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Sintering behavior and microwave dielectric characteristics of $BaO–Sm_2O_3–4TiO_2$ ceramics with B_2O_3 and BaB_2O_4 addition

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Abstract

We studied the low temperature sintering and the reaction in $BaO–Sm_2O_3–4TiO_2$ ceramics with boron-based additives for the application to microwave dielectric devices. The amount of the boride glasses of B_2O_3 and BaB_2O_4 was varied from 1 to 10 wt.% and the green compacts were sintered in the temperature range of 900–1200 °C for 2 h. When B_2O_3 was added, second phases of $Sm_2Ti_2O_7$, $BaTi(BO_3)_2$, $Ba_2Ti_9O_{20}$, and TiO_2 were formed, while BaB_2O_4 addition resulted in the formation of $BaSm_2Ti_4O_{12}$ single phase without second phases. On the basis of these results, it is regarded that the B_2O_3 is a reactive glass and the BaB_2O_4 is a non-reactive glass. The second-phase development, sintering behavior and microwave dielectric characteristics of $BaO–Sm_2O_3–4TiO_2$ ceramics were examined.

Keywords: Dielectric properties; Microstructure final; $BaO–Sm_2O_3–4TiO_2$

1. Introduction

$BaO–R_2O_3–kTiO_2$ ceramics, where R = Sm, Nd, Pr, La are rare earth elements with $k = 3–5$, have received much scientific and commercial attention due to their high dielectric constant, high quality factor and near-zero temperature coefficient of resonant frequency, which are required for the applications as resonators and filters in microwave communication.[1,2] As $k = 4$, the ternary formula of $BaO–R_2O_3–4TiO_2$ solid solution was widely studied to investigate the dielectric properties, structure formula, microstructures and reaction sequences.[3,4] In this system, however, it was found that the secondary phases which are not readily eliminated by conventional ceramic manufacturing process are developed during sintering. Although many successive works have been focused on the phase development, the phase relations are not clearly understood to date.

$BaO–Sm_2O_3–4TiO_2$ has been known to have relatively high dielectric constant ($\varepsilon_r = 70$), excellent quality factor ($Q \times f = 7000$) and good temperature coefficient of resonant frequency ($\tau_f = -15$ ppm/°C).[5] However, high sintering temperature around 1300–1400 °C is one of the disadvantages of the system, which restricts to a wide range of application. For the application to low temperature co-firing technology, low melting glasses were often used for lowering the sintering temperatures. However, the microwave dielectric materials often react with glasses producing undesired second phases, which deteriorate physical properties. Since the microwave dielectric properties depend on not only the microstructure but also the second phases developed, a careful selection of glass is necessary.

In this study, B_2O_3, a well-known liquid former, was employed for low temperature sintering of $BaO–Sm_2O_3–4TiO_2$ ceramics. During sintering, a considerable chemical reaction between the ceramics and the glass was expected to occur because Ba, Sm and Ti components are soluble in B_2O_3. From this point of view, another boron-based low melting glass of BaB_2O_4 is considered in which 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 $BaO–Sm_2O_3–4TiO_2$. The phase development, sintering behavior and microwave dielectric characteristics of $BaO–Sm_2O_3–4TiO_2$ ceramics were examined.

2. Experimental

The $BaSm_2Ti_4O_{12}$(BST) samples were prepared by the general solid-state reaction method of oxides. High purity $BaCO_3$ (99.95%), Sm_2O_3 (99.9%) and TiO_2 (99.9%) powders were

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used as the raw materials. After weighing the raw powders of BaO:Sm_2O_3:$4TiO_2$ to the molar ratio of 1:1:4, the mixture was wet ball milled with ZrO_2 balls in ethanol for 24 h. After drying, calcination of the mixture was conducted at 1250 °C for 2 h in air, and a single phase of $BaSm_2Ti_4O_{12}$ was obtained. Glasses of B_2O_3 and BaB_2O_4 ranging from 1–10 wt.% were added to calcined $BaTi_4O_9$ and dry-mixed for 24 h. The powders were then cold isostatically pressed into pellets under the pressure of 100 MPa. The specimens were sintered in the temperature range of 900–1350 °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 samples to identify the phases. Microstructure observation was conducted by using a scanning electron microscope (JEOL 4500, Japan). The density of the sintered samples was determined by the Archimedes' method. Microwave dielectric properties were measured by the parallel plate method originally proposed by Hakki and Coleman[6] 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 using HP8720C network analyzer.

