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Low firable $BiNbO_4$ based microwave dielectric ceramics

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Abstract

The sintering behavior, the microstructures and the microwave dielectric properties of $Bi(Nb,Ta)O_4$ ceramics with different amount of CuO additions were investigated. The CuO additive, appeared at grain boundary and acted as a sintering aid, could effectively lower the sintering temperature of $BiNbO_4$ ceramics. However, too many CuO additions (>1 wt.%), too long a soaking time (>3 h) or too high a sintering temperature (>960°C) would cause abnormal grain growth resulted in the degradation of densities and dielectric properties of $BiNbO_4$ ceramics. To investigate the microstructures and the dielectric properties of $Bi(Nb,Ta)O_4$ ceramics, 0.5 wt.% CuO addition was selected as a proper sintering aid to reduce the sintering temperature. The dielectric constant ε_r of $BiNb_{(1-x)}Ta_xO_4$ ceramics was not significantly changed with Ta substitution and saturated at 44–45 for dense ceramics. The obtained quality values (Q×f) ranged from 4000 to 21 000 (GHz) were found to be functions of the sintering temperatures and the amount of Ta substitution. The τ_f values were shifted toward negative direction and became more negative with the increase of Ta content. Zero temperature coefficient of resonator frequency could be obtained by properly adjusting the Ta content.

Keywords: A. Sintering; B. Microstructure; C. Dielectric properties

1. Introduction

In recent years, the development of low-temperature-cofiring ceramics (LTCCs) has been getting much interest due to the application of multilayer integrated circuit (MLIC), such as chip LC filters [1]. Most of the well-known commercial microwave dielectric materials exhibited high quality factor values and dielectric constants. However, they are not compatible with silver or copper electrodes due to their high sintering temperatures. To apply the multilayer technology, development of a dielectric material suitable for cofiring with internal conductors below the melting temperature of the metals such as Ag and Cu have become a major focus. The structures of these components consisted of several layers of dielectric ceramics and internal-electric metal conductors. Although some ceramics materials being used for multilayer chip capacitors (MLCCs) showed low sintering temperatures, they possessed high dielectric losses at microwave frequencies [2,3]. Many researchers began with the search for suitable low-firing-temperature dielectrics, and then the modification of their electrical characteristics to meet the desired requirements such as high dielectric constant, low dielectric loss and high temperature stability. Low melting glass additions and chemical processing are two methods normally used in reducing the sintering temperatures of dielectric materials [4,5]. Although glass additions was found to effectively lower the firing temperature of ceramics while they also brought serious degradation in the dielectric properties of dielectric ceramics [4]. The chemical process often required a flexible procedure which increased the cost and time required to fabricate microwave dielectric devices or components [5].

It is well known that bismuth-based dielectric ceramics are low-firing temperature materials and have been studied for piezoelectric materials or multilayer ceramic capacitors [5,6]. The ABO_4 family of compounds ($A = Bi^{3+}$ or Sb^{3+}, and $B = Nb^{5+}$, Ta^{5+} or Sb^{5+}) includes both ferroelectrics and anti-ferroelectrics with the stibiotantalite structure which consists of layers of vertex sharing, distorted BO_6 octahedral parallel to the (001) plane of the orthorhombic unit cell. They are known to

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exhibit multiple structural and dielectric phase transitions and possess excellent ferroelectric, piezoelectric, pyroelectric and electro-optic properties at room temperature [7]. In spite of these interesting properties, Kagata and his co-workers were the first one reported the microwave dielectric properties of $BiNbO_4$ ceramics [8]. They showed $BiNbO_4$ ceramics to be good candidate for low firing microwave ceramics. Little amount of V_2O_5 and CuO were added in $BiNbO_4$ to dense the ceramics and to obtain higher Q×f value. Several works have demonstrated related research [9–12]. However, only pure $BiNbO_4$ ceramics or partial replacement of Nb by Ta were reported. Zero temperature coefficient of resonator frequency was also not properly optimized. In this paper, the sintering behavior and the microwave dielectric properties of CuO-doped $BiNb_{(1-x)}Ta_xO_4$ ceramics (x = 0–1) were investigated. It is desired to clarify these relationships before it can be put on practical applications. In addition, Ta substitution for Nb is expected to improve the microwave dielectric properties of $BiNbO_4$ ceramics due to their same valance (+5) and similar chemical characteristics. The X-ray diffraction (XRD) and the scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and the microstructures of the ceramics.

2. Experiment procedures

Specimen powders were prepared by conventional solid-state reaction technique. The starting materials were high purity (>99.9%) Bi_2O_3, Nb_2O_5 and Ta_2O_5. The powders were first weighed according to the compositions y wt.% CuO-doped $BiNbO_4$ (y = 0, 0.125, 0.25, 0.5, 1 and 2) to optimize the amount of CuO addition. After optimization, powders of compositions $Bi(Nb_{1-x}\ Ta_x)O_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) with 0.5 wt.% CuO addition were mixed according to the desired stoichiometry. All mixtures were ball-milled for 10 h in distill water and then dried. The dried powders were calcined at 800°C for 3 h. The calcined powders were re-milled and then sieved using 100 meshes screen. After adding organic binder, the sieved powders were uniaxially pressed into pellets at 100 kg/cm^2. The pellets were sintered at 860–1010°C for 3–16 h. Typical dimension of the sintered disk was 11 mm in diameter and 5 mm in thickness. The ceramics samples prepared with the sintering aid CuO showed a change in color from white to black.

