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Low temperature sintering and microwave dielectric properties of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with $CuO\text{-}B_2O_3$

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Abstract The effects of $CuO\text{-}B_2O_3$ additive on sintering temperature and microwave dielectric properties of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics prepared by solid-state reaction method have been investigated. The phases and microstructure have also been evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The pure $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics show a high sintering temperature of about 1170 °C. However, the addition of $CuO\text{-}B_2O_3$ lowered the sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics from 1170 to 920 °C due to the $CuO\text{-}B_2O_3$ liquid-phase.The results showed that the microwave dielectric properties were strongly dependent on densification, crystalline phases and grain size. The $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with the addition of 4.0 wt.% CuO + 4.0 wt.% H_3BO_3 sintered at 920 °C afforded excellent dielectric properties of $\varepsilon_r = 45.8$, $Q \times f = 10918$ GHz (at 4.5 GHz) and $\tau_f = 45.6$ ppm/°C, which represent very promising candidates for LTCC dielectric materials.

Keywords Ceramics · Phases · $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ · Dielectric properties

1 Introduction

Low-temperature Co-fired Ceramic (LTCC) technology has received increasing attention by industry and scientific community [1, 2]. A great advantage of LTCC technology is allowing integration of passive components such as resistors, capacitors, inductors, and other functional parts into the co-fired substrates, which leads to highly integrated and multi-functional LTCC modules [3]. In order to increase the integration density and obtain higher processing accuracy, many efforts have been put into the research on component miniaturization. The high dielectric permittivity ($\varepsilon_r > 20$) of microwave dielectric materials is preferred to meet the requirement for miniaturization because the size of the component is inversely related to the $\varepsilon_r^{1/2}$ [4, 5]. Moreover the high quality factor ($Q \times f$ >10000) is required to decrease the dielectric losses. For practical application the microwave dielectric materials need to have low temperature-coefficient of resonant frequency (τ_f) and low sintering-temperature. In order to use base metal electrodes (Ag or Cu), the sintering-temperature of the microwave dielectric ceramics should be lower than 950 °C [6]. However, the conventional microwave dielectric ceramics used for wireless communication systems usually sinter at the ranges from 1200 to 1500 °C.

The sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics is about 1170 °C, which is too high to be applicable to LTCC [7]. Nevertheless, $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics possess very high ε_r of 51, a high $Q \times f$ of 26600 GHz, and acceptable τ_f of 70 ppm/°C, which are favorable for component miniaturization of microwave dielectric applications [8]. It is desirable that the sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ dielectric ceramics could be reduced to 950 °C. Extensive researches have been performed to lower the sintering temperature of the microwave dielectric ceramics: (i) the usage of starting materials with smaller particle

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size synthesized by chemical processes and (ii) the addition of low melting pint sintering aids, including glasses, oxides or mixed-oxides. Since the chemical synthesis is often time consuming and expensive, the most popular and economic method for preparing dense ceramics is the addition of low melting point sintering aids, oxide or mixed-oxide additives such as B_2O_3, V_2O_5, and CuO [9].

CuO is one of the most popular sintering fluxes. Huang et al. have observed that the addition of CuO reduced the sintering temperature of $(Zr_{0.8},Sn_{0.2})TiO_4$ ceramics from 1400 to 1220 °C. The improved microwave dielectric characteristics were obtained from the $(Zr_{0.8},Sn_{0.2})TiO_4$ with 1.0 wt% CuO addition [10]. Gong et al. reduced the sintering temperature of $7NiNb_2O_6$–$9TiO_2$ ceramic from 1200 to 935 °C by adding 3.2 wt% CuO [11]. In our previous work, CuO was first chosen as a sintering aid to lower the firing temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics. We have found that the addition of CuO significantly lowers the sintering temperature from 1200 to 1000 °C. Moreover, stable microwave dielectric properties were obtained in $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with 4.0 wt% CuO sintered at the temperature from 1000 to 1075 °C. However, the sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ + 4.0 wt% CuO ceramics is about 1000 °C, which is still a little high to be applicable to LTCC(<950 °C). It is necessary to further reduce the sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ + 4.0 wt% CuO by adding another sintering aid. The combinatorial addition of B_2O_3 and CuO can be considered as good additives to decrease the sintering temperature of microwave dielectrics materials. Lim et al. have reported that the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics reduced from 1300 to 875 °C with the addition of 10.0 mol% CuO-B_2O_3. Meanwhile, the low-temperature sintered $Ba_2Ti_9O_{20}$ ceramics exhibit very excellent microwave dielectric performance [12]. The sintering temperature of $0.662BaMoO_4$–$0.338TiO_2$ microwave ceramics has also been reduced from 1275 to 850 °C with 5.0 wt% H_3BO_3 and1.0 wt% CuO addition [13].

