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Effect of borate glass additives on the sintering behaviour and dielectric properties of $BaTi_4O_9$ ceramics

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Abstract

Effect of B_2O_3 and BaB_2O_4 addition on microwave dielectric characteristics and sintering behaviours of $BaTi_4O_9$ ceramics were investigated. When B_2O_3 was added, bulk density of the sintered sample decreased as the content of B_2O_3 increased. B_2O_3 addition induced complex reaction with $BaTi_4O_9$ and resulted in the development of second phases such as $Ba_2Ti_9O_{20}$, $BaTi(BO_3)_2$ and TiO_2. When BaB_2O_4 was added, however, relative density increased and the second phases of $Ba_2Ti_9O_{20}$ and $BaTi(BO_3)_2$ were produced. Dielectric characteristics of $BaTi_4O_9$ were also discussed from the viewpoint of bulk density, microstructure and second phases.

Keywords: Sintering; Microstructure-final; Dielectric properties; Borides; $BaTi_4O_9$

1. Introduction

Because of proper microwave dielectric properties of BaO–TiO_2 based systems, a number of researches have been carried out for the development and application for commercial units. In the case of $BaTi_4O_9$, which has superior dielectric properties for high frequency applications, very high sintering temperature around 1300 °C was required for the proper densification. For the application to low temperature co-firing technology, low-melting glasses were often used for lowering the sintering temperatures.

Various kinds of low-melting glasses have been used in $BaTi_4O_9$ ceramics.[1,2] Even though the resultant performance of dielectrics with glass additions greatly depends on the chemical reaction between the glasses and dielectrics, densification and microstructure, no systematic studies have been conducted. In this study, B_2O_3 – a well-known liquid former – was employed for a lower temperature sintering of $BaTi_4O_9$. During sintering considerable chemical reactions between B_2O_3 and $BaTi_4O_9$ were expected to occur when Ba and Ti components were dissolved out form the $BaTi_4O_9$. From this point of view, when another boron based low melting glass of BaB_2O_4 is added, the chemical reaction thought to be different because the Ba component already exists in BaB_2O_4.

In the present study, two kinds of borides, B_2O_3 and BaB_2O_4, were added for lowering the sintering temperature of $BaTi_4O_9$. The phase development behavior, densification, microstructure and dielectric characteristics were examined.

2. Experimental procedure

$BaTi_4O_9$ was prepared by the conventional solid-state reaction process using high purity chemicals of $BaCO_3$ (99.95%) and TiO_2 (99.9%). After ball milling and drying, the mixtures were calcined at 1100 °C for 2 h. BaB_2O_4 was prepared using $BaCO_3$ and B_2O_3 (99.9%) through a heat treatment at 1150 °C for 1 h in a Pt crucible. Calcined $BaTi_4O_9$ and additives of B_2O_3 and BaB_2O_4 were dry-mixed for 24 h. The granulated powders were then pressed into pellets under the pressure of 100 MPa. The specimens were sintered in the temperature range of 900–1100 °C for 2 h in air. Powder X-ray diffraction with nickel-filtered Cu Kα radiation (Mac Science, M03XHF, Japan) was conducted on the sintered specimens to identify the phases. Microstructure observation was conducted by using a scanning electron microscope (JEOL 4500, Japan). Microwave dielectric properties were measured by the parallel plate method originally proposed by Hakki and Coleman[3] utilizing $TE_{01\delta}$ resonant mode using a network analyzer (Agilent 8719ES S-parameter, USA). The quality factor ($Q \times f$) and the temperature coefficient of resonant frequency (τ_f) were measured by the open cavity resonator method[4] using HP8720C network analyzer.

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3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the sintered samples with (a) 9 wt% B_2O_3; and (b) 9 wt% BaB_2O_4 as a function of sintering temperature. In the case of B_2O_3 added samples, it was mostly composed of $BaTi_4O_9$ phase with small amount of $BaTi(BO_3)_2$ and TiO_2 when it was sintered at 800 °C. However, $BaTi_4O_9$ disappeared and $Ba_2Ti_9O_{20}$ phase appeared as the main crystalline phase together with small amount of $BaTi(BO_3)_2$ at the higher sintering temperatures. In the case of the samples with BaB_2O_4 addition, $BaTi_4O_9$ was the major phase at the sintering temperatures of 800 and 900 °C. When the sintering temperature was elevated to 950 °C or above, $Ba_2Ti_9O_{20}$ became dominant and small amount of $BaTi(BO_3)_2$ coexisted.