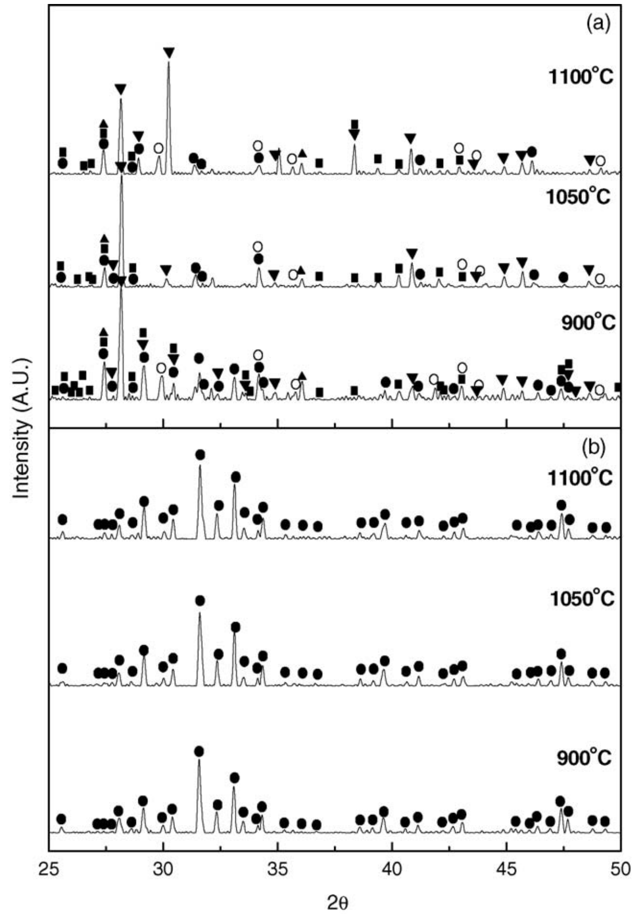

Fig. 1. X-ray diffraction patterns of $BaSm_2Ti_4O_{12}$ with (a) 10 wt.% B_2O_3 and (b) 10 wt.% BaB_2O_4 as a function of sintering temperature. (●)$BaSm_2Ti_4O_{12}$, (○) $BaTi(BO_3)_2$, (■) $Ba_2Ti_9O_{20}$, (▲) TiO_2, and (▼) $Sm_2Ti_2O_7$.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of $BaSm_2Ti_4O_{12}$ (BST) samples with addition of 10 wt.% B_2O_3 and BaB_2O_4 as a function of sintering temperature. When the sample with B_2O_3 was sintered at 900 °C, there exists BST as the main phase and minor phases such as $Sm_2Ti_2O_7$ (ST), $BaTi(BO_3)_2$ (BTB), $Ba_2Ti_9O_{20}$ (BT), and TiO_2 were observed. When the sintering temperature is increased to 1100 °C, the intensity from the ST phase increased and it became the major phase. In the case of BaB_2O_4 addition as shown in Fig. 1(b), the single phase of $BaSm_2Ti_4O_{12}$ was appeared and no particular phase change was observed even at higher sintering temperatures.

The phase evolution of BST with the amount of B_2O_3 at different temperatures is summarized in Table 1. As the amount of B_2O_3 and the temperature increased more kinds of second phases were produced. Because of the low melting temperature of B_2O_3 around 450 °C, when $BaSm_2Ti_4O_{12}$ grains are surrounded by B_2O_3 liquid, Ba, Sm and Ti ions will be concurrently dissolved out into B_2O_3 melts from the solid grains and then forms Ba–Ti–Sm–B–O glass during the sintering process at elevated temperatures. In the Ba–Ti–Sm–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 $BaSm_2Ti_4O_{12}$ grains, which will eventually results in the formation of TiO_2 and Ba-rich B_2O_3 glasses. At the same time,

