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Microstructure and dielectric properties of low temperature sintered $ZnNb_2O_6$ microwave ceramics

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Abstract

Low sintering temperature $ZnNb_2O_6$ microwave ceramics were prepared by doping with mixed oxides of V_2O_5–Bi_2O_3 and V_2O_5–Bi_2O_3–CuO. The effects of additives on the microstructure and dielectric properties of the ceramics were investigated. The results show that doping with V_2O_5–Bi_2O_3 can reduce the sintering temperature of $ZnNb_2O_6$ from 1150 °C to 1000 °C due to the formation of V_2O_5 and Bi_2O_3 based eutectic phases. The combined influence of V_2O_5 and Bi_2O_3 resulted in rod-like grains. Co-doping CuO with 1 wt.% V_2O_5–1 wt.% Bi_2O_3 further lowered the sintering temperature to 880 °C, because eutectic phases could be formed between the CuO, V_2O_5 and Bi_2O_3. A second phase of $(Cu_2Zn)Nb_2O_8$ also forms when the content of CuO is greater than 2.5 wt.%. A pure $ZnNb_2O_6$ phase can be obtained when the amount of CuO was 1.0–2.5 wt.%. The $Q \times f$ values of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO were all higher than 25,000 GHz. The dielectric constants were 22.8–23.8 at microwave frequencies. In addition, the τ_f values decreased towards negative as the content of CuO increased. The ceramic with composition of $ZnNb_2O_6$ + 1 wt.%V_2O_5 + 1 wt.% Bi_2O_3 + 2.5 wt.% CuO sintered at 880 °C exhibited the optimum microwave dielectric properties, ε is 23.4, $Q \times f$ is 46,975 GHz, and τ_f is −44.89 ppm/°C, which makes it a promising material for low-temperature co-fired ceramics (LTCCs).
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Keywords: C. Dielectric properties; Microwave ceramic; Low temperature sintering; Multiplex oxides additives

1. Introduction

Low-temperature co-fired ceramics (LTCCs) are interesting because of their application in novel multilayer communication modules involving microwave components. The major requirements for these materials are the ability to sinter below the Ag/Cu metallization melting temperature, chemical compatibility with the metallization material within the sintering process, and excellent microwave dielectric properties [1,2]. Zinc niobite ($ZnNb_2O_6$) ceramic is one of the candidates for low-temperature sintering microwave dielectrics, with low sintering temperature (~1150 °C) and promising microwave dielectric properties ($Q \times f$ = 87,300 GHz, ε = 25 and τ_f = −56 ppm/°C) [3,4]. Although $ZnNb_2O_6$ ceramics have relatively low sintering temperature, it is still much higher than the melting points of Ag (961 °C) and Cu (1064 °C), which are used as the inner electrodes of LTCCs.

The use of low-melting additives such as glass or oxide is commonly used to reduce the sintering temperature of zinc niobite microwave ceramics [5–7]. V_2O_5, Bi_2O_3, and CuO are the low-melting oxides commonly used as sintering aids [8–10]. However, it has been found that doping with just one low-melting oxide additive does not lower the sintering temperature effectively, and doping glasses as sintering aids can result in the microwave dielectric properties deteriorating seriously. It is expected that $ZnNb_2O_6$ ceramics with multi-oxides additives V_2O_5, Bi_2O_3, and CuO may have excellent microwave properties combined with low sintering temperature [11]. The effects of multi-oxide additives on the sintering temperature and dielectric properties have seldom been reported.

In the present work, $ZnNb_2O_6$ based microwave dielectric ceramics were prepared by a conventional mixed-oxide method. V_2O_5–Bi_2O_3 and V_2O_5–Bi_2O_3–CuO multi-oxide additives were added to lower the sintering temperature. The effects of co-doping with the multi-oxide additives on the sintering temperature, microstructure and microwave dielectric properties of $ZnNb_2O_6$ ceramics were investigated.

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Table 1
Sample identification numbers and quantities of added oxides.

