

The sintering behavior and microwave dielectric properties of Bi(Nb,Sb)O₄ ceramics

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Abstract

Sb₂O₅ were selected to substitute Nb₂O₅ and the effects of substitution on the sintering behavior and the microwave dielectric properties of BiNbO₄ ceramics were studied. Solid solutions formed in sintered BiNb_(1-x)Sb_xO₄ ceramics with x value being no more than 0.4. The unit cell volume of orthorhombic phase BiNb_(1-x)Sb_xO₄ decreased from 331.86 to 324.99 Å³ with x value increasing from 0 to 0.4. The densified temperatures increased from 800 to 940 °C. The microwave dielectric properties of BiNb_(1-x)Sb_xO₄ ceramics were found to be affected by the substitution of Sb for Nb and the sintering temperature. The saturated ϵ_r values first increased from 44.00 to 44.61 with x increasing from 0 to 0.1 and then decreased to 40.69 with x to 0.4. The saturated $Q \times f$ values decreased with increasing of x value. The τ_f values were correlated to the unit cell volume of BiNb_(1-x)Sb_xO₄ and continuously decreased from a positive value of 14.19 ppm/°C for $x = 0$ to a negative value of -30.94 ppm/°C for $x = 0.4$. At a sintering temperature of 820 °C and x value of 0.05, BiNb_(1-x)Sb_xO₄ ceramics exhibited the optimum microwave dielectric properties of $\epsilon_r \sim 44.49$, $Q \times f \sim 14,278$ GHz, and $\tau_f \sim -5.19$ ppm/°C.

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1. Introduction

Recently, the rapid growth of communications using microwave frequencies, such as portable phones and car telephones, has created a demand for the miniaturization of components such as band pass filters and local oscillators. The application of multilayer microwave devices will contribute to 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 needed to co-fire with low loss, low-melting-point conductors such as Ag (melting point = 961 °C) or Cu (1064 °C). (Zr,Sn)TiO₄, Ba₂Ti₉O₂₀, and Ba(MgTa)O₃ systems have excellent microwave dielectric properties and are the most common dielectric materials for ultra-high frequency applications [2–4]. But they are not compatible with the co-fire process because of their high sintering temper-

atures. Low melting glass additions, chemical processing and smaller particle sizes of the starting materials are three methods normally used to reduce 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 for those commercial dielectric materials using these methods are still too high to use low-melting-point electrodes.

Bismuth-based dielectric ceramics are well-known as low-fired materials and have been investigated for the application as multilayer capacitors [9,10]. The microwave dielectric properties of Bi₂O₃–Nb₂O₅ systems were firstly studied by Kagata et al. [11]. The results showed that BiNbO₄ ceramics with CuO/V₂O₅ additions had a Q value of 4260 (at 4.3 GHz), ϵ_r value of 43 and a large τ_f value of 38 ppm/°C (–25 to 20 °C). In order to lower the τ_f values, some lanthanide ions (Ln³⁺, Ln = La, Nd, Sm) were used to substitute for Bi³⁺ in A site of BiNbO₄ and the effects of substitution on densification and microwave dielectric properties of BiNbO₄ ceramics were investigated by several researchers [12–15]. For Ln substitution, the phase transition temperature (orthorhombic to triclinic) of

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BiNbO₄ ceramics was lowered due to the lattice distortion caused by the ionic difference between Ln³⁺ and Bi³⁺. The τ_f values of Ln-modified BiNbO₄ ceramics could be adjusted to near zero. That might be caused by the existence of triclinic phase of BiNbO₄. However, only the Ta was used to substitute for Nb in B site of BiNbO₄ to modify the microwave dielectric properties of BiNbO₄ ceramics by Huang and Weng [16,17]. By adjusting the amount of Ta additive, a near zero τ_f value could also be obtained although no phase transition (orthorhombic to triclinic) occurred in BiNb_(1-x)Ta_xO₄ ceramics.

In this study, BiNbO₄ was used as the host material and Sb₂O₅ was selected to substitute for Nb₂O₅. The influences of Sb substitution for Nb on the sintering behavior and microwave dielectric properties of BiNbO₄ ceramics were investigated. A small amount of CuO–V₂O₅ mixtures (CuO:V₂O₅ = 1:1 in weight ratio) were used as sintering aids. The correlation between the crystal structure and the microwave dielectric properties was also discussed.