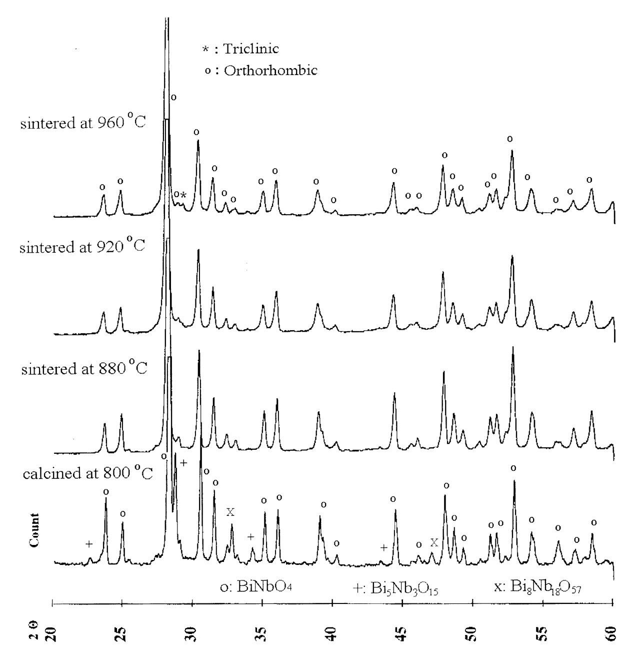


Fig. 1. Typical XRD patterns of 0.5 wt.% CuO added $BiNbO_4$ ceramics at different temperature for 3 h. (o: $BiNbO_4$, +: $Bi_5Nb_3O_{15}$, x: $Bi_8Nb_{15}O_{57}$).

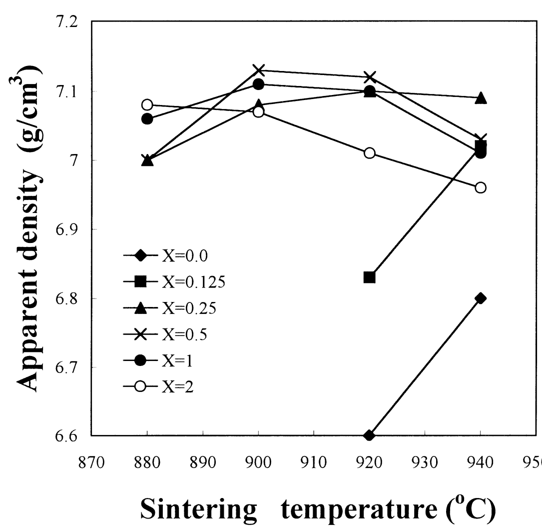


Fig. 2. Densities of $BiNbO_4$ ceramics with x wt.% CuO addition at different sintering temperature.

Table 1
Dielectric properties of $BiNbO_4$ ceramics with CuO addition at different sintering temperature

The amount of CuO (wt.%)	Sintering temperature (°C)	ε_r	Q×f (GHz) at 6.3 GHz	τ_f (ppm/°C)
0.25	880	42.6	5200	–
	900	43.2	8600	–
	920	43.0	9800	–
	940	43.0	9200	–
0.5	880	42.9	8800	–
	900	43.3	13 000	15
	920	42.9	12 500	–
	940	43.0	12 200	–
1.0	880	42.7	8600	–
	900	42.8	7700	–
	920	42.6	6200	–
	940	43.1	5200	–

