln: La, Sm, Nd) systems[7–9] have been studied for the development of the dielectric compositions with a middle dielectric constant (40–80) by using the agents for low-temperature firing. Takada et al.[3] have lowered the sintering temperature of (Zr,Sn)TiO_4 by adding various glasses. Among these glasses, 5ZnO–$2B_2O_3$ glass has effectively densified (Zr,Sn)TiO_4 ceramics and the low-fired (Zr,Sn)TiO_4 ceramics had a high quality factor ($Q \times f \sim 23{,}700$ GHz) at 9.1 GHz, though the ceramics had a low dielectric constant ($\varepsilon_r \sim 15$). Also, Park et al.[9] have added lithium borosilicate glass to MBRT-90 (Fuji Titanium Industry Co., $\varepsilon_r \sim 90$) ceramics and have successfully developed LTCC composition which has a dielectric constant at range of 20–60. MBRT-90 ceramics with 10 wt% lithium borosilicate glass addition was well sintered at 875 °C and had a high dielectric constant of 61.6 at microwave region, though the ceramics had a low quality factor $Q \times f \sim 2500$ GHz. On the above occasions, a high

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quality factor induced the deterioration in the dielectric constant; similarly, a high dielectric constant induced that in the quality factor.

The dielectric properties of $Ba_3Ti_4Nb_4O_{21}$ ceramics have been investigated by Sebastian.[10] He reported that $Ba_3Ti_4Nb_4O_{21}$ ceramics have good microwave dielectric properties with high ε_r of 55, high $Q \times f$ of 9500 GHz (at 5.5 GHz) and τ_f of 100 ppm/°C.[10] The ceramics have a high dielectric constant as well as have a fairly high quality factor. But the sintering temperature of $Ba_3Ti_4Nb_4O_{21}$ ceramic was above 1270 °C, which is too high to be applicable to LTCC. So it is necessary to reduce the sintering temperature. However, the effect on the firing temperature of $Ba_3Ti_4Nb_4O_{21}$ by addition of dopants has not been thoroughly studied.

Then, there have been three approaches to reduce the sintering temperature of the dielectric ceramics: addition of the glass or the oxides of low melting-temperature, chemical processing such as sol–gel and the precipitation method and utilization of ultra-fine particles for raw materials.[11–13] In general, adding the oxides as flux materials has been known to be very inexpensive and effective in order to lower the sintering temperature of the microwave dielectric ceramics. In this work, B_2O_3 and CuO as flux materials were added to the $Ba_3Ti_4Nb_4O_{21}$ ceramics to decrease the sintering temperature for LTCC applications. Furthermore, microstructure and microwave dielectric properties of low-fired $Ba_3Ti_4Nb_4O_{21}$ ceramics with B_2O_3 and CuO additions were also investigated.

2. Experimental procedure

The $Ba_3Ti_4Nb_4O_{21}$ powders were synthesized by conventional mixed oxide methods: $BaCO_3$ (99.9% pure, Milwaukee, WI), TiO_2 and Nb_2O_5 (99.9% pure, High Purity Chemical Laboratory, Saitama, Japan) were mixed homogeneously and calcined at 1100 °C for 2 h. The calcined powders containing a proper amount of B_2O_3 and CuO (99.9% pure, High Purity Chemical Laboratory) were ball-milled for 48 h using ethanol solvent. The milled powders were then dried, granulated and pressed at 100 MPa to yield several disk type pellets (8 mm in diameter and 4 mm in thickness). The pellets were sintered at 850–1000 °C for 2 h with a heating rate of 5 °C/min. The bulk density of the sintered samples was determined by the Archimedes method.

Shrinkage of the specimens during heat treatment was measured using a horizontal loading dilatometer with alumina rams and boats (Model DIL402C, Netzsch Instruments, Germany). Polished and thermally etched surfaces of sintered specimens were examined using field emission scanning electron microscopy (FESEM: Model JSM6330F, Japan Electronic Optics Laboratory, Japan). The crystal structure of sintered samples was investigated using X-ray powder diffraction (Model M18XHF, Macscience Instruments, Japan) in the 2θ range from 20° to 60°. The microwave dielectric properties of sintered samples were measured at x-band frequencies (8–12 GHz) using a network analyzer (Model HP8720C, Hewlett-Packard, Palo Alto, CA, USA).

