Journal of Electroceramics, 14, 67–74, 2005


# Microwave Dielectric Properties of CuO-$V_2O_5$-$Bi_2O_3$-Doped $ZnNb_2O_6$ Ceramics with Low Sintering Temperature

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Submitted January 13, 2003; Revised June 13, 2004; Accepted June 15, 2004

**Abstract.** Microwave dielectric properties of low temperature sintering $ZnNb_2O_6$ ceramics doped with CuO-$V_2O_5$-$Bi_2O_3$ additions were investigated systematically. The co-doping of CuO, $V_2O_5$ and $Bi_2O_3$ can significantly lower the sintering temperature of $ZnNb_2O_6$ ceramics from 1150 to 870°C. The secondary phase containing Cu, V, Bi and Zn was observed at grain boundary junctions, and the amount of secondary phase increased with increasing CuO-$V_2O_5$-$Bi_2O_3$ content. The dielectric properties at microwave frequencies (7–9 GHz) in this system exhibited a significant dependence on the relative density, content of additives and microstructure of the ceramics. The dielectric constant ($\varepsilon_r$) of $ZnNb_2O_6$ ceramics increased from 21.95 to 24.18 with increasing CuO-$V_2O_5$-$Bi_2O_3$ additions from 1.5 to 4.0 wt%. The quality factors ($Q \times f$) of this system decreased with increasing CuO-$V_2O_5$-$Bi_2O_3$ content and ranged from 36118 to 67100 GHz for sintered ceramics, furthermore, all $Q \times f$ values of samples with CuO-$V_2O_5$-$Bi_2O_3$ additions are lower than that of un-doped $ZnNb_2O_6$ ceramics sintered at 1150°C for 2 h. The temperature coefficient of resonant frequency ($\tau_f$) changed from −33.16 to −25.96 ppm/°C with increasing CuO-$V_2O_5$-$Bi_2O_3$ from 1.5 to 4.0 wt%.

**Keywords:** microwave dielectric ceramics, $ZnNb_2O_6$, low temperature sintering

## Introduction

Niobium based, columbite-type compounds such as $MNb_2O_6$ (M = Zn, Mg, Ca, Mn, Cu and Co) have been investigated as microwave dielectric resonators by Maeda et al. [1] and Lee et al. [2, 3]. The evaluations of the microwave dielectric properties of these compounds reveal a high quality factor ($Q \times f$) and a high dielectric constant ($\varepsilon_r$). Among these compounds, $ZnNb_2O_6$ has excellent microwave dielectric properties: $Q \times f = 87300$ GHz, $\varepsilon_r = 25$ and $\tau_f = -56$ ppm/°C [2, 3]. Moreover, its' sintering temperature is only about 1150°C, which can be easily reduced to below 1000°C. Therefore, $ZnNb_2O_6$ ceramics are promising candidates for low-temperature sintering dielectrics applied in multilayer microwave devices.

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CuO and $CaF_2$ have been used for sintering aids to lower the sintering of $ZnNb_2O_6$ ceramics by Lee et al. [4] and Zhang et al. [5]. However, too large amount of dopant would cause decrease of dielectric properties. The melting points of CuO, $Bi_2O_3$ and $V_2O_5$ are 1326, 825 and 678°C, respectively. These oxides have been introduced as sintering aids to create a liquid phase which lowers the sintering temperature and results in good dielectric properties [6, 7]. However, the effects of co-doping with more than two oxides on the sintering behavior of $ZnNb_2O_6$, have not been thoroughly investigated.

In this work, $ZnNb_2O_6$ was selected as the host materials, CuO, $Bi_2O_3$ and $V_2O_5$ were co-added as sintering aids to lower the sintering temperature of $ZnNb_2O_6$ ceramics. The effects of co-doping of CuO, $Bi_2O_3$ and $V_2O_5$ on the low temperature sintering, microstructure and microwave dielectric properties of $ZnNb_2O_6$ ceramics were investigated.

## Experimental Procedure

$ZnNb_2O_6$ powder was synthesized by the conventional mixed oxide method. High purity oxide powders (>99.99%) of ZnO and $Nb_2O_5$ were used as starting materials. They were mixed, according to the composition $ZnNb_2O_6$, and ball-milled in alcohol for 6 h. After drying, the product was calcined at 1000°C for 2 h. The $ZnNb_2O_6$ ceramic powder was mixed with 0.5 wt% CuO, 0.5 wt% $V_2O_5$ and 0.5–3 wt% $Bi_2O_3$ by ballmilling with alcohol for 2 h. The total amount of CuO, $V_2O_5$ and $Bi_2O_3$ ranged from 1.5 wt% to 4.0 wt%. After drying, the powder was pressed into pellets of 10 mm in diameter and 4 mm in thickness at 100 MPa. The pellets were sintered at 790–950°C for 2 h.