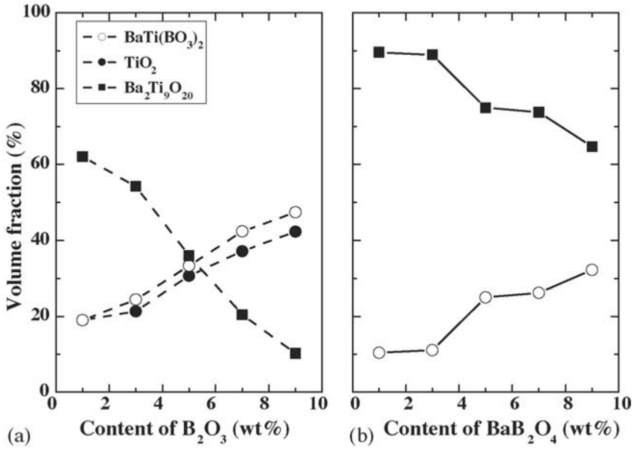

Fig. 2. Change in the volume fraction of the phases in the samples sintered at 1050 °C for 2 h as a function of: (a) B_2O_3; and (b) BaB_2O_4 content.

Fig. 2 shows the volume fraction of the phases in the samples sintered at 1050 °C for 2 h as a function of B_2O_3 and BaB_2O_4 content. These results were determined using the integrated intensity of major X-ray diffraction peaks of respective phases. When the content of B_2O_3 is increased from 1 to 9 wt%, the volume fraction of $Ba_2Ti_9O_{20}$ drastically decreased from 62.1 to 10.2%, but that of $Ba_2Ti_9O_{20}$ slowly decreased from 89.6 to 64.8% when the content of BaB_2O_4 increased. Because of the low melting temperature of B_2O_3 around 450 °C, when $BaTi_4O_9$ grains are surrounded by B_2O_3 liquid, Ba and Ti ions will be concurrently dissolved out into B_2O_3 melts from $BaTi_4O_9$ grains and then forms Ba–Ti–B–O glass during the sintering process at elevated temperatures. In the Ba–Ti–B–O glass, B and Ba component act as glass network former and modifier, respectively. However, because the solubility of Ba in B_2O_3 glass is higher than that of Ti, more Ba will be dissolved out from the $BaTi_4O_9$

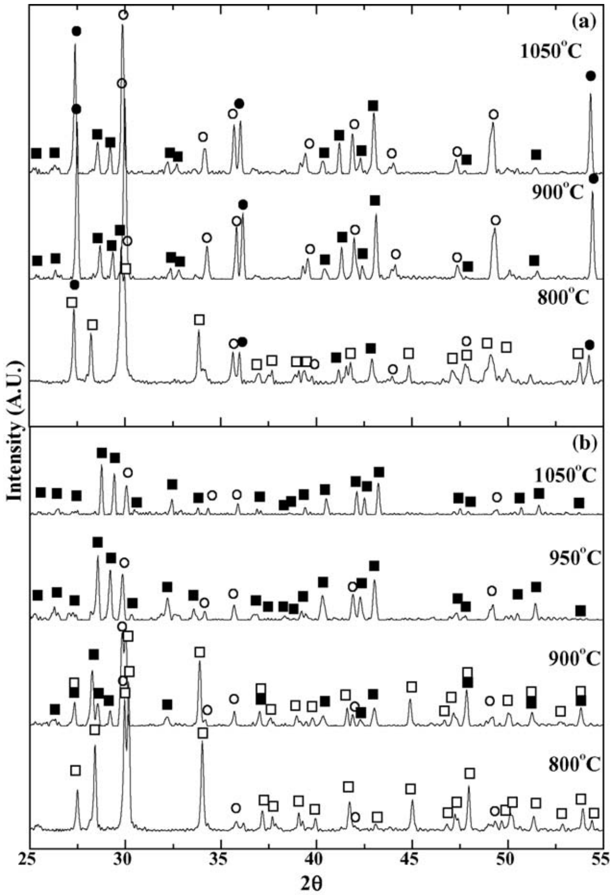

Fig. 1. XRD diffraction patterns of $BaTi_4O_9$ samples as a function of sintering temperature for the cases with: (a) 9 wt% B_2O_3; and (b) 9 wt% BaB_2O_4 (○, $BaTi(BO_3)_2$; ●, TiO_2; ■, $Ba_2Ti_9O_{20}$; □, $BaTi_4O_9$).