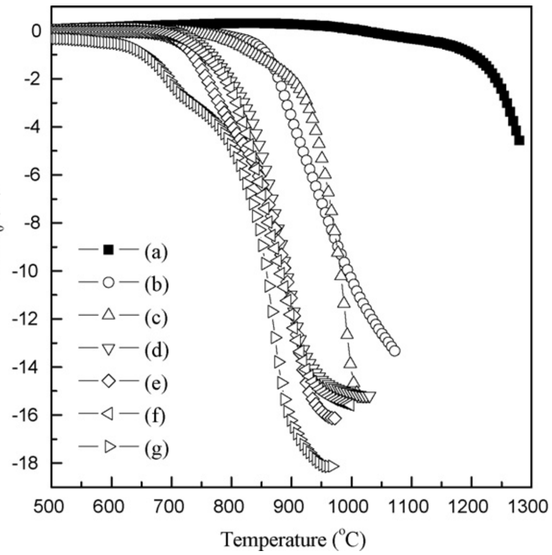

Fig. 1. Shrinkage of $Ba_3Ti_4Nb_4O_{21}$ samples with various contents of B_2O_3 and CuO as a function of temperature: (a) no dopants, (b) 5B, (c) 5C, (d) 1B3C, (e) 2B2C, (f) 3B1C and (g) 5B5C.

3. Results and discussion

3.1. Sintering behaviors

The sintering behavior of $Ba_3Ti_4Nb_4O_{21}$ ceramics with sintering aids (B_2O_3, CuO) was examined by a dilatometer. Fig. 1 shows shrinkage behaviors of $Ba_3Ti_4Nb_4O_{21}$ samples with: (a) no dopants, (b) 5 wt% B_2O_3 (5B), (c) 5 wt% CuO (5C), (d) 1 wt% B_2O_3 and 3 wt% CuO (1B3C), (e) 2 wt% B_2O_3 and 2 wt% CuO (2B2C), (f) 3 wt% B_2O_3 and 1 wt% CuO (3B1C) and (g) 5 wt% B_2O_3 and 5 wt% CuO (5B5C) as a function of temperature. The shrinkage of $Ba_3Ti_4Nb_4O_{21}$ sample without the sintering aids appears to occur slowly at ~1190 °C. Similarly, $Ba_3Ti_4Nb_4O_{21}$ samples with B_2O_3 or CuO showed the apparent shrinkage above 900 °C. However, $Ba_3Ti_4Nb_4O_{21}$ samples with both B_2O_3 and CuO additions exhibited a large shrinkage of 18% at about 900 °C. $Ba_3Ti_4Nb_4O_{21}$ samples with both B_2O_3 and CuO exhibited an onset of shrinkage near 700 °C, reaching maximum value at 950 °C. In other words, though $Ba_3Ti_4Nb_4O_{21}$ sample with 5B or 5C had more or the similar amount of sintering aid, the densification of the sample was poorer than $Ba_3Ti_4Nb_4O_{21}$ sample with 1B3C. These results indicate that the co-additions of B_2O_3 and CuO to $Ba_3Ti_4Nb_4O_{21}$ samples can effectively lower the sintering temperature of the ceramics. So, the lower onset temperatures of densification and the shrinkage rate in the dilatometry curves could be evidence of efficiency to lower the sintering temperature of $Ba_3Ti_4Nb_4O_{21}$ samples by adding both B_2O_3 and CuO simultaneously.

Moreover, according to the phase diagram of CuO–B_2O_3, the compositions with a higher B_2O_3 content easily form a liquid phase at the low temperature (450 °C) and a eutectic point of $Cu_3B_2O_6$–CuB_2O_4 exists as low as at 880 °C.[14] Thus, it can be postulated that the reaction between CuO and B_2O_3 causes the formation of liquid phases and the liquid phases act as the sintering aids for $Ba_3Ti_4Nb_4O_{21}$ samples.