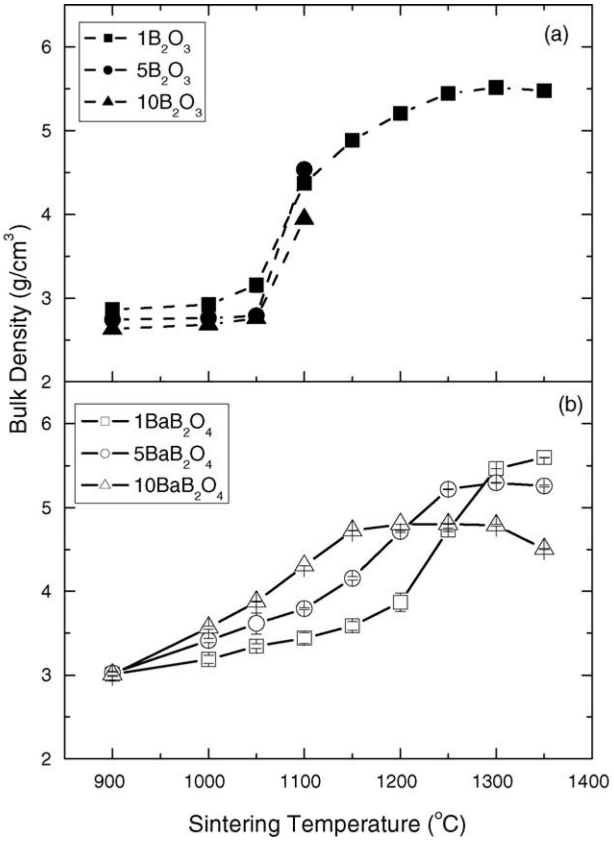

Fig. 2. Bulk density of $BaSm_2Ti_4O_{12}$ as functions of sintering temperature and the amount of (a) B_2O_3 and (b) BaB_2O_4.

Table 1
Phase evolution of $BaSm_2Ti_4O_{12}$ as functions of sintering temperature and the amount of B_2O_3

Temperature (°C)	B_2O_3				
	0 wt.%	1 wt.%	3 wt.%	5 wt.%	10 wt.%
1200	BST	BST	BST, TiO_2, ST	Melt	Melt
1150	BST	BST	BST, TiO_2, ST	Melt	Melt
1100	BST	BST	BST, TiO_2,BT	BST, TiO_2, BT	BST, TiO_2, BT, ST
1050	BST	BST	BST, TiO, BT	BST, TiO, BT	BST, TiO, BT, ST
1000	BST	BST	BST, TiO_2, BT	BST, TiO_2, BT	BST, TiO_2, BT, ST
900	BST	BST	BST	BST, BT	BST, TiO_2, BT, ST

BST: $BaSm_2Ti_4O_{12}$; BTB: $BaTi(BO_3)_2$; BT: $Ba_2Ti_9O_{20}$; TiO_2: TiO_2; ST: $Sm_2Ti_2O_7$.

another reaction among the $BaSm_2Ti_4O_{12}$ grains, many intermediate phases and Ba-rich B_2O_3 glass, $BaSm_2Ti_4O_{12}$ grains and many intermediate phases produced by the reaction will be proceeded, which leads to the formation of various kinds of second phases such as $Sm_2Ti_2O_7$, $BaTi(BO_3)_2$ and $Ba_2Ti_9O_{20}$. In the case of some samples, phase evolution was unavailable due to melting. On the other hand, when BaB_2O_4 is added, less Ba will be dissolved out from $BaSm_2Ti_4O_{12}$ compared to the case of B_2O_3 addition, because BaB_2O_4 can be considered as a material in which the Ba component was already dissolved in B_2O_3. However, it was turned out that there was no phase change when BaB_2O_4 is added. From this result, it can be considered that the B_2O_3 is reactive and the BaB_2O_4 is non-reactive glasses.

The bulk density of the samples as functions of sintering temperature and the amount of B_2O_3 and BaB_2O_4 is illustrated in Fig. 2. In the case of B_2O_3 addition, the density increased with increase of sintering temperature. When sintering temperature reached 1050 °C, a steep increase in density occurred. Considering the melting point of B_2O_3 (450 °C), densification initiated at much higher temperatures. When the glass network former of B_2O_3 is melted at the eutectic temperature, the viscosity of B_2O_3 liquid is very high. When the sintering temperature increased, active dissolving of cations such as Ba, Sm and Ti components