The crystalline phases of the sintered samples were analyzed by X-ray diffraction (XRD) using Cu K$\alpha$ radiation. The densities of the specimens were measured by Archimedes method. Polished and thermal etched surfaces of sintered samples were examined by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The dielectric properties at microwave frequency (6–8 GHz) were measured with a HP8720ES network analyzer using Hakki-Coleman's dielectric resonator method, as modified and improved by Courtney and Kobayashi et al. [8–10].

## Results and Discussions

The XRD patterns of $ZnNb_2O_6$ ceramics doped with CuO-$V_2O_5$-$Bi_2O_3$ sintered at 870°C for 2 h were shown in Fig. 1(a). $ZnNb_2O_6$ ceramics were single phase with a columbite structure when the total amount of CuO-$V_2O_5$-$Bi_2O_3$ less than 3.0 wt%. However, a second phase (marked as '*') was detected in the samples with 3.0–4.0 wt% CuO-$V_2O_5$-$Bi_2O_3$ addition. In order to clarify the secondary phase, 10 wt% CuO-$V_2O_5$-$Bi_2O_3$ additions was added to $ZnNb_2O_6$ ceramics and sintered at 830°C. The XRD patterns were shown in Fig. 1(b). The strongest peak of the secondary phase was observed at 29.28°. However, the secondary phase was not identified in this study because that the reflection peak of the secondary phase was not match to any phase which may be a any combination of five elements including Cu, V, Bi, Zn and O according to EDS analysis results (Fig. 4(d) and (e)). Those results suggest that the secondary phase may be a new phase and has not been reported before. Therefore, the secondary phase is needed to further study in later work.

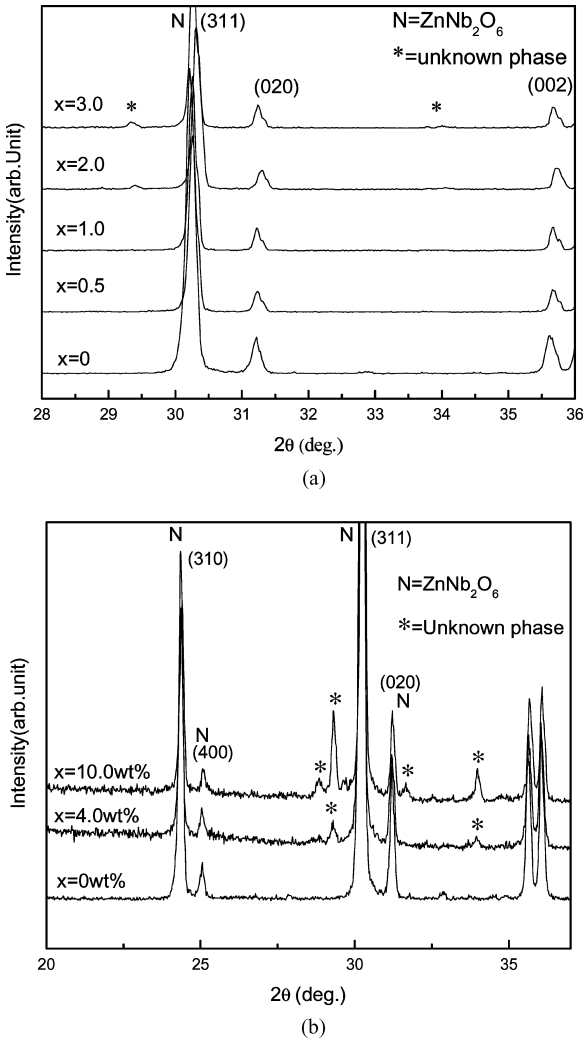



*Fig. 1.* The XRD patterns of $ZnNb_2O_6$ ceramics with 0.5 wt% CuO + 0.5 wt% $V_2O_5$ + ($x$) wt% $Bi_2O_3$ additions sintered at 870°C for 2 h. (b) The XRD patterns of $ZnNb_2O_6$ ceramics with ($x$) wt% CuO-$V_2O_5$-$Bi_2O_3$ additions sintered at 830°C for 2 h.