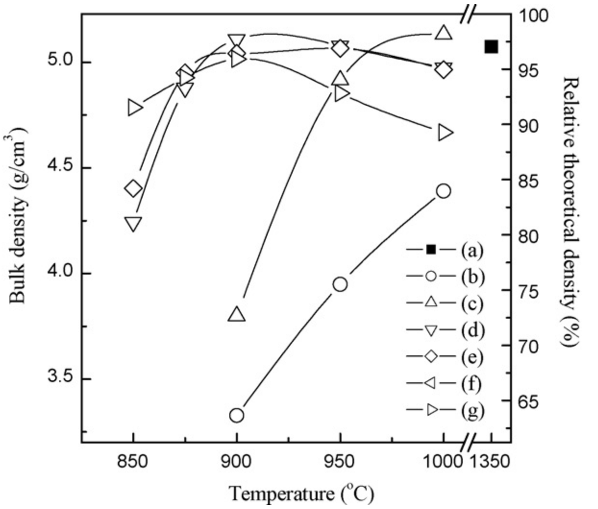

Fig. 2. Bulk density of $Ba_3Ti_4Nb_4O_{21}$ samples with various contents of B_2O_3 and CuO as a function of temperature: (a) no dopants, (b) 5B, (c) 5C, (d) 1B3C, (e) 2B2C, (f) 3B1C and (g) 5B5C.

The bulk densities of $Ba_3Ti_4Nb_4O_{21}$ samples with various contents of B_2O_3 and CuO as a function of sintering temperature are shown in Fig. 2. The bulk density of $Ba_3Ti_4Nb_4O_{21}$ samples with 5B or 5C sintered at 900 °C for 2 h, increased with increasing sintering temperature and reached 3.65 or 4.08 g/cm^3, respectively. In contrast, the bulk densities of $Ba_3Ti_4Nb_4O_{21}$ samples with B_2O_3 and CuO co-additions sintered at 900 °C for 2 h reached almost 5.11 g/cm^3, irrespective of CuO/B_2O_3 ratio. It can be repeatedly observed that the sintering temperature was significantly lowered by the B_2O_3 and CuO additions which enhanced the densification of samples. For example, the bulk density of $Ba_3Ti_4Nb_4O_{21}$ sample with 1B3C reached about 97.7% of the theoretical density of $Ba_3Ti_4Nb_4O_{21}$ samples. If the sintering aids were not added to the ceramics, the pure $Ba_3Ti_4Nb_4O_{21}$ samples of 97.7% theoretical density can be obtained above 1350 °C. Therefore, these results can reveal that significant reduction in the sintering temperature of $Ba_3Ti_4Nb_4O_{21}$ samples is possible with B_2O_3 and CuO co-additions.

The SEM micrographs of: (a) $Ba_3Ti_4Nb_4O_{21}$ sample with no dopants sintered at 1350 °C for 2 h and $Ba_3Ti_4Nb_4O_{21}$ samples with: (b) 5B, (c) 5C, (d) 1B3C sintered at 900 °C for 2 h are shown in Fig. 3. The $Ba_3Ti_4Nb_4O_{21}$ sample with no dopants sintered at 1350 °C showed a dense microstructure with the average grain size of about 5 μm. The $Ba_3Ti_4Nb_4O_{21}$ samples with B_2O_3 or CuO sintered at 900 °C showed the larger amounts of porosity, indicating that the samples were less dense than $Ba_3Ti_4Nb_4O_{21}$ samples with B_2O_3 and CuO co-addition. The dense microstructure of $Ba_3Ti_4Nb_4O_{21}$ ceramics with 1B3C sintered at 900 °C exhibited a rather homogeneous grain size distribution with the small average grain size of 0.7 μm.

Fig. 4 shows the X-ray diffraction patterns of $Ba_3Ti_4Nb_4O_{21}$ sample sintered at 1350 °C for 2 h and $Ba_3Ti_4Nb_4O_{21}$ samples sintered at 900 °C for 2 h with various contents of B_2O_3 and CuO. When a small amount of B_2O_3 (5 wt%) or CuO (5 wt%) was added separately, the BaB_4O_7 or CuO crystalline phase mainly appeared, respectively. The small decrease in the sintering temperature of the $Ba_3Ti_4Nb_4O_{21}$ ceramics could be