Numbers	V_2O_5 (wt.%)	Bi_2O_3 (wt.%)	CuO (wt.%)
BV1#	0.5	0.5	–
BV2#	0.5	1.0	–
BV3#	1.0	0.5	–
BV4#	1.0	1.0	–
BVC1#	1.0	1.0	0.4
BVC2#	1.0	1.0	1.0
BVC3#	1.0	1.0	2.5
BVC4#	1.0	1.0	5.0

2. Experimental

$ZnNb_2O_6$ based ceramics were prepared by the traditional solid-state method. The proportions of V_2O_5, Bi_2O_3 were 0.5–1 wt.%, and CuO was 0.4–5 wt.%, these were designated as BV1-4#, BVC1-4#, respectively, as shown in Table 1. Reagent pure ZnO, Nb_2O_5, V_2O_5, Bi_2O_3 and CuO were used as the starting materials. As the first step, equal moles of ZnO and Nb_2O_5 were ball-milled for 12 h. The mixture was then calcined at 1000 °C for 4 h to synthesize $ZnNb_2O_6$. Then stoichiometric quantities of $ZnNb_2O_6$, V_2O_5, Bi_2O_3 and CuO were weighed and ball-milled for 12 h. After drying, the powder was pressed into two sample types at 120 MPa. One was a disk with 12.0 mm in diameter and 1.0 mm thick, and the other was a cylinder 12.0 mm in diameter and 6.0 mm thick. The samples were sintered at 800–1000 °C for 2 h. The sintered disks were polished and pasted with silver on both surfaces. The sintered cylinders were polished on both surfaces for measuring microwave dielectric properties.

The densities of the sintered samples were measured by the Archimedes method. The phase composition and crystal structure were determined by an X-ray diffraction (Model Panalytical X'Pert PRO, Holland). The microstructure was observed using scanning electron microscopy (SEM, Model Hitachi S-570, Japan) and energy-dispersive X-ray spectroscopy (EDS). The dielectric constant (ε) and dielectric loss (tan δ) were determined at 100 Hz to 2 MHz with a LCR precision electric bridge (Model HP4980A, Hewlett-Packard). The microwave dielectric properties were measured using Hakki and Coleman's dielectric resonator method by a network analysis meter (Model HP8720, Hewlett-Packard) [12,13]. The temperature coefficient of the resonant frequency (τ_f) of the ceramics was determined from 20 °C to 80 °C and calculated as follows:

$$\tau_f = \frac{f_{80} - f_{20}}{60 \times f_{20}} \times 10^6 \ (\text{ppm/°C})$$

3. Results and discussion

3.1. Microstructure and dielectric properties of $ZnNb_2O_6$ ceramics co-doped with V_2O_5–Bi_2O_3

The density curves of the $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3 as a function of sintering temperature are shown in Fig. 1. It can be seen that the densities of the samples increased with increasing sintering temperature. The BV4# sample doped with 1 wt.% V_2O_5 and 1 wt.% Bi_2O_3 densified at 1000 °C, reaching 95% of the theoretical density. Over all, the densities of the ceramics increased steadily with increasing amounts of V_2O_5–Bi_2O_3. Therefore, V_2O_5–Bi_2O_3 additives are good for lowering the sintering temperature. In addition, the density of the sample with increasing amounts of V_2O_5 is higher than that of the equivalent sample with the same amount of Bi_2O_3, which reveals that the effect of V_2O_5 doping is better than that of Bi_2O_3.

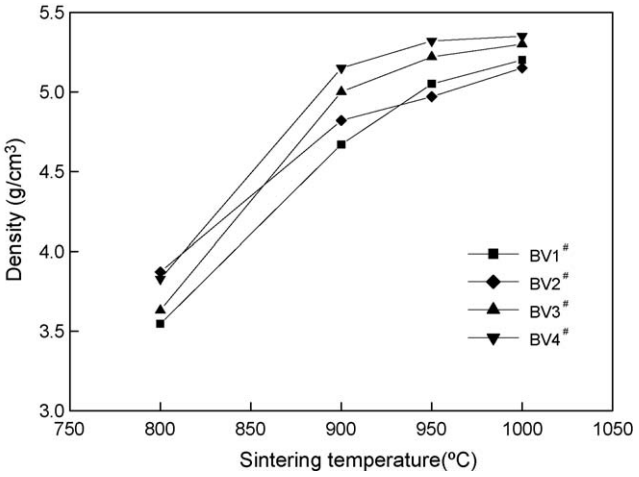

Fig. 1. Densities of V_2O_5–Bi_2O_3 doped $ZnNb_2O_6$ ceramics sintered at different temperatures.

