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Effect of CuO or/and V_2O_5 oxide additives on Bi_2O_3–ZnO–Ta_2O_5 based ceramics

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Abstract

Pure $Bi_2Zn_{2/3}Ta_{4/3}O_7$ (β-BZT) ceramics should be densified above 1000 °C. The sinter ability was improved with the addition of CuO or/and V_2O_5 (express as CuO/V_2O_5) into β-BZT ceramics. The sintering temperature of CuO/V_2O_5 doped β-BZT ceramics was reduced down to 930 °C. The structure of β-BZT doped with CuO was still monoclinic zirconolite structure. The structure of V_2O_5 doped β-BZT was changed. Fluorite phase appeared when doping amount was above 0.3 wt.%. The *Qf* values of β-BZT doped with CuO were higher than that of V_2O_5 doped specimens. By adding 0.05 wt.% CuO together with 0.05 wt.% V_2O_5 into β-BZT ceramics, microwave dielectric properties were $\varepsilon =\sim 63$ and $Qf =\sim 6787$ at ∼5.35 GHz with $\alpha_\varepsilon =\sim 73$ ppm/°C at 1 MHz at a sintering temperature of 930 °C which retained a relative high microwave dielectric properties compared with the undoped β-BZT sintered at 1030 °C.

Keywords: A. Sintering; Bismuth-based ceramics; CuO/V_2O_5; Microwave dielectric properties

1. Introduction

The development of multilayer devices for microwave applications has received wide attraction since multilayer devices have unique characteristics of small size and high volume efficiency. It is well known that high-frequency performance of co-fired multilayer devices is generally dominated by the metal conductivity [1]. In order to reduce the dielectric loss, the electrodes with higher conductivity such as silver have to be used in the co-firing process. At the same time, low sintering temperature and chemical compatibility with the electrode material are needed for host dielectric material during co-firing. Studies of the dielectric properties of bismuth-based pyrochlores have demonstrated that they may be suited toward applications as co-fired dielectric component [2,3,6]. Bi_2O_3–ZnO–Ta_2O_5 (BZT) series ceramics were required to be sintered above 1000 °C to reach high density. For co-firing process, this sintering temperature is too high to use pure silver electrode.

To reduce the sintering temperature of dielectric materials, liquid phase sintering aid was effectively used [4,5]: glass or other low-melting point materials were mixed with dielectric materials. However, the microwave dielectric properties of dielectric materials were also deeply affected by the liquid sintering temperature due to the development of microstructure at low sintering temperature or the reaction between host material and additives. Hiroshi Kagata et al. [6] reported that with the addition of CuO and V_2O_5 into $BiNbO_4$, this ceramics could be sintered at a temperature as low as 875 °C and their properties were improved too. In this paper, CuO/V_2O_5 were chosen as a liquid sintering aid to study the role in densification and microwave dielectric properties of $Bi_2Zn_{2/3}Ta_{4/3}O_7$ (β-BZT) ceramics. The crystalline phases, the microstructures and the microwave dielectric properties of CuO/V_2O_5 doped β-BZT ceramics were presented.

2. Experimental procedures

High purity Bi_2O_3, ZnO and Ta_2O_5 (purity >99%) were used as starting materials to synthesize β-BZT ceramics. The compositions were prepared by conventional powder processing technique. Stoichiometric mixtures were mixed and ball-milled for 20 h with deionized water using zirconia media in polyethylene containers. The mixed slurry was

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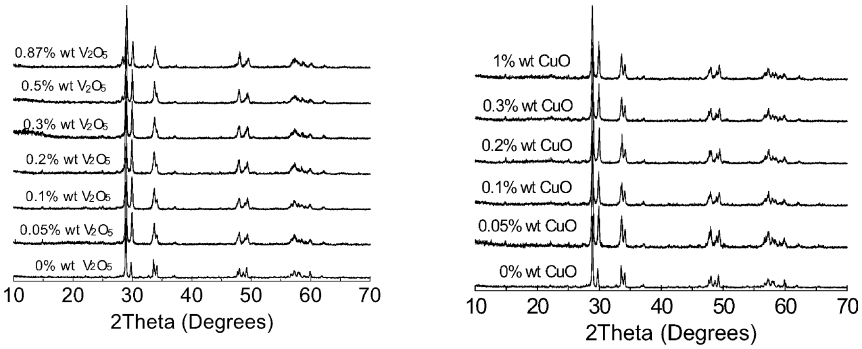

