Effects of ZnO–B₂O₃ Addition on Sintering Behaviors and Microwave Dielectric Properties of Ba₄Sm₉.₃₃Ti₁₈O₅₄ Ceramics

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Abstract—Effects of ZnO–B₂O₃ (ZB) addition on the densification, phase evolution and microwaves dielectric properties of Ba₄Sm₉.₃₃Ti₁₈O₅₄ (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, Sm₂Ti₂O₇ secondary phase appears when ZB addition reaches 2%, and Sm₂Ti₂O₇ 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 \( \varepsilon = 63.4, Q_f = 2830 \, \text{GHz}, \tau_f = -8.8 \, \text{ppm/}°\text{C} \) is obtained for BST ceramics with 1% ZB addition.

Keywords: low temperature sintering, Ba₄Sm₉.₃₃Ti₁₈O₅₄, microwave dielectric properties, ZnO–B₂O₃

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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. Ba₆₋₃ₓLn₈₊₂ₓTi₁₈O₅₄ (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 Ba₆₋₃ₓLn₈₊₂ₓTi₁₈O₅₄ ceramics in the past decades, especially Ba₆₋₃ₓLn₈₊₂ₓTi₁₈O₅₄ (Ln = Nd, Sm, x = 0.5) ceramics. As a good sintering aid, ZnO–B₂O₃ glass is often adopted to reduce the sintering temperature of Ba₆₋₃ₓLn₈₊₂ₓTi₁₈O₅₄ ceramics [11–15]. However, these investigations on low temperature sintering are almost focus on Ba₆₋₃ₓLn₈₊₂ₓTi₁₈O₅₄ (Ln = Nd, Sm, x = 0.5) ceramics. As a good sintering aid, ZnO–B₂O₃ glass is often adopted to reduce the sintering temperature of dielectric ceramics [16–18]. In order to obtain ZnO–B₂O₃ glass powder, but it is required a complicated process of melting, quenching and grinding.

Therefore, ZnO–B₂O₃ (ZB) oxides without treating have been chosen as a sintering aid to reduce the sintering temperature of Ba₄Sm₉.₃₃Ti₁₈O₅₄ (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 BaCO₃ (99%), Sm₂O₃ (99.9%), TiO₂ (99.5%) raw powders. According to the formula Ba₄Sm₉.₃₃Ti₁₈O₅₄, BaCO₃, Sm₂O₃, and TiO₂ 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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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 CuKα-radiation (λ = 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 TE01δ dielectric resonator method [19] with a network analyzer (Agilent 8753 ES), and the temperature coefficient (τf) 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. 1. Densities and shrinkages of BST ceramics with different amount of ZB addition.

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