Fig. 2 shows the XRD patterns of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3 sintered at 950 °C. Besides $ZnNb_2O_6$ phase, trace second phase was detected in BV1#–4# samples. The second phase may be cubic pyrochlore Bi_2O_3–ZnO–Nb_2O_5 (BZN) which was caused by Bi_2O_3 reacting with $ZnNb_2O_6$.

The SEM micrographs of $ZnNb_2O_6$ ceramics sintered at 1000 °C are shown in Fig. 3. It can be found that there are two kinds of grain. One is a rod-like grain, which is resulted when V^{5+} goes into the lattice of $ZnNb_2O_6$ to form a substituted solid

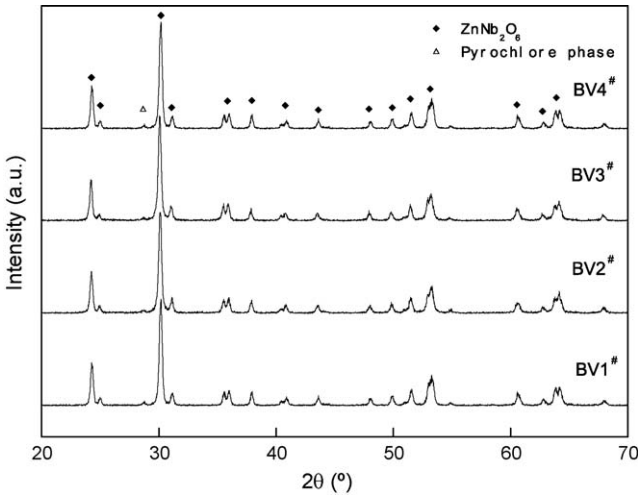

Fig. 2. XRD patterns of V_2O_5–Bi_2O_3 doped $ZnNb_2O_6$ ceramics sintered at 950 °C.

