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Journal of the European Ceramic Society 26 (2006) 2105–2109

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Low-temperature sintering and microwave dielectric properties of $Ba_5Nb_4O_{15}$ with ZnB_2O_4 glass

Jeong-Ryeol Kim[a], Dong-Wan Kim[b], Hyun Suk Jung[a], Kug Sun Hong[a,*]

[a] School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul, Korea
[b] Materials Science & Engineering Division, Korea Institute of Science and Technology, Seoul 136-791, Korea

Available online 6 March 2006

Abstract

The Influence of ZnB_2O_4 glass addition on the sintering temperature and microwave dielectric properties of $Ba_5Nb_4O_{15}$ has been investigated using dilatometry, X-ray diffraction, scanning electron microscopy and network analyzer. It was found that a small amount of glass addition to $Ba_5Nb_4O_{15}$ lowered the sintering temperature from 1400 to 900 °C. The reduced sintering temperature was attributed to the formation of ZnB_2O_4 liquid phase and B_2O_3-rich liquid phases such as $Ba_3B_2O_6$. The $Ba_5Nb_4O_{15}$ ceramics with ZnB_2O_4 glass, sintered at a low temperature, exhibited good microwave dielectric characteristics, i.e., a quality factor ($Q \times f$) = 12,100 GHz, a relative dielectric constant (ε_r) = 40, a temperature coefficient of resonant frequency (τ_f) = 48 ppm/°C. The dielectric properties were discussed in terms of the densification of specimens and the influence of glassy phases such as $Ba_3B_2O_6$ and ZnB_2O_4.

Keywords: Sintering; X-ray method; Dielectric properties; Glass; $Ba_5Nb_4O_{15}$

1. Introduction

Multilayer microwave components have been investigated to miniaturize resonant devices for volume efficiency. To be a useful material for incorporation into multilayer type elements, dielectrics must be capable of being sintered along with electrodes, a process known as cofiring. In multilayer structures, glasses having a low melting point are frequently utilized. Consequently, the dielectrics can be cofired with conducting layers such as silver thick films whose melting point is 961 °C. There have been three approaches to reduce the sintering temperature of the dielectric ceramics: addition of glass having a low melting-temperature, chemical processing, and utilization of ultra-fine particles for raw materials. Liquid-phase sintering with glass additives is the least expensive process among the described method. However, in order to sinter the microwave dielectric ceramics at a low temperature, 20–30 wt% of glass should be contained indispensably, thus the dielectric property such as a quality factor and a relative dielectric constant (ε_r) is diminished significantly.[1] In this sense, the study on searching the suitable glass-dielectric ceramics compositions and on optimizing the sintering conditions for the low temperature sintering and good dielectric properties is essential.

The dielectric properties of a $Ba_5Nb_4O_{15}$ system have been widely investigated and it has been found to be a useful material in microwave communication applications.[2,3] The microwave dielectric properties of $Ba_5Nb_4O_{15}$ have been reported by Sreemoolandgna et al.[4] More recently, Ratheesh et al. measured the microwave dielectric properties of $Ba_5Nb_4O_{15}$ using the whispering gallery mode technique and reported it's outstanding dielectric properties (quality factor = 53,000 GHz at 16 GHz, ε_r = 40, and τ_f = 78 ppm/°C).[5]

However, the sintering temperature of $Ba_5Nb_4O_{15}$ is above 1400 °C, which is too high to be applicable to multilayer microwave components.[4,5] However, the influence of glass addition on the firing temperature and dielectric properties of $Ba_5Nb_4O_{15}$ has not been studied. For the first time, a small amount of ZnB_2O_4 glass was added to lower the sintering temperature of $Ba_5Nb_4O_{15}$ to 900 °C in the present work. The microwave dielectric properties of $Ba_5Nb_4O_{15}$-glass composites sintered at a low temperature were also studied.

