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Low Temperature Sintering of 2.5ZnO-2.5Nb_2O_5-5TiO_2 Ceramics Doped with BaCu(B_2O_5) and its Compatibility with Ag

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Abstract: The effects of different doping amounts of BaCu(B_2O_5) (BCB) on the sintering behavior, dielectric properties and compatibility with Ag of 2.5ZnO-2.5Nb_2O_5-5TiO_2 (ZNT) ceramics were investigated. The sintering temperature of ZNT ceramics was effectively lowered from 1 100 ℃ to 900 ℃ with BCB addition. 3.0wt% BCB doped ZNT ceramic specimens sintered at 900 ℃ for 3 h exhibit optimum dielectric properties with values of ε_r=48, Qf=15 258 GHz, τ_f=41×10^{-6}/℃. Furthermore, no second crystalline phase and no silver migration were detected in the BCB-doped ZNT ceramic specimen co-fired with Ag, which indicates that 3.0wt% BCB doped ZNT ceramics could be a suitable candidate for LTCC applications.

Key words: microwave dielectric ceramics; low temperature sintering; dielectric property

BaCu(B_2O_5)掺杂2.5ZnO-2.5Nb_2O_5-5TiO_2陶瓷的低温烧结及其与Ag的相容性

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摘 要：研究了不同BaCu(B_2O_5)(BCB)掺杂量对2.5ZnO-2.5Nb_2O_5-5TiO_2(ZNT)陶瓷烧结行为、介电性能及与Ag相容性的影响规律。添加BCB可有效地将ZNT陶瓷的烧结温度从1 100 ℃降低至900 ℃。BCB添加量为3.0wt%，900 ℃烧结3 h所制得的ZNT陶瓷的微波性能良好：ε_r=48，Qf=15 258 GHz，τ_f=41×10^{-6}/℃。且在BCB掺杂ZNT陶瓷与Ag共烧样品中未检测到新生相和Ag的扩散，表明3.0wt%BCB掺杂的ZNT陶瓷与Ag的相容性良好，是一种很有潜力的LTCC材料。

关键词：微波介质陶瓷；低温烧结；介电性能
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0 Introduction

Low temperature co-fired ceramic (LTCC) technology has been generating considerable interests due to the miniaturization of multilayer dielectric devices for wireless communications, such as filters and antennas. For practical LTCC applications, the dielectric materials with low sintering temperature were required in order to co-fire with electrodes such as Ag and Cu.

The 2.5ZnO-2.5Nb_2O_5-5TiO_2 (ZNT) ceramics sintered at 1 100 ℃ exhibits good microwave dielectric properties of ε_r=58, Qf=16 300 GHz[1-2]. However, the temperature coefficient of resonance frequency($\tau_f \approx 90\times10^{-6}$/℃) is too high for practical applications[1-3]. Further investigations are mainly focused on the optimization of its microwave dielectric properties. For example, ReO_2 (Re=Sn, Zr, Ce, Bi) was introduced to the ZnO-Nb_2O_5-TiO_2 ceramic system to adjust its τ_f value[2, 4]. However, it must be sintered at 1 100 ℃,

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which is higher than the melting point of silver. Although Zhang et al and Kim et al further lowered the sintering temperature of ZnO-Nb_2O_5-TiO_2-ReO_2 (Re = Sn, Zr, Ce) ceramics to below 900 ℃ by adding V_2O_5-CuO or $FeVO_4$, much deterioration of Qf or silver migration emerged[5-7]. In our primary work, B_2O_3-CuO was added to the ZNT ceramic to lower its sintering temperature, but the result is not satisfactory.

Recently, $BaCu(B_2O_5)$ (BCB) was suggested being one of the promising sintering aids for the densification of dielectric ceramics at relatively low temperatures. For example, the addition of BCB can effectively lower the sintering temperature of $BaTi_4O_9$, BaO-Sm_2O_3-TiO_2 and $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics to 875 ℃[8-10]. However, the effect of BCB addition to the ZNT ceramics has not been reported in the literature concerned. In this paper, the influences of BCB addition on the sintering behavior and microwave dielectric properties of ZNT ceramics were investigated. The chemical compatibility of BCB added ZNT ceramics with silver was also studied.