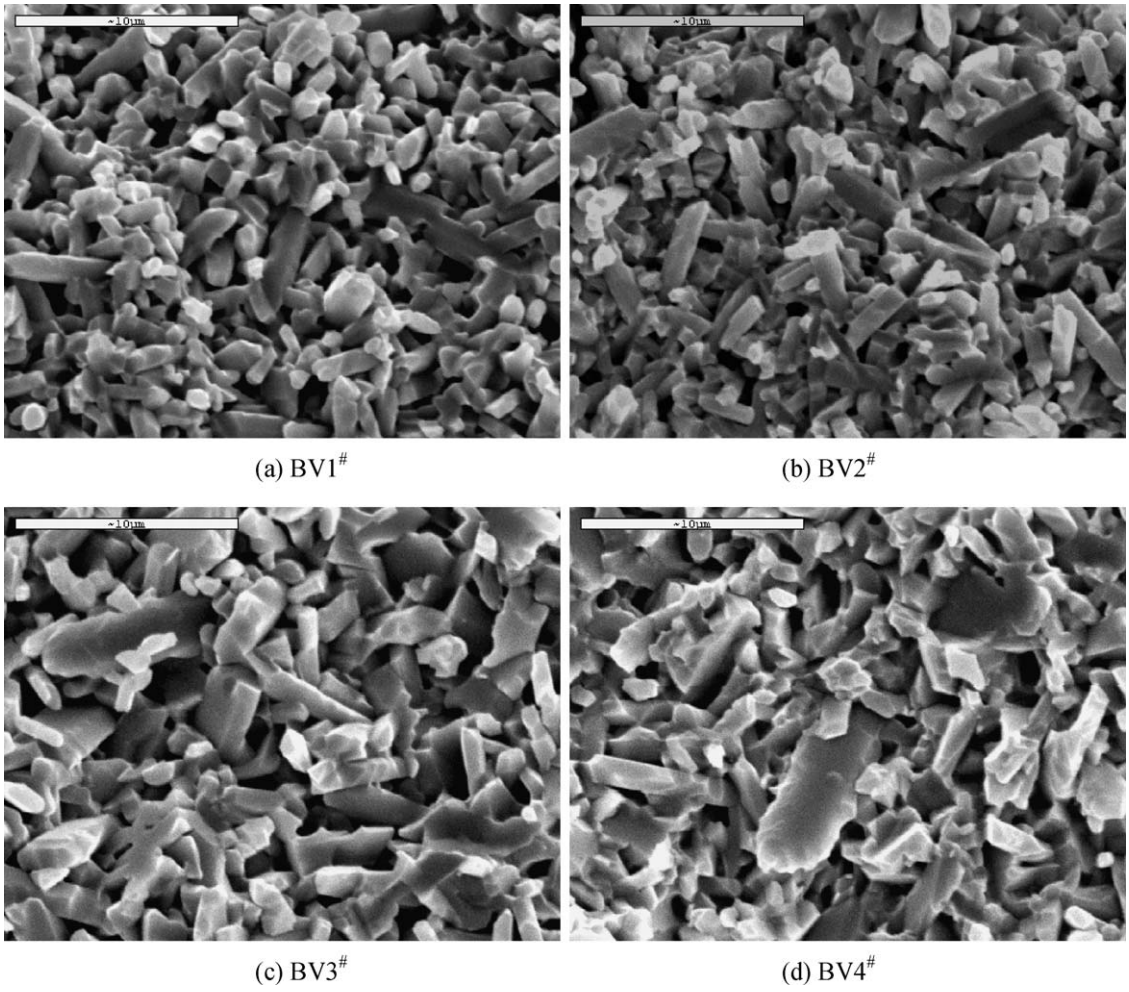

Fig. 3. SEM photographs of V_2O_5–Bi_2O_3 doped $ZnNb_2O_6$ ceramics (sintered at 1000 °C): (a) BV1#; (b) BV2#; (c) BV3#; (d) BV4#.

solution [14]. The other is an equiaxial grain, resulting from the second phase which exists at the grain boundary. The average size of the rod-like grains increased from 2.68 μm to 6.47 μm in length with increasing amounts of V_2O_5–Bi_2O_3, as shown in Table 2.

Fig. 4(a) shows the SEM micrographs of BV4# after polishing and thermal etching. The second phase after thermal etching (in the white circle) was clearly separated from the main phase. The EDS spectrum of the second phase is shown in Fig. 4(b). Abundant amounts of V and Bi were detected in the second phase, and the amount of Nb was more than that of Zn. Since V_2O_5 forms an eutectic with Bi_2O_3, it can be concluded that a liquid eutectic of V_2O_5 and Bi_2O_3 reacted with the $ZnNb_2O_6$ and induced the formation of the second phase.

Table 2
Physical and dielectric properties of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3.

Samples	BV1#	BV2#	BV3#	BV4#
Density (g/cm^3)	5.20	5.15	5.30	5.35
Average grain size (μm)	2.68	3.44	5.76	6.47
ε (1 MHz)	22.29	22.25	22.52	22.91
tan δ (1 MHz)	0.02612	0.01327	0.00049	0.00058

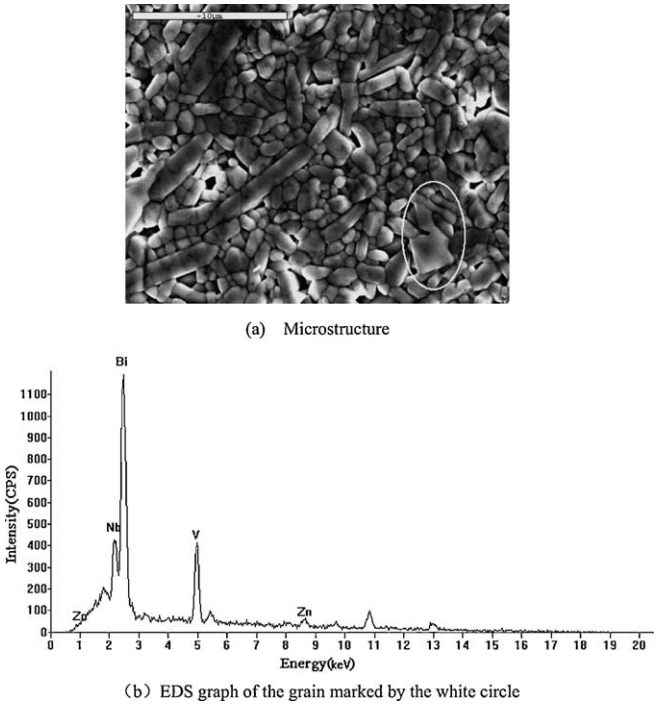

Fig. 4. Thermal etched polish surface and EDS graphs of the ceramic BV4#: (a) microstructure and (b) EDS graph of the grain marked by the white circle.