The relative theoretical densities of $ZnNb_2O_6$ ceramics doped with CuO-$V_2O_5$-$Bi_2O_3$ as a function of sintering temperature were shown in Fig. 2. The densities of samples steadily increased with increasing sintering temperature, and saturated at 850–950°C. It was difficult to densify $ZnNb_2O_6$ ceramics when the sintering temperature is lower than 1150°C. However, the densification temperature of $ZnNb_2O_6$ ceramics decreased with increasing amount of CuO-$V_2O_5$-$Bi_2O_3$.

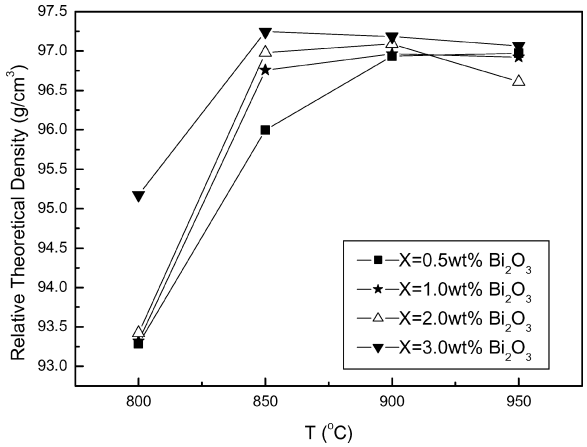



*Fig. 2.* The relative theoretical densities of $ZnNb_2O_6$ ceramics with 0.5 wt% CuO + 0.5 wt% $V_2O_5$ + ($x$) wt% $Bi_2O_3$ additions as a function of sintering temperature.

96% theoretical density could be obtained for all samples when the sintering temperature higher than 870°C. The results suggest that co-doping with CuO, $V_2O_5$ and $Bi_2O_3$ can significantly lower the sintering temperature of $ZnNb_2O_6$ ceramics from 1150 to 870°C.

Typical microstructure of polished and thermal etched $ZnNb_2O_6$ ceramics with CuO-$V_2O_5$-$Bi_2O_3$ are shown in Fig. 3. SEM micrographs show that the grain shape of un-doped $ZnNb_2O_6$ ceramics is equiaxied and uniform. The average grain size is ranged from 8 to 9 $\mu$m (Fig. 3(a)). However, the grain shape change to long column for samples doped with CuO-$V_2O_5$-$Bi_2O_3$, and the average grain size in major axis direction decreased with increasing amount of CuO-$V_2O_5$-$Bi_2O_3$ addition (Fig. 3(b), (c) and (d)). It is suggested that large amount of CuO-$V_2O_5$-$Bi_2O_3$ additives prevent the grain growth of samples.

Figure 4(a) and (b) shows bright-field images and a select-area diffraction pattern of $ZnNb_2O_6$ ceramics with 4.0 wt% CuO-$V_2O_5$-$Bi_2O_3$ sintered at 870°C for 2 h. A triangle intergranular phase (marked at 'a') is observed at the grain boundary junctions (Fig. 4(a)). The ring diffraction pattern of the intergranular phase indicates that it is composed of microcrystals (Fig. 4(b)). Figure 4(c) shows another bright-field images of $ZnNb_2O_6$ ceramics with 1.5 wt% CuO-$V_2O_5$-$Bi_2O_3$ addition sintered at 870°C. A triangle intergranular phase (marked at '2' and '3') is also observed at the grain boundary junctions. In order to clarify the compositions of intergranular phase, EDS results of the intergranular phase (marked as "2" in Fig. 4(c)) and the matrix grains (marked as "1" in Fig. 4(c)) were shown in Fig. 4(d) and (e), respectively. EDS analysis shows the secondary phase at the grain boundary is rich in Cu, V, Bi and Zn (Fig. 4(d)), and those elements except Zn are not observed in matrix grains (Fig. 4(e)). The chemical compositions of the intergranular phase (marked as "2" and "3" in Fig. 4(c)) and the matrix grains (marked as "1", "4" and "5" in Fig. 4(c)) are listed in Table 1. Those results also demonstrate that the secondary phase contains five elements: Cu, V, Bi, Zn and O. furthermore, the content of Zn in secondary phase is higher than those of Cu, V and Bi, while the content of Zn in matrix grains deviate the stoichiometry of $ZnNb_2O_6$ and lower than the normal content according to the ratio of Zn/Nb = 1:2. These results suggest that Zn of $ZnNb_2O_6$ may be react with CuO, $Bi_2O_3$, $V_2O_5$ and form eutectic with liquid phase at high temperature and promote the sintering of $ZnNb_2O_6$ ceramics. The liquid phase then, re-crystallized during cooling [3] The melting point of the secondary phase and appearance temperature of liquid phase were not determined, However the melting point of $ZnNb_2O_6$, CuO, $V_2O_5$ and $Bi_2O_3$ are 1405, 1326, 690 and 825°C, respectively, and the high temperature melting test shows that the melting point of CuO-$V_2O_5$-$Bi_2O_3$ (the ratio is 1:1:1) is 780°C. Therefore, those results suggest that the liquid phase may be formed below 800°C.