In the present work, in order to further reduce the sintering temperature and keep the microwave dielectric properties of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ + 4.0 wt% CuO, the secondary sintering aid B_2O_3 was added to this composition. 4.0 wt% CuO+ (x) wt.%H_3BO_3 (where $x = 1, 2, 4, 6$) was employed as a sintering aid to lower the sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics. The effects of CuO-B_2O_3 addition on the densification, microstructures and microwave dielectric properties of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics were systematically investigated. We have found that the addition of CuO-B_2O_3 significantly lowers the sintering temperature from 1170 to 920 °C. Moreover, very stable microwave dielectric performances were obtained in $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with 4.0 wt.% CuO+ 4.0 wt.% H_3BO_3 sintered at the temperature from 875 to 945 °C.

2 Experimental procedure

The ceramic powders were synthesized by conventional solid-state reaction method from high-purity oxide powders of ZrO_2 (99.0 %),ZnO (99.0 %), Nb_2O_5 (99.99 %), TiO_2 (99.8 %), H_3BO_3 (99.5 %)and CuO (99.0 %). The raw materials were weighed and mixed according to chemical formula $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$+ 4.0 wt.% CuO + ($x$) wt.% H_3BO_3 (where $x = 1, 2, 4, 6$) in ethanol and planetary ball milled using Y_2O_3-stabilised ZrO_2 grinding media for 24 h. After drying and sieving, the milled powders were calcined at 1000 °C for 3.5 h to obtain the pure phase of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ powder. After that, the sintering aids with composition of 4.0 wt.% CuO + (x) wt.% H_3BO_3 (where x =1, 2, 4, 6) were added to $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramic powders. After ball milling for 4 h, the powders were dried, granulated and uniaxially pressed into pellets of 10 mm in diameter. These pellets were sintered at 875–975 °C for 3.5 h in air with the heating rate of 5 °C/min.

The crystal phases of the powders and sintered ceramics were identified by powder X-ray diffraction obtained by a diffractometer (PANalytical B.V., X'Pert PRO, the Netherland) using Cu Kα radiation ($\lambda = 1.5406$ Å) at a voltage and current of 40 kV and 30 mA. XRD data were collected in the range of 20–80° in θ-2θ locked-coupled scanning mode with a 0.02° step and scanning speed of 5°/min. The microstructures were examined by scanning electron microscopy (SEM: Philip, XL30TM). The apparent densities of the sintered ceramics were measured by the Archimedes method using distilled water as the liquid. For the electrical measurements, the sintered pellets were ground, polished, and painted with silver paste, which was fired at 500 °C for 0.5 h. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method by Advantest network analyzer (E5071C) [14]. The temperature coefficient of resonant frequency (τ_f) was also measured by the method sociated with Eq. (1):

$$\tau_f = \frac{(f_{80} - f_{30}) \times 10^6}{(80-30) f_{30}} \,(\mathrm{ppm}/^\circ\mathrm{C}) \tag{1}$$

where f_{80} and f_{30} represent the resonant frequencies at 80 and 30 °C, respectively.

3 Results and discussion

Figure 1 shows the XRD patterns of 4.0 wt% CuO+ 4.0 wt% H_3BO_3-doped $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics sintered at 875–975 °C for 3.5 h. The $ZrTiO_4$ phase was identified as the main phase, which has an α-PbO_2 structure (JCPDS Card NO.34-0415). This means that the zirconium, titanium,