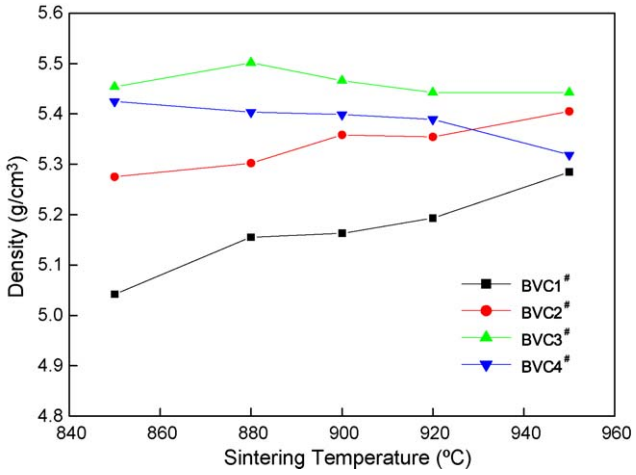

Fig. 5. Densities of V_2O_5–Bi_2O_3–CuO doped $ZnNb_2O_6$ ceramics sintered at different temperatures.

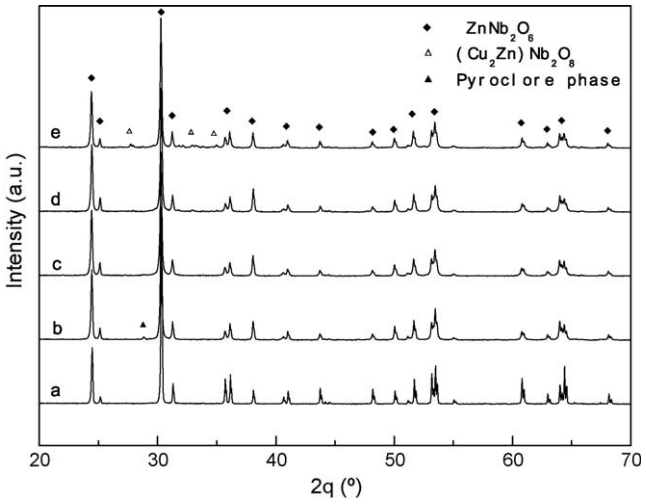

Fig. 6. XRD patterns of V_2O_5–Bi_2O_3–CuO doped $ZnNb_2O_6$ ceramics: (a) pure $ZnNb_2O_6$; (b) BVC1#; (c) BVC2#; (d) BVC3#; (e) BVC4#.

There are two mechanisms that lower the sintering temperature when using oxide sintering aids. One is the formation of a solid solution, which results in lattice distortion and reduces the ion diffusion activation energy. The other is the formation of the liquid phase, which can accelerate the material diffusion and promote rearrangement of grains. Our results demonstrate that the second mechanism plays the main role in lowering sintering temperature of $ZnNb_2O_6$ ceramics.

The dielectric properties (1 MHz) of $ZnNb_2O_6$ ceramics doped with different amounts of V_2O_5–Bi_2O_3 (sintered at 1000 °C) are shown in Table 2. The dielectric constants of the