*Table 1.* Chemical Composition of $ZnNb_2O_6$ ceramics with 4 wt% CuO-$V_2O_5$-$Bi_2O_3$ sintered at 870°C.

| | Composition (mol%) | | | | |
|---|---|---|---|---|---|
| Marked region | Zinc | Niobium | Copper | Bismuth | Vanadium |
| 1 | 27.34 | 72.36 | 0.08 | 0.13 | 0.09 |
| 2 | 31.37 | 2.54 | 22.23 | 16.09 | 27.28 |
| 3 | 36.28 | 3.42 | 20.11 | 18.15 | 22.04 |
| 4 | 28.65 | 71.01 | 0.10 | 0.11 | 0.13 |
| 5 | 30.78 | 68.84 | 0.12 | 0.11 | 0.15 |

Microwave dielectric properties of $ZnNb_2O_6$ ceramics with CuO-$V_2O_5$-$Bi_2O_3$ additives prepared under various temperatures were evaluated in order to clarify the effects of additions and sintering temperature on the microwave dielectric properties. Figure 5 shows the dielectric constant ($\varepsilon_r$) of $ZnNb_2O_6$ ceramics doped with CuO-$V_2O_5$-$Bi_2O_3$ as a function of sintering temperature. The $\varepsilon_r$ values of samples increased with increasing sintering temperature and saturated at 850–900°C, then slightly decreased. These phenomena are attributed to

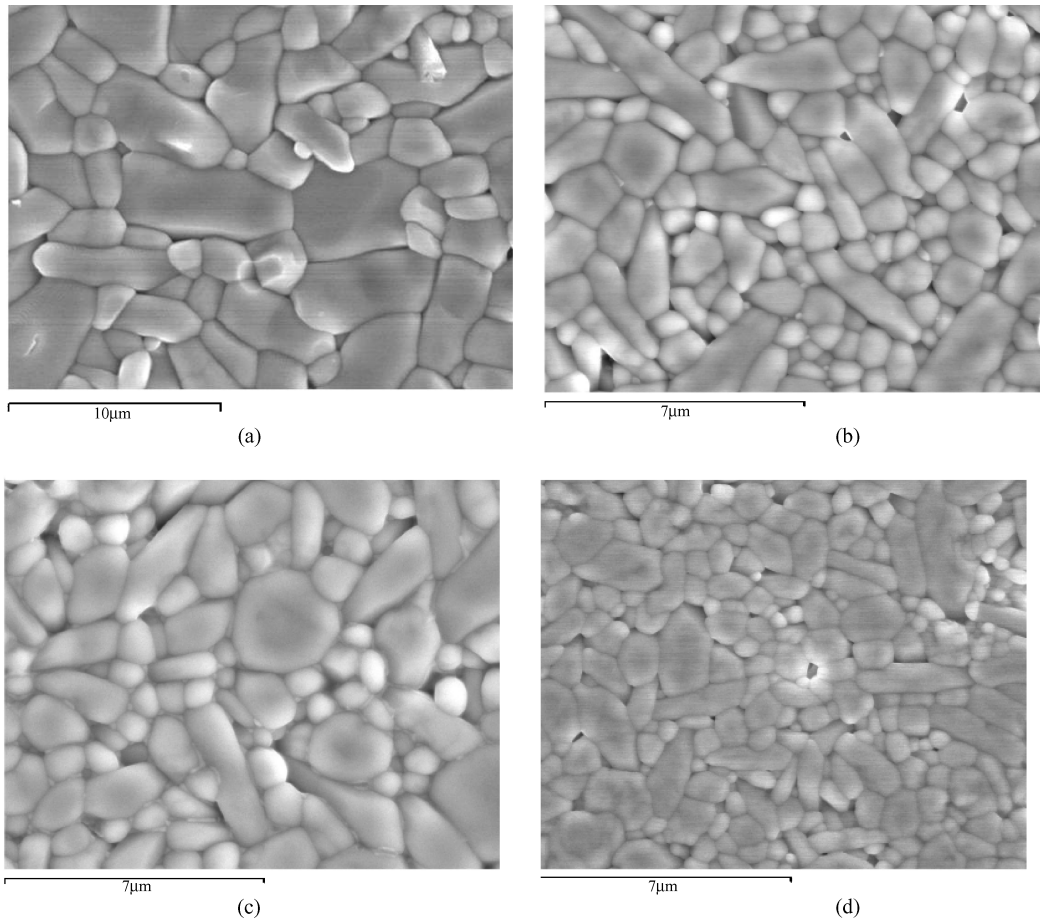
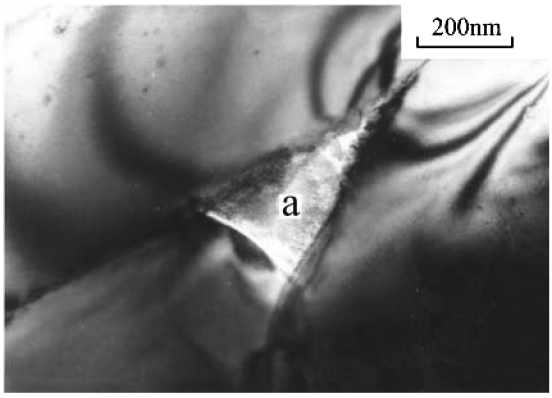