1　Experiment

The BCB ceramic powder was synthesized by solid state reaction using high purity powders (>99%): BaO, CuO and B_2O_3. Proportionate amounts of the above raw materials were mixed in a nylon jar with ZrO_2 balls for 24 h. And then the mixtures were dried and calcined in air at 800 ℃ for 24 h. Specimens of ZNT ceramics were prepared by conventional mixed-oxide routes from high-purity oxide powders (>99%): ZnO, Nb_2O_5 and TiO_2. The raw materials were weighed according to the composition of $2.5ZnO$-$2.5Nb_2O_5$-$5TiO_2$ and were mixed in ethanol medium using ZrO_2 balls for 24 h. And then the mixtures were dried and calcined in air at 1 100 ℃ for 3 h. The calcined powder was remilled with different amount of as-synthesized BCB powder above (noted as $x$wt% BCB, x=2.0, 3.0, 4.0, 5.0) for 24 h. After drying, polyvinyl alcohol (PVA) was added to the calcined powder as a binder. Pellets with 10 mm in diameter and 5-6 mm in thickness were uniaxially pressed under a pressure of 80 MPa. These pellets were sintered in air at 870-960 ℃ for 3 h. The bulk densities of the sintered ceramic were measured by Archimedes′ method. Crystalline phases of the specimens were identified by X-ray powder diffraction patterns (XRD, Philips X′pert Pro MPC, Netherlands, $CuK\alpha_1$). Dielectric behaviors in microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method using a Network Analyzer (8720ES, Agilent, USA) and a temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficient of resonant frequency (τ_f) values were measured in the temperature range from 25 ℃ to 80 ℃, and calculated by the following equation:

$$\tau_f=\frac{\Delta f_0}{f_0\Delta T}=\frac{f_{80}-f_{25}}{f_{25}\times 55} \quad (1)$$

where f_{80} and f_{25} represent the resonant frequencies at 80 ℃ and 25 ℃, respectively.

For the investigation of chemical compatibility with silver, specimens were prepared by printing silver electrode over dense pellets, and then co-fired the specimens at 900 ℃ for 3 h. The phase composition and microstructures of as-sintered specimen were evaluated by XRD and SEM equipped with EDS.

2　Results and Discussion

2.1　Sintering Behavior

Fig. 1 shows the bulk densities of the $x$wt% BCB doped ZNT ceramic specimens (x=2.0, 3.0, 4.0, 5.0) sintered at 870-960 ℃ for 3 h. For the specimens sintered at 870 ℃, the bulk density was comparatively low when 2.0wt% BCB was added, and it increased with the increasing of BCB amount. The maximum bulk density (4.94 g/m^3) was obtained in the 3.0wt% BCB doped ZNT ceramic specimens sintered at 900 ℃ for 3 h. In our preliminary experiment, the saturated bulk density of pure ZNT ceramic specimens sintered at 1 100 ℃ for 3 h was 4.80 g/m^3. It should be noted that the theoretical density of ZNT ceramics is not

available because it is a mixture phase of $ZnTiNb_2O_8$ and $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$. Obviously, after adding BCB, the sintering temperature of the ZNT ceramics was efficiently decreased from 1 100 ℃ to 900 ℃. However, the bulk densities of the sintered specimens decreased as the amount of BCB further increased, which means >3.0wt% BCB is overweighed for the ZNT ceramics.

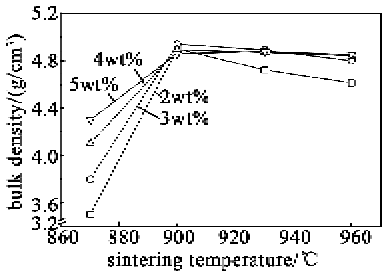

Fig. 1 Bulk density of ZNT ceramics with different BCB contents sintered at 870-960 ℃

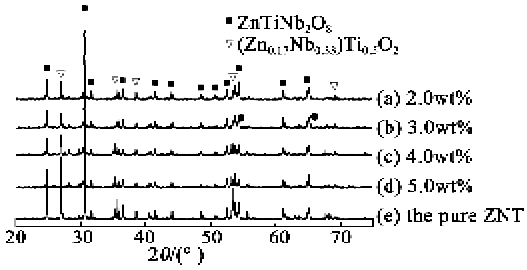

Fig. 2 The typical XRD patterns of the ZNT ceramics sintered at 900 ℃ for 3 h with 2.0wt%, 3.0wt%, 4.0wt%, 5.0wt%, and the pure ZNT ceramics sintered at 1 100 ℃ for 3 h