2. Experimental procedure

The glass was prepared by mixing molar ratio of 1:1 of ZnO (Cerac, Milwaukee, WI) and B_2O_3(High Purity Chemical Labo-

* Corresponding author. Tel.: +822 880 8316; fax: +822 886 4156.
E-mail address: kshongss@plaza.snu.ac.kr (K.S. Hong).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2005.09.065

ratory, Saitama, Japan) in a batch size to yield 30 g of glass. The glass filled in an uncovered Pt crucible was melted at 1000 °C. The melt was homogenized for 1 h and quenched on steel plates.

The $Ba_5Nb_4O_{15}$ powders were synthesized by conventional mixed oxide methods: $BaCO_3$ (Cerac, Milwaukee, WI) and Nb_2O_5 (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 ZnB_2O_4 glass were ball-milled for 48 h using ethanol solvent. The milled powders were then dried, granulated, and pressed at 1000 kg/cm^2 to yield several disk-type pellets (8 mm in diameter and 3 mm in thickness). The pellets were sintered at 850–950 °C for 2 h with a heating rate of 5 °C/min.

Shrinkage of the specimens during heat treatment was measured using a horizontal loading dilatometer with alumina rams and boats (Model DIL402C, Netzsch Instruments, Germany). The bulk density of the sintered samples was determined by the Archimedes method. 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 structures of sintered specimens were investigated using X-ray powder diffraction (Model M18XHF, Macscience Instruments, Japan). 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).

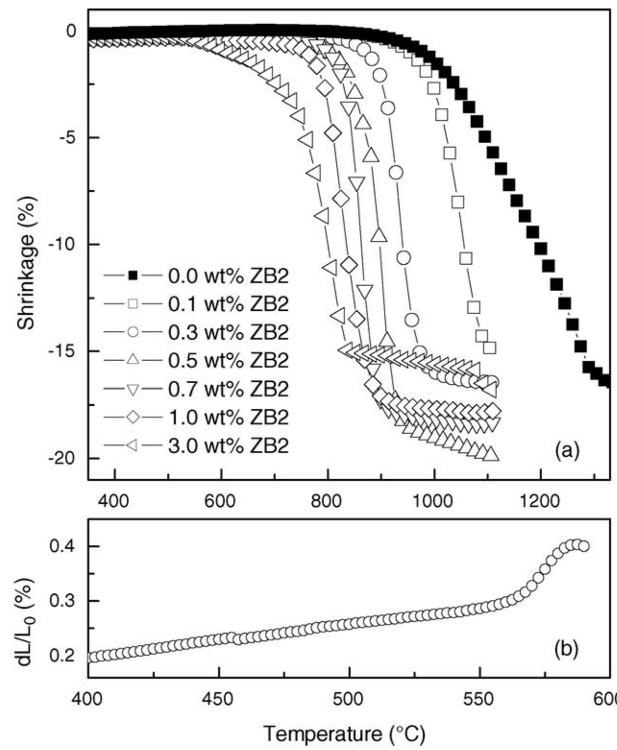

Fig. 1. (a) Shrinkage of the $Ba_5Nb_4O_{15}$ samples with 0.1–3 wt% ZnB_2O_4 glass additions and (b) TMA curve of ZnB_2O_4 glass as a function of temperature.

3. Results and discussion

3.1. Sintering behavior of $Ba_5Nb_4O_{15}$ with ZnB_2O_4 glass additions

Fig. 1(a) shows the change in shrinkage of $Ba_5Nb_4O_{15}$ ceramic with varying amount of ZnB_2O_4 glass. The results demonstrate that the onset temperature of shrinkage is lowered by the small addition of ZnB_2O_4 glass. The shrinkage of $Ba_5Nb_4O_{15}$ without ZnB_2O_4 glass does not occur as rapidly as that with the glass. It is noteworthy that the densification of $Ba_5Nb_4O_{15}$ with 0.5 wt% of ZnB_2O_4 glass addition begins below 800 °C and that the shrinkage reaches a maximum value at approximately 900 °C. For $Ba_5Nb_4O_{15}$ with 3 wt% of ZnB_2O_4 glass addition, the shrinkage begins at ~600 °C but the ultimate shrinkage is lower than that of $Ba_5Nb_4O_{15}$ with 0.5 wt% ZnB_2O_4 glass addition. Fig. 1(b) shows a typical result of thermal mechanical analysis (TMA) measurement of ZnB_2O_4 glass. ZnB_2O_4 glass has a low softening temperature (T_s) = 587 °C and begins to melt above T_s. This result supports that the low temperature densification originates from the formation of liquid phase.