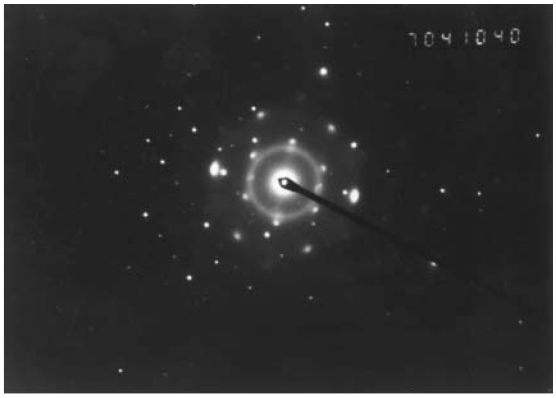

*Fig. 3.* SEM micrograph of polished and thermal etched $ZnNb_2O_6$ ceramics with 0.5 wt% CuO + 0.5 wt% $V_2O_5$ + ($x$) wt% $Bi_2O_3$: (a) undoped $ZnNb_2O_6$, 1150°C, (b) $x = 0.5$ wt%, 870°C, (c) $x = 2.0$ wt%, 870°C, (d) $x = 3.0$ wt%, 870°C.

the increase of relative density ($D_r$) which depends on the sintering temperature. On the other hand, the $\varepsilon_r$ values of the ceramics also increased slightly with increasing amount of CuO-$V_2O_5$-$Bi_2O_3$ additions, and ranged from 22.61 to 24.17. The improvement of $\varepsilon_r$ is closely related to the increase in relative density of ceramics at the same sintering temperature due to the increasing of sintering aids.

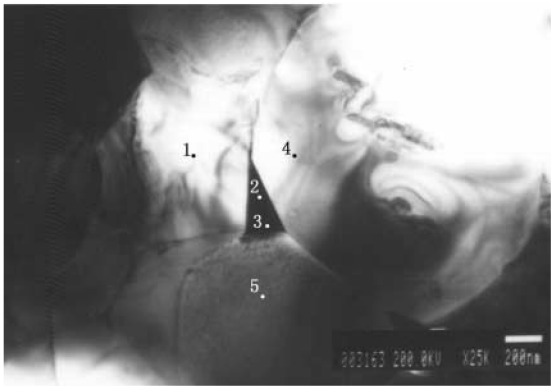
Figure 6 shows the quality factor ($Q \times f$) of $ZnNb_2O_6$ ceramics with CuO-$V_2O_5$-$Bi_2O_3$ additions as a function of sintering temperature. The $Q \times f$ values of $ZnNb_2O_6$ ceramics with different CuO-$V_2O_5$-$Bi_2O_3$ contents also increased with increasing sintering temperature, after reached the maximum values, then decreased. On the other hand, the $Q \times f$ values decreased with increasing amount of CuO-$V_2O_5$-$Bi_2O_3$ and changed from 67100 GHz (1.5 wt%) to 36118 GHz (4.0 wt%), moreover, all $Q \times f$ values of samples with CuO-$V_2O_5$-$Bi_2O_3$ additions are lower than that of undoped $ZnNb_2O_6$ ceramics sintered at 1150°C for 2 h. In general, microwave dielectric loss could be divided into two fields: the intrinsic loss and extrinsic loss. The intrinsic loss was mainly caused by lattice variation modes while the extrinsic loss was mainly dominated by secondary phase, oxygen vacancies, grains sizes and porosity [11]. In this study, the lower $Q \times f$ values for the ceramics with CuO-$V_2O_5$-$Bi_2O_3$ additions are considered to be caused by the crystal defect produced in crystal growth and the impurity effects of the secondary phase. In general, grain growth can improve