2.2 Phase Composition and Microstructure

Fig. 2 illustrates the typical XRD patterns of the pure ZNT ceramics sintered at 1 100 ℃ for 3 h and BCB doped ZNT ceramics sintered at 900 ℃ for 3 h. For BCB doped ZNT ceramic specimens, diffraction peaks could be indexed according to the patterns of $ZnTiNb_2O_8$ phase and $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$ phase. The relative content of $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$ phase in all the BCB-doped ZNT ceramic specimens is much lower than that in pure ZNT ceramic specimen, which indicates that the adding of BCB restrained the crystallization of $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$ in the sintered specimens. However, the relative content of $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$ phase in BCB-doped ZNT ceramic specimens gradually increased with the increasing of BCB addition. Although BCB phase was detected in other microwave dielectric ceramic systems with low melting point sintering aids addition, such as $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$[10-11], no diffraction peaks for BCB phase or other new phase were observed in all the specimens. A similar phenomenon occurred in the BCB doped $BaSm_2Ti_4O_{12}$ and $BaNd_2Ti_5O_{15}$[9]. Lim et al explained it as the fact that BCB liquid phase was not crystallized during cooling and remained as an amorphous phase[9].

Fig. 3 shows the typical SEM images of ZNT ceramics doped with 2.0wt%, 3.0wt%, 4.0wt%, 5.0wt% BCB sintered at 900 ℃ for 3 h. For the ZNT with 2.0wt% BCB addition, a porous microstructure formed due to the insufficient liquid phase. The numbers of pores decreased with the increasing of BCB amount and a dense microstructure without pores was developed in the specimen with 3.0wt% BCB. Furthermore, the grain size of ZNT increased with the increment of BCB. As the BCB increased to 5.0wt%, excessive BCB formed too much liquid phase, which might deteriorate the microwave dielectric properties of the sintered specimens.

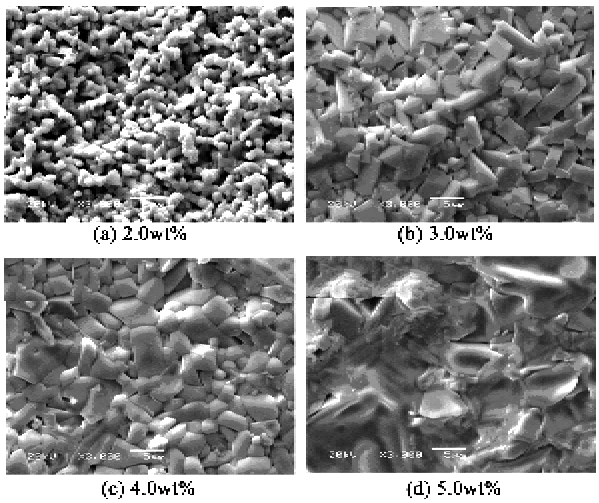

Fig. 3 SEM images of ZNT ceramics with different content of BCB sintered at 900 ℃ for 3 h

2.3 Dielectric Properties

Fig. 4 shows the dielectric properties of the BCB added ZNT ceramics sintered at 900 ℃ for 3 h. The relationship between ε_r value and BCB

content reveals basically a similar trend with that between bulk density and BCB content. Generally, the phase composition and density of the sintered ceramic specimen determine its dielectric constant, due to the differences of the ε_r value between various phase and pores[12]. The ε_r value of $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$ phase (94.5) is much higher than that of $ZnTiNb_2O_8$ phase (34.3) and pores (~1.0)[5,18]. The addition of BCB improved the densification of the ZNT ceramics and restrained the crystallization of $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$, resulting in the decrease of ε_r value of the sintered ZNT ceramic specimens. Another probable explanation for the decrease of ε_r is the addition of BCB, for its ε_r value is only 7.4.

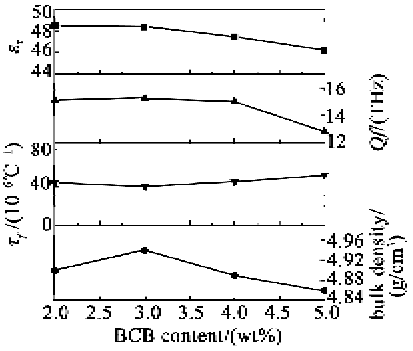

Fig. 4　Dielectric properties of BCB-doped ZNT ceramics sintered at 900 ℃ for 3 h

The Qf of BCB doped ZNT ceramic specimens varied slightly with the BCB content increasing from 2.0wt% to 4.0wt%, and then declined dramatically. This decline might be attributed to the excessive amorphous phase formed in the sintering process.

