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Low temperature sintering and microwave dielectric properties of $Ba_3Ti_5Nb_6O_{28}$ with $ZnO–B_2O_3$ glass additions for LTCC applications

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Abstract

The effects of ZnB_2O_4 glass additions on the sintering temperature and microwave dielectric properties of $Ba_3Ti_5Nb_6O_{28}$ have been investigated using dilatometer, X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and a network analyzer. The pure $Ba_3Ti_5Nb_6O_{28}$ system showed a high sintering temperature (1250 °C) and had the good microwave dielectric properties: $Q \times f$ of 10,600 GHz, ε_r of 37.0, τ_f of −12 ppm/°C. It was found that the addition of ZnB_2O_4 glass to $Ba_3Ti_5Nb_6O_{28}$ lowered the sintering temperature from 1250 to 925 °C. The reduced sintering temperature was attributed to the formation of ZnB_2O_4 liquid phase and B_2O_3-rich liquid phases. Also the addition of ZnB_2O_4 glass enhanced the microwave dielectric properties: $Q \times f$ of 19,100 GHz, ε_r of 36.6, τ_f of 5 ppm/°C. From XPS and XRD studies, these phenomena were explained in terms of the reduction of oxygen vacancies and the formation of secondary phases having the good microwave dielectric properties.

Keyword: Low temperature sintering

1. Introduction

The development of low temperature co-fired ceramics (LTCC) for microwave applications has received much attention, because of the design and functional benefits upon the miniaturization of multilayer devices with high electrical performance by using highly conductive internal electrode metals, such as silver, with a melting point of 961 °C.

In general, in order to sinter ceramics at low temperature, low-melting glasses are added to the ceramics commercially. Among these glasses, Zn–B–O glass has been investigated widely and reported as a low temperature sintering aid. Takada et al.[1] reported sintering behaviors and microwave properties of $BaO–TiO_2–WO_3$ ceramics with commercial $ZnO–B_2O_3$ glass. Their results showed that for 30 wt% glass addition, the density of $BaO–4TiO_2–WO_3$ ceramics reached 98% of the theoretical density at sintering temperature of 900 °C, but the microwave dielectric properties of these low-fired ceramics were significantly deteriorated. Also, Kim et al.[2] investigated the effects of $ZnO–B_2O_3$ glass on the low temperature sintering and the microwave dielectric properties in $BaTi_4O_9$ ceramics. $ZnO–B_2O_3$ glass heat-treated at 900 °C for 2 h crystallized to ZnB_2O_4 and $Zn_3B_2O_6$ phases, and had no reaction with $BaTi_4O_9$ ceramics. The microwave dielectric properties of low temperature fired $BaTi_4O_9$ were dependent on the amount of these $ZnO–B_2O_3$ crystalline phases (ZnB_2O_4 and $Zn_3B_2O_6$). Lee et al.[3] investigated the effects of $3ZnO–B_2O_3$ glass on the microwave dielectric properties and microstructure of $Ba_2Ti_9O_{20}$-based ceramics. The small addition of the $3ZnO–B_2O_3$ glass phase (1 wt%) to the ceramics could effectively lower the sintering temperature (940 °C) and increased the bulk density and dielectric constant of the sintered ceramics. The more addition of the $3ZnO–B_2O_3$ glass enhanced the formation of $BaZr(BO_3)_2$ and Zn_2SiO_4 phases in the ceramics and the second phases significantly affected the microwave dielectric properties and microstructure of the ceramics. However, for $Ca_5Nb_2TiO_{12}$ ceramics, $ZnO–B_2O_3$ glass could not lower the sintering temperature of the ceramics and deteriorated its quality factor and dielectric constant due to the formation of secondary phases (β-$Zn_5B_4O_{11}$).[4]

The dielectric properties of $Ba_3Ti_5Nb_6O_{28}$ ceramics have been investigated by Roberts et al.[5] More recently,

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Sebastian has investigated the microwave dielectric properties of $BaO–TiO_2–Nb_2O_5/Ta_2O_5$ system.[6] He has reported that $Ba_3Ti_5Nb_6O_{28}$ ceramic has high $Q \times f$ of 4500 GHz (at 5.4 GHz), high ε_r of 41 and small τ_f of 8 ppm/°C. The sintering temperature of $Ba_3Ti_5Nb_6O_{28}$ was above 1250 °C, which is too high to be applicable to LTCC. Unfortunately, the effects of sintering aids on the firing temperature of $Ba_3Ti_5Nb_6O_{28}$ ceramics of have not been thoroughly studied.