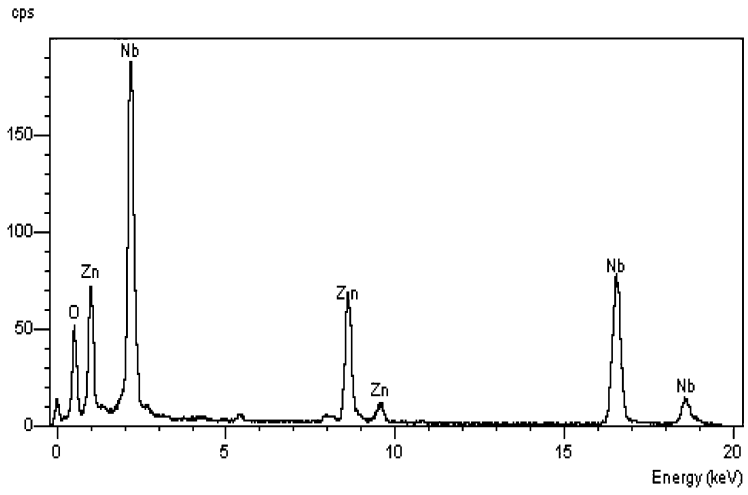

(a)



(b)

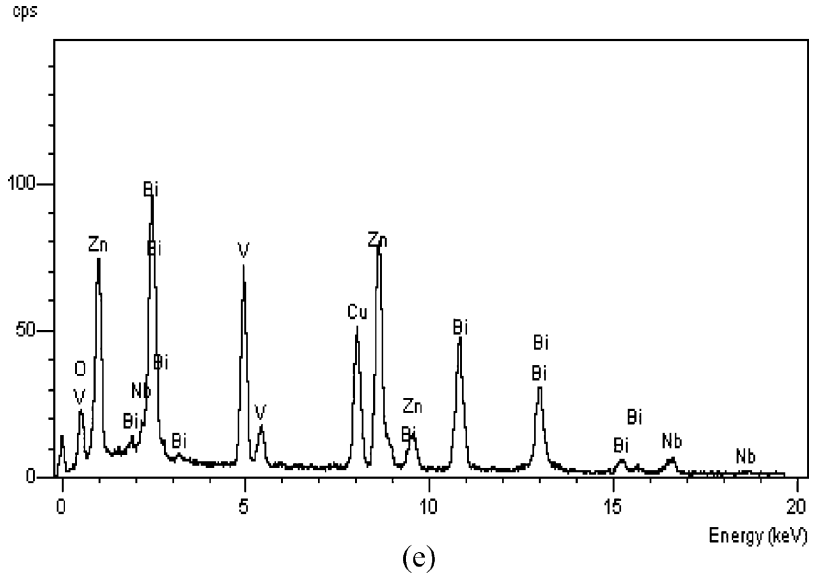



(c)




(d)

*Fig. 4.* TEM micrograph of $ZnNb_2O_6$ ceramics with ($x$) wt% CuO-$Bi_2O_3$-$V_2O_5$ additive sintered at 870°C. (a) Bright-field image, $x = 4$ wt% (b) SAD pattern of the intergranular phase marked as 'a' in (a), (c) Bright-field image, $x = 1.5$ wt%, (d) EDS graph of the intergranular phase marked as '2' in (c), (e) EDS graph of the matrix grains marked as '1' in (c). (*Continued on next page*.)




(e)

*Fig. 4.* (*Continued*).

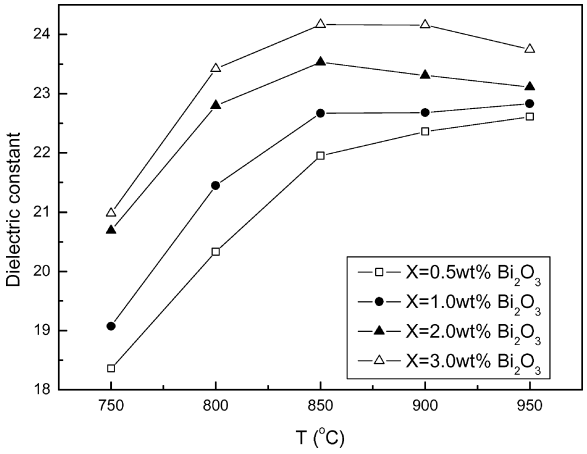



*Fig. 5.* $\varepsilon_r$. values of $ZnNb_2O_6$ ceramics doped with 0.5 wt% CuO + 0.5 wt% $V_2O_5$ + ($x$) wt% $Bi_2O_3$ additions as a function of sintering temperature.