Fig. 1. XRD patterns of CuO/V_2O_5 doped $Bi_2Zn_{2/3}Ta_{4/3}O_7$ ceramics.

dried in an oven at 120 °C for 15 h. The dried powders were calcined in air at 800 °C for 4 h in covered alumina crucibles to form β-BZT crystalline structure as confirmed with X-ray diffractometer. Followed, the β-BZT powder and a certain content of CuO/V_2O_5 powder were mixed, dried and calcined. After granulated, the resultant powders were uniaxially die-pressed into discs having a diameter of 12 mm and thickness of 2 or 6 mm under a pressure of 8 MPa/cm^2. All 6 mm height specimens used for microwave measurements were experienced cold isostatic pressing process. The samples were sintered at various temperatures from 890 to 970 °C for 4 h with a ramping rate of 3 °C/min. The electrodes of samples were coated with silver paste and fired. The bulk density of as-sintered pellets was measured using the METTLER TOLEDO AG285 balance and the density determination kit for balance (Archimedes method).

The structure of sintered pellets was performed by Bruker D8 X-ray diffractometer (XRD). The surface was observed by SEM (JSM-5510LV). The temperature dependence of the dielectric constant and dissipation factor was measured using an automated measurement system consisting a computer, a HP 4284A LCR meter and a temperature chamber. The temperature range was between −60 and 160 °C with a heating rate of 2.5 °C/min. Temperature coefficient of dielectric constant (α_ε, ppm/°C) was calculated from the slope of dielectric constant in the temperature range of 20–85 °C and the dielectric constant at 20 °C. A KEITHLEY 6517A high resistance meter was used to measure the leakage current of the samples under 400 V dc bias for 1 min. Microwave dielectric characteristics of the specimens were measured by the post resonant method, which consisted of parallel conducting plates and coaxial probes. A HP8753E network analyzer was used for the microwave measurement. The dielectric properties were calculated from the frequency of the TE_{011} resonant mode.

3. Results and discussion

The X-ray diffraction patterns of CuO/V_2O_5 doped $Bi_2Zn_{2/3}Ta_{4/3}O_7$ ceramics are shown in Fig. 1. It can be seen that, even at a small amount of V_2O_5 addition, XRD patterns differed from the sample of pure β-BZT. In the vicinity of 32.7–34.7°, the split-peak gradually evolved into single-peak. With V_2O_5 addition higher than 0.3 wt.%, the

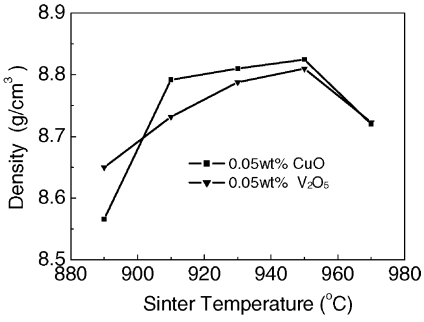

Fig. 2. The density of sample vs. sintering temperature.

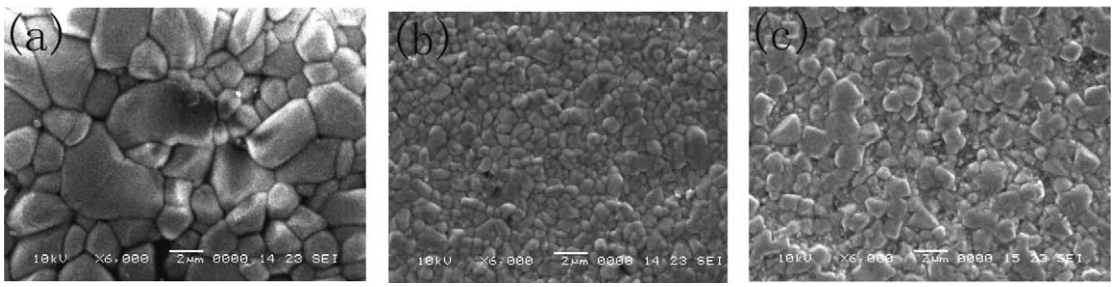

Fig. 3. SEM micrographs of samples (a) β-BZT sintered at 1050 °C/2 h, (b) 0.2 wt.% CuO doped β-BZT sintered at 950 °C/4 h, and (c) 0.2 wt.% V_2O_5 doped β-BZT sintered at 950 °C/4 h.

fluorite structure was observed. However, the crystal structure of all CuO doped samples were characterized as monoclinic zirconolite structure as that of pure β-BZT ceramic, no secondary phase was observed using X-ray diffraction.

