

Sintering behavior and dielectric properties of BZN ceramic powders coated by CuSO_4

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$(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ (BZN) ceramics were synthesized by the traditional solid-state reaction method. Copper oxide is known as a good sintering aid for microwave dielectric ceramics and to be less reactive toward silver. We have introduced the CuO into BZN by modifying BZN surface by a CuO thin layer on the calcined powder instead of mixing CuO directly with BZN powder. A CuO precursor solution of CuSO_4 , was used to prepare the CuO thin layer. This paper describes the effect of CuO layer on the sintering behavior, phase composition and dielectric properties of BZN ceramics. The results showed that appropriate CuO addition could accelerate the sintering process and lower the densification temperature to 900 °C. The optimal concentration of CuSO_4 was found to be 0.5 M. The BZN ceramic sintered at 900 °C presented good microwave dielectric properties i.e. $\epsilon_r = 141$ and $Qf = 426$ GHz, which is much better than those of CuO doped BZN ceramic ($\epsilon_r = 134$ and $Qf = 287$ GHz).

Key words: Microwave dielectric ceramics, Low temperature sintering, Dielectric property.

Introduction

Microwave dielectric ceramics play an important role in the miniaturization of microwave components such as microwave oscillators and filters. With the development of mobile communication, compact size is an essential requirement in many microwave applications. Low temperature co-fired ceramics (LTCC) possessing good microwave dielectric properties have been widely investigated due to the necessity for miniaturization of devices in order to reduce the size of wireless communication system. Thus, low temperature sintering of this pyrochlore type like $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ -based ceramics have been studied [1-3] in order to replace noble metals like Pt or Pd by highly conductive, cheaper and low melting internal electrode metals such as copper (melting point = 1080 °C) or silver (melting point = 961 °C) in LTCC technology. Recently, Cubic bismuth zinc niobate pyrochlore ceramics (BZN) has emerged as a good microwave dielectric material because it exhibits compositionally adjustable temperature coefficients of capacitance (TCC), high permittivity (~ 170), relatively low dielectric loss ($\sim 10^{-4}$) and the lower firing temperature (below 1100 °C). These expect performance make this ceramic a potential candidate for applications in integrated decoupling capacitor, microwave resonator, etc [4-7].

Much work has been performed on reducing the sintering temperature of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$. Its

sintering temperature can be decreased to 950 °C by adding 4wt% silver into BZN [8] and even lower to 900 °C by adding 5 mol% BiVO_4 into BZN (the optimum dielectric properties: $\epsilon_r = 153$; $Q = 2100$; $\tau_f = 350 \times 10^{-6}$) [9]. The 0.5 wt% V_2O_5 doped BZN ceramics sintered at 900 have the optimum dielectric properties; $\epsilon_r = 154$, $\tau_f = -403 \times 10^{-6}/(2 \text{ MHz})$ and $\tan\delta = 0.0033$ [10]. Copper oxide has been known as a good sintering aid for electronic ceramics and less reactive toward silver. However, the other studies have reported that the glasses and oxide dopants exhibited pronounced effects on the microwave dielectric properties and phase composition of the materials. Large and interconnected pores were observed due to the agglomeration of dopants during sintering process [11-14]. The addition of CuO undermined the microwave dielectric properties. it is difficult to not only lower the sintering temperature of BZN ceramics to bellow 1000 °C but also not significantly diminishing of their microwave dielectric properties.

In this work, We have lowered the sintering temperature of BZN microwave ceramics using dissolvable copper salts (CuSO_4), in order to prevent the agglomeration of dopants during sintering process. We propose to introduce the CuO into BZN by modifying the surface of BZN by CuO thin layer on the calcined powder. The process will reduce the amount of sintering aid(CuO) and eliminate the negative impact of sintering aid on microwave dielectric properties such as permittivity and quality factor. Addition of thin-coating has become a new method to lower the sintering temperature of microwave dielectric ceramics. In order to form a contrast, different weight fractions of

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CuO were added to the powder. The sintering temperature, bulk densities, phase composition and microwave dielectric properties have been investigated.

