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Effects of $ZnO–B_2O_3$ Addition on Sintering Behaviors and Microwave Dielectric Properties of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ Ceramics[1]

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Abstract—Effects of $ZnO–B_2O_3$ (ZB) addition on the densification, phase evolution and microwaves dielectric properties of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ (BST) ceramics for low-temperature fired applications have been investigated. The sintering temperature of BST ceramics can be effectively lowered to about 1000°C with introduction of ZB. Tungsten bronze like single phase is observed in the BST ceramics with 0.5 and 1.0% ZB. However, $Sm_2Ti_2O_7$ secondary phase appears when ZB addition reaches 2%, and $Sm_2Ti_2O_7$ phase gradually increases with the increase ZB addition. Microwave dielectric properties of the present ceramics are strongly dependent on phase constitution and density. Optimal microwave dielectric properties of $\varepsilon = 63.4$, $Qf = 2830$ GHz, $\tau_f = -8.8$ ppm/°C is obtained for BST ceramics with 1% ZB addition.

Keywords: low temperature sintering, $Ba_4Sm_{9.33}Ti_{18}O_{54}$, microwave dielectric properties, $ZnO–B_2O_3$

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INTRODUCTION

With the rapid development of mobile and satellite telecommunication system, the considerable attention has been paid to microwave dielectric ceramics because of the wide application in microwave devices, such as resonators and filters [1–5]. Generally, these ceramics are required for high permittivity, high Qf value and near zero temperature coefficient of resonance frequency. Some dielectric ceramics have been found with the above mentioned microwave dielectric properties. $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = Nd, Sm, x = 0.5, 2.3, 0.75) ceramics is the typical currently applied microwave dielectric ceramics system, which displays high permittivity of about 80, high Qf value above 8000 GHz and near zero temperature coefficient of resonance frequency [5–8]. Much attention has been paid to $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ ceramics in the past decades, especially $Ba_4Ln_{9.33}Ti_{18}O_{54}$ (Ln = Nd, Sm). Many investigations on $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = Nd, Sm) are focus on two parts. One is to optimize the microwave dielectric properties such as modification of temperature coefficient, enhancement of Qf values [6–10]. The other is to reduce its sintering temperature, which is too high (~1350°C) for LTCC application [11–15]. Generally, there are three ways to lower the sintering temperature: adding sintering aids, adopting chemical method and using fine powder as starting materials [1]. Taking cost, efficiency and convenience into account, adding oxides with low-melting point or glass is the best choice in these above ways [1]. CuO, BaCu (B_2O_5) and Ba–Zn–B glass have been adopted to reduce the sintering temperature of $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = Nd, Sm) [11–15]. However, these investigations on low temperature sintering are almost focus on $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = Nd, Sm, x = 0.5) ceramics. As a good sintering aid, $ZnO–B_2O_3$ glass is often adopted to reduce the sintering temperature of dielectric ceramics [16–18]. In order to obtain $ZnO–B_2O_3$ glass powder, but it is required a complicated process of melting, quenching and grinding.

Therefore, $ZnO–B_2O_3$ (ZB) oxides without treating have been chosen as a sintering aid to reduce the sintering temperature of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ (BST) ceramics in the present work. And sintering behaviors, crystal phase, microstructure evolution and microwave dielectric properties of BST ceramics have been investigated in details. In addition, the reaction between BST and ZB has also been discussed.

EXPERIMENTAL

BST powder was prepared by the conventional solid-state reaction method from $BaCO_3$ (99%), Sm_2O_3 (99.9%), TiO_2 (99.5%) raw powders. According to the formula $Ba_4Sm_{9.33}Ti_{18}O_{54}$, $BaCO_3$, Sm_2O_3 and TiO_2 powders were weighed, fully mixed and ground by attrition in a polyethylene jar with zirconia balls in de-ioned water for 8 h. After drying, the mix-

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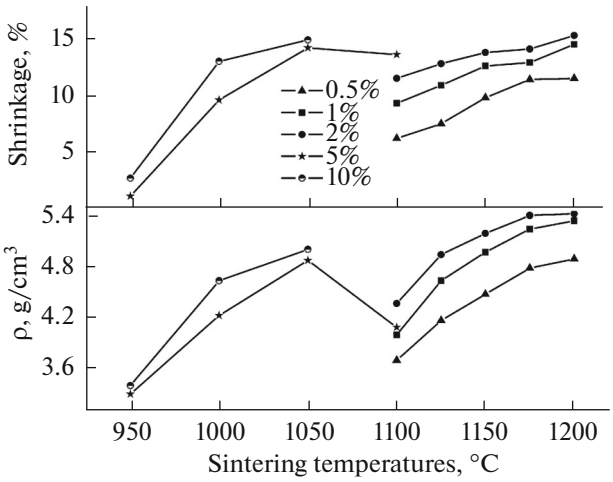

Fig. 1. Densities and shrinkages of BST ceramics with different amount of ZB addition.

tures were calcined at 1200°C for 3 h. Different amount of ZB (0.5–10 wt %) oxides were added to the BST calcined powders, and mixture was reground for 8 h using distilled water. Subsequently, a 5% PVA solution as a binder was added to the dried powder and then the powder was pressed into cylindrical compacts of 10 mm in diameter under a pressure of about 100 MPa. These compacts were sintered at 900–1200°C for 3 h in air.