2. Experimental procedures

Samples of BiNb_(1-x)Sb_xO₄ ($x = 0, 0.05, 0.1, 0.2, 0.4$) were prepared by conventional solid-state reaction methods. High-purity oxide powders: Bi₂O₃ (>99.99%), Nb₂O₅ (>99.97%) and Sb₂O₅ (>99.9%) were used as the 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 crystalline phases of the calcined powder were identified by X-ray diffraction patterns using Cu K α radiation for 2θ from 20 to 60° (Rigaku D/max 2550 V X-ray diffractometer). The calcined powders were added with a small amount of CuO–V₂O₅ mixtures (0.3 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. Typical dimensions of the pellets were 16 mm in diameter and 7 mm in thickness. The pellets were sintered from 780 to 940 °C for 3 h. To prevent from the vaporization of Bi₂O₃, the pellets were placed in a sealed alumina crucible filled with BiNbO₄ powders.

The bulk densities of the sintered ceramics were measured using the Archimedes method and the crystalline phases were also identified by X-ray diffraction patterns as above. To calculate the lattice parameters of the prepared samples, the phase analysis was based on X-ray powder diffraction data from a Guinier-Hägg camera with use of Cu K α_1 radiation and Si as the internal standard. The obtained photographs were evaluated with a computerized scanner system [18]. The determination of unit cells of samples was performed by means of PIRUM program based on Guinier-Hägg film data [19]. Microstructure observation of the sintered surface of BiNb_(1-x)Sb_xO₄ ceramics was performed by scanning electron microscopy (SEM) (JEOL JSM-6700F). The average grain sizes were calculated from

the line intercept method. 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 [20,21]. An Advantest R3767CG network analyzer was employed in the measurement. The temperature coefficient of the resonant frequency τ_f was measured in the temperature range of –25 to +85 °C. The τ_f value was defined as follows:

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

Where f_{85} , f_{-25} , and f_{25} are the TE₀₁₁ resonant frequency at 85, –25, and 25 °C, respectively.

3. Results and discussion

Fig. 1(a)–(c) show the XRD patterns of BiNb_(1-x)Sb_xO₄ powders calcined at 800 °C for 3 h. According to the XRD results, the BiNbO₄ powder after calcination led to the formation of the α -BiNbO₄ (orthorhombic structure, the low temperature form of BiNbO₄) as major crystalline phase and Bi₅Nb₃O₁₅ as minor phase. The diffraction intensity of Bi₅Nb₃O₁₅ phase increased with x value increasing to 0.1 and the BiSbO₄ and β -Bi₃SbO₇ phases could also be identified in the BiNb_{0.6}Sb_{0.4}O₄ calcined powder. Only the orthorhombic phase was revealed in the sintered BiNbO₄ ceramics, as shown in Fig. 1(d). But for $x \geq 0.1$, orthorhombic and triclinic phases were found to be coexisted in sintered specimens and the triclinic peaks intensified with increasing of x value and sintering temperature. It was well-known that the orthorhombic phase, the low temperature phase of BiNbO₄, is stable below 1020 °C and then gradually transforms to the triclinic phase as the temperature is increased [22,23]. The existence of triclinic phase proved that Sb substitution lowered the phase transition temperature,

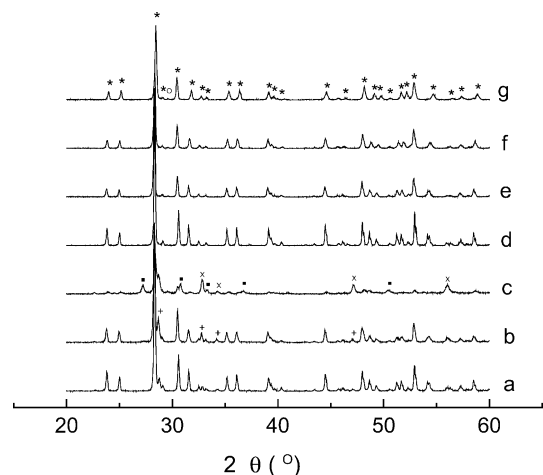


Fig. 1. XRD patterns of BiNb_(1-x)Sb_xO₄ powders calcined at 800 °C with (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.4$, and BiNb_(1-x)Sb_xO₄ ceramics with (d) $x = 0$, (e) $x = 0.1$, (f) $x = 0.2$ sintered at 820 °C, and (g) $x = 0.4$ sintered at 900 °C. (*) α -BiNbO₄; (o) β -BiNbO₄; (+) Bi₅Nb₃O₁₅; BiSbO₄; (x) β -Bi₃SbO₇.

