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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).

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:

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

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

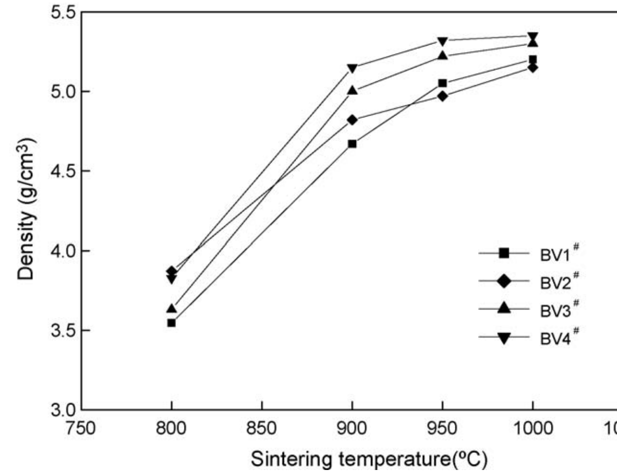

Fig. 1. Densities of V_2O_5–Bi_2O_3 doped $ZnNb_2O_6$ ceramics sintered at different temperatures.

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. 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

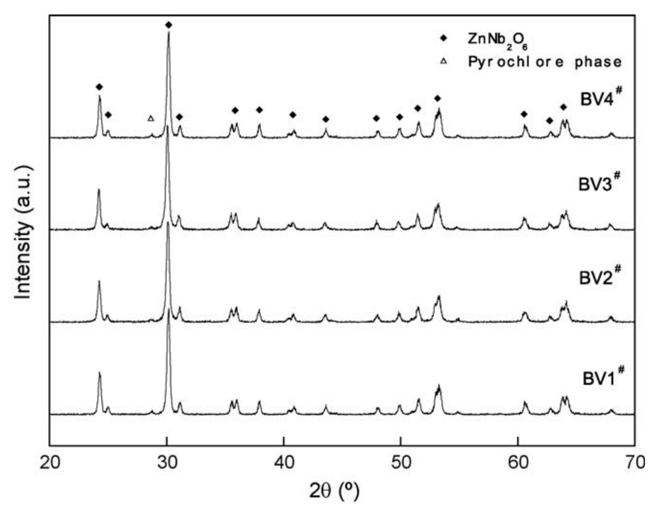

Fig. 2. XRD patterns of V_2O_5–Bi_2O_3 doped $ZnNb_2O_6$ ceramics sintered at 950 °C.