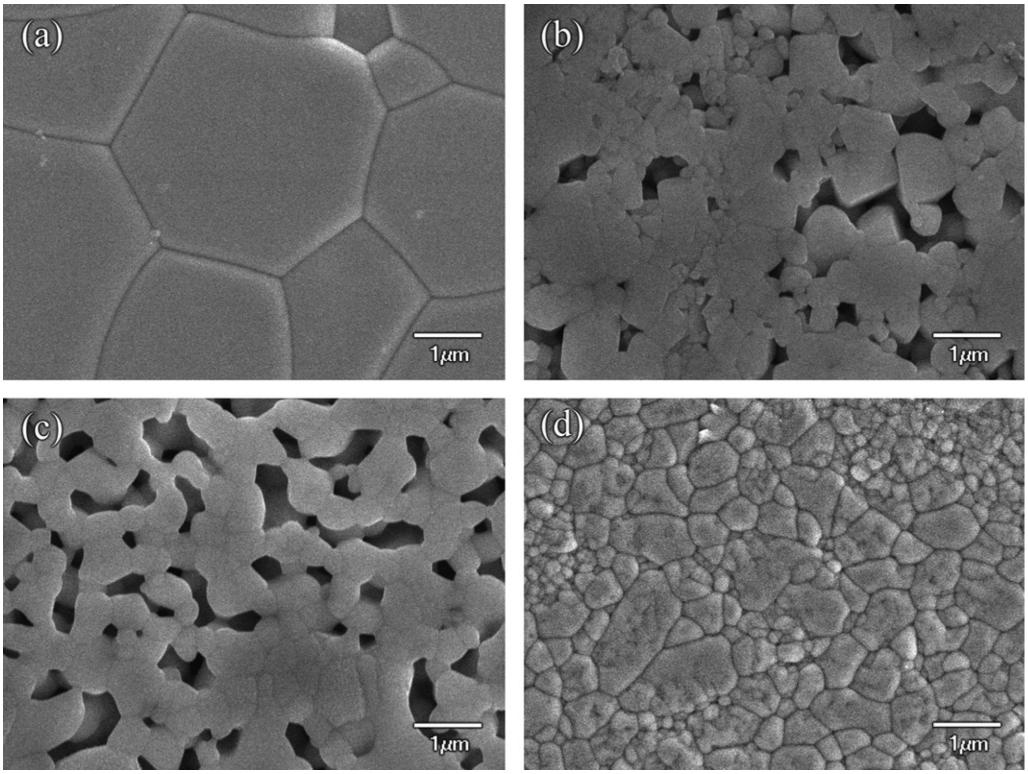

Fig. 3. SEM micrographs of: (a) $Ba_3Ti_4Nb_4O_{21}$ sample sintered at 1350 °C for 2 h and $Ba_3Ti_4Nb_4O_{21}$ samples sintered at 900 °C for 2 h with: (b) 5B, (c) 5C and (d) 1B3C.

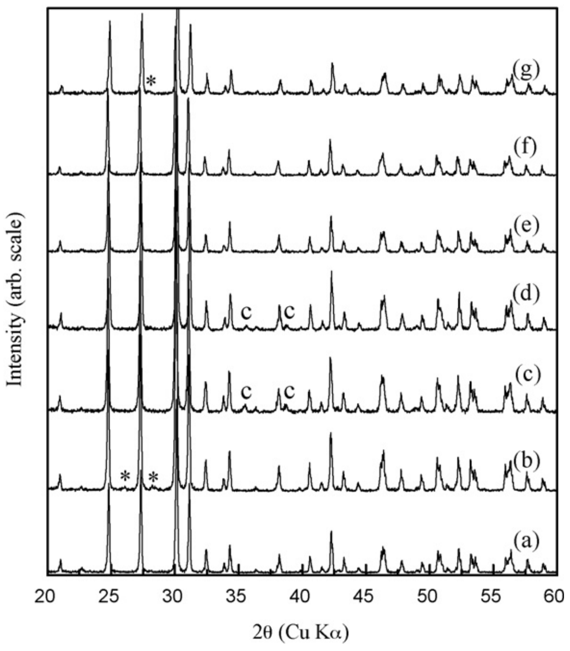

Fig. 4. XRD patterns of: (a) $Ba_3Ti_4Nb_4O_{21}$ sample sintered at 1350 °C for 2 h and $Ba_3Ti_4Nb_4O_{21}$ samples sintered at 900 °C for 2 h with various contents of B_2O_3 and CuO: (b) 5B, (c) 5C, (d) 1B3C, (e) 2B2C, (f) 3B1C and (g) 5B5C (*, BaB_4O_7; C, CuO).

