Low Temperature Sintering of BaTi$_4$O$_9$-Based Middle-*k* Dielectric Composition for LTCC Applications

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Abstract. Effect of glass addition on the low-temperature sintering and microwave dielectric properties of BaTi$_4$O$_9$-based ceramics were studied to develop the middle-*k* dielectric composition for the functional substrate of low-temperature co-fired ceramics. When 10 wt% of glass was added, sufficient densification was obtained and the relative density more than 98% was reached at the sintering temperature of 875°C. The microwave dielectric properties were $k = 32$, Q $\times f = 9000$ GHz, and $t_{cf} = 10$ ppm/°C. As the added amount of glass frit with base dielectric composition, phase changes from BaTi$_4$O$_9$ to BaTi$_5$O$_{11}$ and Ba$_4$Ti$_{13}$O$_{30}$ was observed, which result in the modification of microwave dielectric properties.

Keywords: middle-permittivity, LTCC, BaTi$_4$O$_9$, glass frit

1. Introduction

Low temperature co-fired ceramics (LTCC) technology has been proved to be effective in the development of various modules and substrates in the electronic packaging, especially in wireless and microwave applications. LTCC multilayer structures have been used as 3D wiring circuit board to date, using low-permittivity dielectric compositions (typically, <10). To realize highly integrated and functional LTCC modules, however, it is important to integrate passive components such as resistors, inductors, and resonators in multilayer LTCC structure [1, 2]. Especially, quarter wavelength resonator structures including planar antenna and filters are of important applications. Considering the RF frequency range which is used in current telecommunication system (1–30 GHz) and the desirable chip sizes in the current packaging technologies (2–10 mm), the dielectric compositions the permittivity range of which is 20–100 are most appropriate to realize strip or microstrip resonator structures in LTCC multilayer structure according to the following relationship [3]:

$$k = [c/(\lambda \times f)]^2 \qquad (1)$$

(where, k: effective permittivity, c: light speed, λ: wavelength, f: frequency).

Although there are many dielectric compositions of high microwave quality factor having permittivity range of 20–100, the temperature range of densification are typically in the range of 1300–1500°C [4–7]. To utilize these middle-permittivity dielectric compositions in LTCC technology, it is required to lower the temperature of densification less than 900°C considering that the melting point of Ag, which is the typical internal electrode material in LTCC technology, is ca. 960°C. It has been general and easy way to add glass frits into the microwave dielectric compositions to realize LTCC substrate having good electrical properties together with acceptable densification at the low temperature range. Several microwave dielectric compositions including (Zr,Sn)TiO$_4$ [8], BaO-TiO$_2$-WO$_3$ [9], and BaO-Re$_2$O$_3$-TiO$_2$ (Re: La, Sm, Nd, Eu) systems [10, 11] have been studied for the development of the middle-k LTCC dielectric compositions by using

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glass frits. However, the temperature of densification was higher than 950°C, which is still high for cofiring of Ag inner electrode.

In this study, we are to develop a middle-k LTCC composition based on $BaTi_4O_9$ microwave ceramics. By designing a borosilicate glass frit system carefully, we aim to lower the temperature of densification down to 875°C still maintaining acceptable microwave dielectric properties. The effects of glass addition on the densification, electrical properties, and phase changes in $BaTi_4O_9$-based dielectric composition were examined.

2.   Experimental

A $BaTi_4O_9$-based commercial dielectric composition (Hizirco MWF-38, Hayashi Chemical Industry, Japan) was used as the base dielectric materials. (Hereafter, BT4). Without glass addition, the BT4 can be sintered at 1360°C in the preliminary experiment and exhibits a relative density of more than 98% and good dielectric properties: dielectric constant (k) 38.6, quality factor ($Q \times f$) 44500 GHz, and temperature coefficient of resonant (t_{cf}) + 1.3 ppm/°C. To lower the temperature range of densification of BT4, a series of borosilicate glass system were designed and tested. The designed glass compositions (10–35 wt% of SiO_2, 23–43 wt% of B_2O_3, 33–51 wt% of Li_2O) were fabricated via a conventional glass fabrication process. The glass frits were prepared by melting in a Pt crucible at 1300°C by quenching process with a quench roller. Among those tested, we selected a lithium borosilicate glass system showing optimum sintering properties and electrical properties. The density of the glass frit is ca. 2.3 g/cm³ and the glass transition temperatures (T_g) is in the range of 370–400°C. The dielectric constant is 7.5 and the dielectric loss is typically less than 0.2%.