Experimental

The BZN materials were synthesized via the conventional mixed oxide process, using Bi_2O_3 (> 99%), ZnO (> 99%) and Nb_2O_5 (> 99%) powders as starting materials. The powders were weighed according to the composition and then ball milled using ZrO_2 balls in an ethanol medium for 12 hrs. After drying, the mixtures were put in corundum crucibles and calcined in air at 860°C for 4 hrs. Fig. 1 shows the XRD patterns of BZN sintered at 860°C for 4 hrs.

The calcined powder of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ was coated with different concentration of CuSO_4 solutions. The BZN powder (20 g) was put into CuO precursor solutions (50 ml) (0.1, 0.3, 0.5, 0.7 M CuSO_4). After stirring for 5 min by magnetic stirrer, standing for 5 min, the BZN powder was filtrated by aspirator and dried at 120°C for 10 hrs. Simultaneously, In order to form a comparison and contrast, different content of CuO (> 99%) (1 wt%-5 wt%) were added to the powder and mixed again in an ethanol medium. After drying, the BZN powders were ground well and mixed with a 5.0 wt% of 10% PVA solution, pelletized with a 60 ~ 80 mesh sieve. All samples were prepared using an uniaxial hydraulic press at 14 KN, the samples size were 10 mm diameter and 3 ~ 4 mm height. These samples were sintered at 800°C ~ 950°C in air for 3 hrs to yield the dense ceramics.

The microwave dielectric properties of sintered BZN tablets were evaluated by vector network analyzer (Agilent Technologies Inc, N5230C-220, USA). The crystal phases of the specimens were examined by XRD (Bruker, D8 ADVANCE, Germany, 40 kV-40 mA, $\text{Cu K}\alpha = 0.15406\text{ nm}$). The bulk densities of the sintered pellets were measured using the Archimedes. The relative density was defined as the ratio of the measured

bulk density over the theoretical density, which could be evaluated from the chemical formula and the lattice parameters determined by X-ray diffraction. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (JEOL, JSM-5610LV, Japan) and an energy dispersive X-ray spectrometer (EDS). The sample surface was spray gold by sputter coater (JEOL, JFC-1600, Japan).

Results and Discussion

The variations in density of the BZN- CuO composites are studied as a function of the CuO content and sintering temperature. The density of the CuO -doped and CuSO_4 -coated BZN ceramics sintered at different temperature for 3 hrs is shown in Fig. 2. It is obviously that the density change is strongly dependent on the CuO content and sintering temperature. Initially, the relative density increased with CuO content and sintering temperature due to enlarged grain size as observed in Fig. 4. After reaching the maximum at 900°C with 0.5 M CuSO_4 addition, it slightly decreased owing to the excess liquid phase. The formations of the liquid phases were attributed to the additions of CuO . The amount of liquid phase is very little when a small amount of CuO is added. There is not enough liquid phases to prompt BZN particles slip, rearrangement and dissolution-deposition, so the sample densification is limited. However, excessive amounts of liquid phases will increase the thickness of liquid film between the ceramic particles, leading to ceramic particles dispersed to each other, resulting in a decrease of the density. It seems that the densification of BZN ceramics at low temperatures is attributable to CuO . On the other hand, It is obviously that the mass transfer of solid-sintered process is strongly dependent on the sintering temperature. In fact, the driving force of mass transfer process increases when temperature increases, and diffusion coefficient increase with driving force increment. It seemed that raising the temperature could promote the densification of BZN ceramics. However, an unusually high sintering temperature ($> 900^\circ\text{C}$) could contribute to an abnormal grain growth at a higher CuO content, resulting in a decrease of the density. The density increase is due to the combined effects of higher temperatures and sintering aids as well as reduction in porosity as shown in Fig. 4. It seemed that adding CuO could contribute to the densification of BZN ceramics. The maximum density was found to be 96.9% with 0.5 M CuSO_4 coated and 98.3% with 3 wt% CuO doped.