In the present work, ZnB_2O_4 glass was chosen as a sintering aid to lower the sintering temperature of $Ba_3Ti_5Nb_6O_{28}$ ceramics. The microwave dielectric properties of $Ba_3Ti_5Nb_6O_{28}$ with ZnB_2O_4 glass additions were investigated with the density, the presence of second phases. Also, the enhancement in the quality factor of the low fired $Ba_3Ti_5Nb_6O_{28}$ ceramics was discussed with the absence of oxygen vacancies in the low fired samples.

2. Experimental procedure

The glass was prepared by mixing molar ratio of 1:1 of ZnO (99.9% pure, Cerac, Milwaukee, WI) and B_2O_3 (99.9% pure, High Purity Chemical Laboratory, Saitama, Japan) in a batch size to yield 60 g of glass. The mixed powder was melted at 1000 °C by using an uncovered Pt crucible. The melt was homogenized for 1 h and quenched on steel plates. The glass was milled below −1 μm using a planetary ball mill (Model PM400, Retsch, Germany).

The $Ba_3Ti_5Nb_6O_{28}$ powders were synthesized by conventional mixed oxide methods: $BaCO_3$ (99.9% pure, Cerac, Milwaukee, WI), TiO_2 and Nb_2O_5 (99.9% pure, High Purity Chemical Laboratory, Saitama, Japan) were mixed homogeneously and calcined at 1150 °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 4 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 formation of second phases was 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). X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB spectrometer (Model 220i-XL, VG Scientific Instruments, UK). Peak positions were calibrated by taking the C 1s peak (284.6 eV) as a reference.

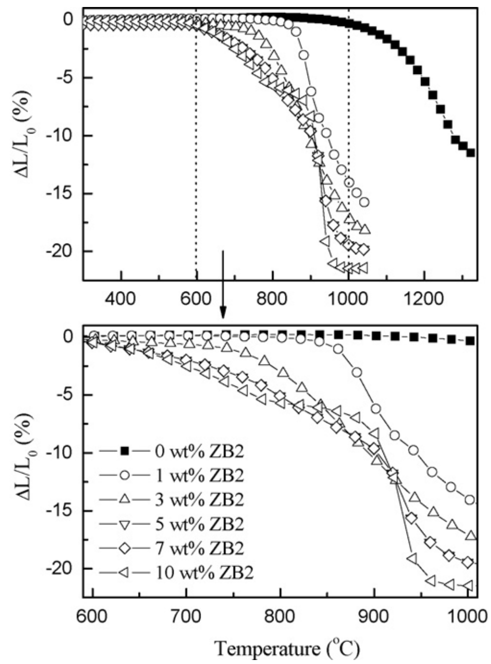

Fig. 1. Shrinkage curves of $Ba_3Ti_5Nb_6O_{28}$ samples with various contents of ZnB_2O_4 glass as a function of temperature.

