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Effects of Ta_2O_5 on microwave dielectric properties of $BiNbO_4$ ceramics

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Abstract

Effects of Ta substitution for Nb on the microwave dielectric properties of $BiNbO_4$ ceramics have been investigated. $BiNb_{(1-x)}Ta_xO_4$ ($x = 0$, 0.1, 0.2, 0.3, 0.4) with 0.3 wt.% $CuO–V_2O_5$ mixtures addition can be densified at very low sintering temperature below 860 °C. The dielectric constants (ε_r) of the Ta-modified $BiNbO_4$ ceramics increase with increasing of Ta contents, but the $Q \times f$ values have no apparent changes. The temperature coefficient of resonant frequency (τ_f) changes from positive to negative with change of x values. The crystalline phase and microstructure of Ta-modified $BiNbO_4$ ceramics have been characterized by X-ray diffraction and scanning electron microscopy respectively.

Keywords: $BiNbO_4$; Ceramics; Low-temperature sintering; Microwave dielectric properties; XRD patterns

1. Introduction

Multilayer microwave devices are becoming increasingly important with the rapid progress of miniaturization in mobile communication systems [1]. In order to satisfy the devices requirement, the microwave dielectric ceramics with low sintering temperature are needed to co-fire with low loss conductors such as Ag or Cu. The sintering temperatures of conventional microwave dielectric ceramics are too high to use the low melting point and low cost electrodes [2–4]. Although addition of low-melting-point glass, chemical processing and smaller particle sizes of starting materials are three methods normally used to reduce the sintering temperature of dielectric materials [5–7], the development of novel low-firing dielectric ceramics is also an effective method.

Recently, bismuth-based dielectric ceramics are attractive due to its relatively low sintering temperature [8,9]. $BiNbO_4$ ceramics with practical microwave dielectric properties were developed by Kagata et al. [10]. $BiTaO_4$ ceramics have a similar crystal structure with $BiNbO_4$ ceramics and its dielectric properties at microwave frequency were studied by Huang and Weng [11]. $BiTaO_4$ ceramics with 0.5 wt.% CuO addition exhibited high $Q \times f$ values (8000 ~ 12000 GHz) and a negative τ_f value (−40 ppm/ °). Its dielectric constant saturated at 43–44. In this paper, $BiNbO_4$ was used as the host materials and Ta_2O_5 was used to substitute for Nb_2O_5. The effects of Ta substitution for Nb on sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics were investigated. The $CuO–V_2O_5$ mixtures were used as sintering aids. The crystalline phases and microstructures of sintered specimens were also characterized.

2. Experimental procedure

The starting materials were high-purity (more than 99.9%) Bi_2O_3, Nb_2O_5 and Ta_2O_5 powders. Samples of $BiNb_{(1-x)}Ta_xO_4$ ($x = 0$, 0.1, 0.2, 0.3, 0.4) were prepared by conventional solid-state reaction method. A small amount of $CuO–V_2O_5$ mixtures (0.3 wt.%) were used as sintering aids. Sintering of the samples was carried out at temperatures between 760 and 890 °C for 3h. The sample was placed in a sealed alumina crucible filled

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with $BiNbO_4$ powders to prevent the evaporation of Bi_2O_3.

The bulk densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were identified by X-ray diffraction (XRD) patterns. Microstructure observation of the sintered surface of $BiNb_{(1-x)}Ta_xO_4$ ceramics was performed by scanning electron microscopy (SEM). The dielectric constants (ε_r) and the quality values Q at microwave frequency were measured using the Hakki-Coleman's dielectric resonator method, as modified and improved by Courtney [12,13]. An Advantest R3767CG network analyzer was employed in the measurement. The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range of −25 to + 85 °C. The τ_f value was defined as follows:

$$\tau_f = (f_{85} - f_{-25})10^6/110f_{25} \quad (\text{ppm}/^\circ\text{C}) \tag{1}$$

where f_{85}, f_{-25}, and f_{25} are the resonant frequencies at 85, −25 and 25 °C respectively.