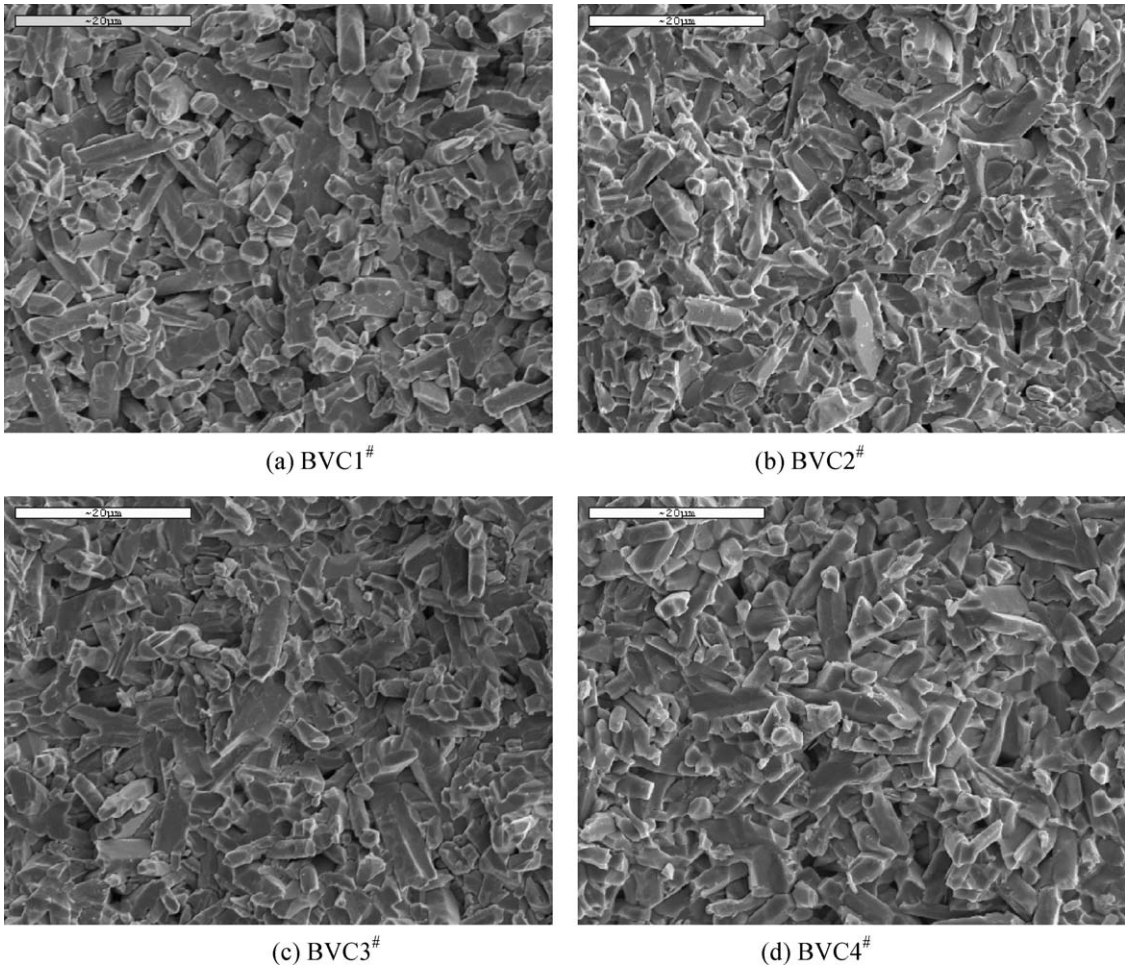

Fig. 7. SEM photographs of V_2O_5–Bi_2O_3–CuO doped $ZnNb_2O_6$ ceramics (2000×): (a) BV1#; (b) BV2#; (c) BV3#; (d) BV4#.

samples were between 22 and 23 and independent of the amounts of V_2O_5 and Bi_2O_3. The dielectric loss clearly changed with the varying proportion of V_2O_5 and Bi_2O_3. The dielectric losses of BV3# and BV4# samples were less than those of BV1# and BV2# because of the higher densities of the BV3# and BV4# samples at 1000 °C. In summary, the sintering temperature of $ZnNb_2O_6$ ceramics can be reduced from 1150 °C to 1000 °C by co-doping with 1 wt.% V_2O_5 and 1 wt.% Bi_2O_3.

3.2. Effects of co-doping with V_2O_5–Bi_2O_3–CuO on the microstructure and dielectric properties of $ZnNb_2O_6$ ceramics

Though the sintering temperature of $ZnNb_2O_6$ ceramic doped with 1 wt.% V_2O_5 and 1 wt.% Bi_2O_3 was below 1000 °C, it still cannot co-fire with the silver inner electrode. Therefore, CuO dopant was also added to the sample with 1.0 wt.% V_2O_5–1.0 wt.% Bi_2O_3.

Fig. 5 shows the density curves of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO as a function of sintering temperatures. The densities of BVC1# and BVC2# increased with increasing sintering temperature and the BVC3# ceramics have the highest density at all sintering temperatures. It can be seen that the BVC3# ceramic reaches its maximum density at 880 °C with the relative density reaching 97%. It is evident that co-doping with V_2O_5, Bi_2O_3, and CuO can effectively lower the sintering temperature of $ZnNb_2O_6$ ceramics.