3. Results and discussion

3.1. Sintering behavior and phase evolution of low-fired $Ba_3Ti_5Nb_6O_{28}$

Fig. 1 shows the change in shrinkage of $Ba_3Ti_5Nb_6O_{28}$ samples with various amount of ZnB_2O_4 glass as a function of temperature. The shrinkage of $Ba_3Ti_5Nb_6O_{28}$ sample without the ZnB_2O_4 glass appeared to occur slowly at approximate 1000 °C and reaches a maximum value at over 1300 °C. For $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass, the shrinkage occurred at 800 °C, moreover, that of $Ba_3Ti_5Nb_6O_{28}$ samples with more amounts of ZnB_2O_4 glass additions occurred approximately at 600 °C. ZnB_2O_4 glass has a low softening temperature (T_s) = 587 °C and begins to melt above T_s.[7] At over 600 °C, ZnB_2O_4 glass can begin to melt and the formed liquid phase can enhance the densification of $Ba_3Ti_5Nb_6O_{28}$ samples. For $Ba_3Ti_5Nb_6O_{28}$ sample with 10 wt% of ZnB_2O_4 glass addition, though the first shrinkage began at 600 °C, the shrinkage rate become low near 800 °C and the ultimate shrinkage started at 900 °C again. This gentle shrinkage near 800 °C could be affected by the crystallization of ZnB_2O_4 glass. The ZnB_2O_4 glass with less than 1 μm in size added to $Ba_3Ti_5Nb_6O_{28}$ samples started to crystallize at over 750 °C (not shown in this study). These results can support that the low temperature densification originates from the formation of ZnB_2O_4 liquid phase and that ZnB_2O_4 glass affects the shrinkage behaviors of $Ba_3Ti_5Nb_6O_{28}$ samples.

Fig. 2 shows the change in bulk density of $Ba_3Ti_5Nb_6O_{28}$ samples with various contents of ZnB_2O_4 glass additions as a function of sintering temperature. The bulk density of $Ba_3Ti_5Nb_6O_{28}$ samples with ZnB_2O_4 glass additions increases sharply with increasing temperature and has a constant value

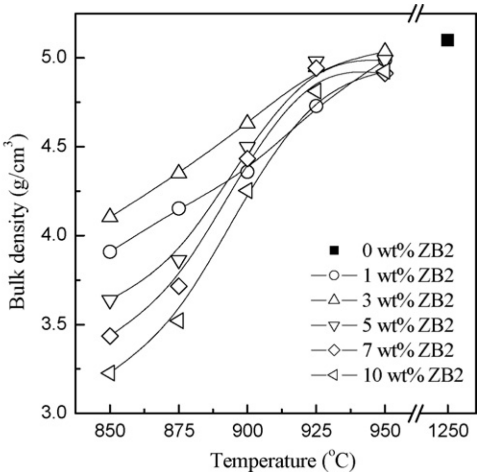

Fig. 2. Changes in the bulk densities of $Ba_3Ti_5Nb_6O_{28}$ samples with various contents of ZnB_2O_4 glass as a function of sintering temperature.

above 925 °C. The bulk density of $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass addition sintered at 925 °C for 2 h reached almost 4.95 g/cm^3. The obtained bulk density of 4.95 g/cm^3 corresponds to the intermediate value between the bulk density (5.10 g/cm^3) of $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C for 2 h and the theoretical density (3.61 g/cm^3) of ZnB_2O_4 crystalline phase (JCPDS #39-1126). Unfortunately, the theoretical density of $Ba_3Ti_5Nb_6O_{28}$ ceramic has not been reported, though the structure of that has been reported (JCPDS #37-1477).[8] Based on these densities, the theoretical density can be calculated approximately at 5.04 g/cm^3 for $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass addition. The obtained bulk density of 4.95 g/cm^3 corresponds to 98.2% of the calculated theoretical density for $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass addition. These results can demonstrate that significant reduction in the sintering temperature of $Ba_3Ti_5Nb_6O_{28}$ samples was possible with ZnB_2O_4 glass additions.

