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Low-temperature sintering of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ microwave dielectric ceramics by B_2O_3 and GeO_2 addition

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Abstract

Tungsten-bronze-type like $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions (BST) have been known to show relatively high dielectric constants ($\varepsilon_r = 80$), excellent quality factor ($Q{\cdot}f = 10{,}700$ GHz) and good temperature coefficient of resonant frequency ($\tau_f = -15$ ppm/K) at $x = 2/3$. However, lower sintering temperature has been asked for the commercial request, since the sintering temperature is higher than 1733 K. In this study, we tried to lower the sintering temperature by several kinds of B_2O_3 and GeO_2 additives. In the all additive systems investigated, the single addition of B_2O_3 ceramic powders was most effective for lowering the sintering temperature of BST ($x = 2/3$). When 0.5 wt.% of B_2O_3 ceramic powder was mixed with starting BST mixtures and sintered at 1473 K, the derived ceramics demonstrated dense microstructure with a large permittivity ($\varepsilon_r = 76$), high quality factor ($Q{\cdot}f = 10{,}500$GHz) and low temperature coefficient of resonant frequency ($\tau_f = -19$ ppm/K). It is noteworthy that the sintering temperature was significantly lowered by 260 K compared with no-additive system, and the derived ceramics maintained the excellent microwave dielectric properties corresponding to pure BST ($x = 2/3$).

Keywords: Dielectric properties; Functional applications; Grain size; Sintering; Tungsten bronze type

1. Introduction

Recently, much attention has been focused on the investigation and development of microwave dielectric materials, and several types of dielectric materials have been developed and put into practical use for microwave filters, oscillators and telecommunications technology. For miniturization of such electronic devices, the following three properties are generally required: (1) high dielectric constant, ε_r; (2) high quality factor, Q; and (3) nearly zero temperature coefficient of resonant frequency, τ_f. We have carried out the series of the work on $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd, Pr and La) solid solution system with high ε_r.[1–5] This solid solution forms a tungsten-bronze-type like crystal structure, and exhibits the highest $Q{\cdot}f$ value at $x = 2/3$, since the Ba and rare earth cations located within different ordering site in the structure.[2] In the case of R = Sm, $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ (BST) showed the most excellent microwave dielectric properties: $\varepsilon_r \approx 80$, $Q{\cdot}f \approx 10{,}700$ GHz, $\tau_f \approx -15$ ppm/K at $x = 2/3$.[5] However, the sintering temperature for BST single phase needs a relatively high temperature as high as 1733 K, and must be reduced for commercial requests. In the previous paper,[3,4] we reported that a slight change in the mixing composition from the solid solutions area to Ti-rich area in the $BaO–Sm_2O_3–TiO_2$ ternary phase diagram lowered the sintering temperature of BST ($x = 2/3$) significantly by 110 K. This new process did not deteriorate the good microwave dielectric properties of BST ($x = 2/3$).[3,4] In the research area of low temperature cofired ceramics (LTCC) technology, low-melting glasses and fine oxide ceramic powders were often used for lowering the sintering temperature. Takada et al.[6] reported reduction of sintering temperature by 160 K in $BaO–TiO_2–WO_2$ systems using addition of B_2O_3 glass, Chung et al.[7] reported low temperature sintering in $BaO{\cdot}La_2O_3{\cdot}4.7TiO_2$ systems due to the addition of $PbO–B_2O_3–SiO_2$ glasses. Moreover, Liu et al.[8] reported reduction in the sintering temperature of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics from 1423 to 1263 K by the addition of B_2O_3 ceramic powder. In the present study, we aim the decrease in sintering temperature of

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BST ($x = 2/3$) solid solution by adding (1) B_2O_3, (2) GeO_2, (3) $B_2O_3 + GeO_2$ ceramic powders and (4) B_2O_3 glassy powders.