3. Results and discussion

Fig. 1(a) and (b) show the XRD patterns of the pure $BiNbO_4$ and $BiNb_{0.6}Ta_{0.4}O_4$ powders calcined at 800 °C. According to the XRD results, the $BiNbO_4$ powder after calcination leads to the formation of the α-$BiNbO_4$ as major crystalline phase and $Bi_5Nb_3O_{15}$ as minor phase. The diffraction intensity of $Bi_5Nb_3O_{15}$ phase increases and the $Bi_3Nb_{17}O_{47}$ phase is also identified for $BiNb_{0.6}Ta_{0.4}O_4$ calcined powder. The typical XRD patterns of $BiNb_{(1-x)}Ta_xO_4$ ceramics

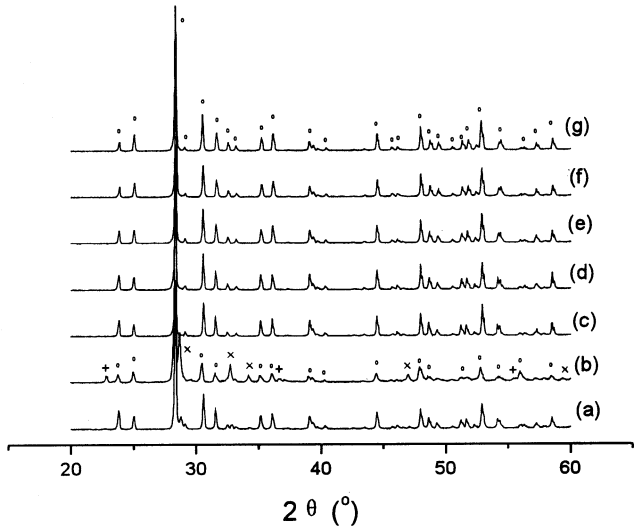

Fig. 1. XRD patterns of $BiNb_{(1-x)}Ta_xO_4$ powders calcined at 800 °C with (a) $x = 0$ (b) $x = 0.4$ and $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 820 °C with (c) $x = 0$ (d) $x = 0.1$ (e) $x = 0.2$ (f) $x = 0.3$ (g) $x = 0.4$ (○: $BiNbO_4$, ×: $Bi_5Nb_3O_{15}$, +: $Bi_3Nb_{17}O_{47}$).

with different x values sintered at 820 °C are also shown in Fig. 1. There is no difference found from the patterns of all compositions. The $Bi_3Nb_3O_{15}$ and $Bi_3Nb_{17}O_{47}$ phases are eliminated and only the low temperature phase of $BiNbO_4$ which is stable below 1020 °C is revealed in sintered $BiNb_{(1-x)}Ta_xO_4$ ceramics, as shown in Fig. 1(c)–(g). This suggests that a complete solid solution is formed in $BiNb_{(1-x)}Ta_xO_4$ ceramics when x is no more than 0.4. It was reported that the phase transition from orthorhombic to triclinic occurs when sintered at 870 °C for $BiTaO_4$ ceramics doped with 0.5 wt.% CuO [11]. The formation of $BiNb_{(1-x)}Ta_xO_4$ solid solution seems to inhibit this phase transition of $BiTaO_4$.

SEM micrographs of the $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 820 °C with different x values are investigated and the results are shown in Fig. 2. The $BiNbO_4$ ceramics without additives cannot be densified and isolated $BiNbO_4$ particles and pores are easily observed even after sintering at 960 °C [14]. With the addition of 0.3 wt.% $CuO–V_2O_5$ mixtures, a much easier densification of $BiNb_{(1-x)}Ta_xO_4$ ceramics is evident, as shown in Fig. 2. The homogeneously fine microstructures with almost no pores are revealed for $BiNb_{(1-x)}Ta_xO_4$ ceramics with all of the x values sintered at 820 °C. The average grain sizes of all compositions were calculated from the line intercept method and all of them are distributed around 0.77–0.86 μm. This suggests that the substitution of Ta for Nb has no apparent effects on grain growth of the well sintered $BiNb_{(1-x)}Ta_xO_4$ ceramics. But an abnormal grain growth, which exhibits large discontinuous grains existing in the fine-grained matrix, can be observed for $BiNb_{0.9}Ta_{0.1}O_4$ ceramics with sintering temperature further increasing to 860 °C (shown in Fig. 2(f)).