The densities of the present ceramics were measured by the Archimedes method. The crystal structures of sintered samples after crushing and grinding were determined by powder X-ray diffraction (XRD, Rigaku Ultima III) analysis, using CuK_α-radiation ($\lambda = 0.15406$ nm) at room temperature. The microstructure was observed by scanning electron microscopy (SEM, ZEISS SUPRA 55). Silver electrodes were coated on the polished ceramics faces for dielectric measurements. Microwave dielectric properties of the present ceramics were measured by $TE_{01\delta}$ dielectric resonator method [19] with a network analyzer (Agilent 8753 ES), and the temperature coefficient (τ_f) of the resonant frequency was measured in the temperature range 25–85°C.

RESULTS AND DISCUSSION

Figure 1 shows the bulk densities and shrinkages of BST ceramics with different amount of ZB ($x = 0.5$–10%) addition. As can be seen, the shrinkage and density gradually ascend with the rising of sintering temperature. The sintering temperature of BST has been reported about 1350°C [6–10]. Sintering temperature is obviously reduced to about 1200°C when a very small amount of ZB (0.5%) is introduced. And with the increasing the ZB addition, shrinkage and density gradually increase as the ZB content is in the range of 0.5–2%. When ZB content reaches 5%, the sintering temperature further reduces to about 1000°C. But the sintering temperature not significantly decrease with ZB addition further increase.

XRD patterns of BST ceramics with different ZB contents are shown in Fig. 2. All the peaks in the XRD patterns can be indexed based on the orthorhombic tungsten bronze type like phase for BST ceramics with

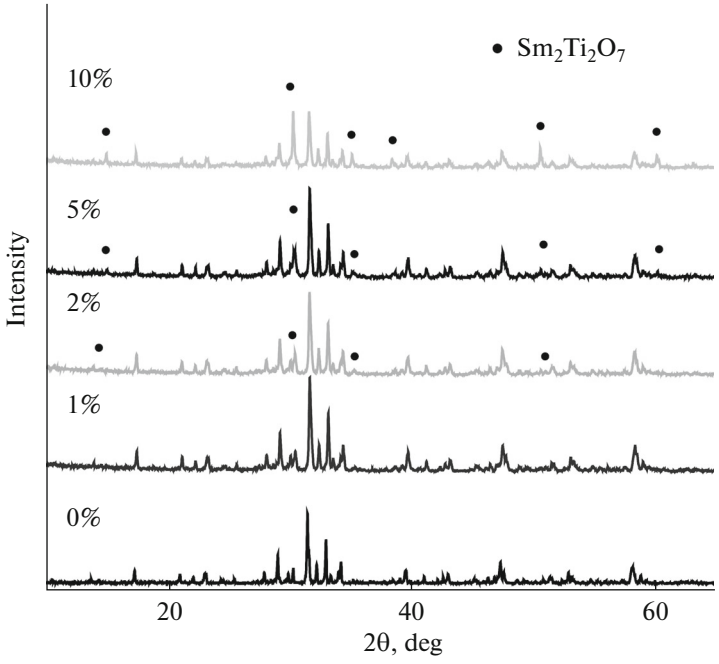

Fig. 2. XRD patterns of the BST ceramics with different ZB content.

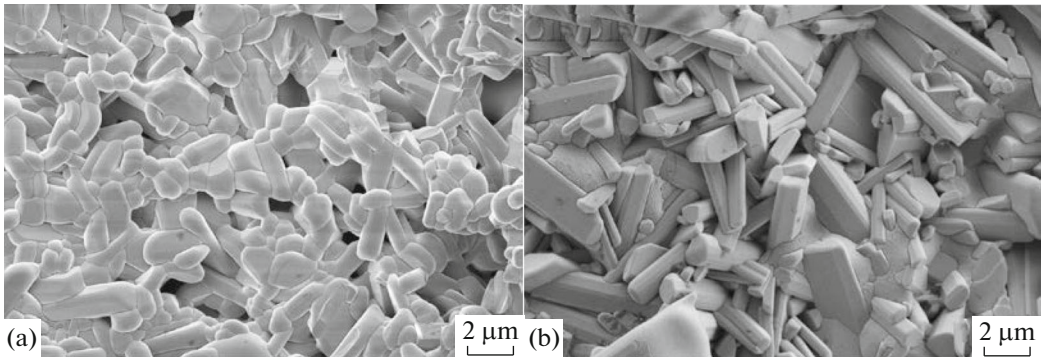

Fig. 3. SEM images of BST ceramics with different amount of ZB, (a) 0.5%, (b) 2%.