2. Experimental

High-purity ceramic powders $BaCO_3$ (99.7%), TiO_2 (99.8%), Sm_2O_3 (99.9%), B_2O_3 (99.9%) and GeO_2 (99.9%) were used as raw materials. The mixture for preparation of BST ($x = 2/3$) was milled with ZrO_2 balls for 24 h in ethanol, then it was dried and calcined in air at 1273 K for 2 h. Oxide additives were subsequently mixed with the calcined BST ($x = 2/3$) powder mixtures in wt.% ranging from 0.3 to 3.0, and the all mixture were again ball-milled for 24 h with distilled water. In this study, (1) B_2O_3, (2) GeO_2, (3) $B_2O_3 + GeO_2$ ceramic powders and (4) B_2O_3 glassy powders were used as oxide additives. B_2O_3 glassy powders were prepared by quenching of molten B_2O_3 solution. The dried powder mixture of BST ($x = 2/3$) and oxide additives were crushed with alumina mortar/bar for 2 h. After adding 3wt% of polyvinyl alcohol as a binder to the powder mixtures, they were passed through a mesh (#300) and uniaxially pressed into disks with 12 mm in diameter and 6 mm in height. The disks were sintered in air at 1423 and 1473 K for 2 h. The sintering temperature was determined using thermo gravimetry and differential thermal analysis (TG-DTA). The crystalline phases of the sintered samples were identified from powder X-ray diffraction (XRD) using Cu-K_α radiation. The microstructure of polished surfaces was investigated by a scanning electron microscope (SEM) after thermal etching. Bulk density was evaluated by the Archimedes method.

Sintered samples were cut and mirror-polished to become the ratios of their diameter and height were 2:1. The polished disks were annealed in air at 1273 K for 2 h. Microwave dielectric properties of ε_r, unloaded $Q \cdot f$ and τ_f were evaluated at a temperature ranging from 293 to 353 K in the TE_{011} mode by Hakki and Colleman's method using a network analyzer (HP-8757C) and parallel conductor boards.[9]

3. Result and discussion

DTA curves of the powder mixtures containing oxide additives showed two endothermic peaks. The first peak appeared around the temperature of 1423 K depending on the kind of oxide additives. On the other hand, the second peak appeared at 1783 K depending on the kind of oxide additives. These two peaks were supposed to be an eutectic point between BST ($x = 2/3$) and oxide additives, and the melting point, respectively. BST single phase shows only an endothermic peak at approximately 1803 K which corresponds to the melting temperature. Therefore, powder compacts in the system BST-oxide additives were sintered at over 1423 K due to the expectation of sintering aids by liquid phase formation.

Fig. 1 shows XRD patterns of BST ($x = 2/3$) with oxide additives (0.5 wt.%). The observed patterns and peak intensities are almost equivalent to those of pure BST ($x = 2/3$), and show no secondary phase besides an