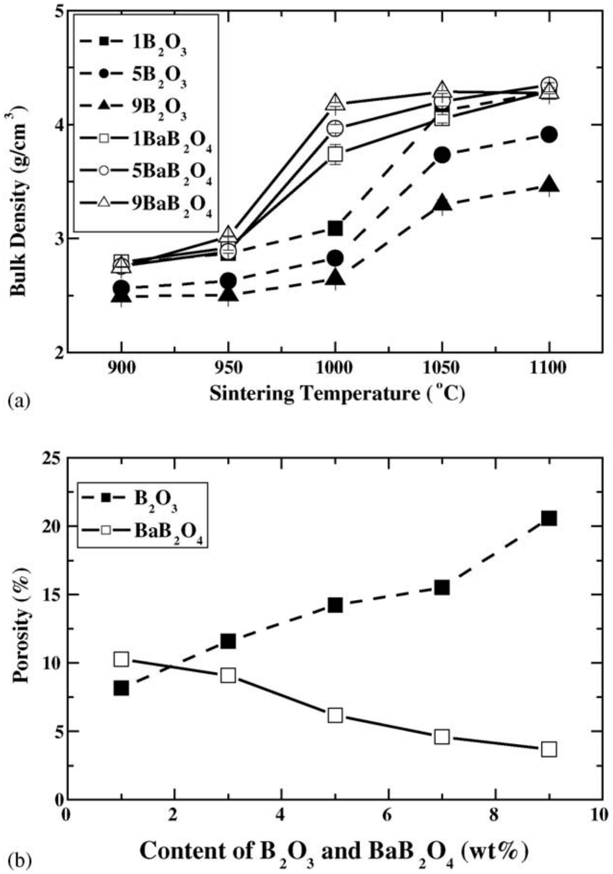

Fig. 3. (a) Bulk density of the $BaTi_4O_9$ samples as functions of temperature and the content of B_2O_3 and BaB_2O_4; (b) porosity of the samples sintered at 1050 °C for 2 h as a function of the content of B_2O_3 and BaB_2O_4.

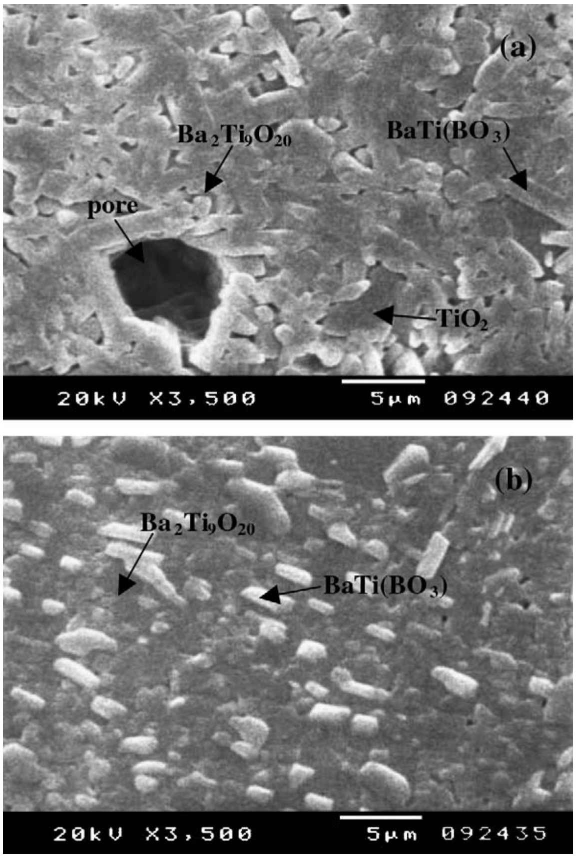

Fig. 4. Microstructures of $BaTi_4O_9$ samples sintered at 1050 °C for 2 h with addition of: (a) 9 wt% B_2O_3; and (b) 9 wt% BaB_2O_4.

which will eventually results in the formation of TiO_2 and Ba-rich B_2O_3 glasses.[5,6] At the same time, another reaction between $BaTi_4O_9$ grains and Ba-rich B_2O_3 glass will be proceeded, that which leads to the formation of the $BaTi(BO_3)_2$ and $Ba_2Ti_9O_{20}$ phases. On the other hand, when BaB_2O_4 is added, less Ba will be dissolved out from $BaTi_4O_9$ comparing to the case of B_2O_3 addition because BaB_2O_4 can be considered as a material that Ba component already dissolved in B_2O_3. In this case, no TiO_2 will be produced but $BaTi(BO_3)_2$ and $Ba_2Ti_9O_{20}$ will be produced.