The bulk density and relative theoretical density of $Ba_5Nb_4O_{15}$ specimens with 0.1–3 wt% of ZnB_2O_4 glass additions are plotted in Fig. 2. The density sharply increased with increasing ZnB_2O_4 glass additions. The bulk density of specimens with the addition of 0.3–1.0 wt% of ZnB_2O_4 glass, sintered at 900 °C for 2 h, increased to 96% of the theoretical density compared with that of $Ba_5Nb_4O_{15}$ (6.293 g/cm^3). These results demonstrate that low-temperature sintering of $Ba_5Nb_4O_{15}$ is successfully achieved by addition of ZnB_2O_4 glass. However, the density of the specimen with the addition of above 3.0 wt% of ZnB_2O_4 glass slightly decreased.

Scanning electron micrographs of $Ba_5Nb_4O_{15}$ with various amounts of ZnB_2O_4 glass sintered at 900 °C for 2 h, are shown in Fig. 3. The sintered $Ba_5Nb_4O_{15}$ specimen containing 0.3 wt% of ZnB_2O_4 glass has elongated grains with a small grain size (1–2 μm) as previously reported by Sreemoolanadhan et al.[4] The SEM micrographs show that the sintered specimens with 0.3–1.0 wt% of ZnB_2O_4 glass have dense microstructures

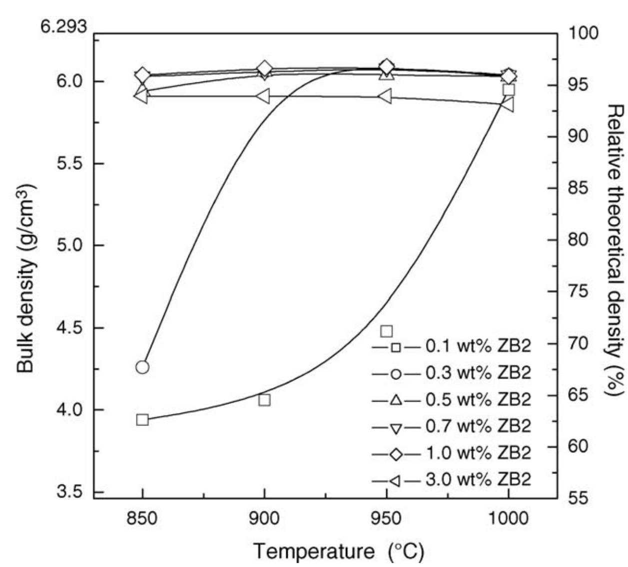

Fig. 2. Bulk density and relative theoretical densities of the $Ba_5Nb_4O_{15}$ samples with 0.1–3 wt% ZnB_2O_4 glass additions as a function of sintering temperatures.