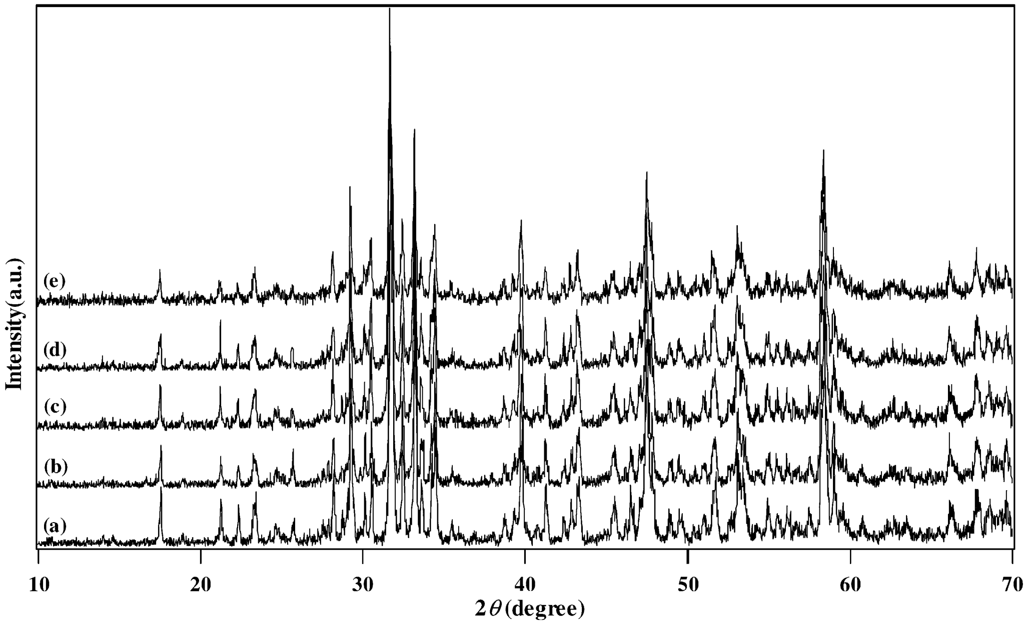

Fig. 1. X-ray powder diffraction patterns of (a) BST ($x = 2/3$) sintered at 1733 K. (b) BST ($x = 2/3$) + B_2O_3 (0.5 wt.%) sintered at 1473 K. (c) BST ($x = 2/3$) + GeO_2 (0.5 wt.%) sintered at 1423 K. (d) BST ($x = 2/3$) + B_2O_3 (0.5 wt.%) + GeO_2 (0.5 wt.%) sintered at 1473 K. (e) BST ($x = 2/3$) + glassy B_2O_3 (0.5 wt.%) sintered at 1473 K.

orthorhombic tungsten-bronze structure of BST. The BST ($x=2/3$) with oxide additives (0.5 wt.%) demonstrated dense sintered body similar to pure BST ($x=2/3$), but larger grains were observed in the BST ($x=2/3$) with glassy B_2O_3 than that with ceramic B_2O_3 addition, as shown in Fig.2.

Fig. 3 shows the apparent density (ρ) and microwave dielectric properties (ϵ_r, $Q{\cdot}f$ and τ_f) of BST ($x=2/3$) sintered at 1423 and 1473 K as a function of B_2O_3 contents. In the figure, plots on the vertical axis at 0wt% show the properties of pure BST ($x=2/3$) sintered at 1733 K. Noteworthy points are that a variation observed in ρ and ε_r has nearly the same trend with increasing additive contents, and that better properties were obtained for the specimen sintered at 1473 K than 1423 K due to liquid-phase sintering aids above the eutectic point. Of all the B_2O_3 contents investigated, 0.5wt% addition demonstrated a highest $Q{\cdot}f$ value