Fig. 3(a) shows bulk density of samples as functions of sintering temperature and the content of B_2O_3 and BaB_2O_4. The bulk density increased as the sintering temperature increased. The overall tendency showed that the density of the samples with BaB_2O_4 addition was higher than that of B_2O_3 addition. Comparing the porosity of the samples sintered at 1050 °C for 2 h as a function of borides content, porosity increased with the content of B_2O_3 in contrast to BaB_2O_4 addition. In addition to the pores, phase development also influenced on the density of the samples. Since more B_2O_3 addition leads to more production of $BaTi(BO_3)_2$ ($\rho = 4.2\ g/cm^3$) and TiO_2 ($\rho = 4.2\ g/cm^3$) phases, which have lower density than $Ba_2Ti_9O_{20}$ ($\rho = 4.6 g/cm^3$) phase, the decrease in bulk density is occurred as shown in Fig. 3(a).

Microstructures of sintered samples with 9 wt% of B_2O_3 and BaB_2O_4 are presented in Fig. 4. When 9 wt% of B_2O_3 is added, large pores were observed. On the basis of energy dispersive spectroscopy (EDS) and X-ray diffraction analysis, the phase of $Ba_2Ti_9O_{20}$, $BaTi(BO_3)_2$ and TiO_2 were distinguishable in the microstructure. The shape of needle like and plate like grains of $BaTi(BO_3)_2$ and $Ba_2Ti_9O_{20}$ are well agreed with the previous observation.[5,7]

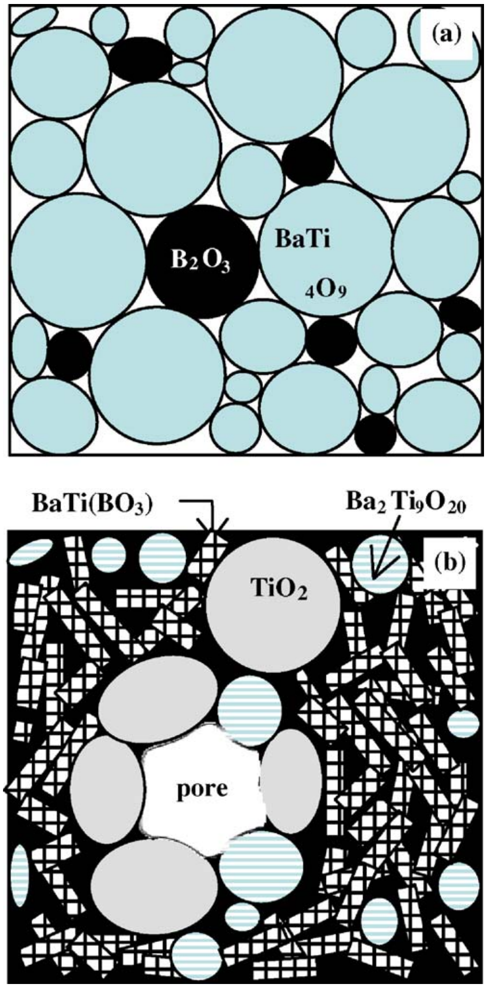

Fig. 5. Schematic diagram of intergranular pore development process: (a) before; and (b) after sintering when a liquid-forming additive of B_2O_3 is added.

Fig. 5 shows the schematic diagram of intergranular pore development process which corresponds to the case of the sample with 9 wt% of B_2O_3 as its microstructure is presented in Fig. 4(a). In a green pellet shown in Fig. 5(a), B_2O_3 and $BaTi_4O_9$ particles are homogeneously distributed. During sintering over the eutectic temperature of B_2O_3, the melts of B_2O_3 will soak into the solid skeleton of $BaTi_4O_9$ grains leaving behind voids at the place where the B_2O_3 existed. Because of the reaction between B_2O_3 and $BaTi_4O_9$, most of the melts of B_2O_3 disappeared and the pore elimination through the liquid flow induced pore filling[8] is not available, which resulted in the generation of large pores observed in Fig. 4(a). From this point of view, it can be considered that the densification and reaction occur simultaneously during sintering process when both B_2O_3 and BaB_2O_4 are added. Since B_2O_3 addition induces complicated and much more chemical reactions than BaB_2O_4 addition, densification might be delayed and densification starts at higher temperature