Fig. 6 shows the XRD patterns of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO sintered at 880 °C. Fig. 6(a) is the XRD pattern of pure ceramic $ZnNb_2O_6$. When the amount of CuO added was 0.4 wt.%, the pyrochlore phase was generated in the $ZnNb_2O_6$ ceramic. When the amount of added CuO increased, the pyrochlore phase disappeared and the ceramics possessed the pure $ZnNb_2O_6$ phase. The reason for this is that, with increasing CuO content, more liquid phase is generated to promote the substitution reaction between CuO and $ZnNb_2O_6$. Both the ionic radius and the valence of Cu^{2+} are similar to those of Zn^{2+}, so the CuO additive will impede the substitution reaction between Bi_2O_3 and $ZnNb_2O_6$. The results show that CuO can restrain the formation of the pyrochlore phase. However, when the CuO content reached 5 wt.%, the $(Cu_2Zn)Nb_2O_8$ phase was detected. The pure $ZnNb_2O_6$ phase was obtained when the amount of CuO was between 1 wt.% and 2.5 wt.%.

The SEM micrographs of the $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO and sintered at 880 °C are shown in Fig. 7. It can be seen that there were many pores in the BVC1# and BVC2# samples, resulting to their low densities. With increasing CuO, the amount of porosity decreased. When the amount of CuO added was more than 2.5 wt.%, few pores were detected. In addition, the rod-like grains formed and the grain size grew larger with increasing amounts of CuO. The formation and growth of rod-like grains demonstrated that the grains grew with the help of the liquid phase at sintering temperature.

Fig. 8 shows the dielectric properties of the $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO as a function of CuO content at frequencies of 1 kHz to 2 MHz. With increasing

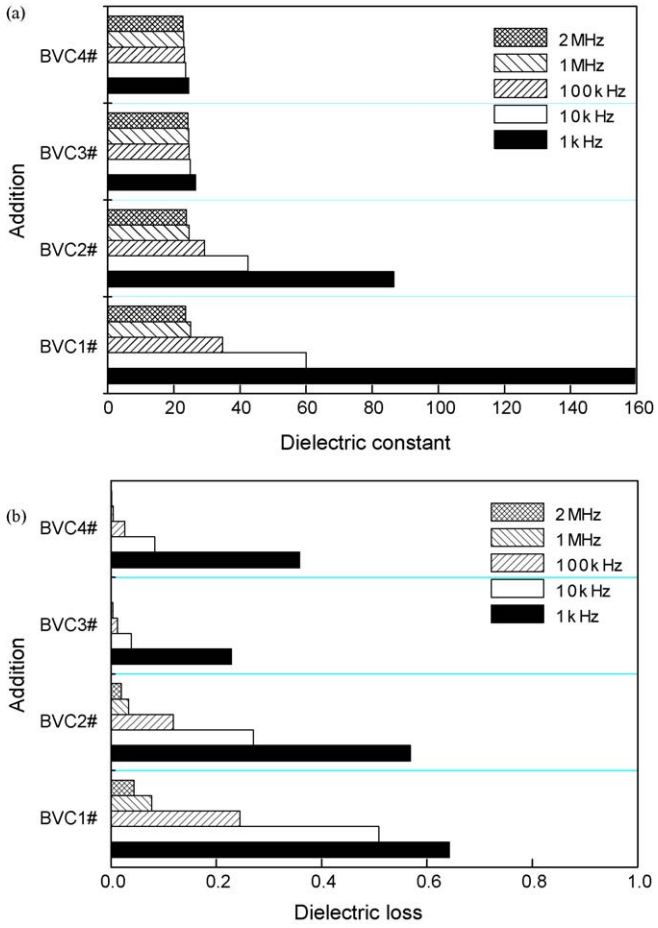

Fig. 8. Dielectric properties of V_2O_5–Bi_2O_3–CuO doped $ZnNb_2O_6$ ceramics: (a) dielectric constant and (b) dielectric loss.

frequency, the dielectric constant and dielectric loss decreased. It can be seen that the dielectric loss decreased with increasing CuO content, and the dielectric loss of BVC3# was clearly less than that of other samples. Since the dielectric loss of ceramics is related to density and the presence of the second ceramic phase, the lower densities of BVC1# and BVC2# lead to higher dielectric loss.

Microwave dielectric properties of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO are shown in Table 3. The dielectric constants of the samples were 22.8–23.8 at microwave frequencies. The $Q \times f$ value of $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO were all greater than 25,000 GHz. The $Q \times f$ value strongly depends on defects, pores and grain boundaries in the ceramics. Firstly with the increasing of CuO, the number of pores and defects decreased

Table 3
Dielectric properties of V_2O_5–Bi_2O_3–CuO doped $ZnNb_2O_6$ ceramics.