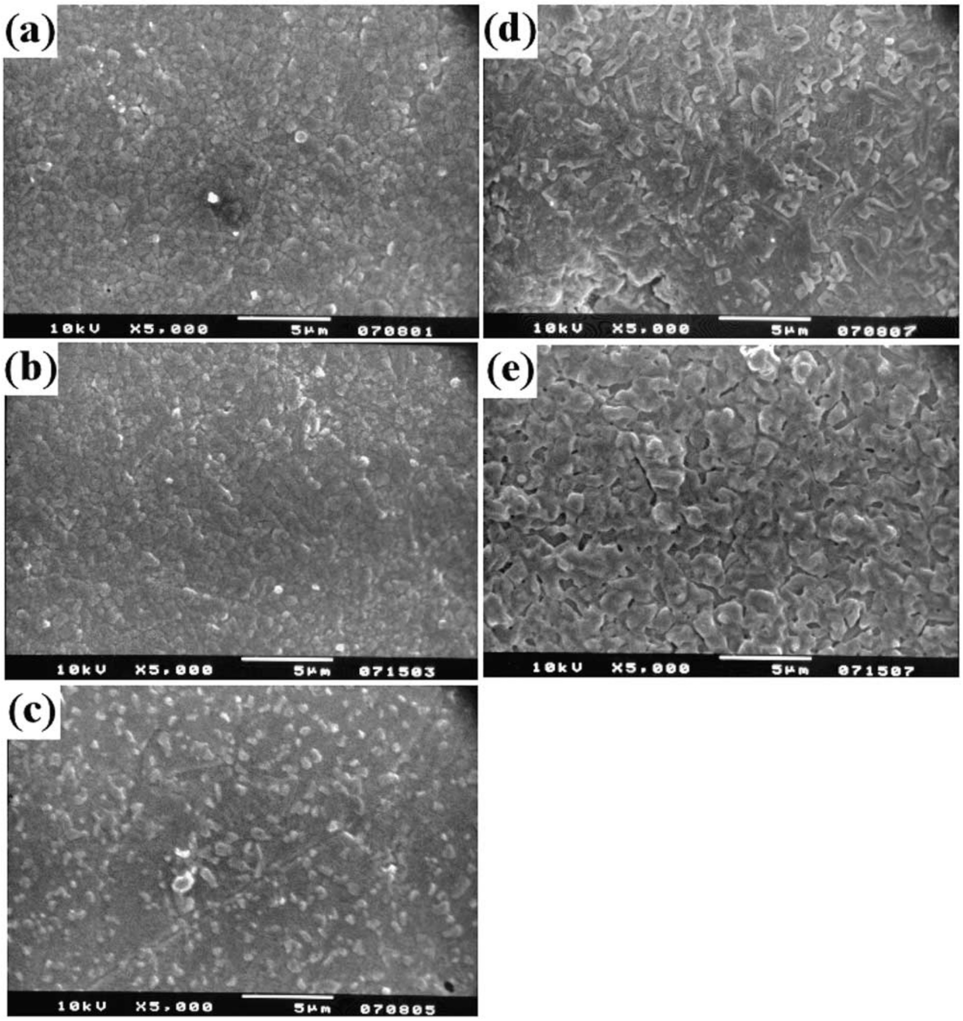

Fig. 2. SEM micrographs of (a) BST ($x=2/3$) and BST ($x=2/3$)+0.5 wt.% of each additive including (b) B_2O_3, (c) GeO_2, (d) $B_2O_3+GeO_2$ and (e) glassy B_2O_3.

Table 1
Microwave dielectric properties and apparent density of BST ($x=2/3$) ceramics

Composition	BST ($x=2/3$)	BST ($x=2/3$) $+B_2O_3$ (0.5 wt.%)	BST ($x=2/3$) $+GeO_2$ (0.5 wt.%)	BST ($x=2/3$) $+B_2O_3$ (0.5 wt.%) $+GeO_2$(0.5 wt.%)	BST ($x=2/3$) +glassy B_2O_3 (0.5 wt.%)
Sintering temperature	1733 K	1473 K	1423 K	1473 K	1473 K
ε_r	80.0	76.1	77.3	75.2	69.6
$Q{\cdot}f$	10,700	10,500	8900	5200	4300
τ_f[ppm/K]	−15.0	−19.4	−19.7	−12.6	−19.2
ρ[g/cm^3]	5.72	5.68	5.77	5.73	5.78

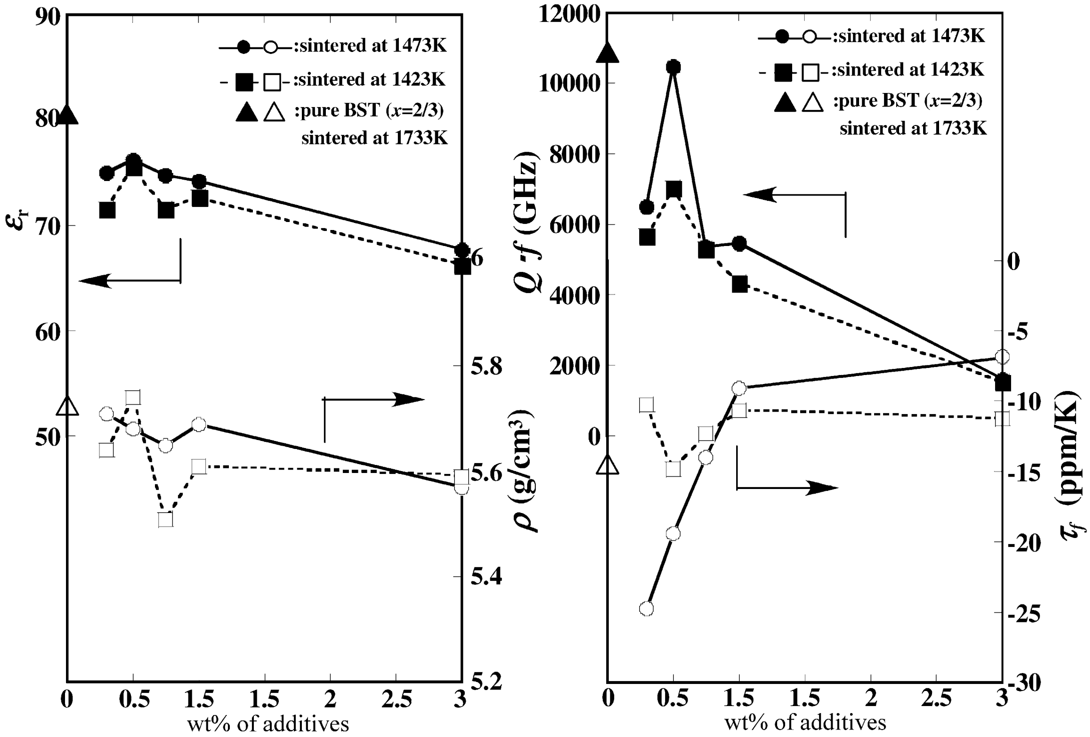

Fig. 3. Microwave dielectric properties and apparent density of BST ($x = 2/3$) ceramics sintered at 1423 and 1473 K with B_2O_3 ceramic powders (0.3–3.0 wt.%). The results of pure BST ceramics prepared at 1733 K are also plotted.