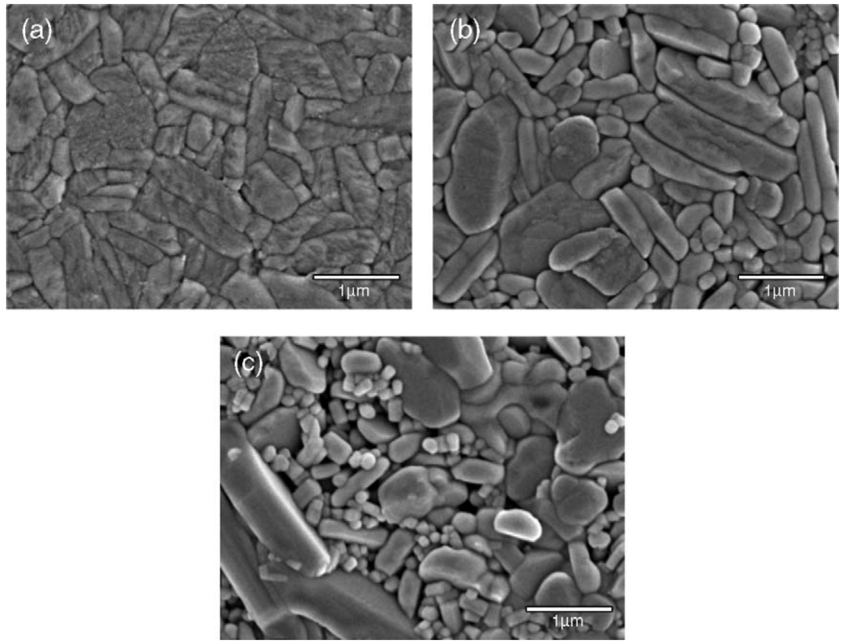

Fig. 3. Scanning electron micrographs of the $Ba_5Nb_4O_{15}$ samples sintered at 900 °C for 2 h with (a) 0.3, (b) 3, (c) 10 wt% ZnB_2O_4 glass addition.

(Fig. 3(a)). However, as shown in Fig. 3(b) and (c), excess addition of ZnB_2O_4 glass (above 3 wt%) induces an abnormal grain growth severely and thereafter results in less dense microstructures, which is in a good agreement with the change in the density as a function of glass contents. The average size of abnormal elongated grains is larger than 5 μm. This abnormal grain growth indicates that the $Ba_5Nb_4O_{15}$–ZnB_2O_4 glass composite involves with liquid-phase sintering.

Fig. 4 shows XRD patterns of $Ba_5Nb_4O_{15}$ specimens with 0.1–10 wt% ZnB_2O_4 glass sintered at 900 °C. The crystalline ZnB_2O_4 phase is found to exist in the XRD pattern of the specimens containing ZnB_2O_4 glass. Above the 0.5 wt% of glass addition, the trace of secondary phases such as crystalline $Ba_3B_2O_6$ phase is observed in the XRD patterns and the intensity increases with the amount of ZnB_2O_4 glass addition. The $ZnNb_2O_6$ phase is found at an excess addition of ZnB_2O_4 glass, also.

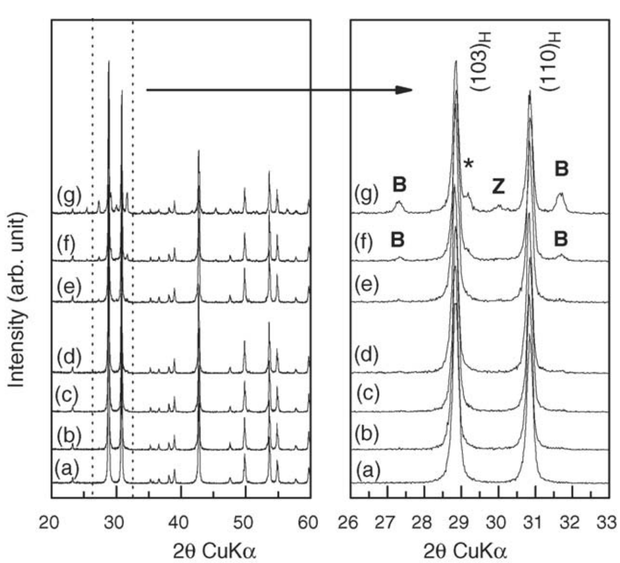

Fig. 4. XRD patterns of the $Ba_5Nb_4O_{15}$ samples with x wt% ZnB_2O_4 glass addition sintered at 900 °C for 2 h. ((*) ZnB_2O_4, B: $Ba_3B_2O_6$, Z: $ZnNb_2O_6$), (x = (a) 0.1, (b) 0.3, (c) 0.5, (d) 0.7, (e) 1, (f) 3, (g) 10).

The $Ba_3B_2O_6$ phase would enhance the densification of $Ba_5Nb_4O_{15}$. In the phase diagram of BaO–B_2O_3, the BaB_8O_{13}–BaB_4O_7, BaB_4O_7–BaB_2O_4, BaB_2O_4–$Ba_3B_2O_6$ eutectics exist as low as 859, 889, 905 °C.[6] The formation of a B_2O_3-rich liquid phase containing $Ba_3B_2O_6$ can assist in the densification of $Ba_5Nb_4O_{15}$.

