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Low temperature reaction-sintering and microwave dielectric properties of $ZnO–Nb_2O_5–2TiO_2$ ceramics

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Abstract Low-temperature fired $ZnO–Nb_2O_5–2TiO_2$ ceramics co-doped with $CuO–V_2O_5$ were fabricated by a reaction-sintering process. $CuO–V_2O_5$ addition effectively lowered the sintering temperature of $ZnO–Nb_2O_5–2TiO_2$ ceramics to 950°C due to the liquid phase sintering. The phase compositions and microwave dielectric properties of $ZnO–Nb_2O_5–2TiO_2$ ceramics depended on the $CuO–V_2O_5$ content and sintering temperatures. Typically, 1.5 wt% $CuO–V_2O_5$ co-doped ceramics sintered at 950°C for 5 h exhibited optimum microwave dielectric properties of $\varepsilon_r = 45.9$, $Q \times f = 12{,}200$ GHz, $\tau_f = -1.8$ ppm/°C. In addition, such sample was compatible with Ag electrode, suitable for the low-temperature co-fired ceramics (LTCC) applications.

1 Introduction

In recent years, along with the rapid growth in wireless communications industry, a variety of microwave devices such as filters, duplexers, resonators and antennas were well developed [1]. Low-temperature co-fired ceramic (LTCC) technology make it possible to integrate many kinds of electronic components in a compact multilayer ceramic structure [2], and silver has been widely used as the internal electrode in the multilayer devices. To realize cofiring with Ag electrode, the processing temperature of the microwave dielectric ceramics must be below 960°C because the melting point of Ag is 960°C [3, 4].

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The $ZnTiNb_2O_8$ ceramics exhibit an excellent quality factor of 42,500 GHz and dielectric constant of 34 [5], which would be one of the new materials suitable for the applications at microwave frequencies. However, the larger negative temperature coefficient of resonant frequency ($\tau_f = -52$ ppm/°C) and higher sintering temperature (1250°C) restrict its application in co-firing ceramic device. Materials with large positive τ_f such as TiO_2 ($\tau_f = +450$ ppm/ °C) were usually used to tune the temperature coefficient to near zero [6]. D.W. Kim et al. reported that $ZnO–2TiO_2–Nb_2O_5$ ceramics have suitable relative permittivity of 58, $Q \times f$ value of 16,300 GHz and τ_f of 10 ppm/ °C [7] at 1100 °C. To reduce the sintering temperatures, the low-melting glasses and low-melting oxide composites are always added to ceramics [8, 9].

Reaction-sintering process is a simple and effective route to synthesize ceramics. The calcination step is by passed and the mixture of the materials is sintered directly [10]. In our previous work, $ZnO–Nb_2O_5–2TiO_2$ (hereafter referred to as ZTN) composite ceramics were prepared by reaction-sintering process at 1100 °C [11]. In this paper, the $CuO–V_2O_5$ (hereafter referred to as CV) were employed as sintering aid for its lower eutectic point (630 °C) [12–14]. The effects of CV addition on phase compositions, sinterablity, and microwave dielectric properties of ZTN composite ceramics were investigated.

2 Experimental procedures

CV co-doped ZTN ceramics were prepared by reaction-sintreing method. High-purity oxide powders (≥99 %) were used as raw materials. Stoichiometric starting powders according to the compositions of $ZnO–Nb_2O_5–2TiO_{2-x}$ wt% ($CuO–V_2O_5$) ($1 \le x \le 2$) were milled in

ethanol with ZrO_2 balls. The mixture powders were dried, granulated with 5 wt% PVA as binder, sieved, and then pressed into pellets ($\Phi = 11.5$ mm × 5.5 mm) under a pressure of 198 MPa. These pellets were sintered from 900 to 1000°C for 5 h in air with a heating rate of 5°C/min.