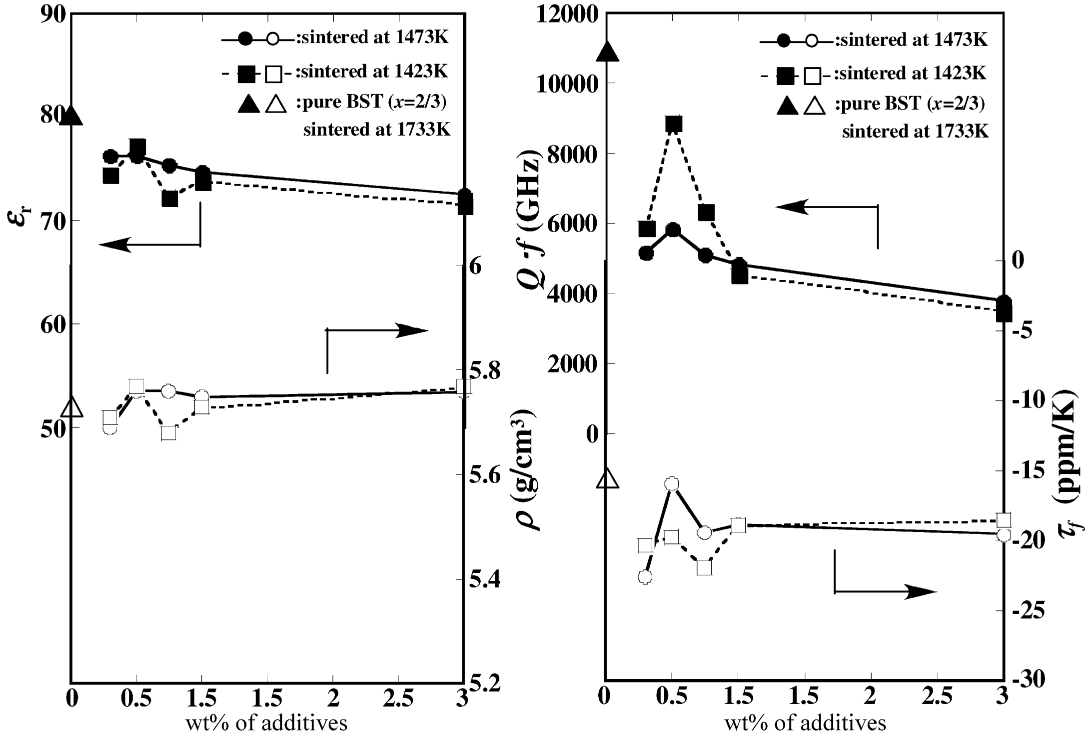

Fig. 4. Microwave dielectric properties and apparent density of BST ($x = 2/3$) ceramics sintered at 1423 and 1473 K with GeO_2 ceramic powders (0.3–3.0 wt.%).