a small amount of ZB additive (<2%), which indicates that no secondary phase is formed. But when ZB content reaches 2%, some weak peaks corresponding to pyrochlore phase $Sm_2Ti_2O_7$ are observed. And these diffraction peaks become stronger for the BST ceramics with more ZB content. Compared with the pure BST ceramics, the diffraction peaks of tungsten bronze type like phase shift towards high angle with the increase of ZB addition, which indicates the unit cell shrinkages.

It is well known that $ZnO-B_2O_3$ glass exhibits a low softening temperature. In the present work, $ZnO-B_2O_3$ based liquid phase may be formed during the sintering when temperature is beyond the melting point. Once the liquid phase appears, $Ba_4Sm_{9.33}Ti_{18}O_{54}$ grains are surrounded by ZB liquid phase. Ba, Sm and Ti ions will be simultaneously dissolved into ZB phase from grains during the sintering process. However, it has been confirmed that the solubility of Ba in ZB glass is higher than that of Ti by authors [20]. Thus, more Ba atom is dissolved from the BST grains than Ti atom, which results in Ba-deficiency BST grains. So the volume of the unit cell decreases due to the decrease of large Ba atom. Corresponding variation is diffraction peaks shift to the higher angle. Eventually, secondary phase forms when Ba deficiency in BST grains is beyond a certain extent. So $Sm_2Ti_2O_7$ phase is observed in the BST ceramics with 2% ZB addition.

SEM images of the specimens are shown in Fig. 3. Apparent difference on the grain morphologies is observed in the BST ceramics with 0.5 and 2% ZB addition. The BST ceramics with 0.5% ZB addition displays columnar grains, which is similar the BST pure ceramics in many investigations [16–18]. And a few pores are also observed, which consists well with the lower density. But the two kinds of grains with different sizes are observed in the BST ceramics with 2% ZB addition. The large columnar grain can be ascribed to abnormal grain growth in the liquid phase sintering. It is also noticed that there is not clear grain boundary between some small columnar grains, which implies the appearance of liquid phase during sintering. Meantime, this specimen also exhibits the denser microstructure. As stated above, the increase of ZB addition is helpful to enhance the densification of BST ceramics.

Microwave dielectric properties of BST ceramics with different ZB addition sintered at optimum temperature are shown in Fig. 4 to Fig. 6. As shown in Fig. 4, the permittivity initially increases with the increasing of ZB amount, and then rapidly drops. As stated above, in the range of 0.5–2%, density obviously increases with the increase of ZB content. At the same time, the crystal phases do not nearly change. As reported previously, permittivity is mainly affected by the density and the second phases. So the permittivity is proportional to the density for the BST ceramics with 0.5–2% ZB. Permittivity ε of BST sample with ZB addition increases from 53.4 for 0.5% to 64.7 for 2%. However, the more secondary phase $Sm_2Ti_2O_7$ with low permittivity [21] is formed in the BST ceramics with more ZB addition (5, 10%), which results in a drop of permittivity. So the variation of permittivity is

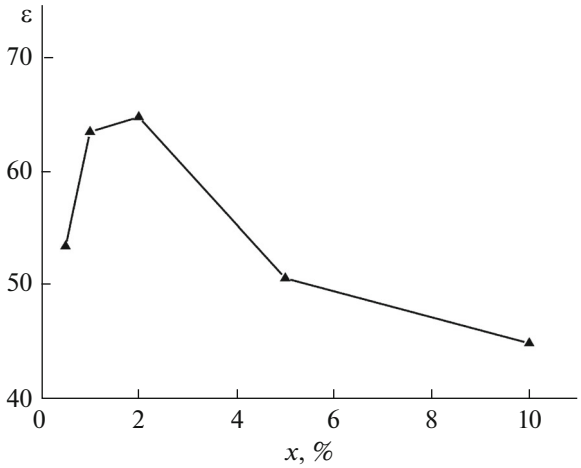

Fig. 4. Permittivity of BST ceramics as a function of ZB content.