The τ_f of pure ZNT ceramics sintered at 1 100 ℃ for 3 h in our work is $90\times10^{-6}/℃$, much higher than the result of Kim's $(10\times10^{-6}/℃)$[2]. This difference might be attributed to the factors affecting the microwave dielectric properties of ceramic materials, such as measurement method, raw materials, experiment procedure, et c. Furthermore, the τ_f of the BCB doped ZNT ceramic specimens is almost invariant with increasing BCB. In general, the optimum microwave dielectric properties of $\varepsilon_r=48$, $Qf=15\ 258$ GHz, $\tau_f=41\times10^{-6}/℃$ were obtained in the 3.0wt% BCB doped ZNT ceramic specimen sintered at 900 ℃ for 3 h.

2.4　Compatibility with Silver

The chemical compatibility of the ceramic composite and silver is essential if it has to be used as a multilayer device with silver electrode for LTCC applications. Fig. 5 shows the XRD patterns of (a) the 3.0wt% BCB added ZNT ceramics sintered at 900 ℃ for 3 h and (b) the 3.0wt% BCB added ZNT ceramics co-fired with Ag electrode at 900 ℃ for 3 h. Only peaks of the ZNT ceramic phase ($ZnTiNb_2O_8$, $(Zn_{0.17}Nb_{0.33})Ti_{0.5}O_2$) and a pure silver phase were detected. This indicates that the ZNT ceramics did not react with silver and no other phase formed at 900 ℃. The silver migration of the 3.0wt% BCB doped ZNT ceramics was further investigated by SEM and EDS (Fig. 6). The silver profile sharply increased at the interface between ZNT ceramics and Ag electrodes. In addition, the concentrations of Zn, Nb and Ti in the Ag electrodes were very low. Combined with the XRD results, it can be concluded that the 3.0wt% BCB doped ceramic does not react with silver at 900 ℃. This makes 3.0wt% BCB doped ZNT ceramic a kind of promising dielectric material for LTCC technology.

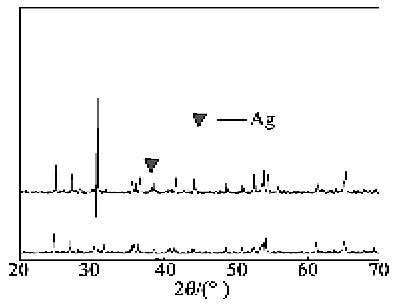

Fig. 5 XRD patterns of the 3.0wt% BCB-added ZNT ceramics sintered at 900 ℃ for 3 h, 3.0wt% of BCB-added ZNT ceramics sintered with Ag electrodes at 900 ℃ for 3 h

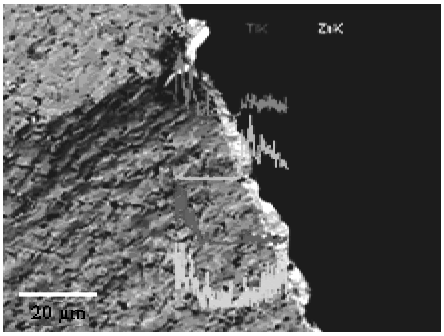

Fig. 6　SEM image and EDS of the interface between 3.0wt% BCB-added ZNT ceramics and Ag electrode

3 Conclusion

In this study, the effects of BCB addition on the sintering behavior and microwave dielectric properties of 2.5ZnO-2.5Nb_2O_5-5TiO_2 (ZNT) ceramics were investigated. The ZNT ceramics with proper BCB addition can be well sintered at 900 ℃ due to the liquid phase effect. Obviously, BCB could be a suitable sintering aid improving the densification of ZNT ceramics. The 3.0wt% BCB doped ZNT ceramic specimens sintered at 900 ℃ for 3 h has optimum dielectric properties of $\varepsilon_r=48$, $Qf=15\ 258$ GHz, $\tau_f=41\times10^{-6}/℃$. Furthermore, only ZNT ceramic phase as well as silver phase and no silver migration were detected in the BCB-doped ZNT ceramic specimen co-fired with silver, which indicates that 3.0wt% BCB doped ZNT ceramics could be a suitable candidate for LTCC applications.

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