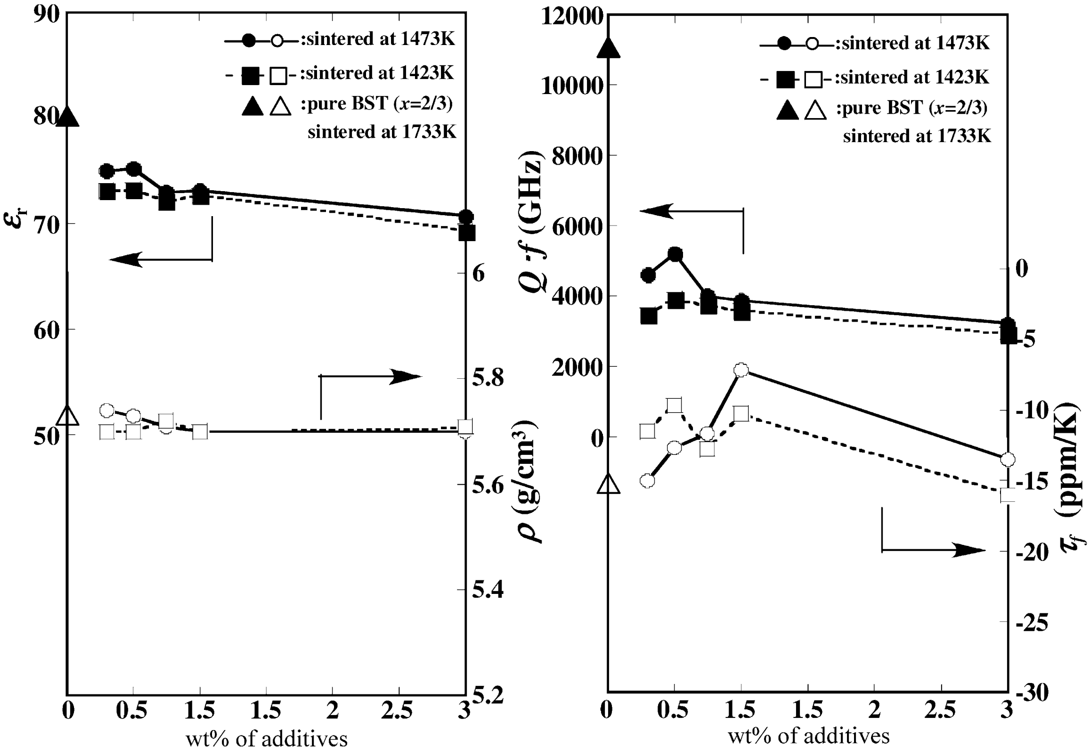

Fig. 5. Microwave dielectric properties and apparent density of BST ($x=2/3$) ceramics sintered at 1423 and 1473 K with 0.5 wt.% of B_2O_3 and GeO_2 ceramic powders (0.3–3.0 wt.%).

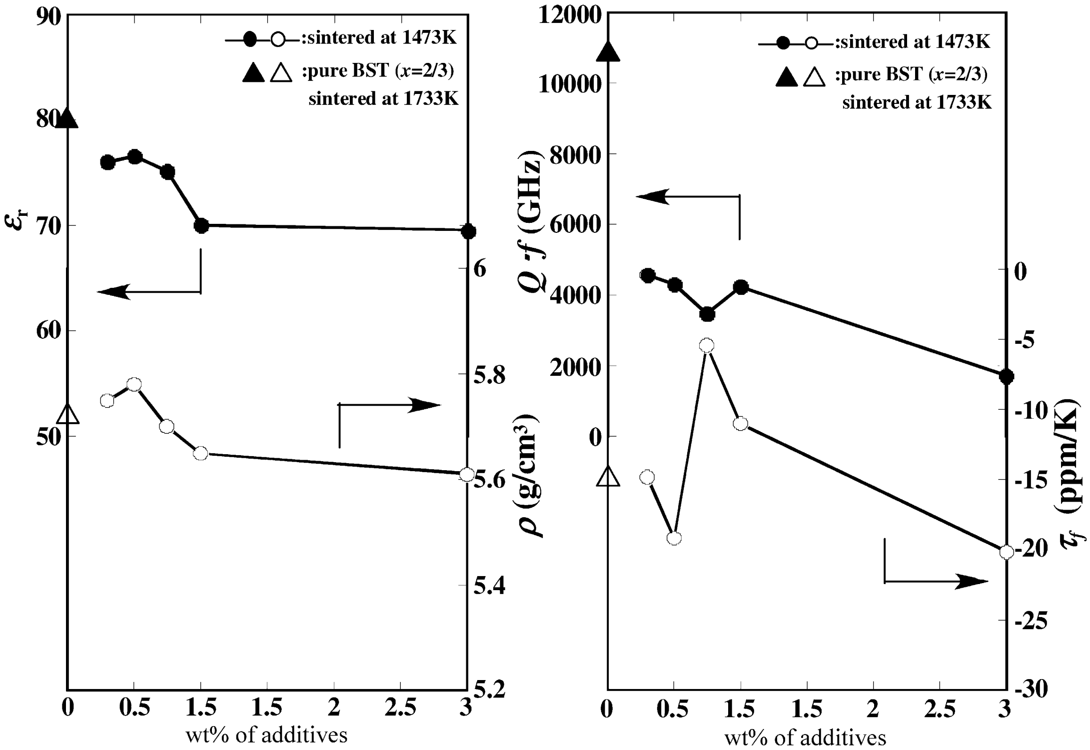

Fig. 6. Microwave dielectric properties and apparent density of BST ($x=2/3$) ceramics sintered at 1473 K with B_2O_3 glassy powders (0.3–3.0 wt.%).