3.2. Microwave properties of $Ba_5Nb_4O_{15}$ sintered at a low temperature

In the present work, the $Ba_5Nb_4O_{15}$ specimen without ZnB_2O_3 glass shows a ε_r of 40.8, a quality factor of 50,000 GHz, and a temperature coefficient of resonant frequency (τ_f) of 50 ppm/°C.

Fig. 5(a) shows ε_r of the $Ba_5Nb_4O_{15}$ specimens sintered at 900 °C for 2 h as a function of ZnB_2O_4 glass content. Relative dielectric constant (ε_r) of $Ba_5Nb_4O_{15}$ with 0.1 wt% ZnB_2O_4 glass is 19.6 which is attributed to a low bulk density as shown in Fig. 2. However, ε_r of $Ba_5Nb_4O_{15}$ with 0.3 wt% ZnB_2O_4 glass is 40.7, same to that of pure $Ba_5Nb_4O_{15}$ specimen. Excess additions of ZnB_2O_4 glass (above 0.3 wt%) cause a slight decrease of ε_r, which can be interpreted with the dielectric constants of the secondary phases such as ZnB_2O_4, $ZnNb_2O_6$, and $Ba_3B_2O_6$ which were detected in the XRD analysis. Lee et al. reported that $ZnNb_2O_6$ had a low ε_r of 25.[7] Also, Wu et al. made a systematic study of dielectric properties of ZnB_2O_4 glass system at microwave frequencies.[8] According to their studies, ZnO–B_2O_3 glass with molar ratio of 1:1 showed a low ε_r of 6.88. Although

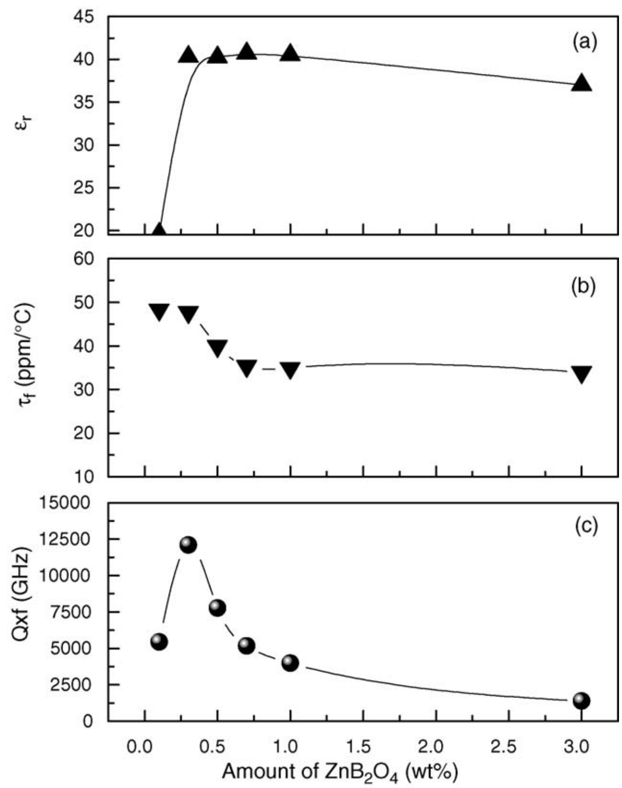

Fig. 5. Microwave dielectric properties of the $Ba_5Nb_4O_{15}$ samples sintered at 900 °C for 2 h as a function of ZnB_2O_4 glass: (a) relative dielectric constant (ε_r), temperature coefficient of resonant frequency (τ_f), (c) quality factor ($Q \times f$).

the dielectric properties of crystalline $Ba_3B_2O_6$ is not fully characterized, BaO–B_2O_3–SiO_2 glass with a molar ratio of 5:4:1 exhibited a low ε_r of 9.15. Therefore, it can be suggested that slight reduction of ε_r observed in the low-temperature sintered $Ba_5Nb_4O_{15}$ can be attributed to the low ε_r of secondary phases, which were slightly contained in $Ba_5Nb_4O_{15}$ specimens.