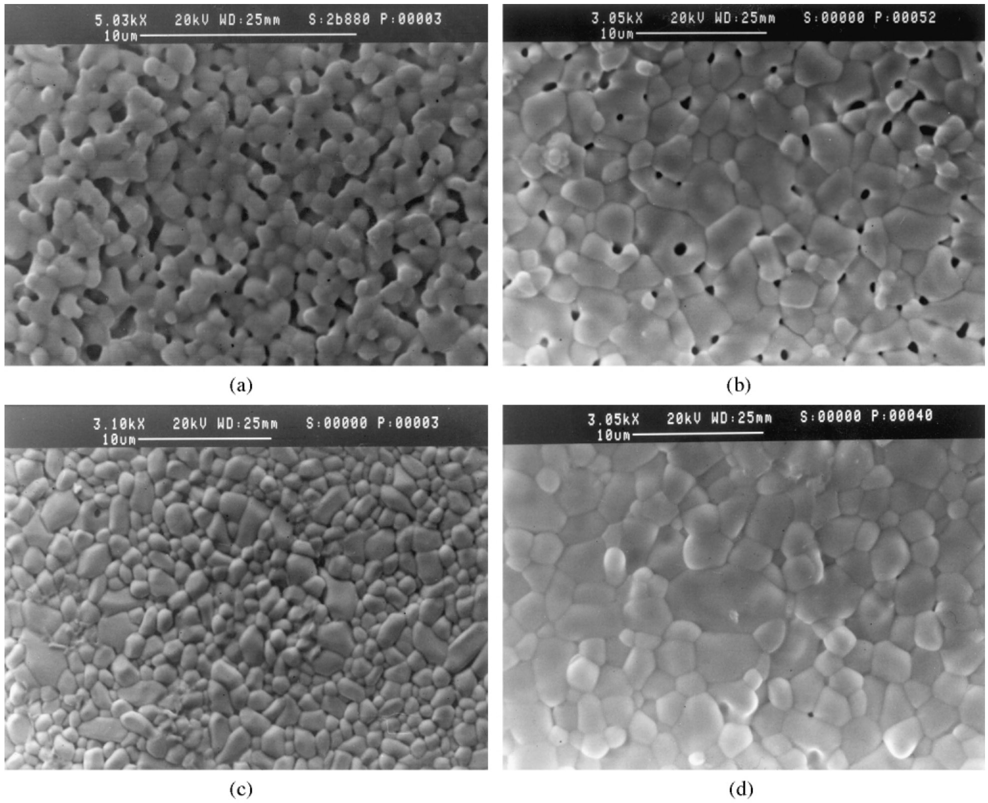


Fig. 3. SEM micrographs of $BiNbO_4$ ceramics without CuO addition sintered at (a) 980°C, (b) 1010°C and with 0.5 wt.% CuO addition sintered at (c) 880°C, (d) 920°C for 3 h.

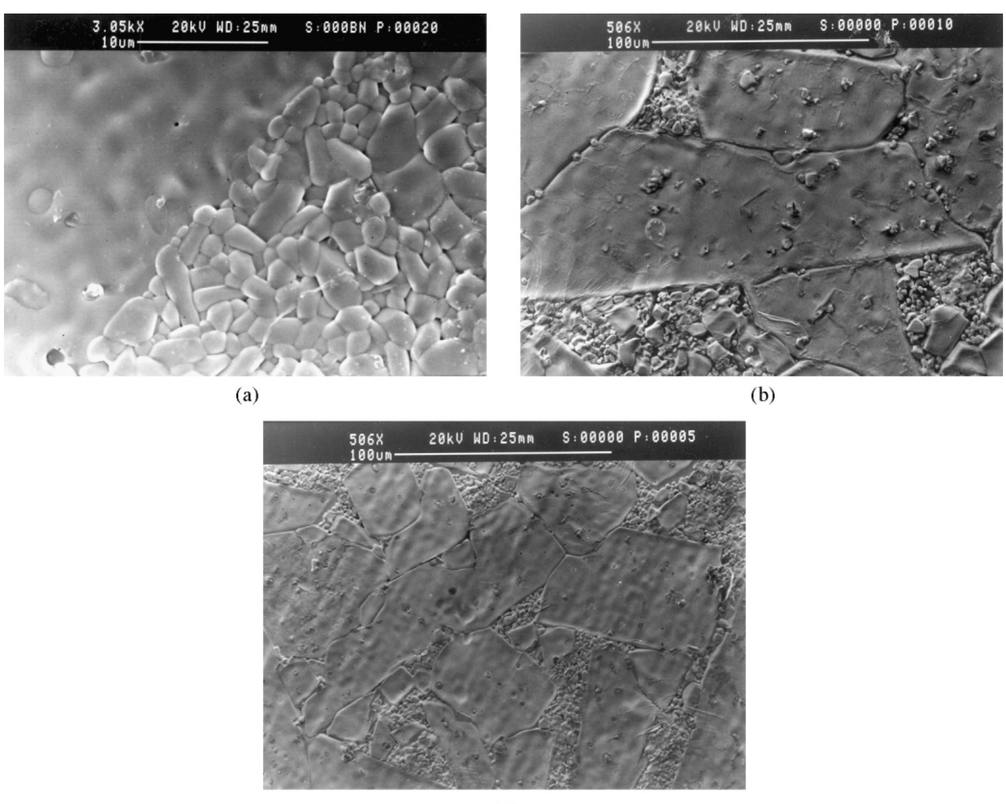


Fig. 4. SEM micrographs of $BiNbO_4$ ceramics with 0.5 wt.% CuO addition sintered at (a) 920°C/6 h, (b) 960°C/3 h and (c) with 2 wt.% CuO addition sintered at 920°C/3 h.