The BT4 dielectric composition and 0–10 wt% of glass frit were mixed by ball-milling for 24 h. The slurry was dried at 90°C for several hours and granulated with 3 wt% of PVA (poly-vinyl alcohol) solution. The granulated powders were pressed into disk shapes and sintered in the temperature range of 800–950°C for 2 h. Apparent porosity and bulk density of the sintered samples were examined by the Archimedes principle. The linear shrinkage ratio was determined from the direct measurement with micrometer.

The microwave dielectric properties of sintered samples were examined using a network analyzer

(Model HP8720C, Hewlett-Packard, USA) in the frequency ranged of 8–16 GHz. Dielectric constant was measured by a parallel plate resonator method. The microwave quality factor ($Q \times f$) and temperature coefficient of the resonant frequency (t_{cf}) were examined using an invar cavity at the temperature range from 25 to 80°C [12].

3.   Results and Discussion

Figure 1 shows the effects of the added amount of glass frit and firing temperature on the sintering behavior of BT4 ceramics. As the amount of the glass frit increases, both the linear shrinkage and bulk density increases at the temperature range of 850–900°C as shown in (a). When 10 wt% of the frit was added, significant densification was achieved at 875°C. As the amount
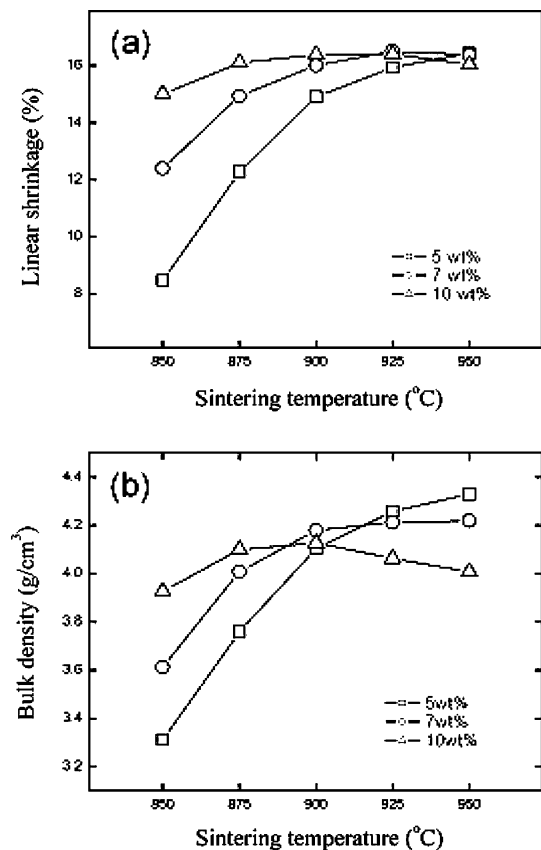

Fig. 1. Effects of glass additions and firing temperature on the sintering behavior of BT4 ceramics. All samples were sintered for 2 h at peak temperature range: (a) linear shrinkage, and (b) bulk density.

of added frit increases, the higher densification was achived at less than 850°C whereas the final density of the sintered body decreases at the temperatures higher than 900°C.

When 10 wt% of glass frit was added at 875°C, the density of 4.11 g/cm^3 (relative density 98%), linear shrinkage 16.1%, open porosity 0.165% were obtained. The fact that the density decreases with increasing the amount of frit in the temperature range of 900–950°C could be ascribed to the low density of glass itself. As the firing temperature of middle-k LTCC composition

should be less than 900°C to be compatible with Ag inner electrode, the added amount of glass frit used in this study should be higher than 7 wt%.