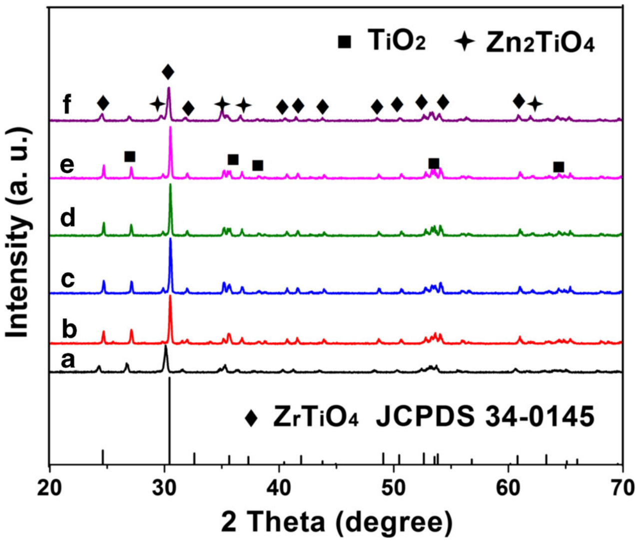

Fig. 1 XRD patterns of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with 4.0 wt% CuO+ 4.0 wt% H_3BO_3 addition sintered at different temperature: **a** 875 °C, **b** 890 °C, **c** 920 °C, **d** 945 °C, **e** 960 °C, **f** 975 °C for 3.5 h

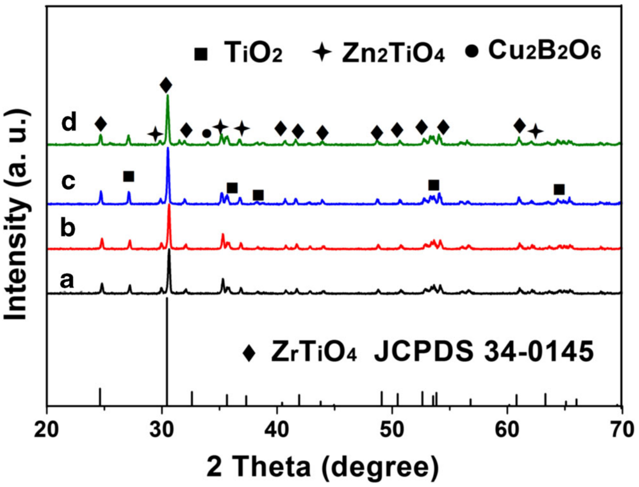

Fig. 2 XRD patterns of the $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with different amount of CuO and H_3BO_3 addition sintered at 920 °C: **a** 4.0 wt.% CuO + 1.0 wt.% H_3BO_3, **b** 4.0 wt.% CuO + 2.0 wt.% H_3BO_3, **c** 4.0 wt.% CuO + 4.0 wt.% H_3BO_3, and **d** 4.0 wt.% CuO +6.0 wt.% H_3BO_3 for 3.5 h

zinc, and niobium in the α-PbO_2 structure ions are randomly distributed in the oxygen octahedron. The second phase is rutile (TiO_2) (JCPDS file no. 76-0324), the third phase is Zn_2TiO_4 (JCPDS file no. 73-0578). It was observed that both of the rutile and Zn_2TiO_4 phase content creased and then decreased with the increasing sintering temperatures and reached a maximum at 920 °C. Jeon and Lin have found that the effectiveness of sintering aids is greatly affected by the sintering temperatures [15].

Figure 2 shows the XRD patterns of the $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$+ 4.0 wt.% CuO + ($x$) wt.% H_3BO_3 (where $x = 1,2,4,6$) sintered at 920 °C for 3.5 h. As can be seen from the graph, the different doping diffraction pattern of samples is relatively consistent. Ceramic main crystal phase, the second phase and the third phase also are $ZrTiO_4$, rutile (TiO_2) and Zn_2TiO_4 phase [16]. However, there has been found the $Cu_3B_2O_6$ phase in the pellets doped with 4.0 wt.% CuO + 6.0 wt.% H_3BO_3. For the 6.0 wt.% H_3BO_3 added $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics, a liquid phase containing $Cu_3B_2O_6$ was formed during the sintering and assisted in the densification of the $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics at 920 °C.