The crystalline phases were analyzed by means of an X-ray powder diffraction method using Cu–K_α radiation from 20° to 60° in 2θ. The microstructure analysis and element analysis were observed by a scanning electron microscope (SEM) and an energy dispersive spectra (EDS). The densities of sintered ceramics were measured using the Archimedes method. Measurements of the dielectric constant and the unloaded Q-values on TE_{011} mode at 6–8 GHz were accomplished using the post resonant method developed by Hakki and Coleman

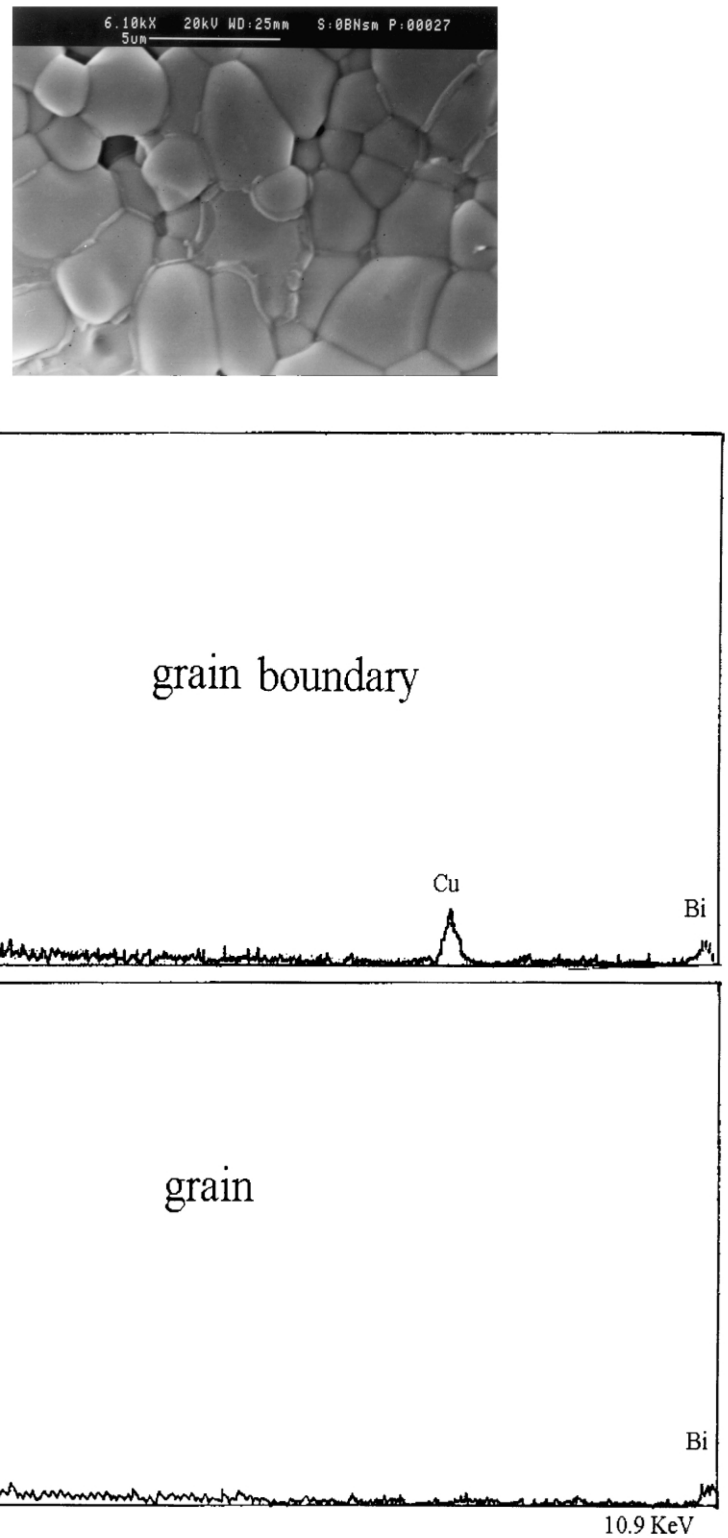


Fig. 5. EDS of grain and grain boundary for 0.5 wt.% CuO added $BiNbO_4$ ceramics sintered at 920°C/3 h.