The bulk densities of the ZTN composite ceramics were measured by Archimedes method. The theoretical densities were calculated by the following formula:

$$\rho_{theo} = \frac{W_1 + W_2}{W_1/\rho_1 + W_2/\rho_2} \quad (1)$$

where ρ_1, ρ_2 and W_1, W_2 are the theoretical densities and weight fractions of material 1 and material 2 respectively. The crystal structures were analyzed using X-ray diffraction (XRD) with Cu Ka radiation (Rigaku D/MAX2550, Japan). In order to analyze the microstructure, the sintered specimens were polished and thermally etched at 200°C lower than their sintering temperatures. Microstructures were performed by scanning electron microscope (FEI Co. Eindhoven, Netherlands). The microwave dielectric properties were measured by the $TE_{01\delta}$ shielded cavity method using a vector network analysis (ZVB20, Rohde & Schwarz, Germany). The temperature coefficient of resonant frequency (τ_f) was calculated with the following equation:

$$\tau_f(ppm/^oC) = \frac{f_{80} - f_{25}}{f_{25} \times (80 - 25)} \times 10^6 \quad (2)$$

where f_{80} and f_{25} were the $TE_{01\delta}$ resonant frequency measured at 80 and 25°C, respectively.

3 Results and discussions

Figures 1 and 2 show the XRD patterns of the ZTN specimens sintered at different temperatures and doped with various amount of CV, respectively. For comparison, the XRD pattern of undoped ZTN ceramics sintered at 1100°C is given in Fig. 2. As shown in Figs. 1 and 2, all the samples contain two phases: $ZnTiNb_2O_8$ (JCPDS#88-1973) and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (ICDD–PDF#39-0291). According to XRD analysis and the literatures [11, 15], the following reaction formulae (3) hold during the sintering process.

$$ZnO + Nb_2O_5 + TiO_2 \rightarrow ZnTiNb_2O_8,\ ZnTiNb_2O_8 + TiO_2 \rightarrow Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2 \quad (3)$$

The quantitative ratios of $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phases calculated from the major peak intensities of the two phases are listed in Table 1. As shown in Table 1, for the ZTN specimens doped with 1.5 wt% CV, with increasing sintering temperatures, the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase content increases accompanying with the

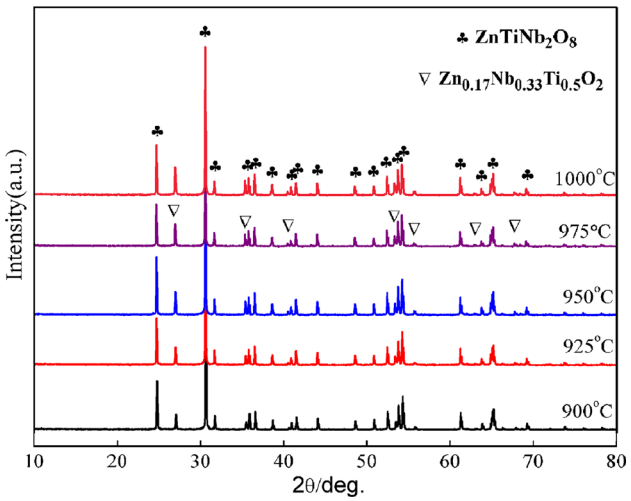

Fig. 1 X-ray diffraction patterns of ZTN ceramics added with 1.5 wt% CV sintered at different temperature

decreases of $ZnTiNb_2O_8$ phase. The content of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase reaches 24.94 % for the ZTN ceramic sintered at 1100 °C. For CV-doped ZTN ceramics sintered at 950 °C, $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase content shows the highest value at $x = 1.5$. Thus, sintering temperature and CV content are two important factors to control the quantitative ratios of $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$.

Figure 3 shows the SEM micrographs of CV-doped ZTN ceramics after polishing and thermal etching. With increasing sintering temperature and CV content, it can be observed that pores of specimens decrease and the grain sizes increase. Well-dense microstructures are obtained at 950 °C as $x \geq 1.5$, indicating that CV is an effective sintering aid to lower the sintering temperature of ZTN

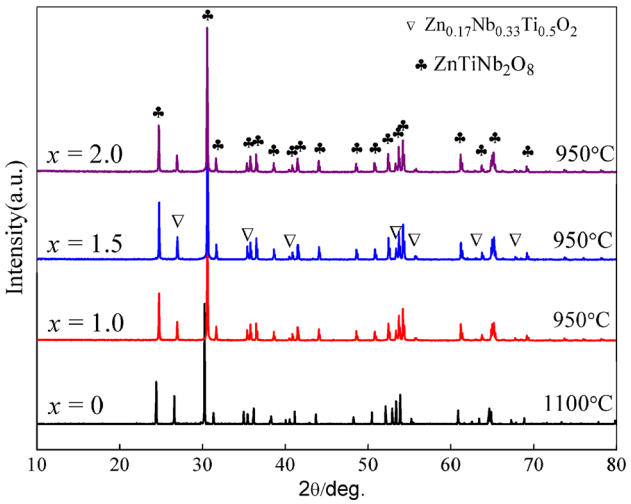

Fig. 2 X-ray diffraction patterns of ZTN ceramics added with different amount of CV sintered at 950 °C and the undoped ZTN sintered at 1100 °C