Fig. 3 shows the XRD patterns of CuSO_4 precursors coated ceramics sintered at 900°C for 3 hrs. The X-ray diffraction patterns of the BZN ceramics have not significant change with various CuSO_4 precursors coated, and second phase was not observed. Even when the concentration of CuSO_4 is as high as 0.7 M, no

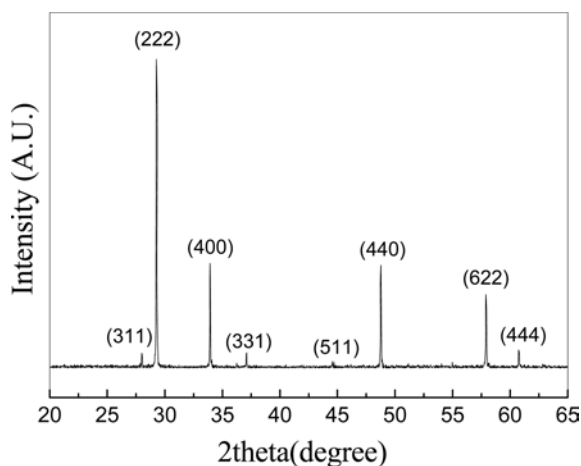


Fig. 1. XRD patterns of BZN sintered at 860°C for 4 hrs.

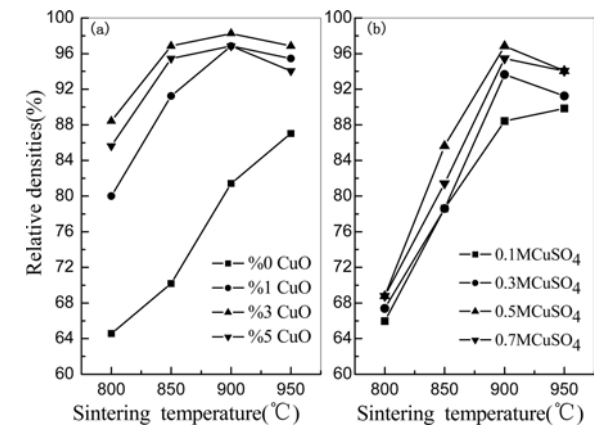


Fig. 2. Relative densities of:(a)CuO doped BZN,(b)CuSO₄ coated BZNceramics sintered at different temperature for 3 hrs.

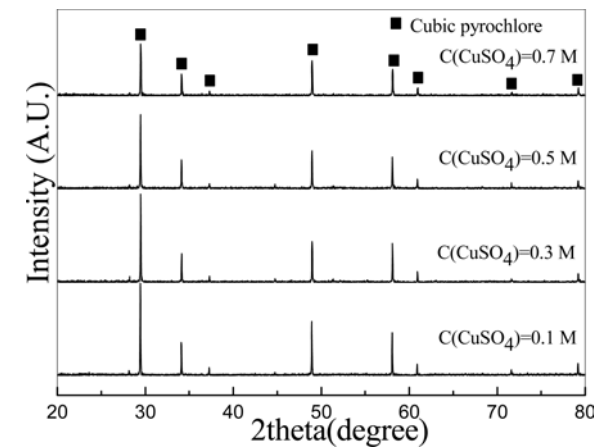


Fig. 3. XRD patterns of CuSO₄ precursors coated on (Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O₇ powders sintered at 900 °C for 3 hrs.

extra peaks are observed in the XRD pattern and CuO phase is not found either, which is due to the fact that CuO liquid phase is not crystallized during the cooling process.

The surface microstructural photographs of (Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O₇ ceramics with different concentration of CuSO₄ solution coated were demonstrated in Fig. 4. The

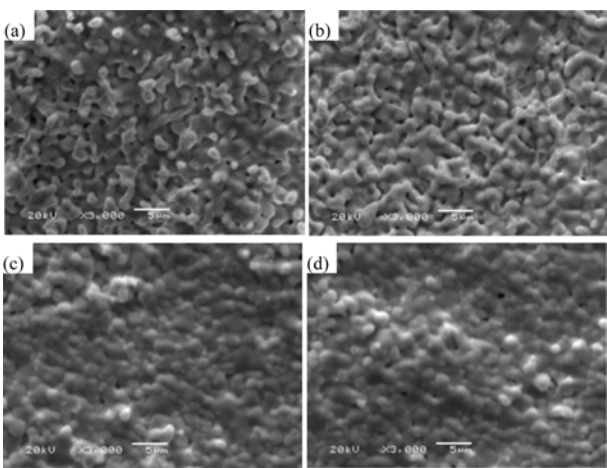


Fig. 4. SEM of (a) 0.1MCuSO₄ coated BZN, (b) 0.3MCuSO₄ coated BZN (c) 0.5MCuSO₄ coated BZN (d) 0.7MCuSO₄ coated BZN. All samples were processed at 900 °C for 3 hrs,

grain size increased with increasing the concentration of CuSO₄ due to the liquid phase effect. At the level of 0.1 M CuSO₄ solution addition, porous specimens were observed, due to the amount of the liquid phase was insufficient for sintering of the ceramics as shown in Fig. 4(a). The microstructure became dense with increasing CuSO₄ content. At 0.5 M, the pores were eliminated, resulting in a homogeneous distribution of grains. However, abnormal grain growth was detected for BZN specimens incorporating 0.7 M CuSO₄ solution at 900 °C, which might directly affect the microwave dielectric properties of BZN samples.