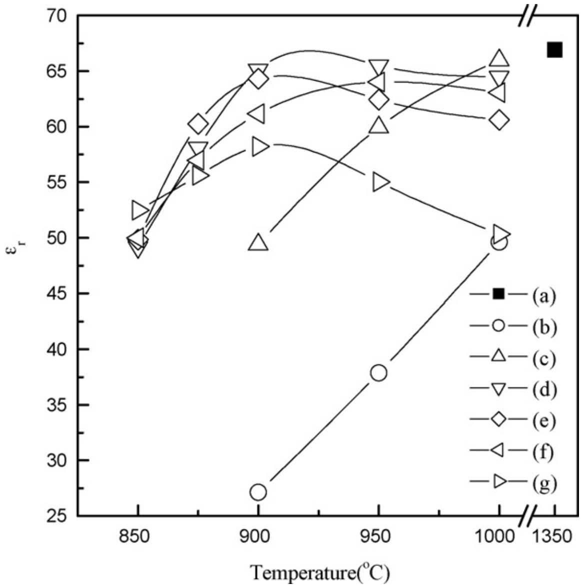

Fig. 5. Relative dielectric constant of $Ba_3Ti_4Nb_4O_{21}$ sample with various contents of B_2O_3 and CuO as a function of temperature: (a) no dopants, (b) 5B, (c) 5C, (d) 1B3C, (e) 2B2C, (f) 3B1C and (g) 5B5C.

somewhat explained by the presence of BaB_4O_7 or CuO second phase. But these secondary phases existing in the $Ba_3Ti_4Nb_4O_{21}$ ceramics could not decrease the sintering temperature below 1100 °C. When both B_2O_3 and CuO were added, the additions lowered the sintering temperature to 900 °C and the amount of BaB_4O_7 or CuO secondary phase decreased. It can be expected that the low-temperature fired $Ba_3Ti_4Nb_4O_{21}$ samples with 1B3C are a mixture of $Ba_3Ti_4Nb_4O_{21}$, remaining CuO and a small amount of liquid phases, mainly. Thus, although it is extremely difficult to detect a minor phase by X-ray, it can be assumed that the reaction between CuO and B_2O_3 causes the formation of liquid phases and the liquid phases act as the sintering aids for $Ba_3Ti_4Nb_4O_{21}$ samples.

3.2. *Microwave dielectric properties of low-fired $Ba_3Ti_4Nb_4O_{21}$*

Sebastian reported that $Ba_3Ti_4Nb_4O_{21}$ ceramic has good microwave dielectric properties with high ε_r of 55, high $Q \times f$ of 9500 GHz (at 5.5 GHz) and τ_f of 100 ppm/°C.[10] The pure $Ba_3Ti_4Nb_4O_{21}$ ceramic in this study has the similar excellent microwave dielectric properties previously reported. Fig. 5 shows the relative dielectric constant of low-fired $Ba_3Ti_4Nb_4O_{21}$ as a function of B_2O_3 and CuO contents. The bulk density of low-fired $Ba_3Ti_4Nb_4O_{21}$ had maximum value when 1B3C was added. The relative dielectric constant (ε_r) of the low-fired $Ba_3Ti_4Nb_4O_{21}$ samples with 1B3Cu sintered at 900 °C was 65 similar to that of pure fired $Ba_3Ti_4Nb_4O_{21}$ sample sintered at 1350 °C. The relative dielectric constants of low-fired $Ba_3Ti_4Nb_4O_{21}$ exhibited the same behavior as the bulk densities of the ceramics with sintering temperature as shown in Figs. 2 and 5. In Fig. 5, ε_r of low-fired $Ba_3Ti_4Nb_4O_{21}$ with B_2O_3 or CuO shows a decrease in value from that (67.0) of pure $Ba_3Ti_4Nb_4O_{21}$ sintered at 1350 °C for 2 h, because of the poor densification at low temperatures. In contrast, ε_r of low-fired $Ba_3Ti_4Nb_4O_{21}$ samples with both B_2O_3 and CuO co-additions is higher than that of low-fired $Ba_3Ti_4Nb_4O_{21}$ with B_2O_3 or CuO, because of high densification. Though the secondary phases with a low dielectric constant[15] like CuO and BaB_4O_7 crystalline phase exist in low-fired $Ba_3Ti_4Nb_4O_{21}$ samples, the small amount of the secondary phases may not affect the dielectric constants.