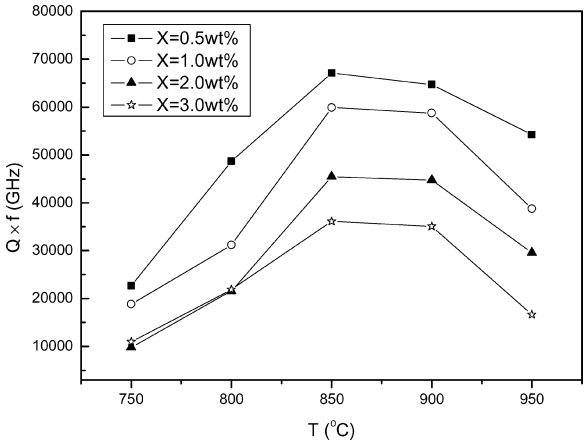



*Fig. 6.* $Q \times f$ values of $ZnNb_2O_6$ ceramics doped with 0.5 wt% CuO + 0.5 wt% $V_2O_5$ + ($x$) wt% $Bi_2O_3$ additions as a function of sintering temperature.

the $Q \times f$ values, because as the grain size increased, the pores and grain boundary area decreased, which can reduce the lattice imperfections and increase the $Q \times f$ values [12, 13]. In this study, the average grain size is about 8 $\mu$m for undoped samples, the grain boundaries are very clear and no secondary phase observed, therefore, the $Q \times f$ value was very high for un-doped sample, while the average grain size in major axis direction of $ZnNb_2O_6$ ceramics decreased from 6 to 4 $\mu$m as the content of CuO-$V_2O_5$-$Bi_2O_3$ additions ranged from 1.5 to 4.0 wt% (Fig. 3(b) and (d)), and the $Q \times f$ values decreased from 67100 to 36118 GHz (Fig. 6). Those results suggest that too large an amount of CuO-$V_2O_5$-$Bi_2O_3$ addition inhibit the grain growth, and form a small grain in comparison with those of un-doped sample or samples with small amount additives, which maybe decreased the $Q \times f$ values of $ZnNb_2O_6$ ceramics. On the other hand, the secondary

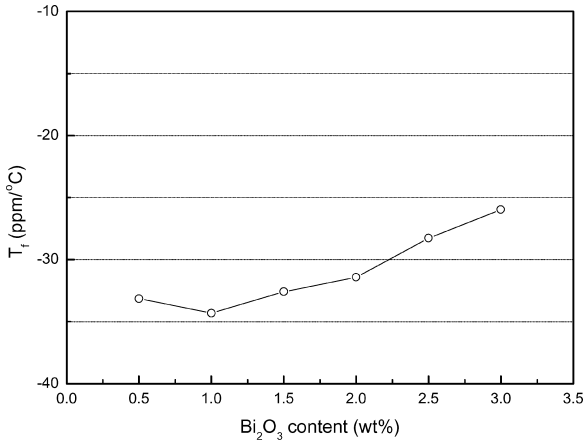



*Fig. 7.* $\tau_f$ values of $ZnNb_2O_6$ ceramics doped with 0.5 wt% CuO + 0.5 wt% $V_2O_5$ + ($x$) wt% $Bi_2O_3$ addition sintered at 870°C.

phase which is rich in Cu, V, Bi and Zn may bring the impurity to the ceramics, and thus anharmonicity in phonon vibration may increase with increasing of the secondary phase due to the adding of CuO-$V_2O_5$-$Bi_2O_3$ additions, which may cause the decrease of $Q \times f$ value.