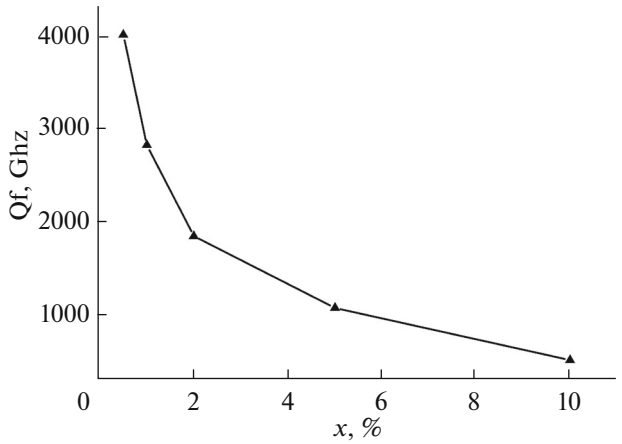

Fig. 5. Qf values of BST ceramics as a function of ZB content.

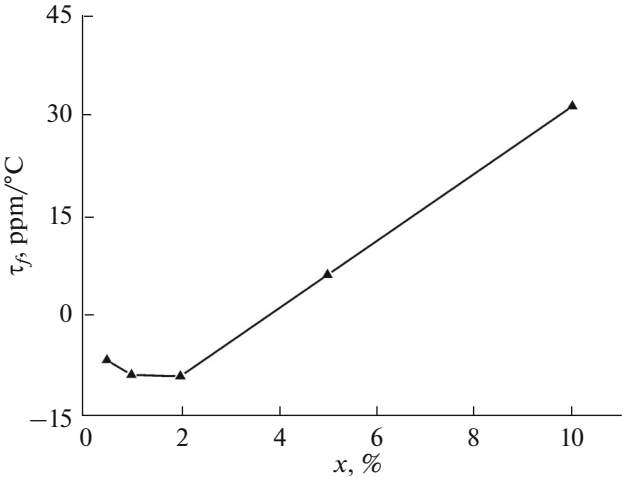

Fig. 6. Temperature coefficients of BST ceramics with ZB addition.

well consistent with the variation of density and phase evolution for the present ceramics.

Figure 5 shows the variation of Qf value of BST with ZB addition sintered at optimum temperature. As the ZB addition is introduced, the Qf value rapidly declines. Generally, Qf value is usually affected by the combination of intrinsic and extrinsic factors together. Intrinsic factor is related to the anharmonic interaction of the electric field and the crystal phonons. While extrinsic factors are related to imperfect microstructures, such as pores, secondary phases, oxygen vacancy, inner stress and density [15] The density variation shows that the density increases with the increase of ZB content when x is less than 5%, while the Qf value obviously reduces. This is linked to the phase and structure evolution. As stated in XRD section above, barium atom dissolution into the liquid phase during the sintering. That results in Ba-deficiency in BST crystallite. Subsequently, the dielectric losses of BST ceramics rapidly increase, and Qf value decreases. In addition, when ZB content reaches 2%, the high loss phase $Sm_2Ti_2O_7$ is formed, which is commonly used as a dielectric in the solid oxide fuel cell (SOFC) due to its oxygen ion conductivity [22]. Therefore, the Qf value drops to below 1000 GHz when a large amount of $Sm_2Ti_2O_7$ phase is formed for BST ceramics with more than 5% ZB addition.

Temperature coefficients of resonant frequency (τ_f) of BST ceramics are shown in Fig. 6. With the increase of ZB addition, τ_f first has little variation (~ −10 ppm/°C), and then shifts to positive value when ZB content is more than 2%. The variation of τ_f can be explained by phase evolution of the present ceramics. As stated above, there is almost single phase BST with near zero τ_f when ZB content is not beyond 2%. Otherwise, the secondary phase $Sm_2Ti_2O_7$ with high positive τ_f (about 250 ppm/°C) is formed, which results in the τ_f value shift to positive.

CONCLUSIONS

BST ceramics with different amount of ZB addition is prepared by solid-state reaction method. Effects of ZB addition on sintering behaviors, structure evolution and microwave dielectric properties of BST ceramics have been investigated. The ZB addition significantly reduces the sintering temperature of BST ceramics from 1350°C to about 1000°C. A very small amount of second phase $Sm_2Ti_2O_7$ is formed in BST ceramics with 2% ZB addition, and $Sm_2Ti_2O_7$ phase content increases with the further increase of ZB addition. The relationship between microwave dielectric properties and phase evolution has been discussed. The BST ceramics with 1% ZB addition exhibits excellent microwave dielectric properties of $\varepsilon = 63.4$, Qf = 2830 GHz and $\tau_f = -8.8$ ppm/°C.

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