Fig. 3 shows the plots of the bulk densities of $BiNb_{(1-x)}Ta_xO_4$ ceramics with different x values versus their sintering temperatures. As the sintering temperature increases, the bulk densities of $BiNb_{(1-x)}Ta_xO_4$ ceramics increase and reach the saturated values. The sintering temperatures of $BiNb_{(1-x)}Ta_xO_4$ ceramics required for obtaining the maximum densities increase from 820 to 860 °C as the x values increase from 0 to 0.4. The higher sintering temperature of $BiTaO_4$ than that of $BiNbO_4$ ceramics is account for this result. The saturated densities of $BiNb_{(1-x)}Ta_xO_4$ ceramics increase from 7.19 to 7.88 g/cm^3 with increasing of x value from 0 to 0.4. It is worth noting that the densities of sintered ceramics decrease with further increasing in firing temperature and this maybe due to the abnormal grain growth in ceramics.

The dielectric constants of $BiNb_{(1-x)}Ta_xO_4$ ceramics as a function of sintering temperature and x value are shown in Fig. 4. The ε_r value exhibits the similar trend as that for the bulk densities as demonstrated in Fig. 3. It implies that the increase for ε_r values of

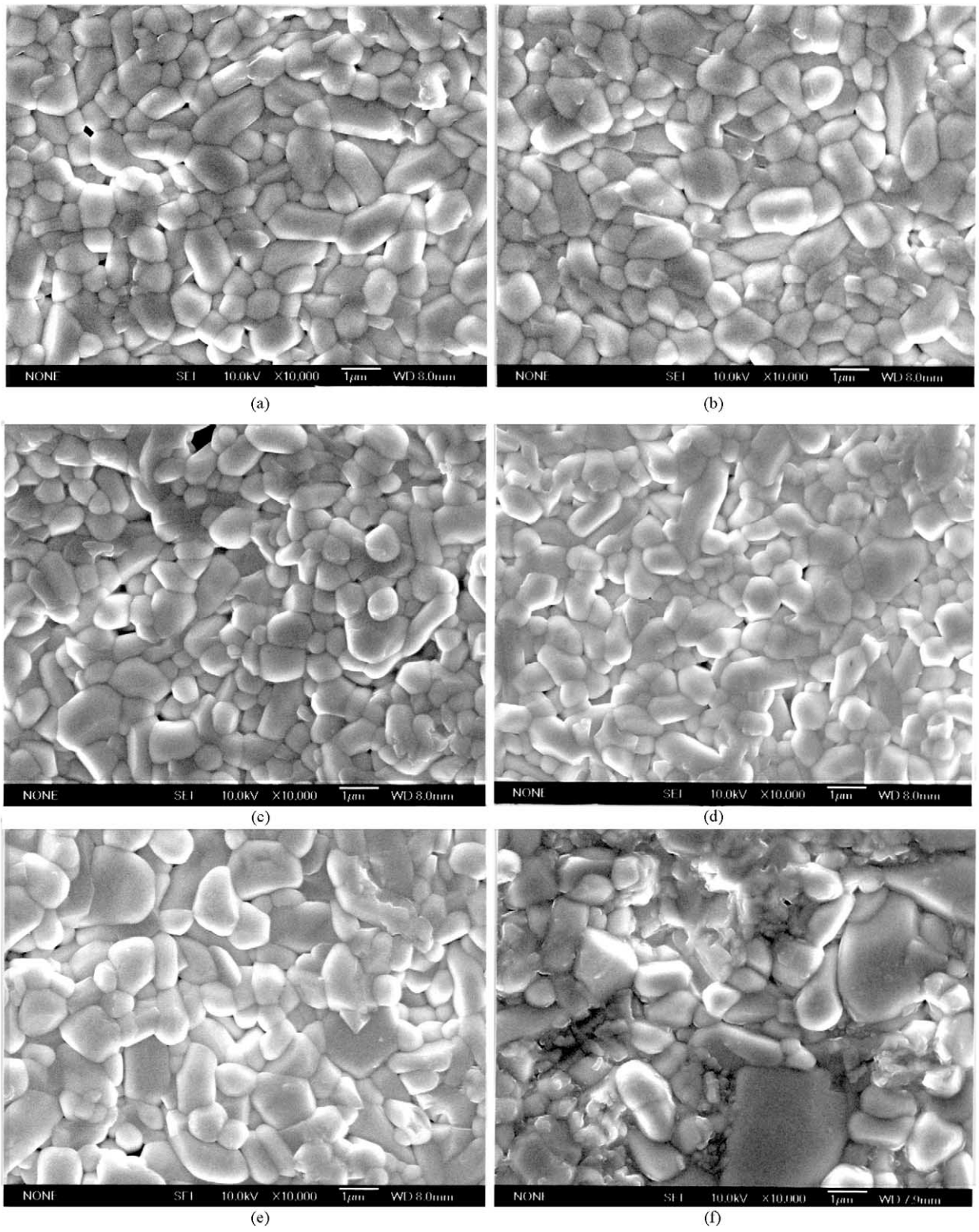

Fig. 2. SEM micrographs of $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 820 °C with (a) $x = 0$ (b) $x = 0.1$ (c) $x = 0.2$ (d) $x = 0.3$ (e) $x = 0.4$ and sintered at 860 °C with (f) $x = 0.1$.

$BiNb_{(1-x)}Ta_xO_4$ ceramics with increasing sintering temperature is due to the increase of density. The ε_r values are also correlated to Ta content in $BiNb_{(1-x)}Ta_xO_4$ ceramics. The saturated ε_r value increases from 43.95 to 45.63 with the increase of x value from 0 to 0.4.