Figure 7 shows the temperature coefficient of resonant frequency ($\tau_f$) of $ZnNb_2O_6$ ceramics with different amount of CuO-$V_2O_5$-$Bi_2O_3$ additions sintered at 870°C. The $\tau_f$ values of samples shift to zero direction with increasing amount of CuO-$V_2O_5$-$Bi_2O_3$ additions. In general, $\tau_f$ value is known to be related with the temperature coefficient of dielectric constant ($\tau_\varepsilon$) and the thermal expansion coefficient ($\alpha_l$) of which the value is approximately 10 ppm/°C in the microwave dielectric ceramics. And Lee et al. also reports that the $\tau_f$ values of $MNb_2O_6$ ceramics are considered to depend on the crystal structure on a basis of the relationship between $\tau_\varepsilon$ and unit cell volumes [3]. However, in the case of CuO-$V_2O_5$-$Bi_2O_3$-doped $ZnNb_2O_6$ ceramics, $\tau_f$ values may be primary influenced by the composition and content of the secondary phase if the crystal structure influence is ignored. The compositions of the secondary phase are very complex according to the results of XRD and EDS, there are no way to obtain the $\tau_f$ value of the secondary phase, therefore, it needs to be further studied for the secondary phase using other measure methods.

It is of interesting to investigate the co-fired behavior between the $ZnNb_2O_6$ ceramics and internal silver electrodes because $ZnNb_2O_6$ ceramics with CuO-$V_2O_5$-$Bi_2O_3$ additions shows good sintering properties below 900°C and excellent dielectric properties. Figure 8 shows SEM micrographs and EDS line scan of the interface between the $ZnNb_2O_6$ ceramics with CuO-$V_2O_5$-$Bi_2O_3$ additions and the silver electrode co-fired at 870°C for 2 h. SEM micrographs show that the silver internal electrodes were well formed and the reaction between the $ZnNb_2O_6$ ceramics and the silver electrode was not observed. Furthermore, EDS line scan also demonstrate this result. Therefore, low-firing $ZnNb_2O_6$ ceramics with CuO-$V_2O_5$-$Bi_2O_3$ additions

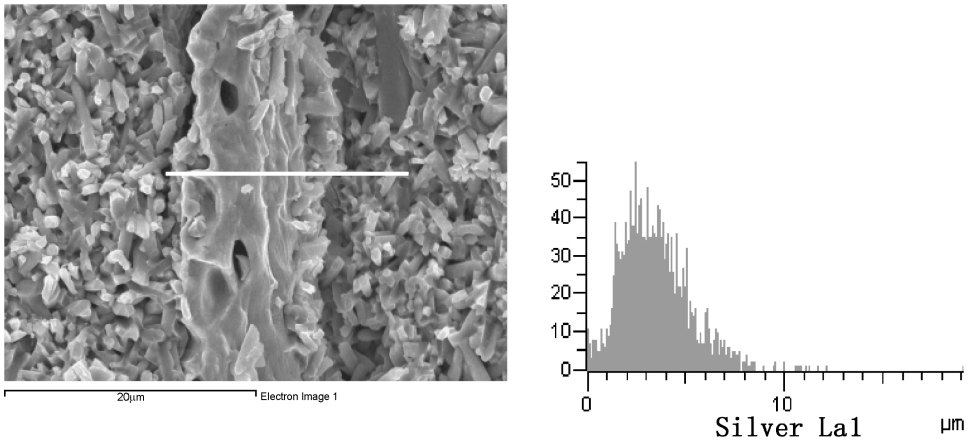



*Fig. 8.* SEM micrograph and EDS line scan of the interface between a silver electrode and the ceramic co-fired at 870°C.

are promising candidates for low-temperature sintering dielectrics applied in multilayer microwave devices.

## Conclusions

The sintering temperature of $ZnNb_2O_6$ ceramics was significantly reduced from 1150 to 870°C by the co-doping of CuO, $Bi_2O_3$ and $V_2O_5$. The secondary phase containing Cu, V, Bi and Zn were observed at grain boundary junction. The mechanism of low temperature sintering may be caused by that CuO, $Bi_2O_3$, $V_2O_5$ and $ZnNb_2O_6$ forming a eutectic liquid phase (richen in Cu, V, Bi and Zn) at high temperature and promoting the sintering of $ZnNb_2O_6$ ceramics. The $ZnNb_2O_6$ ceramics doped with 1.5 wt% CuO-$V_2O_5$-$Bi_2O_3$ additives exhibit excellent microwave dielectric properties: $\varepsilon_r. = 32.69$, $Q \times f = 67100$ GHz and $\tau_f = -32.69$ ppm/°C. CuO-$V_2O_5$-$Bi_2O_3$-doped $ZnNb_2O_6$ ceramics is chemically compatible with Ag electrode for multilayer microwave devices applications.

## Acknowledgment

This work has been financially supported by the High technology Research and Development Project of the People's Republic of China (No. 2001AA325100) and the National Mayor Fundamental Research Project of China (No. 2002CB613307).

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