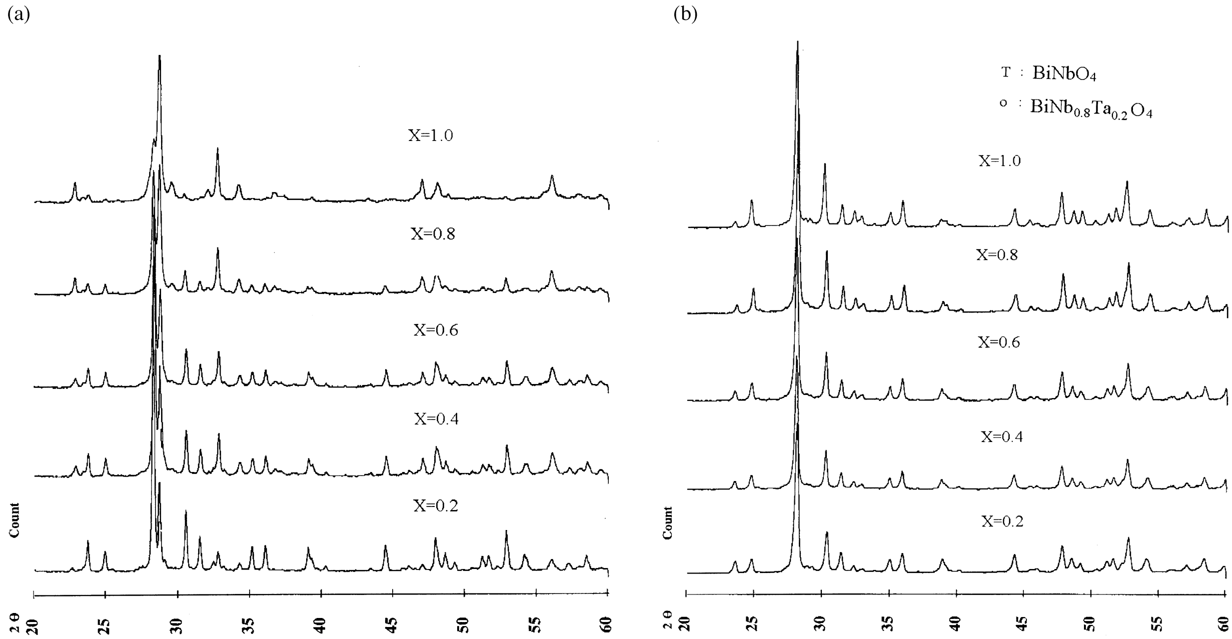


Fig. 6. Typical XRD patterns of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics (a) calcined at 800°C/3 h and (b) sintered at 940°C/3 h.

[13]. It consisted of two parallel conducting plates and coaxial probes connected to a HP8757D network analyzer and a HP8350B sweep oscillator. By measuring the $TE_{01\delta}$ resonant frequency at 25°C(f_25) and 80°C (f_{80}), the temperature coefficient of resonant frequency could be obtained as

$$\tau_f = (f_{80} - f_{25})/(55 \times f_{25}) \times 10^6 \quad (ppm/°C) \tag{1}$$

3. Results and discussion

3.1. CuO-doped $BiNbO_4$ ceramics

Fig. 1 illustrates the typical X-ray diffraction patterns of 0.5 wt.%-CuO-doped $BiNbO_4$ ceramics calcined at 800°C/3 h and sintered at 880–960°C/3 h. The calcined powder at 800°C exhibited orthorhombic $BiNbO_4$ phase as the main crystalline phase with the existence of some other minor phases. After sintering at temperatures 880–920°C, the samples exhibited single orthorhombic Bi NbO_4 phase without any second phase or impurity phase. However, small amount of triclinic $BiNbO_4$ phase appeared at $2\theta = 29.3$ for samples sintered at 960°C. Same X-ray pattern were obtained for $BiNbO_4$ ceramics with different amount of CuO additions. $BiNbO_4$ is known to have an orthorhombic-$SbTaO_4$ type crystal structure below 1020°C [7], and will transform to triclinic phase at higher temperature. It suggested that the CuO addition enhanced the densification and a little lowered the phase transition temperature of $BiNbO_4$ ceramics.

Fig. 2 shows the densities of $BiNbO_4$ ceramics with various amount of CuO addition at different sintering temperature for 3 h. It was observed that pure $BiNbO_4$ ceramics was not dense and possessed a density of 6.8 g/cm^3 at 940°C. With 0.125 wt.% CuO addition, $BiNbO_4$ ceramics was still not well dense while it seemed excess with 2 wt.% CuO addition due to the fact that the densities of $BiNbO_4$ ceramics decreased with increasing sintering temperature. With 0.25–1 wt.% CuO additions, the densities of $BiNbO_4$ ceramics initially increased with increasing sintering temperature and then decreased. It