As mentioned above, specimens based on composition of $Bi_2Zn_{2/3}Ta_{4/3}O_7$ were sintered at 1030 °C. After doping CuO/V_2O_5 into β-BZT, the sintering temperature of the samples decreased below 950 °C. This could be attributed to the liquid-phase sintering that promoted the densification of β-BZT ceramics very effectively [7]. The effects of 0.05 wt.% CuO/V_2O_5 on the densification of β-BZT ceramics sintered at different temperature are shown in Fig. 2. The density increased continually below 950 °C and then started to decrease slightly. All other specimens that doped with various CuO/V_2O_5 additions had a same change tendency. The bulk density reaches a maximum at a fixed temperature with a certain addition. The larger amount of additions was used, the lower the temperature was. For V_2O_5 doped specimens, the density gradually decreases with increasing of V_2O_5 content. The decrease of density maybe associates with the change of phase structure in the finished specimen. The density of all CuO doped β-BZT specimens are above 8.82 g/cm^3.

The SEM micrographs are shown in Fig. 3. The grain size of undoped sample was about 2–5 μm. The grain size decreased and the microstructure became dense with doping of CuO/V_2O_5. These results suggested that the doping of CuO/V_2O_5 substantially decrease the grain size and change the microstructure of β-BZT ceramics.

Pure β-BZT and V_2O_5 doped ceramics had excellent electrical resistivity higher than 10^{13} Ω cm. These high values represent very good insulation resistance and hence very small leakage current in capacitor devices. For CuO doped specimens, the electrical resistivity decreased from 10^{13} to 10^8 Ω cm with increasing of the amount of CuO.

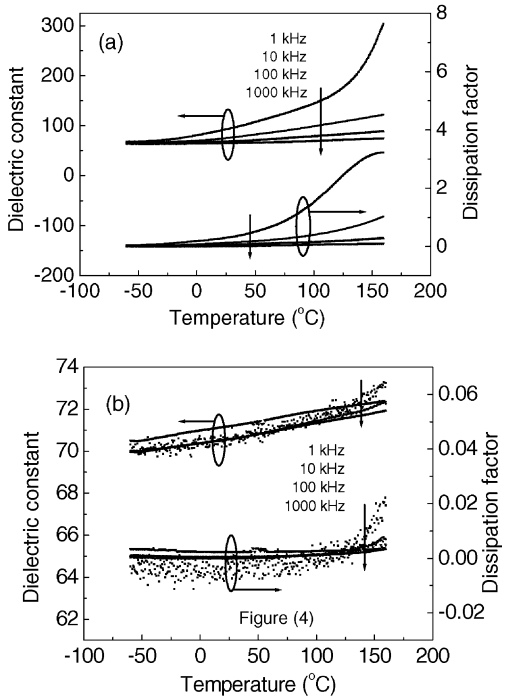

Fig. 4. Temperature dependence of ε and $\tan\delta$ for (a) 1 wt.% CuO doped β-BZT and (b) 0.87 wt.% V_2O_5 doped β-BZT at 1, 10, 100 and 1000 kHz.

Temperature dependence of dielectric constant (ε) and dissipation factor ($\tan\delta$) is presented in Fig. 4. When CuO content added to 0.2 wt.% and above, the temperature