The densification of the low-fired $Ba_3Ti_5Nb_6O_{28}$ ceramics was confirmed by a SEM study. Fig. 3 shows SEM micrographs of (a) $Ba_3Ti_5Nb_6O_{28}$ sample without ZnB_2O_4 glass sintered at 1250 °C for 2 h, and $Ba_3Ti_5Nb_6O_{28}$ samples with (b) 1 wt%, (c) 3 wt%, and (d) 10 wt% ZnB_2O_4 glass additions sintered at 925 °C for 2 h. $Ba_3Ti_5Nb_6O_{28}$ sample containing 1 wt% ZnB_2O_4 glass had some pores and the average size of the grains (0.4 μm) was less than that (1.3 μm) of $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C. $Ba_3Ti_5Nb_6O_{28}$ sample containing 3 wt% ZnB_2O_4 glass had a dense microstructure and the average size of the grains was about 0.8 μm. The higher the amount of glass added was, the larger the average size of the grains was. Moreover, the excess addition of ZnB_2O_4 glass induced an abnormal grain growth and some large pores. The size of the grains grown abnormally was larger than 5 μm for $Ba_3Ti_5Nb_6O_{28}$ sample containing 10 wt% ZnB_2O_4 glass. The abnormal grain growth can interfere with densification of ceramics.[9] The results indicate that $Ba_3Ti_5Nb_6O_{28}$ sample containing ZnB_2O_4 glass could involve with liquid-phase sintering and that the proper amounts of glass are needed in order to obtain dense microstructure.

Fig. 4 shows XRD patterns of (a) $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C for 2 h and $Ba_3Ti_5Nb_6O_{28}$ samples sintered at 925 °C for 2 h with various contents of ZnB_2O_4 glass additions ((b)–(f)). And Fig. 4(g) shows XRD pattern of the ZnB_2O_4 glass powder quenched at 925 °C. Fig. 4 indicates that the second phases containing crystalline phases of ZnB_2O_4 and BaB_8O_{13} (JCPDS #20-0097) appeared. The intensity of the second phase peaks slightly increases with increasing amounts of

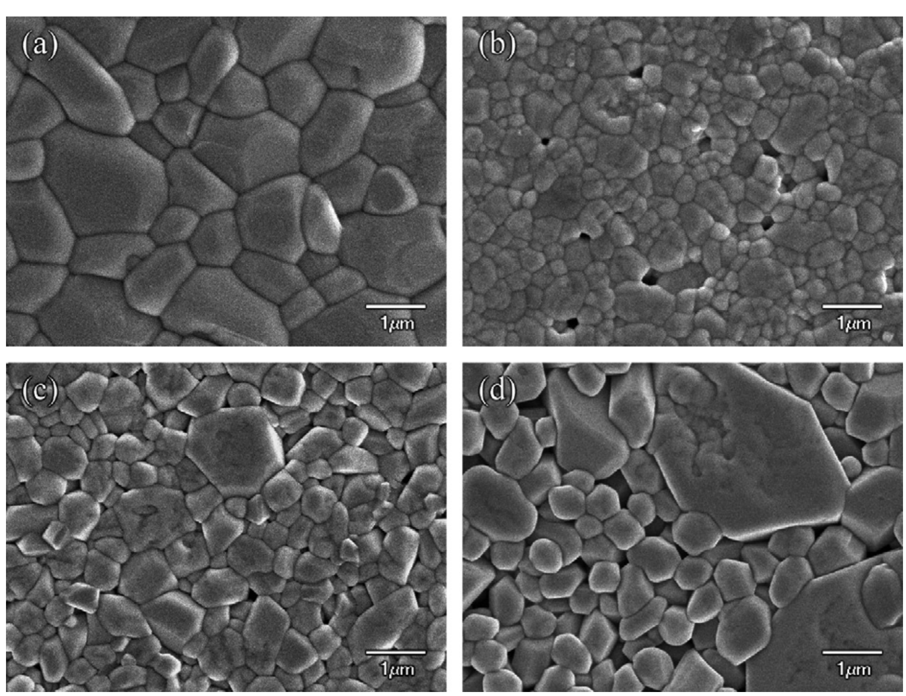

Fig. 3. SEM micrograph of $Ba_3Ti_5Nb_6O_{28}$ samples with (a) 0 wt% ZnB_2O_4 glass sintered at 1250 °C for 2 h, (b) 1 wt%, (c) 3 wt%, and (d) 10 wt% ZnB_2O_4 glass sintered at 925 °C for 2 h.