Figure 2 shows scanning electron microscope (SEM) images of the BT4 ceramics with different amount of glass and sintering temperature. As the added amount of glass frit and firing temperature increase, the average grain size also increases. The effect of the amount of frit seems to be more crucial that the firing temperature. Figure 3 shows electron probe micro analysis (EPMA) results of the BT4 with 10 wt%
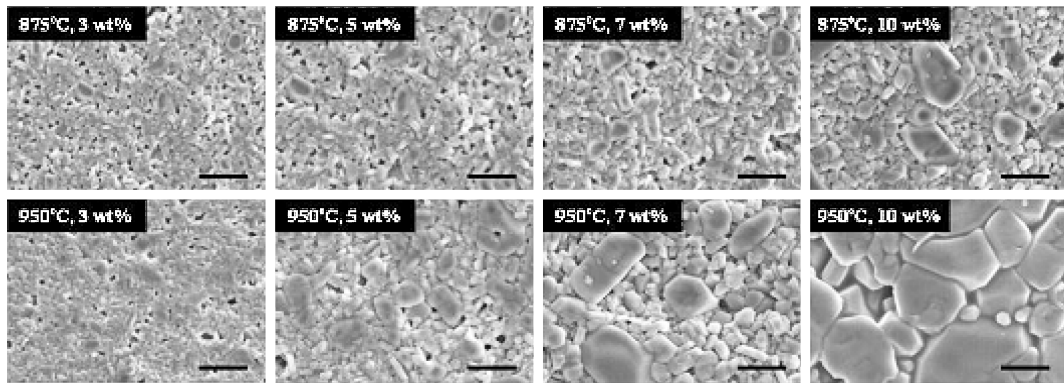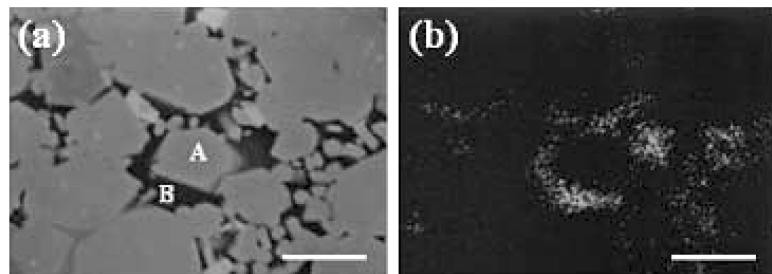

Fig. 2. Scanning electron microscope (SEM) images of BT4 ceramics with the different amount of glass and sintering temperature for 2 h. (Scale bar: 5 μm).

(c)

Position	Element	Atomic %	Phase
A	Ba	15.9	BaO–TiO$_2$
	Ti	84.1	
B	Ba	8.5	BaO–TiO$_2$
	Ti	42.7	
	Si	48.8	Glass

Fig. 3. Electron probe micro analysis (EPMA/WDS) results of BT4 ceramics with 10 wt% glass addition sinterd at 950°C for 2 h. (a) Backscattered electron images, (b) elemental X-ray maps for Si-ion, and (c) a summarized table of quantitative analysis. (Scale bar: 10 μm).
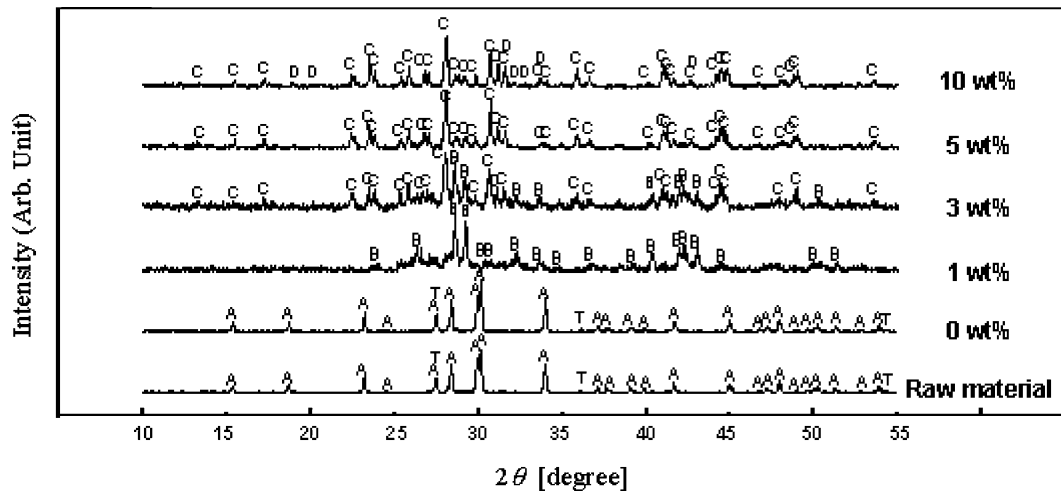
Fig. 4. X-ray powder diffraction (XRD) patterns of BT4 ceramics with different amount of glass contents heat-treated at 950°C for 2 h. (A: $BaTi_4O_9$, B: $Ba_2Ti_9O_{20}$, C: $BaTi_5O_{11}$, D: $Ba_4Ti_{13}O_{30}$).

glass addition sintered at 950°C for 2 h. The analysis shows that the composition of the grains consist of $BaO\text{-}TiO_2$ phases whereas there is Si phase in the grainboundary, which is believed to be a glass phase. From these observations in microstructural change and elemental analysis, the densification seems to be accelerated by the liquid phase during firing resulting from the softened glass frit.