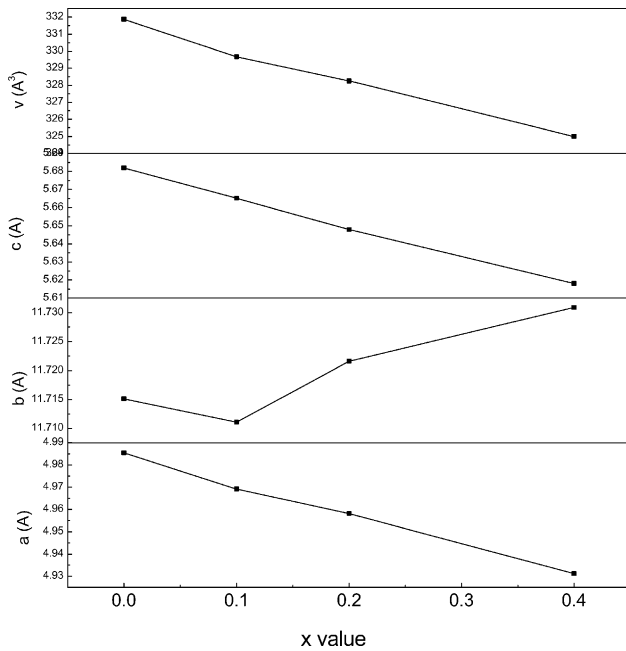


Fig. 2. Lattice parameters of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ as a function of x value.

not as Ta substitution did [16,17]. The difference in ionic radii between Sb^{5+} (0.62 \AA) and Nb^{5+} (0.69 \AA), which is larger than that between Ta^{5+} (0.68 \AA) and Nb^{5+} , might account for this result [24]. However, the ratio (R) values of $I_{\text{tri}}/[I_{\text{tri}}+I_{\text{ortho}}]$, where I_{tri} and I_{ortho} are intensities of triclinic (202), (-210) and orthorhombic (040) reflection peaks of XRD patterns, respectively [12–14], of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with different x values at different sintering temperatures were all less than 0.1. This suggests that the degree of triclinic phase transition of Sb substitution for Nb in BiNbO_4 ceramics is far smaller than that of Ln substitution for Bi in BiNbO_4 ceramics, although the amount of substitution for Sb to Nb is more than that of Ln to Bi [12–15]. It was worth noting that only the two forms of BiNbO_4 phases were present and the BiSbO_4 and $\beta\text{-Bi}_3\text{SbO}_7$ phases were not found in sintered $\text{BiNb}_{0.6}\text{Sb}_{0.4}\text{O}_4$ ceramics (Fig. 1(g)). This result shows that the solid solutions still can be formed in $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with x value being no more than 0.4. Further investigation showed that the BiNbO_4 and BiSbO_4 phases were co-existed and the solid solutions did not form in the sintered $\text{BiNb}_{0.4}\text{Sb}_{0.6}\text{O}_4$ ceramics (which will be discussed in other place).

Ignoring the peaks of the triclinic phase because of their very weak intensities, the lattice parameters of $\alpha\text{-BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ in sintered specimens were calculated and the results are shown in Fig. 2. The a -axis and c -axis decreased and b -axis increased with increasing of Sb substitution. The unit cell volume of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ solid solutions also linearly decreased from 331.86 to 324.99 \AA^3 with x value increasing from 0 to 0.4. The substitution of large Nb^{5+} cations by smaller Sb^{5+} cations will account for this result. The changes of lattice parameters also reflect the formation of solid solutions, as shown in Fig. 1.

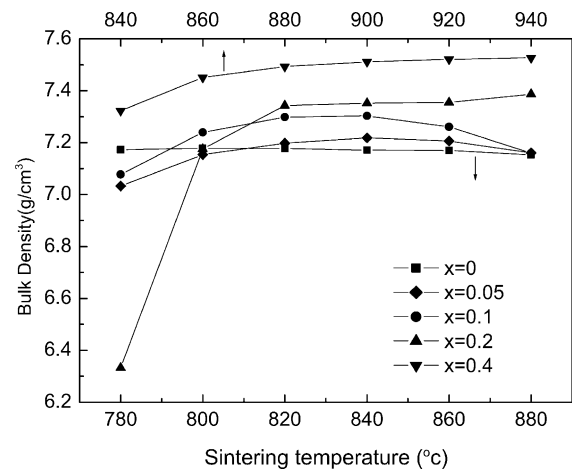


Fig. 3. SEM micrographs of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics.