Figs. 5(a) and 5(b) shows the EDS spectra of BZN specimen with 0.5 M CuSO₄ solution and with 0.3 wt% CuO additions, respectively. It revealed that the surface of the ceramics have the same element Bi, Zn, Nb, Cu, and O. The regions of Fig. 5(b) were Cu and O rich compared with the region of Fig. 5(a). The formations of the liquid phases were attributed to the additions of CuO. In addition, high CuO additions also produce more liquid phase, which is believed to significantly affect the microwave dielectric properties of the

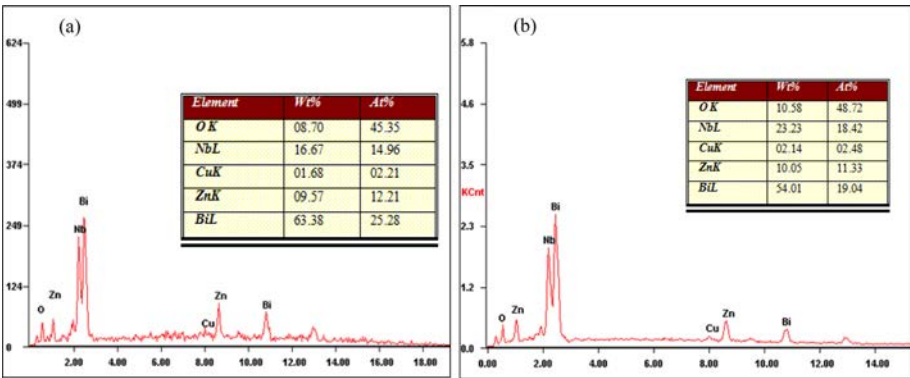


Fig. 5. EDS spectra of (a) 0.5MCuSO₄ coated BZN (b) 0.3 wt% CuO doped BZN. All samples were processed at 900 °C for 3 hrs,

ceramic samples. The liquid coating method can reduce the amount of sintering aid and minimized the negative impact of sintering aid on dielectric properties.

Fig. 6 shows the relative density, ϵ_r , Qf of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ ceramics with different concentration of CuSO_4 solution coated. The relationships between dielectric constant (ϵ_r) value and the concentration of CuSO_4 solution reveal the same trend with those between densities and the concentration of CuSO_4 solution because higher density means lower porosity. In fact, the number of polarons per unit volume of ceramics increases when density increases, and dielectric constant increase with density increment. The ϵ_r value at 0.1 M CuSO_4 was small at 118, due to the porous microstructure. The slightly increase in the dielectric constant was attributed to a higher density. The highest dielectric constant was obtained for 0.5 M CuSO_4 coated BZN ceramics at 950 °C. However, it slightly reduces when the CuSO_4 content exceeded 0.5 M. The dielectric constant was slightly decreased with increasing the concentration of CuSO_4 solution due to a reduction in the density.

At the level of 0.1 ~ 0.5 M CuSO_4 , the Qf values of BZN ceramics slightly increased with increasing the concentration of CuSO_4 . However, the Qf value

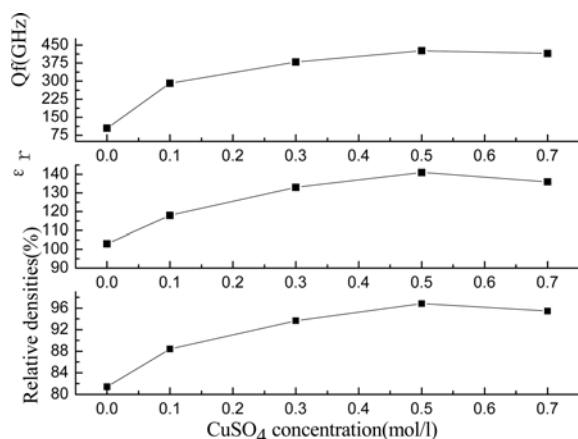


Fig. 6. The relative density, ϵ_r , Qf of CuSO_4 coated $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ ceramics sintered at 900 °C for 3 hrs.

