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Effects of Y_2O_3 on Sintering Behavior and Microwave Dielectric Properties of BiNbO$_4$ Ceramics

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Y_2O_3 was selected as a substitute for Bi_2O_3 and the effects of substitution on the sintering behavior and microwave dielectric properties of BiNbO$_4$ ceramics were studied. With the addition of 0.5 wt% CuO–V_2O_5 mixtures, all $Bi_{(1-x)}Y_xNbO_4$ ceramics could be densified below 900°C. The triclinic phases were identified in $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0.03$ and the intensities of triclinic peaks increased with increasing x and sintering temperature. Saturated bulk density decreased from 7.17 g/cm³ to 6.99 g/cm³ and ε_r from 44.21 to 37.32 with increasing x from 0 to 0.1 for $Bi_{(1-x)}Y_xNbO_4$ ceramics. $Q \times f$ was mainly influenced by sintering temperature. τ_f changed with x and sintering temperature. The τ_f values of dense $Bi_{(1-x)}Y_xNbO_4$ ceramics continuously decreased from 28.32 ppm/°C to -8.78 ppm/°C with the increase in x from 0 to 0.1. [DOI: 10.1143/JJAP.42.3514]

1. Introduction

With the rapid progress in commercial wireless communication, the downsizing of mobile communication terminals has become increasingly important for convenience of use. Therefore, the components used in those terminals must also be miniaturized. The application of multilayer microwave devices will contribute to the realization of this goal.[1] In the fabrication of multilayer microwave devices, low-firing microwave dielectric materials with high dielectric constant ε_r, low dielectric loss and near-zero temperature coefficient of resonant frequency τ_f are necessary for co-firing with low-loss, low-melting-point conductors such as silver and copper. (Zr, Sn)TiO$_4$, Ba$_2$Ti$_9$O$_{20}$, and Ba(MgTa)O$_3$ systems have excellent microwave dielectric properties and are the most commonly used dielectric materials in ultra high-frequency applications.[2–4] However, they are not compatible with the co-firing process because of their high sintering temperature. Low-melting-glass addition, chemical processing and use of small-particle sizes of the starting materials are three methods generally used in reducing the sintering temperature of dielectric materials.[5–8] However, they also result in the deterioration of microwave dielectric properties, or require a flexible procedure. Furthermore, the sintering temperatures of those commercial dielectric materials using these methods are still too high for the use of low-melting-point electrodes.

Bismuth-based dielectric ceramics are low-fired materials and have been investigated as materials of multilayer capacitors.[9] Kagata et al. first studied the microwave dielectric properties of the Bi_2O_3–Nb_2O_5 system.[10] Their results showed that BiNbO$_4$ ceramics with Cuo/V_2O_5 addition could be densified at 875°C and had a Q of 4260 (at 4.3 GHz), ε_r of 43 and large τ_f of 38 ppm/°C (-25–20°C). In order to lower τ_f, Nd_2O_3 and La_2O_3 were substituted for Bi_2O_3 and the effects of substitution on the densification and microwave dielectric properties of BiNbO$_4$ ceramics were investigated by Choi et al. and Huang et al., respectively.[11,12] For Nd or La substitution, the phase transition temperature (orthorhombic to triclinic) of BiNbO$_4$ ceramics decreased due to the lattice distortion caused by the ionic difference between Ln^{3+} (Ln = Nd, La) and Bi^{3+}. The $Q \times f$ and τ_f of Ln-modified BiNbO$_4$ ceramics were

assumed to correlate with phase transformation ratio. The valence of Y^{3+} is the same as that of Bi^{3+} but its ionic radius (0.892 Å) is smaller than that of Bi^{3+} (1.02 Å) or Nd^{3+} (0.995 Å).[13] Since the ionic difference between Ln^{3+} and Bi^{3+} plays an important role in the phase transition and microwave dielectric properties of Ln-modified BiNbO$_4$ ceramics, it motivated us to investigate the influence of Y substitution for Bi on the sintering behavior and microwave dielectric properties of BiNbO$_4$ ceramics. A small amount of CuO–V_2O_5 mixture was used as sintering aids. The crystalline phases and microstructures of the sintered specimens were also characterized.