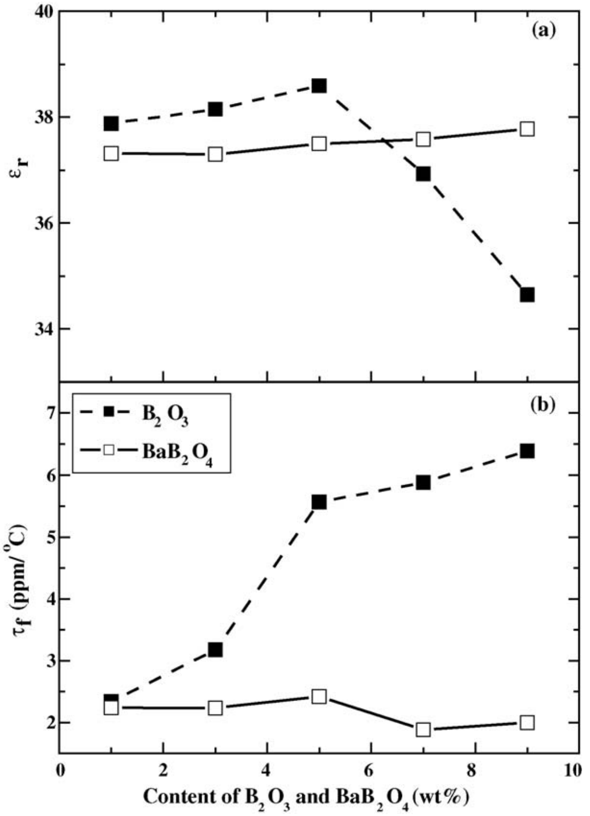

Fig. 6. (a) Dielectric constant; and (b) temperature coefficient of resonant frequency of samples sintered at 1050 °C for 2 h as a function of B_2O_3 and BaB_2O_4 content.

when B_2O_3 is added as revealed in Fig. 3(a). Note that a great increase in densification occurred at 1000 and 1050 °C when BaB_2O_4 and B_2O_3 were added, respectively.

The dielectric constant of the samples sintered at 1050 °C for 2 h as a function of B_2O_3 and BaB_2O_4 is presented in Fig. 6(a). For the B_2O_3 added samples, dielectric constant slowly increased from 37.9 to 38.4 as the content increased from 1 to 5 wt%. Further addition of B_2O_3 over 5 wt% resulted in a great decrease in dielectric constant. The increase in dielectric constant is thought to be originated from the formation of TiO_2 phase, which has high dielectric constant around 105. The great decrease in dielectric constant over 5 wt% of B_2O_3 is believed to be caused by poor densification since B_2O_3 produces many large pores. As the content of BaB_2O_4 is increased from 1 to 9 wt%, dielectric constant revealed almost constant value around 37.5 but showed an increasing tendency with BaB_2O_4 content. Even though the formation of the $BaTi(BO_3)_2$ was expected to reduce the dielectric constant due to its low dielectric constant around 11.5, the dielectric constant was not decreased. The negative effect of $BaTi(BO_3)_2$ phase on dielectric constant seems compensated by the accelerated densification effect of BaB_2O_4. The quality factor ($Q \times f$) of the samples decreased with increasing the content of B_2O_3 and BaB_2O_4. When the content of B_2O_3 is increased from 1 to 9 wt%, even though the figure is not presented, the quality factor decreased from 36,350 to 24,140, while the quality factor decreased from 38,860 to 33,370 as the content of BaB_2O_4 increased from 1 to 9 wt%. Fig. 6(b) shows the temperature coefficient of resonant frequency (τ_f) of the samples sintered at 1050 °C for 2 h as a function of borides content. τ_f increased with increasing of B_2O_3 content. Since B_2O_3 addition led to the formation of TiO_2, it is thought that the TiO_2 second phase is attributed to the increase in τ_f because TiO_2 has high positive τ_f value. When BaB_2O_4 is added, the τ_f is nearly independent of the amount of BaB_2O_4.

4. Conclusion

The effect of low temperature glasses of borides addition on microwave dielectric characteristics and sintering behavior of $BaTi_4O_9$ ceramics was examined. When B_2O_3 was added, active dissolution of Ba and Ti into B_2O_3 liquid from $BaTi_4O_9$ led to the formation of many second phases during sintering process. Moreover, B_2O_3 produced many large pores in the microstructure. These results made the dielectric characteristics of $BaTi_4O_9$ deteriorated. When BaB_2O_4 was added, chemical reaction between the glass and $BaTi_4O_9$ seems to be suppressed and densification was improved, which results in superior dielectric characteristics than the case of B_2O_3 addition.

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