Fig. 6 shows the $Q \times f$ value of low-fired $Ba_3Ti_4Nb_4O_{21}$ with various B_2O_3 and CuO additions at different sintering

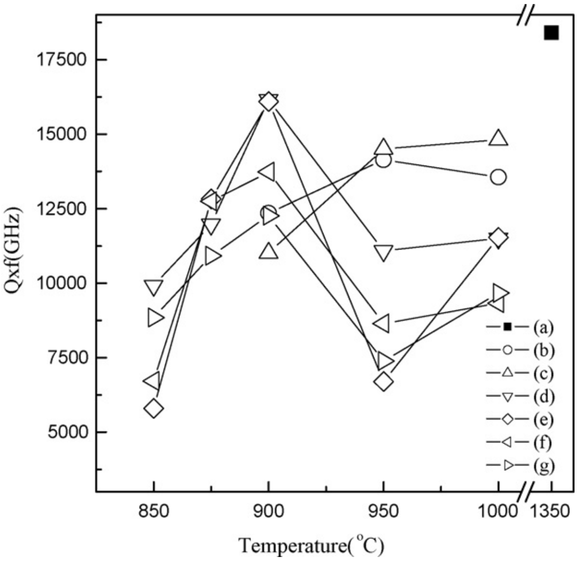

Fig. 6. Quality factor of $Ba_3Ti_4Nb_4O_{21}$ samples with various contents of B_2O_3 and CuO as a function of temperature: (a) no dopants, (b) 5B, (c) 5C, (d) 1B3C, (e) 2B2C, (f) 3B1C and (g) 5B5C.

temperatures. The $Q \times f$ value of the specimens increased with increasing sintering temperature and also considerably increased with the bulk densities of the low-fired $Ba_3Ti_4Nb_4O_{21}$ samples. However, it decreased when the temperature was increased higher than 900 °C. The deterioration in the quality factor may be induced by the change of the secondary phases like CuO and BaB_4O_7 crystalline. The temperature coefficients of resonant frequency of the low-fired $Ba_3Ti_4Nb_4O_{21}$ samples were around 100 ppm/°C. Unfortunately, the research about the temperature stability of the resonant frequency is essential, and this work is in progress. In this study, the good microwave dielectric properties of $\varepsilon_r = 65$, $Q \times f = 16{,}000$ GHz and $\tau_f = 101$ ppm/°C can be obtained for the $Ba_3Ti_4Nb_4O_{21}$ sample with 1 wt% B_2O_3 and 3 wt% CuO additions sintered at 900 °C for 2 h.

4. Conclusion

The sintering behaviors and dielectric properties of $Ba_3Ti_4Nb_4O_{21}$ ceramics were investigated as a function of B_2O_3–CuO content. When B_2O_3 or CuO was added separately to $Ba_3Ti_4Nb_4O_{21}$, the ceramic did not sinter below 1100 °C. But, it was found that simultaneous additions of both B_2O_3 and CuO to $Ba_3Ti_4Nb_4O_{21}$ enable to reduce the sintering temperature from 1350 to 900 °C without remarkable deterioration of microwave dielectric properties. The amount of the BaB_4O_7 second phase, which existed in the $Ba_3Ti_4Nb_4O_{21}$ ceramics with B_2O_3, decreased with the addition of both B_2O_3 and CuO. Therefore, it can be inferred that CuO reacted with B_2O_3 forming the CuO–B_2O_3 liquid phase, which assisted in the sintering of the $Ba_3Ti_4Nb_4O_{21}$ ceramics at 900 °C. $Ba_3Ti_4Nb_4O_{21}$ sample with 1 wt% B_2O_3 and 3 wt% CuO additions sintered at 900 °C for 2 h has a high quality factor and a high dielectric constant ($\varepsilon_r = 65$, $Q \times f = 16{,}000$ GHz and $\tau_f = 101$ ppm/°C). Therefore, the CuO and B_2O_3 added $Ba_3Ti_4Nb_4O_{21}$ ceramic is a good candidate material for the LTCC applications.

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