The densities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with different x values as a function of sintering temperatures are shown in Fig. 3. As the sintering temperature increased, the densities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics increased and reached the maximum values. The sintering temperatures of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics required for obtaining their maximum densities (defined as the densified temperatures) increased from 800 to $940 \text{ }^\circ\text{C}$ as the x value increased from 0 to 0.4. This suggests that the substitution of Sb for Nb reduces the sinterability of BiNbO_4 ceramics. Further increasing the sintering temperature above the densified temperatures caused the densities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics decreased slightly. The saturated bulk densities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics increased from 7.18 g/cm^3 (97.75% TD, TD is defined as the theoretical density) to 7.53 g/cm^3 (97.58% TD) with the increase of x value from 0 to 0.4 owing to the substitution of heavier Sb atoms for lighter Nb atoms.

The SEM micrographs of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with various x values sintered at different temperatures are shown in Fig. 4. The homogeneously fine microstructures with almost no pores were revealed for $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with $x = 0\text{--}0.2$ sintered at $820 \text{ }^\circ\text{C}$ (Fig. 4(a)–(c)). The average grain sizes of all those compositions were distributed around $0.77\text{--}0.86 \mu\text{m}$. The $\text{BiNb}_{0.6}\text{Sb}_{0.4}\text{O}_4$ ceramics with 0.3 wt.% $\text{CuO-V}_2\text{O}_5$ mixtures could not be densified until sintered at $920 \text{ }^\circ\text{C}$ for 3 h, as shown in Fig. 3. Fig. 4(d) shows the SEM micrograph of as-sintered surface of $\text{BiNb}_{0.6}\text{Sb}_{0.4}\text{O}_4$ ceramic at $920 \text{ }^\circ\text{C}$. The average grain sizes of this ceramic were also $0.86 \mu\text{m}$ but the amount of bar shape grains were more than that of above three shown in Fig. 4(a)–(c). This resulted from the growth anisotropies of BiNbO_4 grains and the higher sintering temperature. The amount of bar shape grains increased for $\text{BiNb}_{0.9}\text{Sb}_{0.1}\text{O}_4$ ceramics with the sintering temperature increasing from 820 to $840 \text{ }^\circ\text{C}$ and an abnormal grain growth, which exhibited large discontinuous grains existing in the fine-grained matrix, could be observed with temperature further increasing to $860 \text{ }^\circ\text{C}$ (Fig. 4(e) and (f), respectively). This means