Figure 3 demonstrates the SEM micrographs of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with 4.0 wt.% CuO +4.0 wt.% H_3BO_3 sintered at different temperature: (a) 875 °C, (b) 890 °C, (c) 920 °C, (d) 945 °C, (e) 960 °C, (f) 975 °C. For the $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics sintered at 890 °C, many distinct pores were easily found [17]. However, pores decreased significantly and much larger grains were observed in pellets sintered at 920 °C as shown in Fig. 3c. The grain size increased rapidly with the increasing of sintering temperature, which can be attributed partly to the

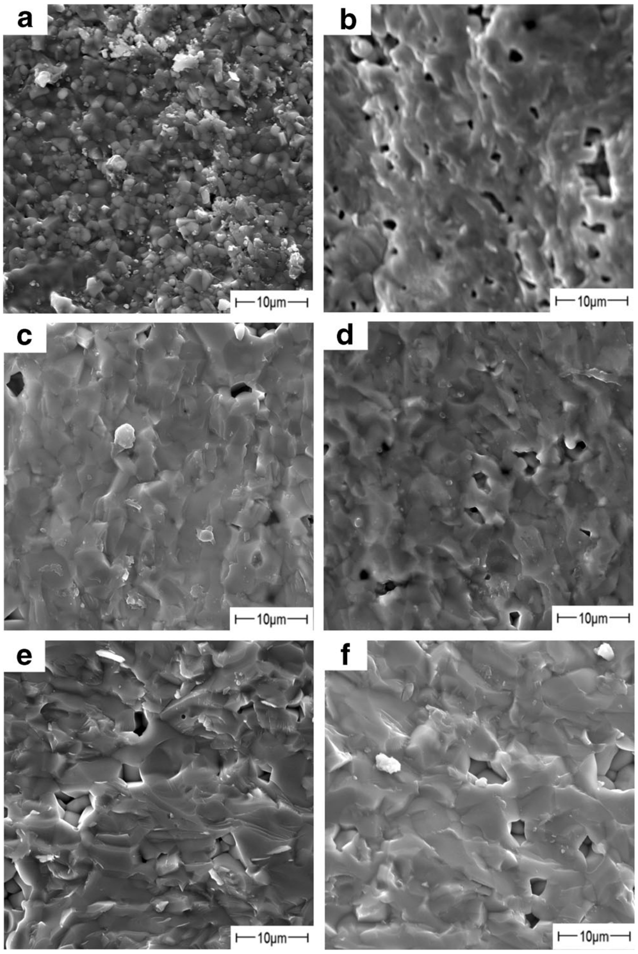

Fig. 3 SEM micrographs of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with 4.0 wt.% CuO +4.0 wt.% H_3BO_3 addition sintered at different temperature: **a** 875 °C, **b** 890 °C, **c** 920 °C, **d** 945 °C, **e** 960 °C, **f** 975 °C for 3.5 h

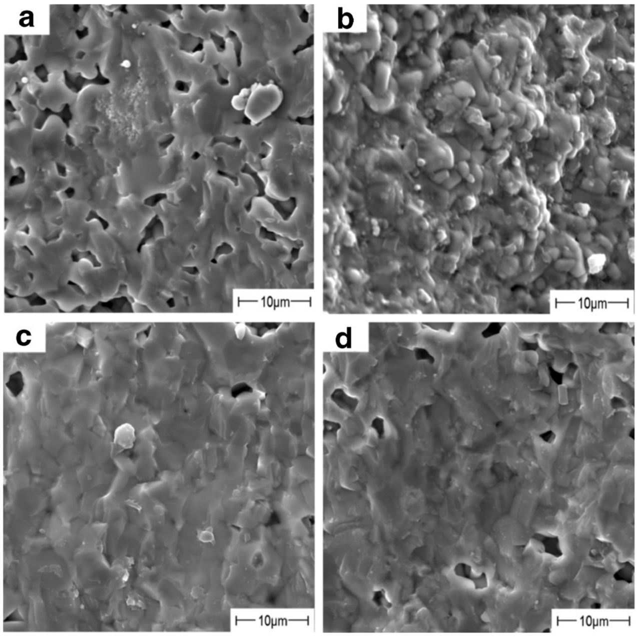

Fig. 4 SEM micrographs of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with 4.0 wt.% CuO + (*x*) wt.% H_3BO_3 addition sintered at 920 °C for 3.5 h

presence of liquid phase. Figure 3e shows the liquid-phase of CuO-B_2O_3 was overproduced in the pellets sintered at 960 °C. Because of the excess liquid-phase and generating volatile of B_2O_3, gases in the pellets couldn't be evacuated in time, so that the microwave dielectric properties became worse at 975 °C [18].