(10500 GHz) which nearly corresponds to $Q{\cdot}f$ value of 10700 GHz for pure BST ($x=2/3$) (Table 1). Compared with the variation observed in ρ and ε_r, both $Q{\cdot}f$ and τ_f remarkably changed with increasing amount of B_2O_3 addition. Secondary phases formed by B_2O_3 addition seems have affected both properties significantly, although apparent emergence of new peaks or pattern change were not observed in XRD because of the existence of BST ($x=2/3$) structure with many peaks.

Fig. 4 presents the results obtained for BST ($x=2/3$) with GeO_2 addition. Property change with increasing GeO_2 amount is similar in behavior to the case of B_2O_3 addition, as shown in Fig. 3, but the variation step with increasing GeO_2 addition is smaller than that with B_2O_3 addition. This is because an additive amount for the former case was smaller than that of the latter case in molar%. Nevertheless, an interesting point is that $Q{\cdot}f$ demonstrated its top value at 0.5 wt.% addition the same as in the case of B_2O_3. However, the $Q{\cdot}f$ value (8900 GHz) was lowered from that of pure BST ($x=2/3$) (Table 1).

When GeO_2 was added to BST ($x=2/3$)+0.5 wt%. B_2O_3 powders for trial, properties obtained in the sintered specimen never exceeded those of the BST ($x=2/3$) +0.5 wt.% B_2O_3 specimen, but was lowered gradually with increasing GeO_2 addition (Fig. 5). This indicates that B_2O_3 is better than GeO_2 as an additive source for maintaining good microwave dielectric properties as well as lowering sintering temperature of BST ($x=2/3$).

As mentioned above, B_2O_3 has been often used for lowering sintering temperature of microwave dielectric ceramics, B_2O_3 used in the above research was either a glassy powder[6,7] or a crystalline ceramic powder.[8] Fig. 6 deals with the effect of glassy B_2O_3 addition on the properties of BST ($x=2/3$). Sintering temperature was fixed to 1473 K. When the data plotted in Fig. 6 are compare with those plotted in Fig. 3, one can see an apparent difference in $Q{\cdot}f$ and τ_f. In the case of glassy B_2O_3 addition, a steep rise in $Q{\cdot}f$ at around 0.5 wt.% addition is not observed, and $Q{\cdot}f$ value monotonously decreases with increasing grassy B_2O_3 addition. On the other hand, the variation in τ_f demonstrates an opposite trend to that observed in the case of ceramic B_2O_3 addition. As presented in Fig. 2, the grain size of sintered specimens was markedly different between the two specimens. Large BST ($x=2/3$) grains were preferably formed in the specimen with glassy B_2O_3 addition. This seems to indicate that liquid phase sintering occurred actively in the BST specimen, when glassy B_2O_3 was added. Actually, apparent density of the BST ($x=2/3$) specimen with glassy B_2O_3 addition was relatively higher than that of the specimen with the ceramic powder (Table 1). It is also considered that intergranular amorphous phases resulting from glassy B_2O_3 addition might have affected $Q{\cdot}f$ and τ_f values significantly. Further research on microscopic evaluation is urgently needed.

4. Conclusion

The additive effects of (1) B_2O_3, (2) GeO_2, (3) $B_2O_3+GeO_2$ ceramic powders and (4) B_2O_3 glassy powders upon the microstructures and microwave dielectric properties of BST ceramics ($x=2/3$) were investigated to reduce the sintering temperature. These additives significantly lowered sintering temperature of BST ($x=2/3$). When 0.5 wt.% of B_2O_3 ceramic powder was added to BST ($x=2/3$) and sintered 1473 K, nearly the same excellent dielectric properties were obtained. B_2O_3 worked as a better sintering aid in BST ($x=2/3$) microwave dielectric ceramics than GeO_2. It is noteworthy that the sintering temperature of BST ($x=2/3$) was significantly lowered by over 260 K from 1733 K to 1473 K by the selection of B_2O_3 ceramic powder.

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