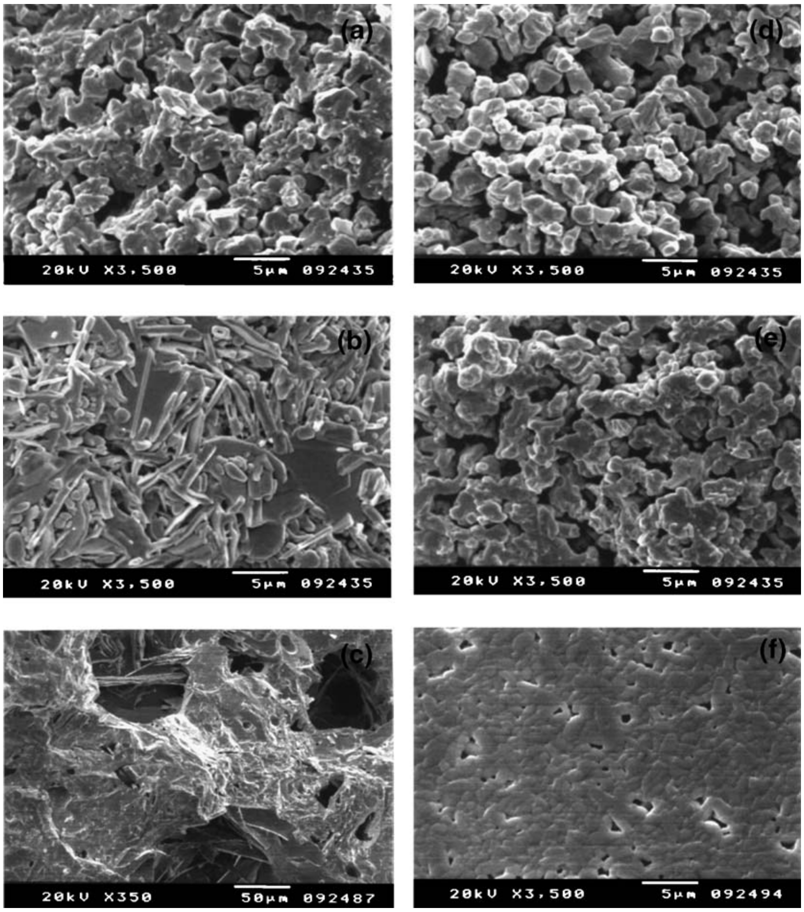

Fig. 3. Microstructure of $BaSm_2Ti_4O_{12}$ sintered at 1100 °C for 2 h with addition of (a) 1 wt.% B_2O_3, (b) 5 wt.% B_2O_3, (c) 10 wt.% B_2O_3, (d) 1 wt.% BaB_2O_4, (e) 5 wt.% BaB_2O_4 and 10 wt.% BaB_2O_4.

may lead to lowering of viscosity of liquid. Otherwise, liquid phases from many intermediate second phases produced by the chemical reaction might produce a liquid phase and contribute to the densification at that temperature. Decrease in the bulk density was observed as the amount of B_2O_3 increased, which is mostly attributed to the lower theoretical density of B_2O_3 (1.819 g/cm^3) than that of $BaSm_2Ti_4O_{12}$ (5.909 g/cm^3). Some of the samples with high content of B_2O_3 were melted down at high temperature and the measurement of density was not available. On the other hand, in the case of BaB_2O_4 addition, almost linear increase in density was observed in accordance with the increase of sintering temperature. The densification at low temperature was accelerated showing increased slopes of density as the amount of BaB_2O_4 increased, which is caused by the increased liquid volume.

Fig. 3 shows SEM images of the samples sintered at 1100 °C for 2 h as a function of the amount of B_2O_3 and BaB_2O_4. The irregular shape of particles in the sample with B_2O_3 suggests that second phases with different crystal structure exist. In the case of Fig. 3(c), which shows a low magnification view, many large pores are observed. In the pores, there exist flake-shaped grains. During the liquid phase sintering, more dissolution of Ba component and the capillary soaking of the liquid into adjacent solid grains will induce the formation of Ba-deficient second phases near the pores, which will result in compositional inhomogeneity in the sample. Because of the chemical reaction between B_2O_3 liquid and solid grains, most of the B_2O_3 melts disappeared and the liquid filling of pores is not available. Moreover, because the flake-shaped grains hinder moving and sliding of grains densification through particle rearrangement process might be inhibited. However, in the case of BaB_2O_4 addition, high densification was achieved when 10 wt.% of BaB_2O_4 is added.