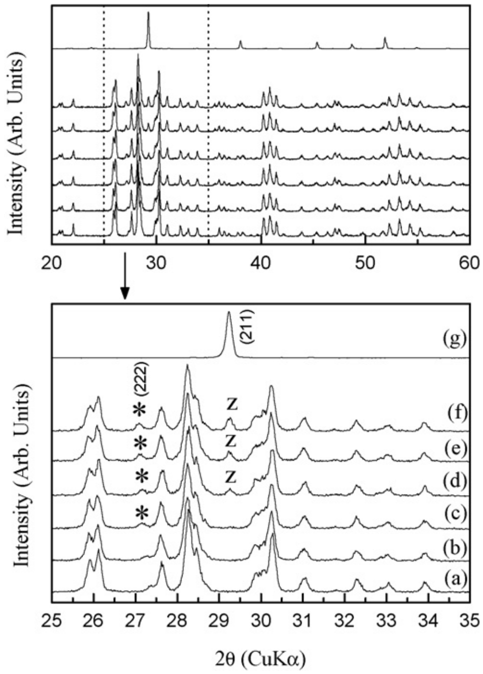

Fig. 4. XRD patterns of (a) $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C for 2 h and $Ba_3Ti_5Nb_6O_{28}$ samples sintered at 925 °C for 2 h with various contents of ZnB_2O_4 glass: (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt%, (f) 10 wt%. And XRD pattern of (g) crystalline ZnB_2O_4 quenched at 925 °C (Z: crystalline ZnB_2O_4, *: BaB_8O_{13}).

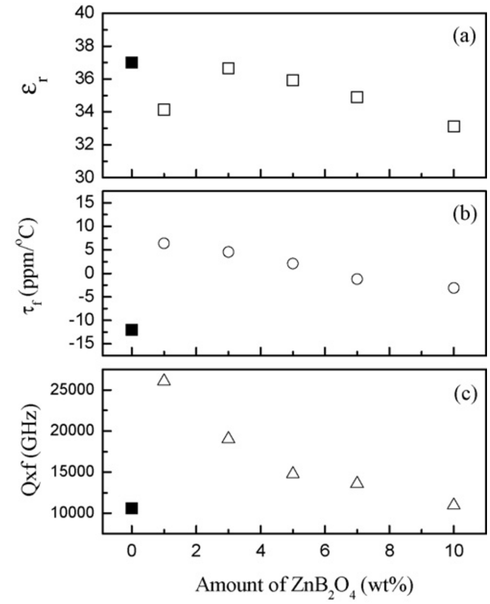

Fig. 5. Microwave dielectric properties of the $Ba_3Ti_5Nb_6O_{28}$ samples sintered at 925 °C for 2 h as a function of ZnB_2O_4 glass: (a) relative dielectric constant (ε_r), temperature coefficient of resonant frequency (τ_f), (c) quality factor ($Q \times f$).

ZnB_2O_4 glass additions. The BaB_8O_{13} phase could enhance the densification of $Ba_3Ti_5Nb_6O_{28}$ samples such as ZnB_2O_4 glass could. In the phase diagram of $BaO–B_2O_3$, $BaB_8O_{13}–BaB_4O_7$, $BaB_4O_7–BaB_2O_4$, and $BaB_2O_4–Ba_3B_2O_6$ eutectics exist as low as 859, 889, 905 °C.[10] The formation of ZnB_2O_4 and a B_2O_3-rich liquid phase containing BaB_8O_{13} can assist in the densification of $Ba_3Ti_5Nb_6O_{28}$ ceramics.

3.2. Microwave dielectric properties of low-fired $Ba_3Ti_5Nb_6O_{28}$

In this study, the $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C for 2 h had the relative dielectric constant (ε_r) of 37.0, a quality factor ($Q \times f$) of 10,900 GHz, and a temperature coefficient of resonant frequency (τ_f) of −12 ppm/°C, similar to the previous studies.[5–6]