2. Experimental

Samples of $Bi_{(1-x)}Y_xNbO_4$ ($x = 0$, 0.01, 0.03, 0.05, 0.10) were prepared by conventional solid-state reaction methods. High-purity oxide powders, Bi_2O_3 (>99.99%), Y_2O_3 (>99.99%) and Nb_2O_5 (>99.97%), were used as starting materials. These powders were mixed according to the desired stoichiometry and ball-milled for 24 h with deionized water in a nylon bottle with agate balls. The mixtures were dried and calcined at 800°C for 3 h. The calcined powders were mixed with a small amount of CuO–V_2O_5 mixture (0.5 wt%) and then remilled for 24 h. After drying, the powders with 6 wt% PVA binder were uniaxially pressed into pellets in a steel die. The pellets were 16 mm in diameter and 7 mm in thickness. The pellets were sintered from 780°C to 900°C for 3 h. To prevent the vaporization of Bi_2O_3, the pellets were placed in a sealed alumina crucible filled with BiNbO$_4$ powder.

The bulk densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were identified based on X-ray diffraction patterns using Cu–K$_\alpha$ radiation for 2θ from 20 to 60° (Rigaku D/max 2550V X-ray diffractometer). The microstructural observation of the sintered surface of $Bi_{(1-x)}Y_xNbO_4$ ceramics was performed by scanning electron microscopy (SEM) (JEOL JSM-6700F). The average grain sizes were calculated by the line intercept method. Dielectric constant ε_r and quality value Q at the microwave frequency were measured using Hakki–Coleman's dielectric resonator method, as modified and improved by Courtney.[14,15] An Advantest R3767CG network analyzer was employed in the measurement. The
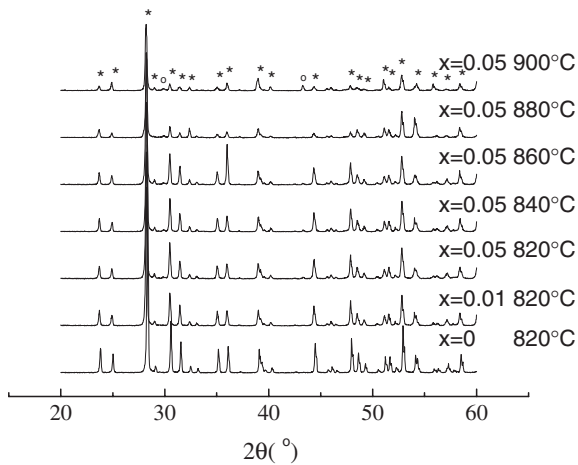
Fig. 1. XRD patterns of $Bi_{(1-x)}Y_xNbO_4$ ceramics with different x values sintered at different temperatures [*: orthorhombic, o: triclinic].

Fig. 2. Bulk density of $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0$–0.1 as a function of sintering temperature.

temperature coefficient of the resonant frequency τ_f was measured in the temperature range of $-25°C$ to $+85°C$. τ_f was defined as follows:

$$\tau_f = \frac{f_{85} - f_{-25}}{110 \times f_{25}} \times 10^6 \quad (\text{ppm}/°C), \quad (1)$$

where f_{85}, f_{-25} and f_{25} are the TE_{011} resonant frequencies at $85°C$, $-25°C$ and $25°C$ respectively.