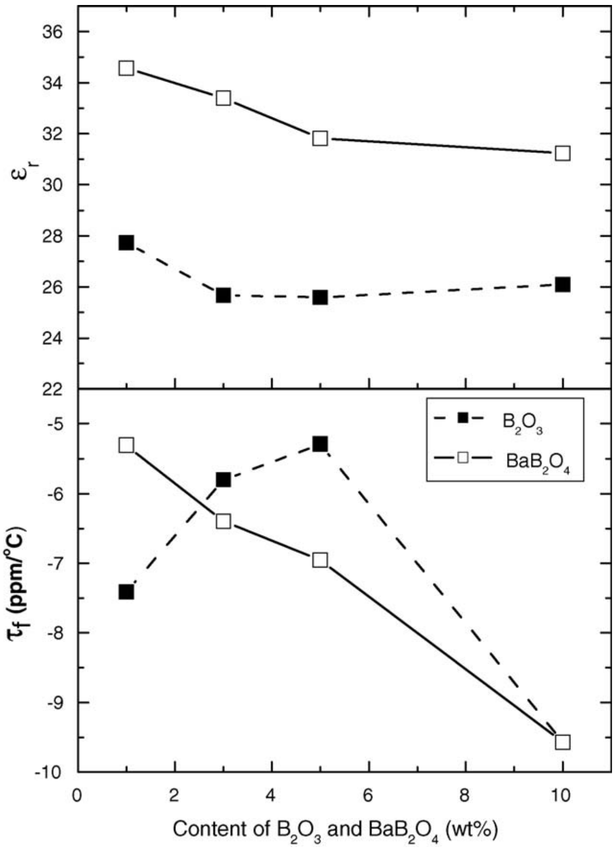

Fig. 4. (a) Dielectric constant and (b) temperature coefficient of resonant frequency of $BaSm_2Ti_4O_{12}$ sintered at 1100 °C for 2 h as a function of the amount of B_2O_3 and BaB_2O_4.

Dielectric constant of $BaSm_2Ti_4O_{12}$ samples sintered at 1100 °C for 2 h as a function of the amount of B_2O_3 and BaB_2O_4 is presented in Fig. 4(a). Dielectric constant of the samples with BaB_2O_4 was higher than that of the samples with B_2O_3 added samples. In the case of B_2O_3 addition, poor densification and the various kinds of second phases are the reasons of the low dielectric constant. In the case of BaB_2O_4 addition, dielectric constant slowly decreased as the amount of BaB_2O_4 increased probably due to the more incorporation of BaB_2O_4 liquid phase. Temperature coefficient of resonant frequency (τ_f) of the samples is also presented in Fig. 4(b). The increase in τ_f with increase of B_2O_3 from 1 to 5 wt.% is believed to be caused from the generation of TiO_2 second phase, which has high positive τ_f value. A drastic decrease in τ_f with addition of 10 wt.% B_2O_3 is believed to be caused by poor densification and inhomogeneous compositional distribution in the sample. On the other hand, in the case of BaB_2O_4 addition, τ_f decreased linearly in accordance with the amount of BaB_2O_4. Concerning $Q \times f$ values of the specimens, it greatly decreased from 15,400 to 7700 as the amount of BaB_2O_4 increased from 1 to 10 wt.%. When B_2O_3 was added, the $Q \times f$ values also showed a decreasing tendency with the values from 14,600 to 11,800 as the amount of B_2O_3 increased from 1 to 10 wt.%.

4. Conclusion

Low temperature sintering and microwave dielectric characteristics of $BaO–Sm_2O_3–4TiO_2$ ceramics were examined when reactive glass of B_2O_3 and non-reactive glass of BaB_2O_4 is added. Addition of reactive B_2O_3 induced the development of various second phases such as $Sm_2Ti_2O_7$, $BaTi(BO_3)_2$, $Ba_2Ti_9O_{20}$, and TiO_2. The chemical reaction between the glass and the ceramics induced inhomogeneous compositional distribution and microstructure, which resulted in deteriorated microwave dielectric characteristics. In the case of non-reactive BaB_2O_4 addition, no second phase was produced and it contributed to high densification as well as proper dielectric characteristics.

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