Fig. 5(a) shows ε_r of the $Ba_3Ti_5Nb_6O_{28}$ samples sintered at 925 °C for 2 h as a function of ZnB_2O_4 glass contents. For low-fired $Ba_3Ti_5Nb_6O_{28}$ samples with ZnB_2O_4 glass, ε_r has been affected by the density and the second phases. For $Ba_3Ti_5Nb_6O_{28}$ sample with 1 wt% ZnB_2O_4 glass, ε_r is 34.1, which is attributed to a low bulk density as shown in Fig. 2. However, ε_r of the dense $Ba_3Ti_5Nb_6O_{28}$ with 3 wt% ZnB_2O_4 glass is 36.6, similar to that of pure $Ba_3Ti_5Nb_6O_{28}$ sample. More additions of ZnB_2O_4 glass cause a slight decrease of ε_r, which can be interpreted with the dielectric constants of the secondary phases such as ZnB_2O_4 and BaB_8O_{13}, which were detected in the XRD analysis. Wu et al.[11] made a systematic study of dielectric properties of the glass systems including ZnB_2O_4 at microwave frequencies. According to their studies, $ZnO–B_2O_3$ glass with molar ratio of 1:1 showed a low ε_r of 6.88. Although the dielectric properties of crystalline BaB_8O_{13} is not fully characterized, $BaO–B_2O_3–SiO_2$ glass with a molar ratio of 3:6:1 exhibited a low ε_r of 7.31. Therefore, the slight reduction of ε_r observed in the low-temperature sintered $Ba_3Ti_5Nb_6O_{28}$ with 3–7 wt% ZnB_2O_4 glass additions can be attributed to the low ε_r of secondary phases though the densities of those samples were similar. Because $Ba_3Ti_5Nb_6O_{28}$ sample with 10 wt% ZnB_2O_4 glass had a low density and more secondary phases, ε_r is the lowest value, 33.1.

The change in τ_f of the low-fired $Ba_3Ti_5Nb_6O_{28}$ samples as a function of ZnB_2O_4 glass content is shown in Fig. 5(b). The higher contents of ZnB_2O_4 glass added is, the lower τ_f of the low-fired $Ba_3Ti_5Nb_6O_{28}$ samples is. Secondary phases having a low τ_f such as ZnB_2O_4 (−10 ppm/°C)[11] would contribute to the slight decrease in τ_f of ZnB_2O_4 glass-added $Ba_3Ti_5Nb_6O_{28}$ system. Unfortunately, the reason why τ_f of low-fired $Ba_3Ti_5Nb_6O_{28}$ samples including secondary phases with a low τ_f was high in comparison with −12 ppm/°C for pure $Ba_3Ti_5Nb_6O_{28}$ sample is not clear.

Fig. 5(c) shows the change in the quality factor of low-fired $Ba_3Ti_5Nb_6O_{28}$ samples as a function of ZnB_2O_4 glass content. The further addition of ZnB_2O_4 glass diminished the quality factor, significantly. Considering that the bulk densities of specimens with 3–7 wt% ZnB_2O_4 glass addition were almost same, the secondary phases (i.e. ZnB_2O_4, 1733 GHz)[11] could mainly deteriorate the quality factor. The similar behavior was reported by Takada et al.[1] They reported that sintering studies and microwave property measurements were performed on $BaO–TiO_2–WO_3$ ceramics with additions of $5ZnO–2B_2O_3$ glass. Their results showed that the theoretical densities of $BaO–4TiO_2–0.1WO_3$ ceramics were similar at sintering temperature of 900 °C, but the quality factor of those specimens was significantly affected by secondary phases.

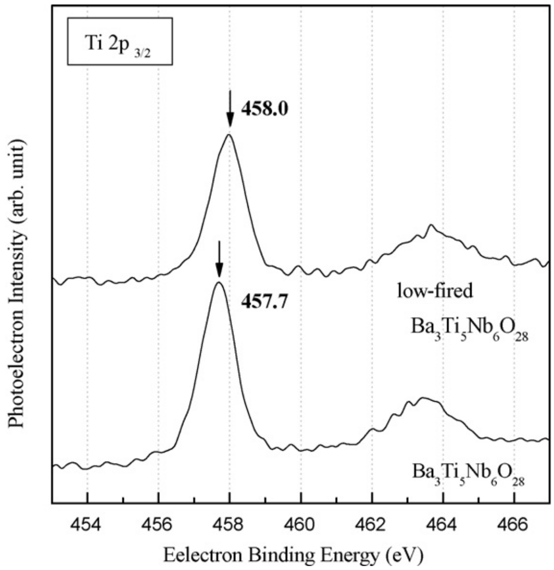

Fig. 6. XPS spectra of Ti $2p_{2/3}$ for $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C for 2 h and low-fired $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass sintered at 925 °C.