Table 1 Quantitative ratios between $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phases, average grain sizes and microwave dielectric properties of ZTN ceramics with different CV content sintered at various temperatures

Sintering temperature	900 °C	925 °C	950 °C	975 °C	950 °C	950 °C	1100 °C
x value	1.5	1.5	1.5	1.5	1.0	2.0	0
$ZnTiNb_2O_8$ (wt%)	90.1	87.9	85.8	82.9	86.1	87.3	75.1
$Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (wt%)	9.9	12.1	14.2	17.1	13.9	12.7	24.9
Average grain size (μm)	1.6	1.9	2.5	2.9	1.8	3.2	4.5
ε_r	42.4	43.0	45.9	46.3	42.5	40.8	49.3
$Q \times f$ (GHz)	10,000	11,400	12,200	12,100	10,000	6800	22,000
τ_f (ppm/ °C)	−18.2	−11.2	−1.8	3.4	−5.8	−14.8	10.4

% of $ZnTiNb_2O_8 = I_1/(I_1 + I_2) \times 100$ %; % of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2 = I_2/(I_1 + I_2) \times 100$ %

I_1 intensity of the major peak of $ZnTiNb_2O_8$ at 2θ around 15.259°, I_2 intensity of the major peak of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ at 2θ around 13.515°

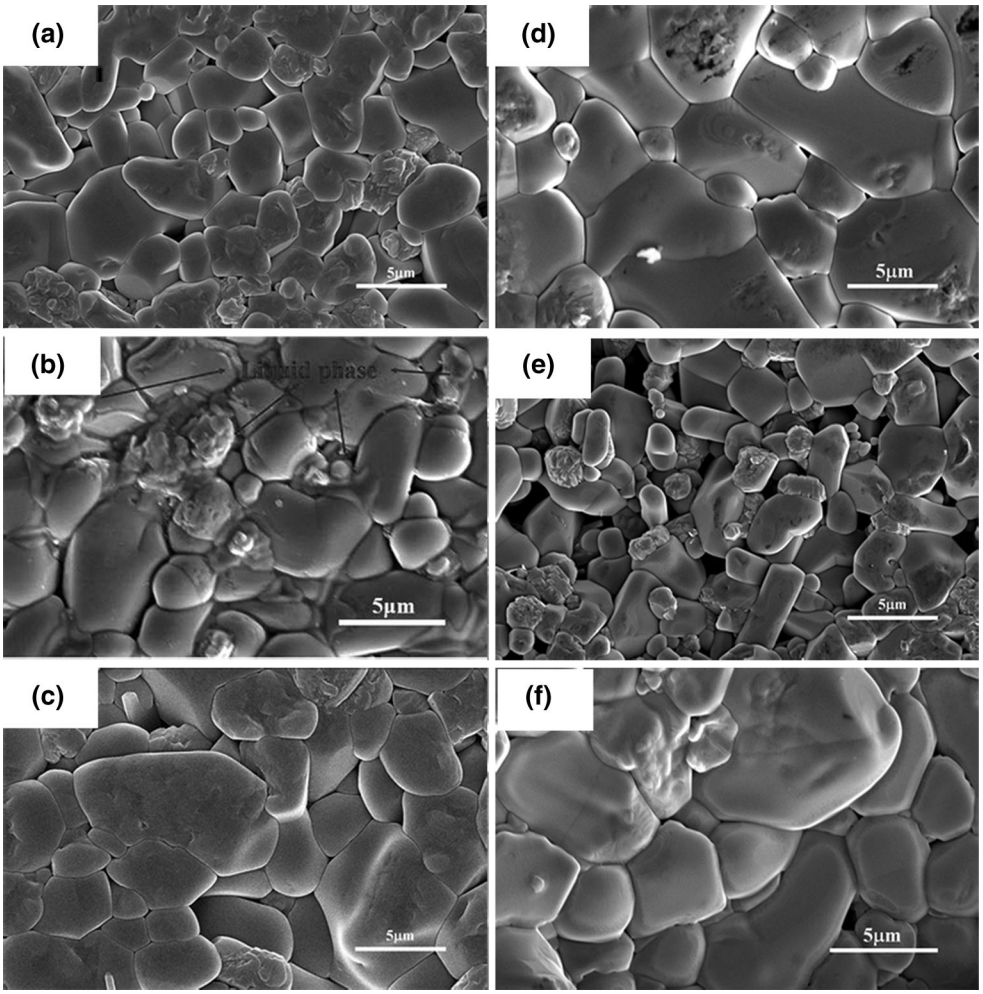

Fig. 3 SEM micrographs of ZTN ceramics: added with 1.5 wt% CV sintered at **a** 925 °C; **b** 950 °C; **c** 975 °C; **d** the undoped ZTN ceramic sintered at 1100 °C **e** added with 1.0 wt% CV sintered at 950 °C, **f** added with 2.0 wt% CV sintered at 950 °C

ceramics. In order to obtain the average grain sizes, the statistics of average grain size were calculated on the more than 300 particles in each sample, and the mean grain sizes are listed in Table 1. The grain size of the undoped ZTN (Fig. 3d) is in the range of 4–6 μm. The average grain size of the CV-doped specimens are in the range of 1.6–3.2 μm.