3. Results and Discussion

Figure 1 shows the typical XRD patterns of $Bi_{(1-x)}Y_xNbO_4$ ceramics with different x values sintered at different temperatures. Only the orthorhombic phase was revealed in the sintered $BiNbO_4$ and $Bi_{0.99}Y_{0.01}NbO_4$ ceramics, as shown in Figs. 1(a) and 1(b). However, for $x \geqslant 0.03$, orthorhombic and triclinic phases were found to coexist in sintered specimens and the triclinic peaks intensified with increasing Y content and sintering temperature. The orthorhombic phase, i.e., the low temperature phase of $BiNbO_4$, is stable below $1020°C$ and then gradually transforms to the triclinic phase as the temperature increases.[16,17] The existence of the triclinic phase proves that Y substitution could effectively lower the phase transition temperature. The lattice distortion caused by the ionic difference between Y^{3+} (0.892 Å) and Bi^{3+} (1.02 Å) appears to account for this result.[11,12] The phase transition temperature of Y-modified $BiNbO_4$ ceramics is lower than that of Nd or La-modified $BiNbO_4$ ceramics. This suggests that the large difference in ionic radius between Y^{3+} and Bi^{3+} induces more lattice distortion. However, the ratios (R) of $I_{tri}/[I_{tri} + I_{ortho}]$, where I_{tri} and I_{ortho} are the intensities of triclinic (202), $(\bar{2}10)$ and orthorhombic (040) reflection peaks of the XRD pattern, respectively,[11,12] of $Bi_{(1-x)}Y_xNbO_4$ ceramics with different x values at different sintering temperatures were all small. Even for $x = 0.1$ and sintering temperature of $900°C$, the R of Y-modified $BiNbO_4$ ceramics was only 0.19. The amount of Y substitution for Bi was small (less than 0.1) and the phase transition of $Bi_{(1-x)}Y_xNbO_4$ ceramics was limited when sintered at below $900°C$ for 3 h.

The densities of $Bi_{(1-x)}Y_xNbO_4$ ceramics with different x values as a function of sintering temperature are shown in
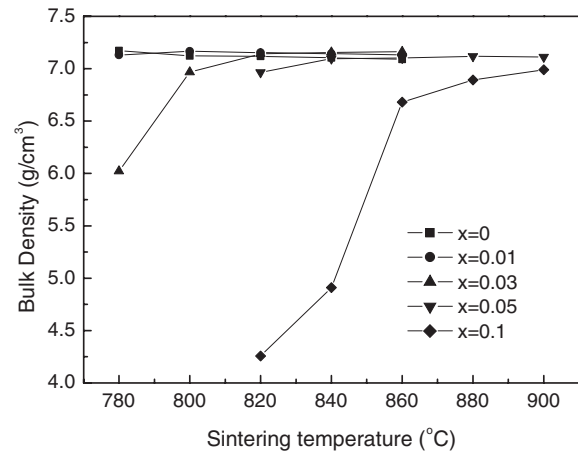
Fig. 2. The sintering temperatures of $Bi_{(1-x)}Y_xNbO_4$ ceramics required for obtaining their maximum densities increased from $780°C$ to $900°C$ as x increased from 0 to 0.10. The increase of the coexisting amount of the triclinic phase in $Bi_{(1-x)}Y_xNbO_4$ ceramics might account for this result because mass transportation in a sintering behavior is easily disturbed by second-phase generation. The densities of $BiNbO_4$ ceramics decreased from 7.17 g/cm^3 to 7.09 g/cm^3 with increasing sintering temperature from $780°C$ to $860°C$. For $x = 0.01$, the densities increased from 7.13 g/cm^3 at $780°C$ to a maximum of 7.16 g/cm^3 at $800°C$, and then slightly decreased with further increase in temperature. The saturated bulk densities of $Bi_{(1-x)}Y_xNbO_4$ ceramics decreased from 7.17 g/cm^3 to 6.99 g/cm^3 with the increase in x from 0 to 0.10 owing to the substitution of heavier Bi atoms by lighter Y atoms.