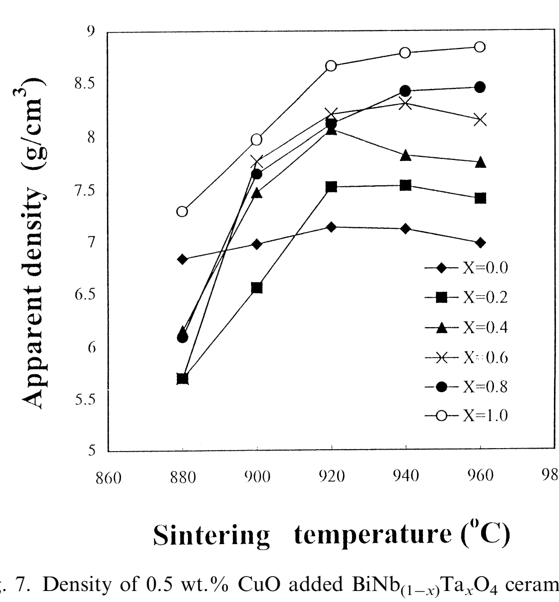
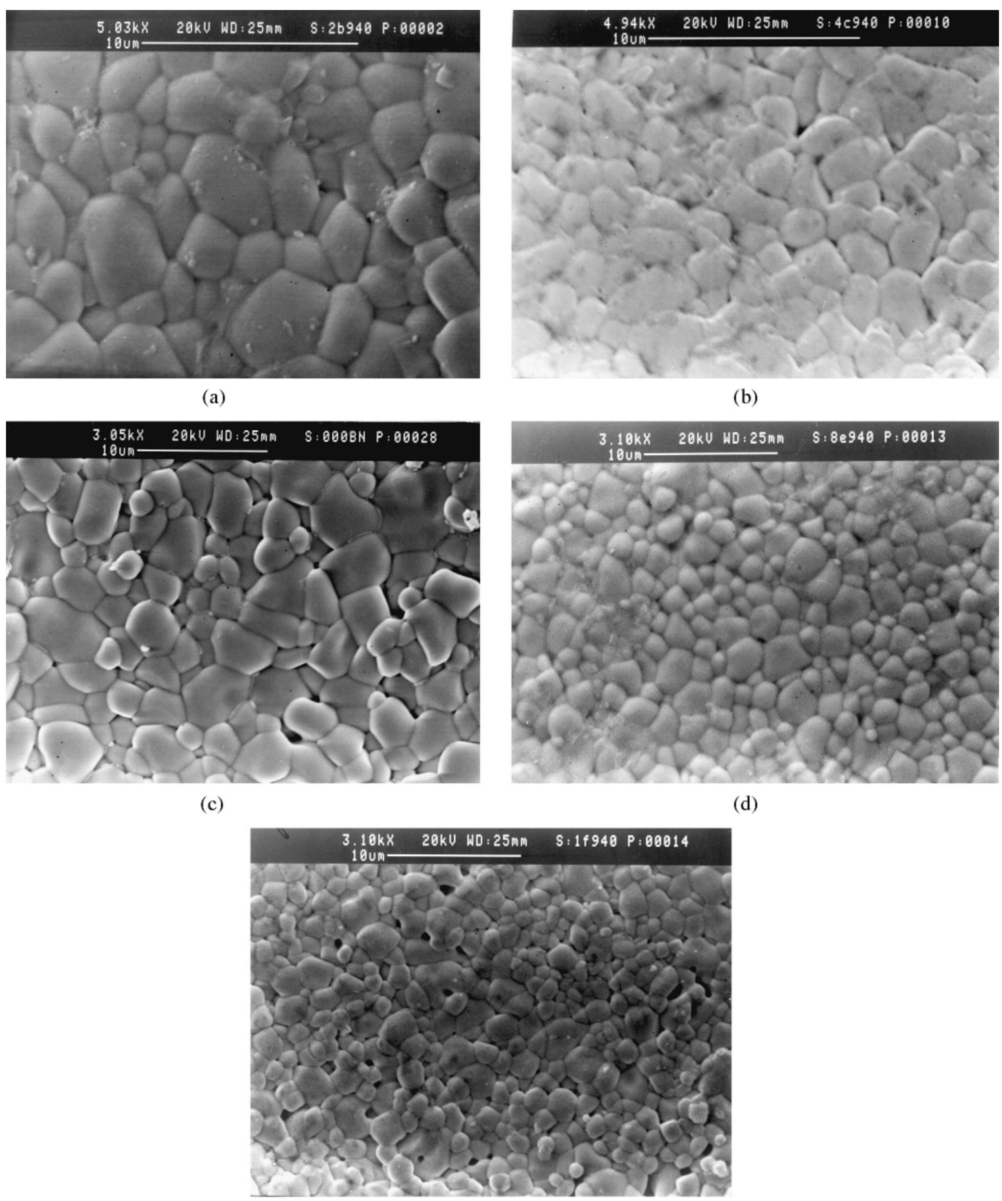


Fig. 7. Density of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics at different sintering temperature.

suggested that suitable amount of CuO addition for $BiNbO_4$ ceramics were in the range of 0.25–1 wt.%. A maximum density of 7.11 g/cm^3 was obtained for $BiNbO_4$ ceramics with 0.5 wt.% CuO addition sintered at 900°C for 3 h.

The SEM micrographs of $BiNbO_4$ ceramics with/without CuO addition at different sintering temperature are shown in Fig. 3. $BiNbO_4$ ceramics was not dense and the grain did not grow at 980°C/3 h. Although the grain of undoped $BiNbO_4$ ceramics grew at 1010°C/3 h, many pores existed in grain boundary and triple point. With 0.5 wt.% CuO addition, the pores were almost eliminated at 880°C/3 h and the grain size increased with increasing sintering temperature. In the past, suggestion sometimes was made to increase the sintering temperature or prolong the soaking time to increase the density of ceramics resulted in the improvement of the dielectric properties. However, over soaking, over sintering or over adding sintering aid would cause abnormal grain growth of ceramics. Evidence for the statement was observed in Fig. 4. Fig. 4(a–c) represented the conditions over soaking, over sintering and over adding sintering aid, respectively. Abnormal grain growth or formation of secondary recrystallization were observed due to over soaking, over sintering or over adding sintering aid resulted in a decrease in density [14]. The grain size was around 50 μm for all the cases. The phenomenon agreed with the results as discussed in Fig. 2. To clear the



(e)

Fig. 8. Typical SEM micrographs of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 940°C/3 h with (a) $x=0.2$, (b) $x=0.4$, (c) $x=0.6$, (d) $x=0.8$ and (e) $x=1.0$.

location of CuO, EDS of grain and grain boundary for 0.5 wt.% CuO added $BiNbO_4$ ceramics sintered at 920°C/3 h is demonstrated in Fig. 5. It indicated that the CuO additive appeared at the grain boundary but not inside the grain. $BiNbO_4$ ceramics with different amount (< 2 wt.%) of CuO additions exhibited the same results.