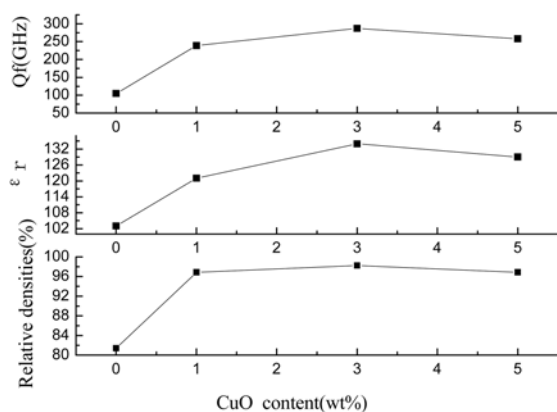


Fig. 7. The relative density, ϵ_r , Qf of CuO doped $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ ceramics sintered at 900 °C for 3 hrs.

decreased from 426 to 415 GHz as the concentration of CuSO_4 solution increased from 0.5 M to 0.7 M. The microwave dielectric loss is mainly caused not only by the intrinsic loss (lattice vibrational modes), but also by the extrinsic loss (a second phase, grain sizes, oxygen vacancies, and porosity or densification). Relative density also plays an important role in controlling the Qf values. The degradation of the Qf value was attributed to a decrease in density. In fact, a decreased Qf with higher CuSO_4 coated ceramics could be related to abnormal grain growth and grain boundary phases, as observed in Fig. 4. Due to not only the observed grains of BZN ceramics with 0.5 M CuSO_4 solution being more uniform than those of others but also a revealed decrease in lattice imperfection and porosity. Moreover, the decrease in the Qf values for highly CuSO_4 coated BZN ceramics could be a result of the low Qf of the liquid phase. Apparently, a decrease in the Qf value for the sample with 0.7M CuSO_4 could be attributed to excessive CuSO_4 content. The 0.5 M CuSO_4 coated BZN ceramics exhibits the best properties; $\epsilon_r = 141$, Qf = 426 GHz.

Fig. 7 shows the relative density, ϵ_r , Qf of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ ceramics with various CuO additions sintered at 900 °C for 3 hrs. The ϵ_r and Qf value of BZN ceramics with 3 wt% CuO addition was found to be higher than the one with 5 wt% CuO addition. Higher CuO contents would degrade the ϵ_r and Qf value of BZN ceramics since the grain boundary phases and abnormal grains were pronounced products at higher CuO contents. The 3 wt% CuO doped BZN ceramics exhibits the best properties; $\epsilon_r = 124$, Qf = 287 GHz. The CuSO_4 coated BZN sintered at 900 °C has exhibited better microwave dielectric properties ($\epsilon_r = 141$, Qf = 426 GHz) than those of CuO doped BZN ($\epsilon_r = 134$, Qf = 287 GHz). The thin layer dopant coating process has been found to be a very effective way to lower ceramic sintering temperature without the significant decrease in its dielectric properties.

Conclusions

BZN powders were coated with a CuO thin layer using a precursor solution of CuSO_4 . The sintering temperature of BZN ceramic was lowered to 900 °C. That is, this process allows employing BZN ceramics as LTCC using silver as internal electrode. The process reduces the amount of sintering aid but obtained superior dielectric properties as compared with the BZN ceramic specimen doped by CuO through conventional oxide solid mixing method. The thin layer dopant coating process has been found to be a very effective way to lower ceramic sintering temperature without the significant decrease in its dielectric properties. The $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ ceramic composite could be well sintered at 900 °C for 3 hrs when 0.5 M CuSO_4

solution coated and showed good dielectric properties i.e. $\epsilon_r = 141$ and $Qf = 426$ GHz. This result is superior to by conventional CuO oxide solid mixing method ($\epsilon_r = 134$, $Qf = 287$ GHz).

Acknowledgments

This work was supported by the Henan Provincial Natural Science Foundation (122102210431) and the Educational Commission of Henan Province (12A430001).

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