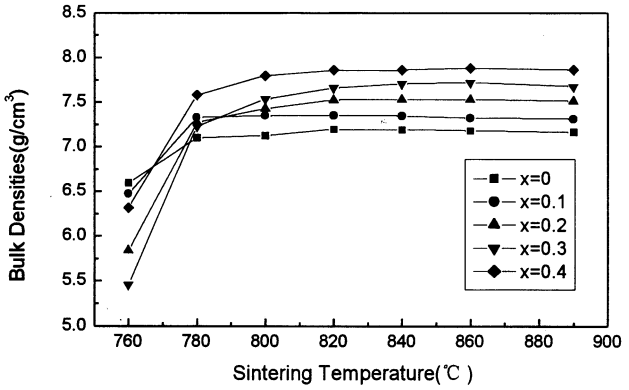

Fig. 3. Bulk densities of $BiNb_{(1-x)}Ta_xO_4$ ceramics with $x = 0$–0.4 as a function of sintering temperature.

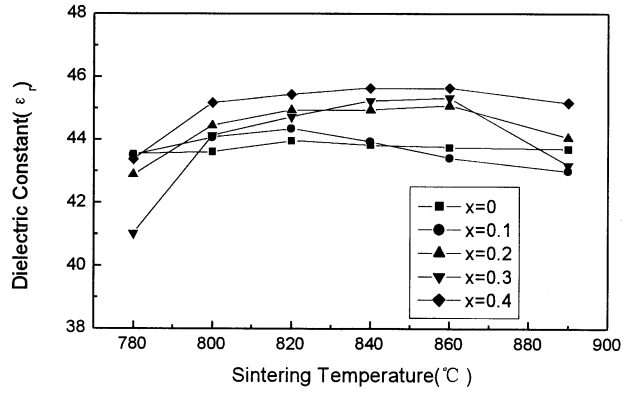

Fig. 4. Dielectric constants of $BiNb_{(1-x)}Ta_xO_4$ ceramics with $x = 0$–0.4 as a function of sintering temperature.

The $Q \times f$ values of $BiNb_{(1-x)}Ta_xO_4$ ceramics with various x values at different sintering temperatures are plotted in Fig. 5. The $Q \times f$ values of all compositions increase with sintering temperature and then decrease after reaching their maximum values. The increase in $Q \times f$ values maybe caused by the increase in densities and grain growth. It is known that there are intrinsic loss and extrinsic losses for dielectric ceramics at microwave region. The intrinsic loss is caused by the anharmonic phonon decay process in the pure crystal lattice while the extrinsic losses are caused by crystal defects and grain boundaries etc [15]. The amounts of pores and grain boundaries decrease with increasing of the density and grain size and then the lattice imperfections and dielectric losses are reduced. However too high a sintering temperature causes the microstructure of $BiNb_{(1-x)}Ta_xO_4$ ceramics inhomogeneous, which leads to the increase in the crystal defect and the decrease in the $Q \times f$ values, as shown in Fig. 2(f). The saturated $Q \times f$ values of $BiNb_{(1-x)}Ta_xO_4$ ceramics range between 11 900 and 12 300 GHz regardless of x value. The substitution of Ta_2O_5 for Nb_2O_5 has no apparent influence on the $Q \times f$ values of $BiNb_{(1-x)}Ta_xO_4$ ceramics.