Figure 4 presents the relative density of the CV-doped ZTN ceramics sintered at different temperatures. The dot on the vertical axis shows the relative density of the undoped ZTN ceramic sintered at 1100°C. As shown in Fig. 4, the samples doped with 1.0 wt% CV display the lower relative densities, indicating that 1.0 wt% CV doping

is not enough to efficiently densifying the ceramics at these sintering temperatures. Furthermore, the relative densities of samples with 1.5 and 2.0 wt% were more than 95 % at 950°C, which means that the CV is a very effective low-temperature additive.

Figure 5a shows the ε_r values of CV-doped ZTN ceramics sintered at different temperatures. The dielectric constant values in Fig. 5a are corrected by following equation [16]:

$$\varepsilon_r = \varepsilon_{obs}(1 + 1.5P),\ P = 1-R \tag{4}$$

where ε_{obs} is the measured dielectric constant value, R is the relative density, P is the porosity. The theoretical dielectric constant values of 1.5 wt% CV doped ZTN ceramics calculated by Lichtenecker empirical logarithmic mixing rule [17]:

$$\ln \varepsilon_r = \upsilon_1 \ln \varepsilon_1 + \upsilon_2 \ln \varepsilon_2 \tag{5}$$

where ε_1 and ε_2 are the dielectric constant values of $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$; $\upsilon_1$and are their volume fraction. The theoretical permittivities given in Fig. 5a are different from the corrected ones, but are close to each other, which indicates that the trend of ε_r values of CV-doped ZTN ceramics is depended on sintering temperature and CV content, which is consistent with that of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ content ($\varepsilon_r = 95$ [18]).

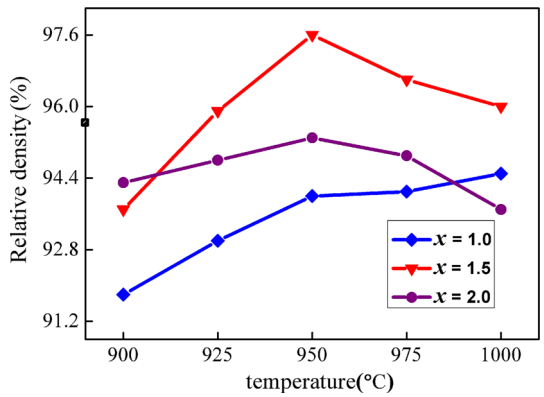

Fig. 4 The relative densities of the ZTN ceramics with the addition of CV sintered at different temperatures

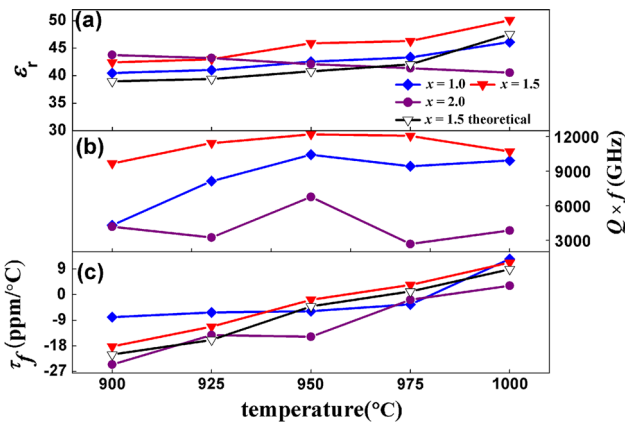

Fig. 5 The microwave dielectric properties of CV-doped ZTN ceramics sintered at various temperatures