The SEM images of $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0.01$, 0.03, 0.05 and 0.1 sintered at different temperatures are shown in Fig. 3. The grain morphology of the $Bi_{0.99}Y_{0.01}NbO_4$ ceramic sintered at $780°C$ was uniform and distinct, as shown in Fig. 3(a1). The average grain sizes remained almost unchanged for the $Bi_{0.99}Y_{0.01}NbO_4$ ceramic with increasing sintering temperature from $780°C$ to $800°C$, an abnormal grain growth, which exhibited large discontinuous grains existing in a fine-grained matrix, could be observed with further increase in sintering temperature to $820°C$ [Figs. 3(a2) and 3(a3), respectively]. For the $Bi_{0.97}Y_{0.03}NbO_4$ ceramic sintered at $780°C$, the as-sintered surfaces were porous and the grains did not grow [Fig. 3(b1)]. The pores were still easily observed on the surfaces of the $Bi_{0.97}Y_{0.03}NbO_4$ ceramic as-sintered at $800°C$ [shown in Fig. 3(b2)]. This suggests that the substitution of Y for Bi reduces the sinterability of $BiNbO_4$ ceramics, as shown in Fig. 2. The number of pores decreased and the grain size increased with increasing sintering temperature from $800°C$ to $840°C$ for $Bi_{0.97}Y_{0.03}NbO_4$ ceramics [Figs. 3(b3) and 3(b4)]. The average grain sizes of dense $Bi_{(1-x)}Y_xNbO_4$ ceramics (the samples reached their maximum relative densities) with various x values sintered at different temperatures, i.e., $800°C$ for $x = 0.01$ [Fig. 3(a2)], $840°C$ for $x = 0.03$ [Fig. 3(b4)], $860°C$ for $x = 0.05$ [Fig. 3(c)] and $900°C$ for $x = 0.1$ [Fig. 3(d)], ranged from approximately
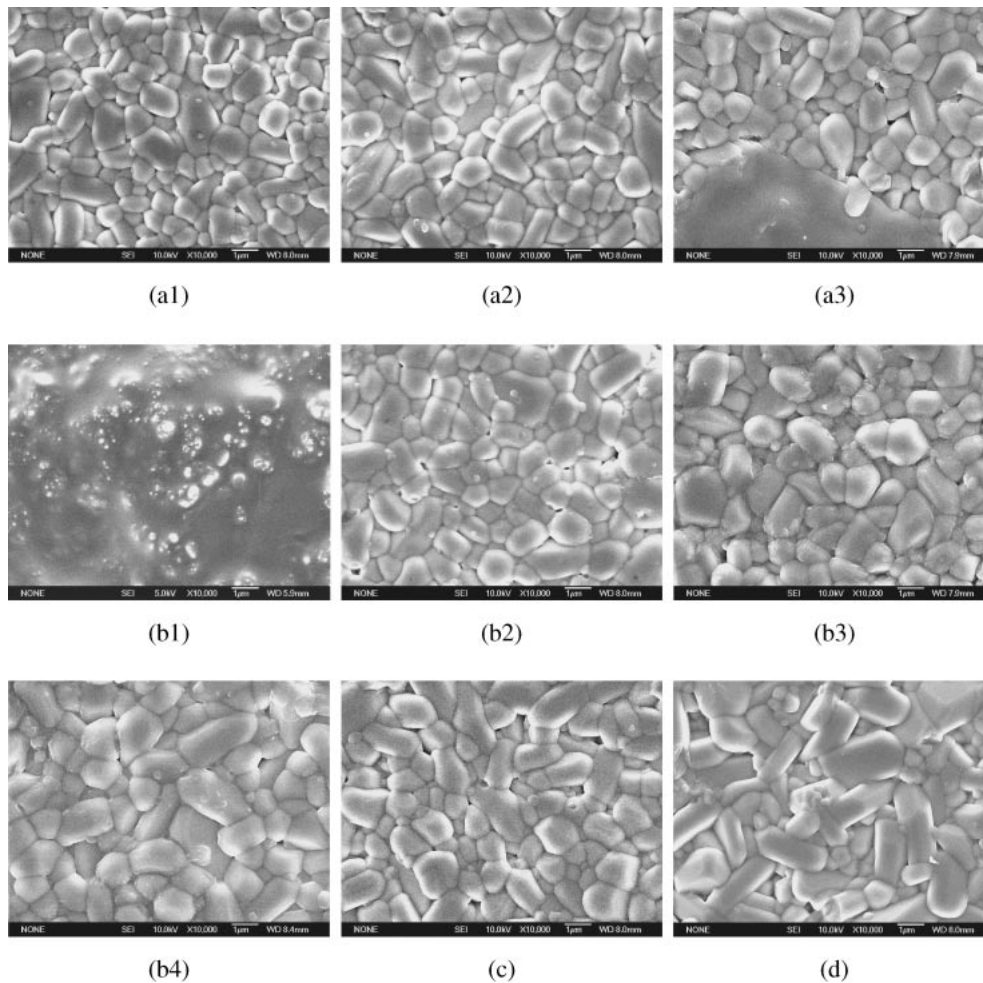
Fig. 3.   SEM images of $Bi_{(1-x)}Y_xNbO_4$ ceramics for $x = 0.01$ sintered at (a1) 780°C, (a2) 800°C and (a3) 820°C; for $x = 0.03$ sintered at (b1) 780°C, (b2) 800°C, (b3) 820°C and (b4) 840°C; for $x = 0.05$ sintered at (c) 860°C; and for $x = 0.1$ sintered at (d) 900°C.
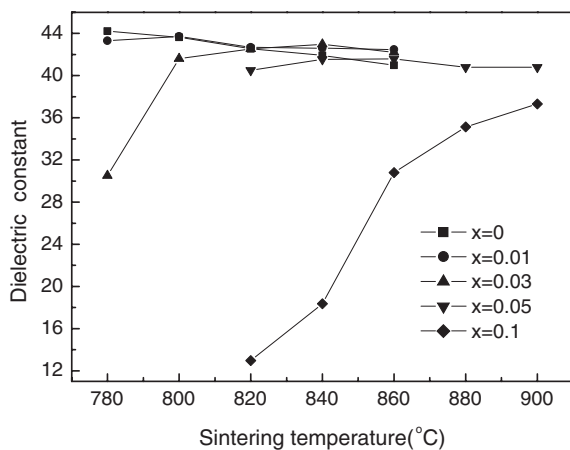