Figure 4 shows the SEM micrographs of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with 4 wt.% CuO + (*x*) wt.% H_3BO_3 (where $x = 1,2,4,6$) sintered at 920 °C. The grain sizes of these bulk ceramics increased gradually with the increasing of H_3BO_3 from 1.0 wt.% to 6.0 wt.%. Besides, more liquid-phase of CuO-B_2O_3 could be found with the increase of CuO-B_2O_3 content. It can be concluded that the introduction of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics doped with CuO-B_2O_3 increased the grain sizes and promoted the densification at a lower temperature. However, it should be noted that excess CuO-B_2O_3-liquid phase might also lead to a decline in the microwave dielectric properties of the bulk ceramics [19].

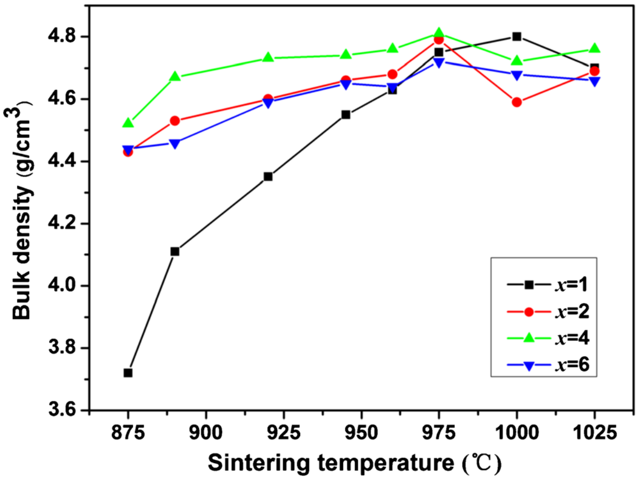

Fig. 5 The relative density of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ bulk ceramics with 4.0 wt.% CuO + (*x*) wt.% H_3BO_3 addition sintered at 875–1025 °C for 3.5 h

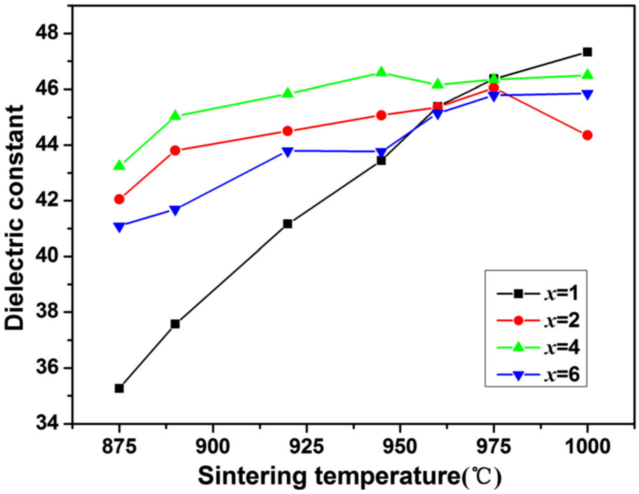

Fig. 6 The dielectric constant of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with 4.0 wt.% CuO + (*x*) wt.% H_3BO_3 addition sintered at 875–1025 °C for 3.5 h

Figure 5 shows the bulk densities of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramic doped with different amount of CuO-B_2O_3 sintered at different temperatures for 3.5 h The density of the ceramic samples sintered below 925 °C was low, but increased with increasing sintering temperature to a maximum and slightly declined thereafter. The increase in density is attributed to the reduction in porosity and uniform grain growth. The addition of CuO-B_2O_3 is responsible for the low-temperature densification of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics. It might be a liquid sintering mechanism for this system.The decrease in density can be attributed to the liquid-phase effect induced by the over-sintering, which is

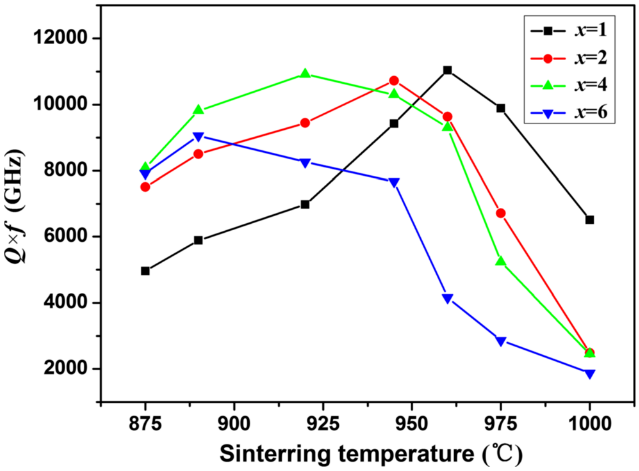

Fig. 7 The $Q{\times}f$ values of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with 4.0 wt.% CuO + (*x*) wt.% H_3BO_3 sintered at 875–1025 °C for 3.5 h