Figure 5b illustrates the $Q \times f$ values of CV-doped ZTN ceramics sintered at different temperatures. With increasing sintering temperature, the $Q \times f$ values initially increase and then decrease thereafter. It is believed that the density play an important role in controlling dielectric loss, as found in other microwave dielectric materials [19–21]. In addition, the decrease of $Q \times f$ values at higher temperature(≥950 °C) is due to the increase of the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ ($Q \times f = 15{,}000$ GHz [18]) phase content. Thus, both density and the $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ phase content affect the $Q \times f$ values of the ceramics. The deterioration in $Q \times f$ values of the ZTN specimens with 2.0 wt% CV can be attributed to the presence of excess liquid phases, which may induce more significant deterioration in dielectric properties of ceramics [6].

The τ_f values of CV-doped ZTN ceramics sintered at different temperatures are given in Fig. 5c. As known to all, the mixing rule of τ_f values can be described as follows:

$$\tau_f = \upsilon_1\tau_{f1} + \upsilon_2\tau_{f2} \tag{6}$$

where τ_{f1} and τ_{f2} represent the τ_f values of $ZnTiNb_2O_8$ and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$, respectively, υ_1 and are their volume fraction. For 1.5 wt% CV added ZTN ceramics sintered at different temperature, the measured τ_f values are close to the theoretical ones. As shown in Table 1, an increase in τ_f values consistent with the increase of secondary phase content is observed, which means the secondary phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ ($\tau_f = +237$ ppm/°C [18]) is the dominating factor to control τ_f values of ZTN ceramics.

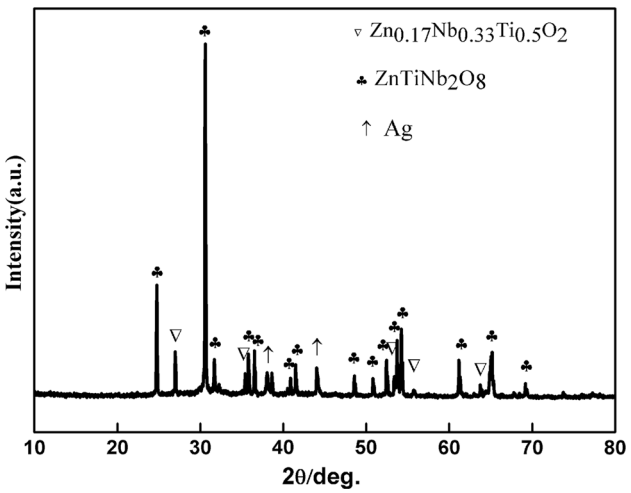

Fig. 6 XRD pattern of 1.5 wt % CV added ZTN sample co-fired with Ag powders at 950°C

Typically, the ZTN ceramics with 1.5 wt% CV and sintered at 950°C have excellent microwave dielectric properties of $\varepsilon_r = 42.9$, $Q \times f = 12{,}200$ GHz, $\tau_f = -1.8$ ppm/°C.

Figure 6 show the crystalline phases of the 1.5 wt% CV-doped ZTN sample co-fired with 20 wt% Ag powders at 950°C. From the XRD pattern, Ag powders does not produce a new phase in the sample, which means the CV-added ZTN ceramics are able to match with the Ag electrode well.

4 Conclusion

ZTN composite ceramics co-doped with CV ceramics could be synthesized by a reaction-sintering process. The sintering behavior, phase compositions and the microwave dielectric properties of the composite ceramics were investigated. The ZTN ceramics with small amounts of CV addition can be well sintered at 950 °C. The change of second phase $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ content depend on CV content and sintering temperature, which ultimately affect the microwave dielectric properties of CV-doped ceramics. The ZTN dielectrics with 1.5 wt% CV sintered at 950 °C showed the optimum microwave dielectric properties: $\varepsilon_r = 45.9$, $Q \times f = 12{,}200$ GHz, $\tau_f = -1.8$ ppm/ °C. The XRD result of co-fired sample showed that the ZTN ceramics were chemical compatible with Ag at 950 °C.

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