Fig. 4.   Dielectric constant of $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0$–0.1 as a function of sintering temperature.

0.98 to 1.11 µm. This means that Y substitution for Bi has no effect on the grain growth of the well-sintered $Bi_{(1-x)}Y_xNbO_4$ ceramics.

Figure 4 shows the plots of the dielectric constant of $Bi_{(1-x)}Y_xNbO_4$ ceramics as a function of sintering temperature for various x values. The ε_r of $BiNbO_4$ ceramics decreased from 44.21 to 40.99 with increasing sintering temperature from 780°C to 860°C. The ε_r of $Bi_{(1-x)}Y_xNbO_4$ ceramics with x ranging from 0.01 to 0.1 first increased with sintering temperature and saturated at 800°C–900°C depending on x, then decreased with further increase in sintering temperature. The relationship between sintering temperature and ε_r was found to be the same as that between sintering temperature and density. The increase in ε_r with sintering temperature is due to the well-known effects of grain growth and reduced porosity (the dielectric constant of pore equals 1.0). The decrease in ε_r above the densification temperature is associated with abnormal grain growth and increasing porosity, as shown in Fig. 3. It was found that ε_r of $Bi_{(1-x)}Y_xNbO_4$ ceramics also correlate to x. Saturated ε_r decreased with increasing Y content. For pure $BiNbO_4$ ceramics doped with 0.5 wt% CuO–V_2O_5 mixture, ε_r could reach 44.21 at a sintering temperature of 780°C. However the ε_r of $Bi_{0.9}Y_{0.1}NbO_4$ ceramics sintered at 900°C critically decreased to 37.32. At microwave frequencies the dielectric constant of the ceramics is closely related to the sum of electronic and ionic polarizabilities of components. According to the ionic polarizabilities reported by Shannon, the polarizabilitiy of Y^{3+} (3.81) is smaller than that of Bi^{3+} (6.12).[18] Furthermore, the amount of triclinic phase β-$BiNbO_4$ increased with the increase in the amount of Y substitution for Bi in $Bi_{(1-x)}Y_xNbO_4$ ceramics. The unit cell volume of β-$BiNbO_4$ is known to be smaller than that of α-
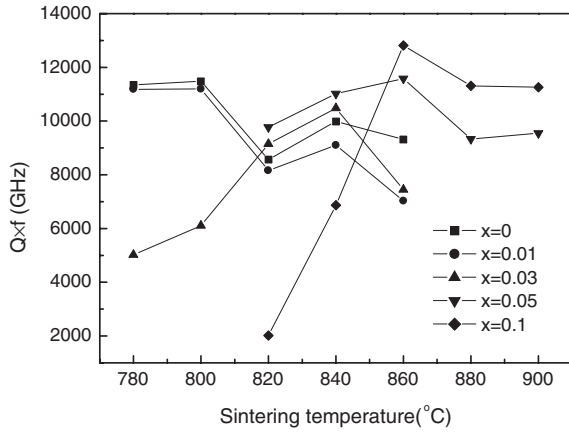
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Fig. 5. $Q \times f$ of $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0$–0.1 as a function of sintering temperature.