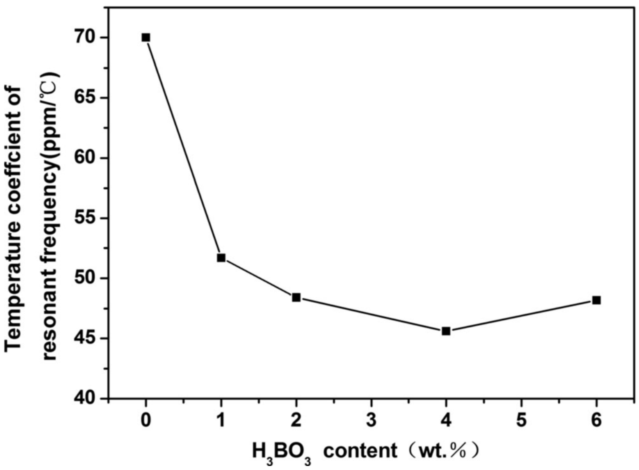

Fig. 8 The temperature coefficient of resonant frequency (τ_f) *of* $_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ ceramics with different amount of 4.0 wt.% CuO + (x) wt.% H$_3$BO$_3$ (where $x = 1,2,4,6$) sintered at 920 °C for 3.5 h

clearly observed from the microstructure of the sample shown above. Therefore, the addition of CuO-B$_2$O$_3$ improved the sinter ability of Zr$_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ ceramics and reduced their sintering temperature by more than 250 °C. When the sintering temperature was above 920 °C ($T \geq 920$ °C), the density of the samples with the H$_3$BO$_3$ content more than 2.0 wt.% reached above 4.58 g/cm , indicating that the samples sintered above 925 °C were very dense as shown in Figure. This ceramic can be cofired with a low cost electrode to meet the requirements of LTCC technology.

Figure 6 shows the dielectric constant of Zr$_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ ceramics doped with different amount of CuO-B$_2$O$_3$ sintered at varies temperatures for 3.5 h. The variation of ε_r value was consistent with that of density. The dielectric constant of the pellets sintered below 920 °C was low. As the sintering temperature increased, the dielectric constant of all the samples increased, followed by a slight decrease. Moreover, it is observed that the dielectric constant of Zr$_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ ceramics increased to a maximum value and decreased thereafter. A small amount of liquid or the increase of temperature causes the ceramic pores reduce the grain growth, resulting in the high densification and increased the ε$_r$. The decrease in dielectric constant was caused by the decrease in density, which was closely linked to the overproduction of the CuO-B$_2$O$_3$ liquid phase and the volatile B$_2$O$_3$. Li-Xia Pang and Di Zhou also observed similar results for B$_2$O$_3$–CuO doped Li$_2$MO$_3$ (M = Ti, Zr, Sn) ceramics [20].The maximum ε_r value of 46.6 was obtained for the specimen doped with 4.0 wt% CuO + 4.0 wt% H$_3$BO$_3$ sintered at 945 °C. The stable ε_r values ranging from 45.1 to 46.6 were obtained in pellets doped with 4.0 wt% CuO+ 4.0 wt% H$_3$BO$_3$ sintered at the temperature from 875 to 975 °C.

Figure 7 shows the Q×f values of Zr$_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ ceramics with (x) wt.% H$_3$BO$_3$ (where $x = 1,2,4,6$) sintered at 875–1025 °C for 3.5 h. Since the sintering temperature has a significant influence on the microwave dielectric properties of ceramics, the effect of different sintering temperatures on microwave dielectric properties was investigated. With the increasing sintering temperature, the Q×f value of pellets increased to a maximum value and decreased thereafter,which showed a similar trend with that of density. It is also observed that the Q×f value increased to a maximum value and decreased thereafter at the temperature from 875 to 975 °C. The dramatically increase of Q×f values can be attributed partly to a structural change from α-PbO$_2$ to rutile structure with the increasing sintering temperature and/or CuO-B$_2$O$_3$ content. Moreover, Q×f values are known to be affected by the morphology of the samples, such as grain size, porosity, and density. A note worthy fact is that the Q×f value of the sample may also decrease with an oversize grain, which can be related to the presence of liquid-phase of CuO-B$_2$O$_3$ in grain boundary [21, 22]. So the Q×f value increased with the increase of CuO-B$_2$O$_3$ addition first and then decreased when