It is noteworthy that low-fired $Ba_3Ti_5Nb_6O_{28}$ samples with ZnB_2O_4 glass additions possess a high $Q \times f$, in comparison with that of pure $Ba_3Ti_5Nb_6O_{28}$ sample. In general, the addition of additives for low temperature sintering is accompanied by a significant decrease in the microwave dielectric properties. Fig. 6 shows Ti $2p_{3/2}$ spectra of $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C and $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass sintered at 925 °C. The binding energy of Ti $2p_{3/2}$ peak for $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C and $Ba_3Ti_5Nb_6O_{28}$ sample with 3 wt% ZnB_2O_4 glass sintered at 925 °C is 457.7 and 458.0 eV, respectively. It is reported that the binding energy of Ti $2p_{3/2}$ peak for Ti_2O_3 (Ti^{3+}) and TiO_2 (Ti^{4+}) is 457.3 and 458.8 eV, respectively.[12] These results suggest that $Ba_3Ti_5Nb_6O_{28}$ sample sintered at 1250 °C could have the more oxygen vacancies due to reduction of Ti^{4+} than low-fired $Ba_3Ti_5Nb_6O_{28}$ samples. It has been reported that, although there is only a very limited reduction of the TiO_2, the reduction is sufficient to deteriorate the quality factor in TiO_2 containing ceramics.[13–15] Therefore, the higher $Q \times f$ of $Ba_3Ti_5Nb_6O_{28}$ samples sintered at low temperature than that of pure $Ba_3Ti_5Nb_6O_{28}$ sample can be attributed to the absence of oxygen vacancies, i.e., Ti^{4+} reductions.

4. Conclusion

The sintering behaviors, phase evolution and microwave dielectric properties of $Ba_3Ti_5Nb_6O_{28}$ ceramics were investigated as a function of ZnB_2O_4 glass content. It was found that the proper additions of ZnB_2O_4 glass to $Ba_3Ti_5Nb_6O_{28}$ ceramics enabled a reduction in sintering temperature from 1250 to 925 °C. During sintering of $Ba_3Ti_5Nb_6O_{28}$ ceramics with ZnB_2O_4 glass, $Ba_3Ti_5Nb_6O_{28}$ was found to react with ZnB_2O_4 glass, primarily forming BaB_8O_{13} crystalline phase. The low temperature sintering was suggested to originate from the formation of B_2O_3-rich liquid phases including BaB_8O_{13} as well as ZnB_2O_4 liquid phase. The microwave dielectric properties of low-fired $Ba_3Ti_5Nb_6O_{28}$ samples with ZnB_2O_4 glass additions mainly depended on the densification and the second phases such as crystalline ZnB_2O_4 and BaB_8O_{13}. The enhancement of the quality factor in low-fired $Ba_3Ti_5Nb_6O_{28}$ samples would be due to less oxygen vacancies than in $Ba_3Ti_5Nb_6O_{28}$ samples sintered at 1250 °C. $Ba_3Ti_5Nb_6O_{28}$ ceramic with 3 wt% ZnB_2O_4 glass additions sintered at 925 °C had good microwave dielectric properties: $Q \times f = 19{,}100$ GHz, $\varepsilon_r = 36.6$, $\tau_f = 5$ ppm/°C. Therefore, $Ba_3Ti_5Nb_6O_{28}$ ceramic with 3 wt% ZnB_2O_4 glass can be a suitable candidate for low temperature co-fired ceramic (LTCC), in the points of its low sintering temperature and outstanding microwave dielectric properties.

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