Fig. 6. τ_f of $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0$–0.1 as a function of sintering temperature.

Fig. 7. τ_f of dense $Bi_{(1-x)}Y_xNbO_4$ ceramics as a function of x.

$BiNbO_4$ (i.e., $V_{\beta\text{-BiNbO4}} = 324.0\,\text{Å}^3$ and $V_{\alpha\text{-BiNbO4}} = 330.9\,\text{Å}^3$).[16] The decrease in unit cell volume promotes the shrinkage of the octahedral and decreases the ionic polarizabilities of $BiNbO_4$. Thus the saturated ε_r of $Bi_{(1-x)}Y_xNbO_4$ ceramics decreases with increasing Y content.

Figure 5 illustrates the $Q \times f$ of $Bi_{(1-x)}Y_xNbO_4$ ceramics as a function of sintering temperature. The $Q \times f$ values of all samples increased with increasing sintering temperature. After reaching their maximum, the $Q \times f$ values decreased slightly. Many factors are believed to affect microwave dielectric loss, which can be classified into two types, i.e., intrinsic loss and extrinsic loss.[19] Intrinsic loss is caused by an anharmonic phonon decay process in a pure crystal lattice while extrinsic loss is caused by the existence of crystal defects, grain boundaries, second phases and pores.[20] The densities and grain sizes of $Bi_{(1-x)}Y_xNbO_4$ ceramics increased with increasing sintering temperature and then the number of pores and grain boundary areas decreased, which meant less lattice imperfections and lower dielectric loss. Abnormal grain growth, which occurred in sintered $Bi_{(1-x)}Y_xNbO_4$ ceramics with further increase in sintering temperatures above the densification temperatures, led to the increase in the extent of crystal defects and the decrease in $Q \times f$. Choi *et al.* suggested that the $Q \times f$ of $BiNbO_4$ ceramics rapidly increases as the triclinic transition ratio (R) is between 0.4 and 0.6 with Nd substitution for Bi.[11] Huang *et al.* found that $Q \times f$ of $BiNbO_4$ ceramics appears to increase with increasing grain size for a given R with La substitution for Bi.[12] The R of Y-modified $BiNbO_4$ ceramics was less than 0.2 in this experiment. The saturated $Q \times f$ of $Bi_{(1-x)}Y_xNbO_4$ ceramics decreased from 11483 GHz to 10480 GHz with increasing x from 0 to 0.03, and then increased to 12814 GHz with further increase in x to 0.1. From the results of XRD patterns, we observed no triclinic phase (for $x = 0$, 0.01) or the R was very small (0.017 for $x = 0.03$ sintered at 840°C). The decrease in the $Q \times f$ of $Bi_{(1-x)}Y_xNbO_4$ ceramics with increasing x from 0 to 0.03 might arise from substitutional impurity effects, which enhance the anharmonicity of phonon vibrations.[21–23] However, the increase in saturated $Q \times f$ with further increase in x from 0.03 to 0.1 might be related to the increase in the intensity of triclinic phase. The maximum $Q \times f$
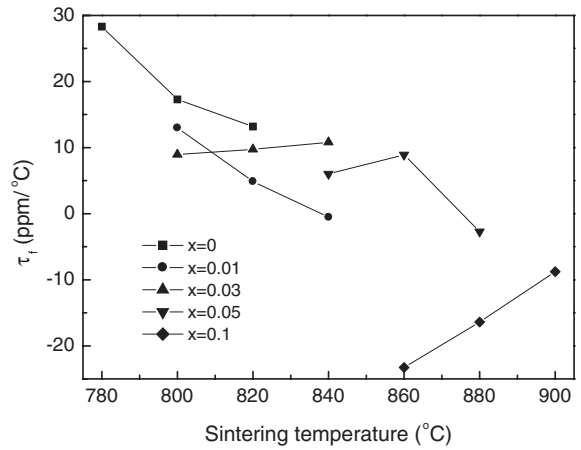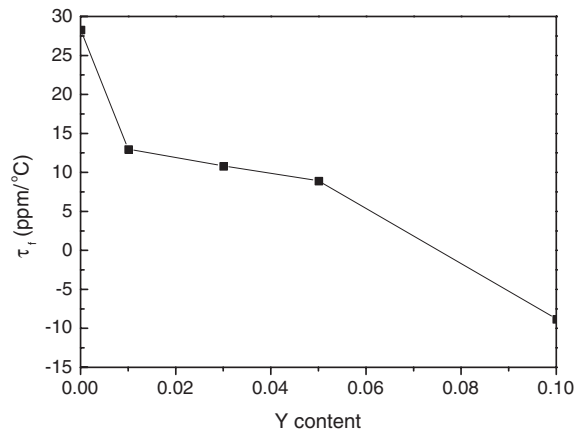
could be obtained when R ranged between 0.03 and 0.06 in Y-modified $BiNbO_4$ ceramics with CuO–V_2O_5 mixture addition.