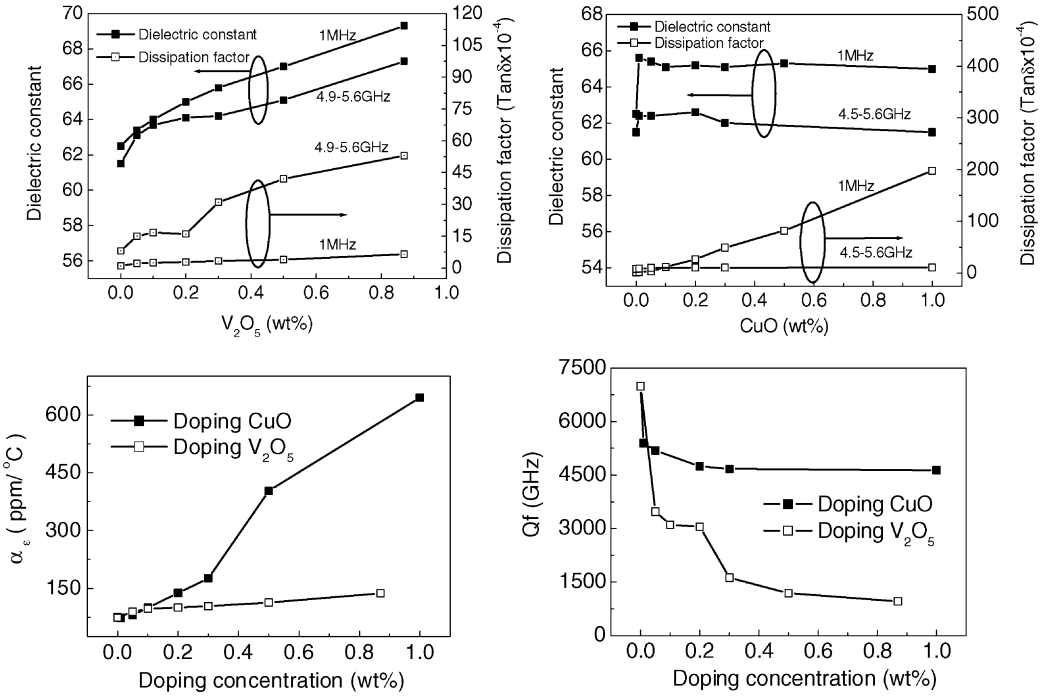

Fig. 5. Microwave dielectric properties of different CuO/V_2O_5 doped samples.

dependence of dielectric behaviors showed that the tan δ at low frequency increases with increasing of temperature. Combined with the electrical resistivity measurement, this phenomenon could be attributed to the conductance loss [8].

Fig. 5 shows the microwave dielectric properties of different CuO/V_2O_5 doped samples. As increasing V_2O_5 doping content, the dielectric constant and dissipation factor increased continuously both at 1 MHz and 4.9–5.6 GHz. Also, with increasing of V_2O_5 content, the obvious change was the increase of the α_ε at 1 MHz from 75 to 137 ppm/°C and the decrease of *Qf* value from 6987 to 957. This result was due to the formation of the secondary phase. The enhanced dielectric constant in V_2O_5 added β-BZT ceramics also could attribute to the contribution from the secondary phase.

For CuO doped samples, the dissipation factor and temperature coefficient of dielectric constant were found to be sensitive to CuO addition. With increasing of CuO content the α_ε and tan δ increased at 1 MHz. The *Qf* values of β-BZT doped with CuO were higher than that of V_2O_5 doped specimens, but they were lower than pure β-BZT. In general, *Qf* values are affected by the oxygen vacancies and electron concentration, impurities, grain boundaries, and microstructure [9]. The decrease of *Qf* value of CuO doped specimens was probably due to impurity grain boundaries and the decrease of grain size as confirmed by SEM photographs. Also, the lower electrical resistivity of the ceramics resulted in a higher conductance loss and thus lowered the *Qf* value.

When both 0.05 wt.% CuO and 0.05 wt.% V_2O_5 were added into β-BZT, the sintering temperature of ceramics specimens were also reduced down to 930 °C. The microwave dielectric properties were: $\varepsilon =\sim 63$ and $Qf =\sim 6787$ at ~5.35 GHz with $\alpha_\varepsilon =\sim 73$ ppm/°C at 1 MHz.

4. Conclusions

The structure and dielectric properties of CuO/V_2O_5 doped β-BZT ceramics were investigated. The structure of CuO doped β-BZT ceramics was characterized as monoclinic zirconolite structure as that of pure β-BZT ceramic. The structure of V_2O_5 doped β-BZT ceramics cannot maintain the monoclinic zirconolite structure even at lower doping amount. Therefore, CuO/V_2O_5 were effective to lower the sintering temperature of β-BZT, while the microwave dielectric properties of the specimens were deteriorated by excess amount of CuO/V_2O_5. At room temperature and 1 MHz, as the addition of CuO increased from 0.01 to 1 wt.%, the dielectric constant of all the specimens was about 65.5, but dielectric loss and temperature coefficient of the dielectric constant gradually increased to a maximum value. With increase of V_2O_5 content, a decrease in microwave dielectric properties was obtained. When both 0.05 wt.% CuO and 0.05 wt.% V_2O_5 were added into β-BZT, the microwave dielectric properties were: $\varepsilon =\sim 63$ and $Qf =\sim 6787$ at ~5.35 GHz with $\alpha_\varepsilon =\sim 73$ ppm/°C at 1 MHz.

Acknowledgements

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