Fig. 5(b) shows τ_f of the $Ba_5Nb_4O_{15}$ samples sintered at 900 °C for 2 h as a function of ZnB_2O_4 glass content. τ_f decreased slightly to 34 ppm/°C with the 3 wt% of ZnB_2O_4 glass addition in comparison with 50 ppm/°C for pure $BaNb_4O_{15}$. Secondary phases having a small τ_f such as ZnB_2O_4 (−10 ppm/°C) and $ZnNb_2O_6$ (−56 ppm/°C) would contribute to the slight decrease in τ_f of ZnB_2O_4 glass-added $Ba_5Nb_4O_{15}$ system, also.

The quality factors of the $Ba_5Nb_4O_{15}$ specimens, sintered at 900 °C for 2 h, were plotted in Fig. 5(b) as a function of ZnB_2O_4 glass content. The small quality factor (5500 GHz) of the $Ba_5Nb_4O_{15}$ with 0.1 wt% of ZnB_2O_4 glass is correlated with the poor densification, which is same to the case in dielectric constant. The quality factor of the $Ba_5Nb_4O_{15}$ with 0.3 wt% of ZnB_2O_4 glass showed a maximum value, 12,100 GHz. However, further addition of ZnB_2O_4 glass diminished the quality factor, significantly. The change in quality factor corresponds to the formation of secondary phases as shown in Fig. 4. It is notable that the onset point of secondary phase is same to that of decrease in quality factor. The trace of $Ba_3B_2O_6$ was found at 0.5 wt% of ZnB_2O_4 glass addition and the quality factor diminished, simultaneously. Considering that the bulk densities of specimens with 0.3–1.0 wt% of glass addition are almost same, the secondary phases critically deteriorate the quality factor. The similar behavior was reported by Takada et al. They reported that sintering studies and microwave property measurements were performed on BaO–TiO_2–WO_3 ceramics with additions of either 5ZnO–$2B_2O_3$ glass.[1] Their results showed that the density of BaO–$4TiO_2$–$0.1WO_3$ ceramics reached 98% of the theoretical density at sintering temperature of 900 °C, but the quality factor of those specimens significantly decreased. The significant deterioration of quality factor in $Ba_5Nb_4O_{15}$ specimens with an excess addition of ZnB_2O_4 glass is related to the formation of secondary phases having the lower quality factors, i.e., ZnB_2O_4 (1,733 GHz) and $Ba_3B_2O_6$ (1,221 GHz).

4. Conclusion

It was found that a small addition of ZnB_2O_4 glass to $Ba_5Nb_4O_{15}$ enabled a reduction in sintering temperature from 1400–900 °C. ZnB_2O_4 glass with ∼587 °C of softening point (T_s), starts to melt at approximately 600 °C. During sintering of $Ba_5Nb_4O_{15}$–ZnB_2O_4 glass composites, $Ba_5Nb_4O_{15}$ was found to react with ZnB_2O_4 glass, primarily forming $Ba_3B_2O_6$ crystalline phase and $ZnNb_2O_6$. The low temperature sintering was suggested to originate from the formation B_2O_3-rich liquid phases including $Ba_3B_2O_6$ as well as ZnB_2O_4 liquid phase. Moreover, the secondary phases such as $Ba_3B_2O_6$ were found to critically influence the microwave dielectric properties of low temperature sintered $Ba_5Nb_4O_{15}$. As a result of optimizing the glass addition content (0.3 wt%), the $Ba_5Nb_4O_{15}$–ZnB_2O_4 glass composite, sintered at a low temperature, 900 °C, showed a dense structure and outstanding dielectric properties: quality factor = 12,100 GHz, $\varepsilon_r = 40$, $\tau_f = 48$ ppm/°C. These results demonstrate that the $Ba_5Nb_4O_{15}$–ZnB_2O_4 glass composite is a promising candidate for low temperature cofired ceramics (LTCC).

Acknowledgements

This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology, Republic of Korea.

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