Dielectric properties of $BiNbO_4$ ceramics with CuO addition at different sintering temperature are demonstrated in Table 1. In general, the dielectric constant ε_r were correlated with the densification and saturated at 42–44 for dense $BiNbO_4$ ceramics. The Q×f values varied in the range from 5000 to 13 500 corresponding to different amount of sintering aid and sintering condition. Higher Q×f values were obtained for $BiNbO_4$ ceramics with 0.5 wt.% CuO addition due to denser ceramics and well developed microstructure such as more clear grain boundary and larger grain size. A τ_f value of 15 ppm/°C for $BiNbO_4$ ceramics with 0.5 wt.% CuO addition was obtained. It was observed that $BiNbO_4$ ceramics with 0.5 wt.% CuO addition sintered at 900°C/3 h illustrated better microwave dielectric properties (ε_r~43.3, Q×f~13 000 at 6.3 GHz, and τ_f~15 ppm/°C) in this system. From previous discussion, 0.5 wt.% CuO addition and 3 h firing were selected as sintering aid and soaking time, respectively, to further investigate the microwave dielectric properties of $BiNb_{(1-x)}Ta_xO_4$ ceramics.

3.2. 0.5 Wt.% CuO-doped $BiNb_{(1-x)}Ta_xO_4$ ceramics

Fig. 6 illustrates typical XRD patterns of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics calcined at 800°C/3 h and sintered at 940°C/3 h. The crystal structures of $BiNbO_4$ and $BiTaO_4$ are known as the low-temperature α-$SbTaO_4$ type below 1020°C. As Bi_2O_3 and Nb_2O_5 powders calcined at 800°C, $BiNbO_4$ was presented as the main crystalline phase associated with miner phases $Bi_8Nb_{18}O_{59}$ and $Bi_5Nb_3O_{15}$. The crystalline phases of all compositions showed similar results when Nb is partially substituted by Ta, i.e. the $Bi(Nb,Ta)O_4$ phase dominated the crystalline phase combined with other minor phases. As shown in Fig. 6b, no phase difference was observed for sintered $BiNb_{(1-x)}Ta_xO_4$ ceramics at different x-value. Since the difference of ion radius of Ta^{5+} (0.068 nm) is near but smaller than that of Nb^{5+} (0.069 nm), $BiNbO_4$ and $BiTaO_4$ would form a complete solid solution when Ta is used as substitution for the Nb sites of $BiNbO_4$ ceramics.

Fig. 7 shows the density of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics at different sintering temperature. It suggested that Ta-rich compositions needed higher sintering temperature to densify. The temperature needed to densify $BiNb_{(1-x)}Ta_xO_4$ ceramics increased from 900 to 960°C as the x-value increased from 0 to 1.0. For each composition, too high a sintering temperature leaded the densities of sintered ceramics to decrease due to the inhomogeneous microstructure evolution. Fig. 8 illustrated the typical SEM micrographs of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 940°C/3 h. It was observed that the grain size of $BiNb_{(1-x)}Ta_xO_4$ ceramics with $x = 0.2$ is larger than that with $x = 1$ due to higher sinterability.

The dielectric constant of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics as functions of the sintering temperature is shown in Fig. 9. The dielectric constant ε_r often exhibited the same trend with the density since that dense ceramics had less pores (air, $\varepsilon_r = 1$) to decay the ε_r value of the dielectrics. The ε_r value of $BiNb_{(1-x)}$-Ta_xO_4 ceramics all saturated at 44–45 in spite of their x-values. Fig. 10 demonstrated the plots of the Q×f values of 0.5 wt.% CuO added $BiNb_{(1-x)}Ta_xO_4$ ceramics versus

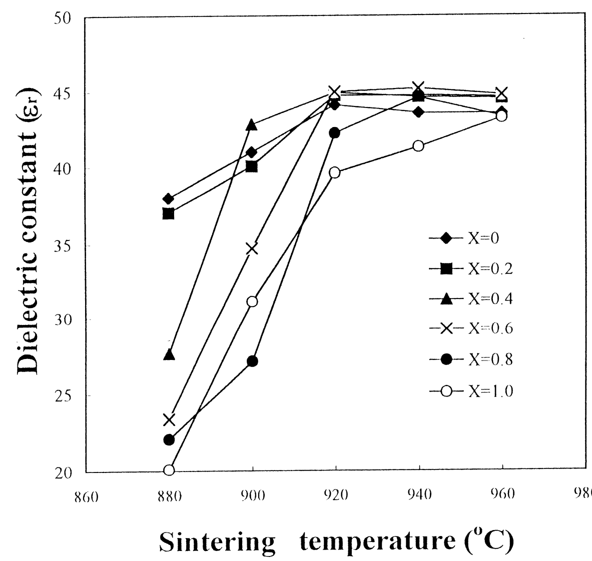


Fig. 9. Dielectric constant of $BiNb_{(1-x)}Ta_xO_4$ ceramics with 0.5 wt.% CuO addition at different sintering temperature.