Figure 4 shows the X-ray diffraction (XRD) patterns of the BT4 ceramics, with different amount of glass contents, heat-treated at 950°C for 2 h. When heat-treated at 950°C without glass addition, only the $BaTi_4O_9$ phase was identified. As the added amount of the glass frit increases, the $BaTi_4O_9$ phase changes into $Ba_2Ti_9O_{20}$ and $BaTi_5O_{11}$ in sequence. From the fact that the mole percentage of Ti becomes richer along this sequence, it seems that glass frit in which alkali is rich, absorbs Ba more preferably than Ti.

Table 1 summarizes all the crystalline phases in BT4 ceramics with variation of the amount of glass frit and firing temperature. As the amount of glass frit increases, the on-set temperature of decomposition from the $BaTi_4O_9$ phase to other second phases decreases. For examples, BT4 composition exhibits only the $BaTi_4O_9$ phase up to the temperature of 1350°C whereas the $BaTi_4O_9$ phase in the BT4 composition with 10 wt% of frit start to decompose to $BaTi_5O_{11}$ and $Ba_4Ti_{13}O_{30}$ phases at the temperature of 700°C. As the EPMA analysis indicates that the local composition of the grains and grainboundaries are different slightly from point to point, it is believed that the phases co-exist at a certain experimental condition as listed in Table 1 are not always thermodynamically mixed phase. They could rather result from the compositional fluctuations according to the local inhomogeneity of the mixing ration of BT4 and glass frit. Every sequence in the phase

Table 1. A summarized list of the crystalline phases in BT4 ceramics with variation of the amount of glass frit. All samples were sintered for 2 h at peak temperature range.

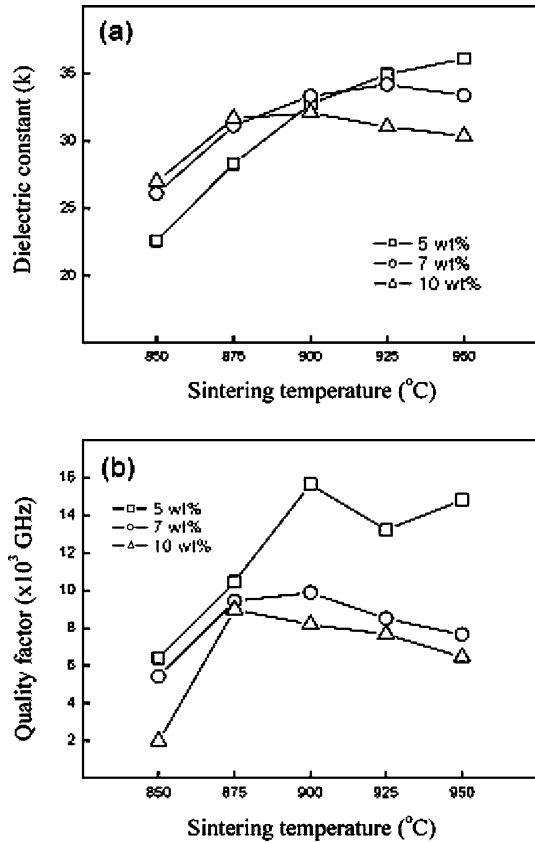|	R.T.	600°C	700°C	800°C	875°C	950°C	1350°C
BT4	BT_4	BT_4	BT_4	BT_4	BT_4	BT_4	BT_4
BT4 + 1 wt% frit	BT_4	BT_4	BT_4	BT_4	$BT_4 + BT_5 + B_2T_9$	B_2T_9	–
BT4 + 3 wt% frit	BT_4	BT_4	BT_4	$BT_4 + BT_5$	$BT_5 + B_2T_9$	$BT_5 + B_2T_9$	–
BT4 + 5 wt% frit	BT_4	BT_4	$BT_4 + BT_5$	BT_5	BT_5	BT_5	–
BT4 + 7 wt% frit	BT_4	BT_4	$BT_4 + BT_5$	BT_5	BT_5	BT_5	–
BT4 + 10 wt% frit	BT_4	BT_4	$BT_4 + BT_5 + B_4T_{13}$	$BT_5 + BT_4 + B_4T_{13}$	$BT_5 + B_4T_{13}$	$BT_5 + B_4T_{13}$	–

Fig. 5. Effects of glass addition on the microwave dielectric properties of (a) dielectric constant (k) and (b) quality factor ($Q \times f$). All samples were sintered for 2 h at peak temperature range.

change with increasing the amount of glass frit at a certain firing temperature, in Table 1, indicates that Ti-rich phases evolve with increasing the amount of glass frit.