Table 1 Properties of microwave dielectric ceramics

Material	Firing (°C)	Q×f (GHz)	ε_r	τ_f (ppmK^{-1})	Reference
(Zr$_{0.8}$,Sn$_{0.2}$)TiO$_4$ + 1.0 wt%CuO	1220	50000	38	3	[10]
7NiNb$_2$O$_6$–9TiO$_2$ + 3.2 wt%CuO	935	10039	60.5	62	[11]
Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ + 0.5 wt%B$_2$O$_3$	1500	195000	34.2	4.74	[23]
MgTiO$_3$ + 0.5 wt%V$_2$O$_5$	1110	85600	15.8	12	[24]
BiSbO$_4$ + 1.0 wt%CuO-V$_2$O$_5$	930	33380	19.7	−71.5	[25]
Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ + 5 mol%B$_2$O$_3$-10 mol%CuO	870	11000	26	0	[26]
Ba$_2$Ti$_9$O$_{20}$ + 10.0 mol%CuO-B$_2$O$_3$	875	16000	36	9.11	[12]
Li$_2$ZnTi$_3$O$_8$ + 0.25CuO-1.5Bi$_2$O$_3$-1.5V$_2$O$_5$	900	53400	25.6	−5.27	[27]
Zr$_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ + 4 wt.% CuO	1000	18544	46.2	38.4	This Work
Zr$_{0.3}$(Zn$_{1/3}$Nb$_{2/3}$)$_{0.7}$TiO$_4$ + 4 wt.% CuO-4 wt.% H$_3$BO$_3$	920	10918	45.8	45.6	This Work

the H_3BO_3 content more than 4.0 wt%. Only if we find the ceramics which has no porosity, moderated grain size, high density and suitable liquid components, can we get a better $Q{\times}f$ value. It is observed that stable $Q{\times}f$ values can be obtained in the pellets doped with 4.0 wt% CuO+ 4.0 wt% H_3BO_3 sintered at the temperature from 875 to 945 °C.

Figure 8 shows the temperature coefficient of resonant frequency (τ_f) of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with various amount of 4.0 wt.% CuO + (x) wt.% H_3BO_3 (where $x=0,1,2,4,6$) sintered at 920 °C for 3.5 h. In contrast to the pure $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with the τ_f of 70 ppm/°C, the τ_f values decreased as the CuO-B_2O_3 was added. This is because the temperature coefficient of resonant frequency (τ_f) may be related to the rutile (TiO_2) phase and the liquid phase. It is observed that the τ_f values did not change much with different different amount of 4.0 wt.% CuO + (x) wt.% H_3BO_3 (where $x=1,2,4,6$) in this experiment.

Table 1 gives a list of 10 typical microwave dielectric ceramics doped with low-melting point sintering aids and their properties. Compared with other additives, a large reduction of the sintering temperature (above 300 °C) can be achieved with the addition of CuO-B_2O_3 and the system showed good microwave dielectric properties. Therefore, the CuO-B_2O_3 doped $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramic is a good candidate material for low-temperature cofiring ceramics.

4 Conclusions

The effects of CuO-B_2O_3 additive on sintering temperature and microwave dielectric properties of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics have been investigated. The phases and microstructure have also been evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the microwave dielectric properties were strongly dependent on densification, crystalline phases and grain size, which were all influenced by the sintering temperature and the amount of CuO-B_2O_3.The addition of CuO-B_2O_3 lowered the sintering temperature of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics from 1170 to 920 °C due to the CuO liquid-phase. Moreover, high dielectric constant and stable Q×f values were obtained for the bulk sample doped with 4.0 wt.% CuO + 4.0 wt.% H_3BO_3 sintered at the temperature 875 to 945 °C. The $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics with the addition of 4.0 wt.% CuO +4.0 wt.% H_3BO_3 sintered at 920 °C afforded excellent dielectric properties of $\varepsilon_r=45.8$, $Q{\times}f=10918$ GHz (at 4.5 GHz) and $\tau_f=45.6$ ppm/°C, which represent very promising candidates for LTCC dielectric materials.

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