The τ_f values of $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 820 °C as a function of Ta content are shown in Fig. 6. As the x value changes from 0 to 0.4, the τ_f value steadily changes from a positive value of 15.85 ppm/ °C to a negative value of −27.32 ppm/ °C. According to the XRD patterns, the $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 820 °C exhibit a single crystalline phase of α-$BiNbO_4$ which is stable below 1020 °C. Therefore, the changes of the τ_f values are considered to be attributed to the effects of Ta substitution. A small τ_f values of 0.52 ppm/ °C is obtained for $BiNb_{0.9}Ta_{0.1}O_4$ ceramics at 820 °C.

4. Conclusion

In this paper, the sintering behavior and microwave dielectric properties of $BiNb_{(1-x)}Ta_xO_4$ ceramics have been studied. The $BiNb_{(1-x)}Ta_xO_4$ ceramics doped with 0.3 wt.% CuO–V_2O_5 mixtures can be densified to 97%TD below 860 °C. The dielectric constants of $BiNb_{(1-x)}Ta_xO_4$ ceramics slightly increase from 43.95 to 45.63 and the temperature coefficients of resonant frequency decrease from 15.85 to −27.32 ppm/ °C with

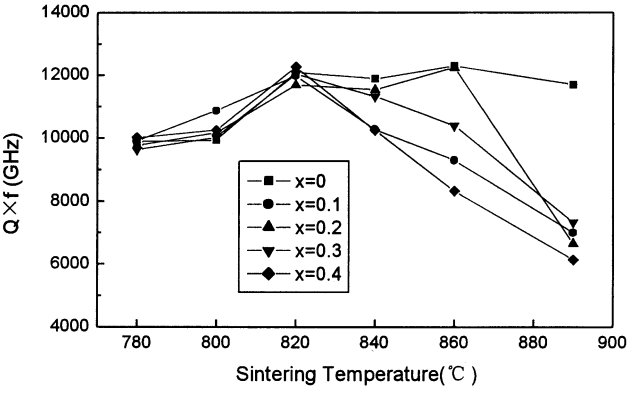

Fig. 5. $Q \times f$ values of $BiNb_{(1-x)}Ta_xO_4$ ceramics with $x = 0$–0.4 as a function of sintering temperature.

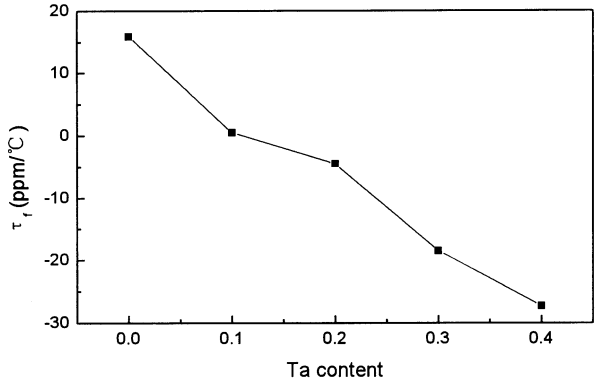

Fig. 6. τ_f values of $BiNb_{(1-x)}Ta_xO_4$ ceramics sintered at 820 °C as a function of Ta content.

the increase of x value from 0 to 0.4. The $Q \times f$ value saturates at 11 900–12 300 GHz regardless of Ta content. The $BiNb_{0.9}Ta_{0.1}O_4$ ceramics sintered at 820 °C show the best microwave dielectric properties of $\varepsilon_r \sim 44.35$, $Q \times f \sim 11\,978$ GHz and $\tau_f \sim 0.52$ ppm/ °C. It can be used as dielectric materials for multilayer microwave devices with Cu or Ag inner conductors.

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