Figure 5 shows the effects of glass addition on the microwave dielectric properties in BT4 ceramics. As the added amount of the frit increases, the magnitude of dielectric constant (k) increases at the temperature range of 850–900°C. This could be attributed to the densification with glass addition as discussed in Fig. 1. However, at the temperature range of 900–950°C, k decreases. This might be related to the relatively low k of glass frit itself ($\sim$7.5) as the magnitude of k in all the BaO-TiO$_2$ phases including BaTi$_5$O$_{11}$, Ba$_2$Ti$_9$O$_{20}$, and Ba$_4$Ti$_{13}$O$_{30}$ are in the similar range [13, 14]. Also, the decrease of k could be ascribed to the increase of apparent porosity.

The increase of $Q \times f$ with increasing the firing temperature should be ascribed to the accelaration of densification at the elevated temperatures. The fact that the magnitude of $Q \times f$ rather decreased with increasing glass frit, at the temperatures higher than 900°C, could be related to the formation of second phases generated from the reaction between dielectric composition and glass frits [15] together with the low $Q \times f$ of glass itself. The $Q \times f$ values of glass frits used in this study were typically 500–1500, which were far lower than that of BT4.

As was discussed, second phases including BaTi$_5$O$_{11}$, Ba$_2$Ti$_9$O$_{20}$, and Ba$_4$Ti$_{13}$O$_{30}$ phases were identified by XRD analysis at higher temperatures higher than 900°C due to the reaction between BaTiO$_4$ and glass frits.

Figure 6 shows the effects of the glass addition and the sintering temperature on the temperature coefficient of resonant frequency (t_{cf}) of BaTi$_4$O$_9$-based ceramics. The low t_{cf} at 1 wt% of glass frit could be related to the fact that Ba$_2$Ti$_9$O$_{20}$ phase, which has t_{cf} of +2 ppm/°C, is dominant as summarized in Table 1. As the glass frit increases by more than 1 wt%, t_{cf} increases. This might be attributed to the high t_{cf} of BaTi$_5$O$_{11}$ (+40 ppm/°C) [13, 14], which were generated by the phase decomposition at that range of glass frit. When the amount of glass frit increases by more than 5 wt%, t_{cf} decreases monotonically. This decrease of t_{cf} with increasing glass frits can be ascribed to the negative t_{cf} of glass frits. Typically, the glass compositions in this study exhibit the t_{cf} of −70 ppm/°C.
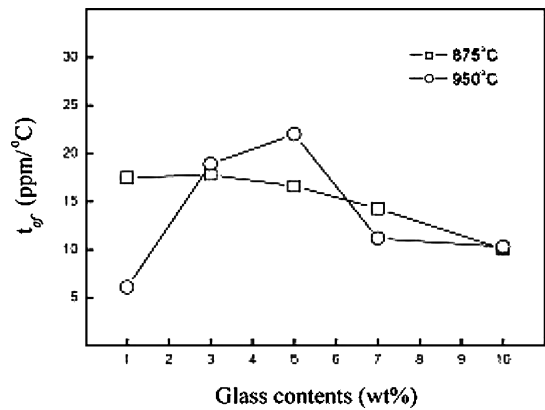

Fig. 6. Effects of glass contents and sintering temperature on the temperature coefficient of resonant frequency (t_{cf}) of BT4 ceramics. All samples were sintered for 2 h at peak temperature range.

4. Conclusion

In this study, middle-*k* LTCC dielectric compositions were developed. The effects of borosilicate-based glass addition on the densification and the microwave properties of commercial BaTi$_4$O$_9$-based dielectric ceramics were studied at the sintering temperature of 850–950°C. Importantly, with 10 wt% of the glass frit, the sample exhibit 98% of relative density and the dielectric properties of $k = 32$, $Q \times f = 9000$ GHz, and $t_{cf} = 10$ ppm/°C were obtained. The effects of density, microstructure, phase change on the electrical properties of the dielectric ceramics were discussed. Especially, it was observed that the glass phase and the second phases can modify the microwave properties significantly. Thus, when one designs middle-*k* LTCC composition with glass frits, the phase changes and related electrical properties should be examined and designed carefully.

Acknowledgment

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