Samples	BVC1#	BVC2#	BVC3#	BVC4#
ε (1 MHz)	25.1	24.6	24.4	22.9
tan δ (1 MHz)	0.0768	0.0336	0.00334	0.00426
ε (~7.5 GHz)	22.8	23.8	23.4	22.8
$Q \times f$ (GHz)	25823	30558	46975	40181

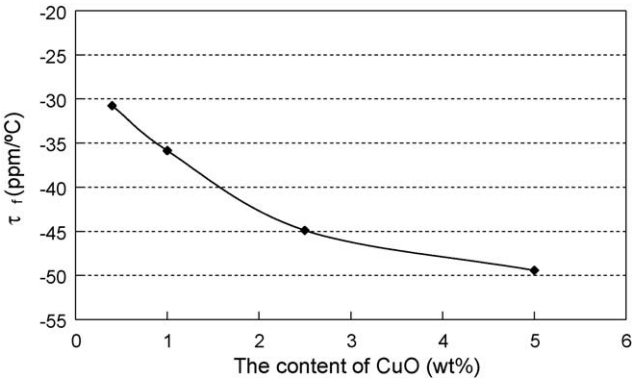

Fig. 9. The temperature coefficient of the resonant frequency of V_2O_5–Bi_2O_3–CuO doped $ZnNb_2O_6$ ceramics.

and $Q \times f$ increased. When the proportion of CuO reached 2.5 wt.%, the $Q \times f$ value reaches its maximum value, 46,975 GHz. Then the second phase $(Cu_2Zn)Nb_2O_8$ was formed, which results in decreasing $Q \times f$.

Fig. 9 shows the temperature coefficient of the resonant frequency (τ_f) of the ceramics as a function of CuO content. It can be seen that the τ_f values decreased from −30.75 ppm/°C to −49.44 ppm/°C continuously with increasing CuO. It has been reported that the τ_f value is related to the tilting of the octahedrons in the perovskite structure [14]. These results suggested that the substitution of Cu^{2+} for Zn^{2+} in $ZnNb_2O_6$ could cause the tilting of octahedrons. This may be attributed to the smaller ionic radius of Cu^{2+} (0.072 nm) compared with Zn^{2+} (0.074 nm) and A-site vacancies caused by non-stoichiometric substitution.

In summary, $ZnNb_2O_6$ ceramics doped with V_2O_5–Bi_2O_3–CuO not only have low sintering temperature, but also have good microwave dielectric properties, indicating a promising candidate material for LTCC applications.

4. Conclusions

Co-doping with 1.0 wt.%V_2O_5 and 1.0 wt.% Bi_2O_3 can lower the sintering temperature of $ZnNb_2O_6$ ceramics from 1150 °C to1000 °C, due to the eutectic phase formed by V_2O_5 and Bi_2O_3. Because of the co-effect of V_2O_5 and Bi_2O_3, there were rod-like and equiaxial grains coexisting in the $ZnNb_2O_6$ ceramics. Co-doping with CuO and V_2O_5–Bi_2O_3 can lower the sintering temperature of $ZnNb_2O_6$ ceramics even further. When the amount of CuO was more than 1.0 wt.%, the sintering temperature of $ZnNb_2O_6$ ceramics decreased from 1000 °C to 880 °C with a relative density more than 97%. A second phase $(Cu_2Zn)Nb_2O_8$ also forms when the CuO content is greater than 2.5 wt.%. The pure $ZnNb_2O_6$ phase can be obtained when the amount of CuO was between 1.0 wt.% and 2.5 wt.%. The mechanism of lowering of the sintering temperature is through the formation of liquid phases between CuO, Bi_2O_3 and V_2O_5. With increasing CuO content, the temperature coefficient of the resonant frequency τ_f values decreased continuously towards negative values. In the present work, the ceramics with composition of $ZnNb_2O_6$ + 1.0 wt.% V_2O_5 + 1.0 wt.% Bi_2O_3 + 2.5 wt.% CuO can be sintered at 880 °C, and exhibited excellent microwave dielectric properties, ε is 23.4, τ_f is −44.89 ppm/°C and $Q \times f$ is 46,975 GHz.

Acknowledgments

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