The τ_f values of $Bi_{(1-x)}Y_xNbO_4$ ceramics with various x values at different sintering temperatures are shown in Fig. 6. τ_f was influenced by sintering temperature. Compared with Fig. 4 and Fig. 6, the change in τ_f with sintering temperature was in accordance with the change in ε_r with sintering temperature. τ_f is related to the temperature coefficient of dielectric constant τ_ε and that of linear expansion α_L by[24]

$$\tau_f = -\tau_\varepsilon/2 - \alpha_L \qquad (2)$$

α_L is nearly constant for well-sintered ceramics. Thus, τ_f depends only on τ_ε, which generally increases with increasing dielectric constant ε_r. The change in τ_f with sintering temperature for a given x value was caused by the change in ε_r, as shown in Fig. 4. Figure 7 shows the τ_f of dense $Bi_{(1-x)}Y_xNbO_4$ ceramics as a function of x. The τ_f continuously decreased from 28.32 ppm/°C to -8.78 ppm/°C with increasing x from 0 to 0.1. This implies that τ_f can be adjusted to near zero by substituting a suitable amount of Bi with Y in $BiNbO_4$ ceramics.

4. Conclusions

The microstructure and the microwave dielectric proper-

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ties of $Bi_{(1-x)}Y_xNbO_4$ ceramics doped with $0.5\,wt\%$ CuO–V_2O_5 mixture were investigated. The phase transition temperature of $BiNbO_4$ ceramics was reduced to below $900^\circ C$ by the substitution of Y for Bi. The densification temperatures increased from $780^\circ C$ to $900^\circ C$ with increasing x from 0 to 0.1. Bulk density and ε_r increased with sintering temperature, reached their maximum values and then decreased with further increase in temperature. The saturated bulk density and ε_r of $Bi_{(1-x)}Y_xNbO_4$ ceramics decreased with increasing of x. $Q \times f$ was dependent on sintering temperature. τ_f was also dependent on sintering temperatures and x. A near zero τ_f could be obtained by carefully adjusting Y content. The $Bi_{(1-x)}Y_xNbO_4$ ceramics with $x = 0.05$ sintered at $860^\circ C$ showed good microwave dielectric properties of $\varepsilon_r \sim 41.58$, $Q \times f \sim 11579\,GHz$ and $\tau_f \sim 8.93\,ppm/^\circ C$.

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