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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.

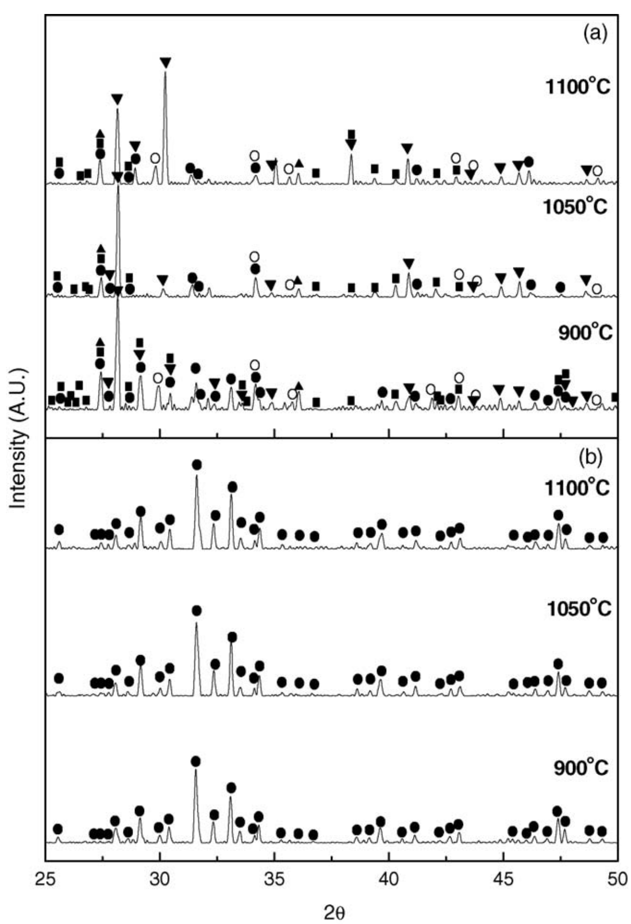

Fig. 1. X-ray diffraction patterns of $BaSm_2Ti_4O_{12}$ with (a) 10 wt.% B_2O_3 and (b) 10 wt.% BaB_2O_4 as a function of sintering temperature. (●)$BaSm_2Ti_4O_{12}$, (○) $BaTi(BO_3)_2$, (■) $Ba_2Ti_9O_{20}$, (▲) TiO_2, and (▼) $Sm_2Ti_2O_7$.

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,

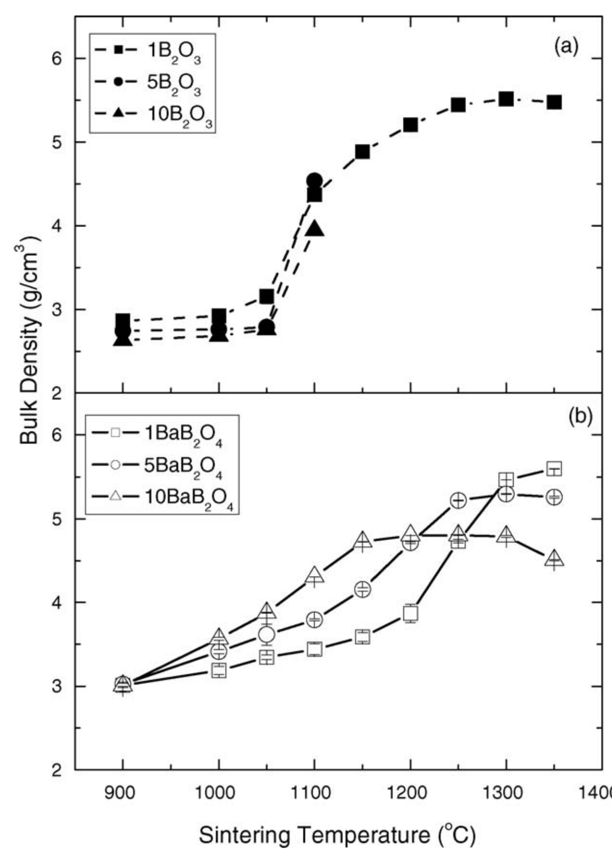

Fig. 2. Bulk density of $BaSm_2Ti_4O_{12}$ as functions of sintering temperature and the amount of (a) B_2O_3 and (b) BaB_2O_4.