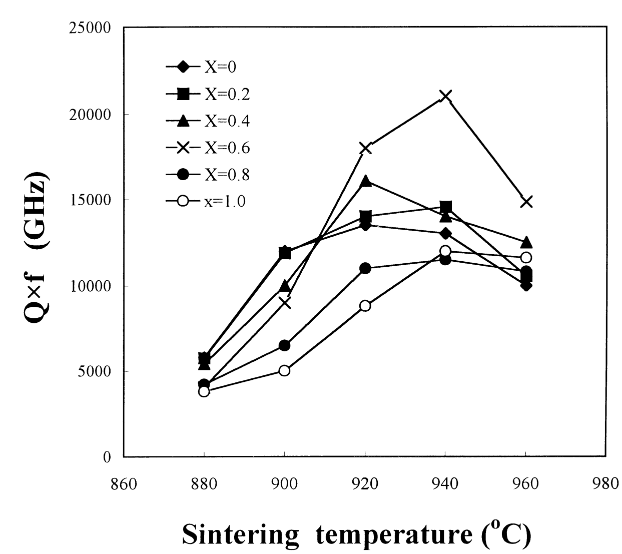


Fig. 10. Q×f values of $BiNb_{(1-x)}Ta_xO_4$ ceramics with 0.5 wt.% CuO addition at different sintering temperature.

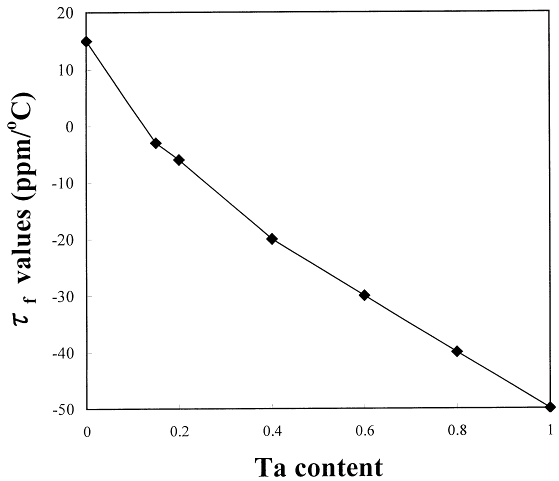


Fig. 11. τ_f Value of $BiNb_{(1-x)}Ta_xO_4$ ceramics with 0.5 wt.% CuO addition as a function of Ta content at 940°C/3 h.

their sintering temperatures. The Q×f value is an important index for the applications of dielectric ceramics at microwave frequencies since higher Q×f value means lower loss for microwave devices. For x-values less than 0.6, the Q×f values of $BiNb_{(1-x)}Ta_xO_4$ ceramics were functions of Ta content and varied from 9000 (GHz) to 21 000 (GHz) at the sintering temperatures ranged from 900 to 940°C. However, it decreased for sintering temperature over 940°C due to the decrease of density, i.e. inhomogeneous grain growth. A maximum Q×f value of 21 000 (GHz) was revealed for $BiNb_{0.4}Ta_{0.6}O_4$ composition sintered at 940°C/3 h. Fig. 11 illustrates the τ_f value of 0.5 wt.% CuO added Bi $Nb_{(1-x)}Ta_xO_4$ ceramics sintered at 940°C/3 h. The τ_f value rapidly decreased with the increase of Ta content. It varied from 15 ppm/°C at $x=0$ to -50 ppm/°C at $x=1$. With $x=0.12$, a τ_f value of -0.2 ppm/°C was measured. It implied that zero temperature coefficient of resonator frequency could be obtained by properly adjusting the Ta content.

4. Conclusions

A systematical study of low-temperature co-firing microwave dielectric ceramics material CuO-doped Bi(Nb,Ta)O_4 was investigated. The dielectric constant ε_r saturated at 44–45 in spite of CuO addition or Ta substitution for dense ceramics. The Q×f value of $BiNb_{(1-x)}Ta_xO_4$ ceramics was affected by the CuO additive, the Ta substitution and the sintering condition. With 0.5 wt.% CuO addition and $x=0.6$, it increased from 9000 to 21 000 (GHz) as the sintering temperature increased from 900°C to 940°C and then decreased to 14 000 (GHz) when further increased the sintering temperature to 960°C. For practical applications, zero τ_f value can be obtained by properly adjusting the Ta content. With $x=0.12$, $BiNb_{(1-x)}Ta_xO_4$ ceramics possessed a τ_f value of -0.2 ppm/°C.

Acknowledgements

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