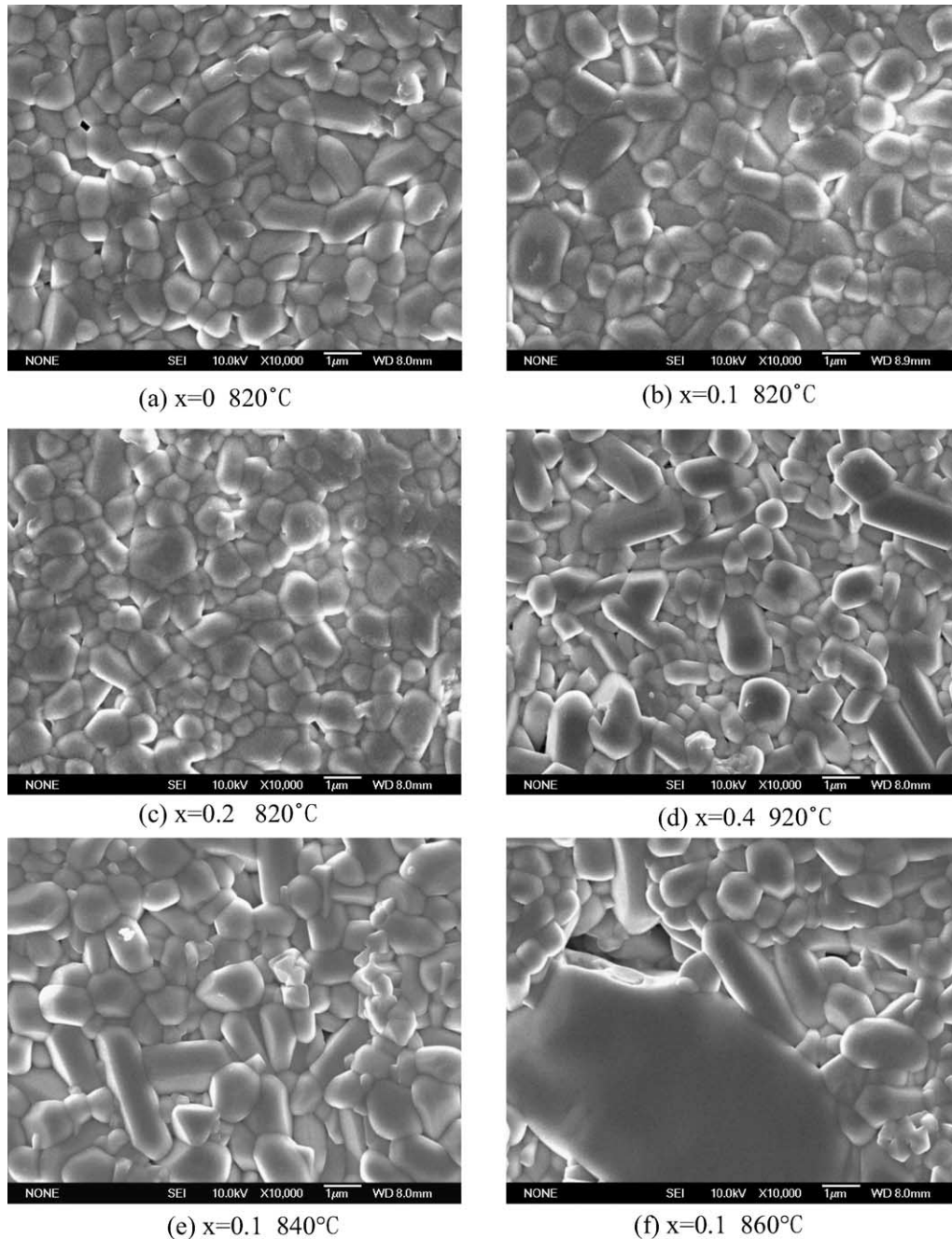


Fig. 4. Bulk densities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with $x = 0-0.4$ as a function of sintering temperature.

that too high a sintering temperature is unnecessary for this system.

Fig. 5 shows the plots of the dielectric constants of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics as a function of sintering temperatures for various x values. The ϵ_r values of all $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics increased with sintering temperature and saturated at 800–940 °C depending on the x value, then decreased with further increasing in temperature. The relationships between sintering temperatures and ϵ_r values revealed the same trend with those between sintering temperatures and densities. It implies that the increase for ϵ_r

values of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with sintering temperature is due to the increase of density and reduced porosity (the dielectric constant of pore equals 1.0). The decrease in ϵ_r values above the densified temperatures is associated with the abnormal grain growth and the increase of porosity, as shown in Fig. 4. It was found that the ϵ_r values of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics were also correlated to x values. The saturated ϵ_r values first increased from 44.00 to 44.61 with x increasing from 0 to 0.1 and then decreased to 40.69 with x to 0.4. At microwave frequencies the dielectric constant of ceramic is closely related with the sum of electronic

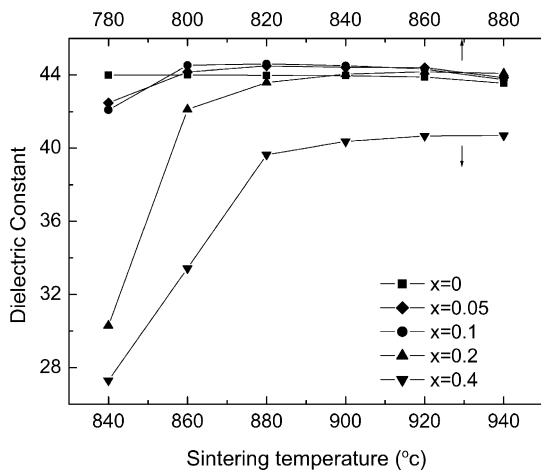


Fig. 5. Dielectric constants of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with $x = 0\text{--}0.4$ as a function of sintering temperature.

and ionic polarizabilities of components. The slight increase in ϵ_r value might result from the increase of electronic polarizabilities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with the increase of x value. The lattice parameters of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics decreased with increasing the amount of Sb substitution for Nb, as shown in Fig. 2. The decrease of the lattice parameters promotes the shrinkage of the octahedral and decreases the ionic polarizabilities of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics. It also decreases the dielectric constant indirectly.

Fig. 6 illustrates the $Q \times f$ values of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics as a function of the sintering temperatures. The $Q \times f$ values of all samples increased with increasing of sintering temperatures. After reaching the maximum values, the $Q \times f$ values decreased. Many factors are believed to affect the microwave dielectric losses of dielectric ceramics and can be divided into two fields, i.e. intrinsic loss and extrinsic loss [25]. The intrinsic loss is caused by anharmonic phonon decay process in the pure crystal lattice while the ex-

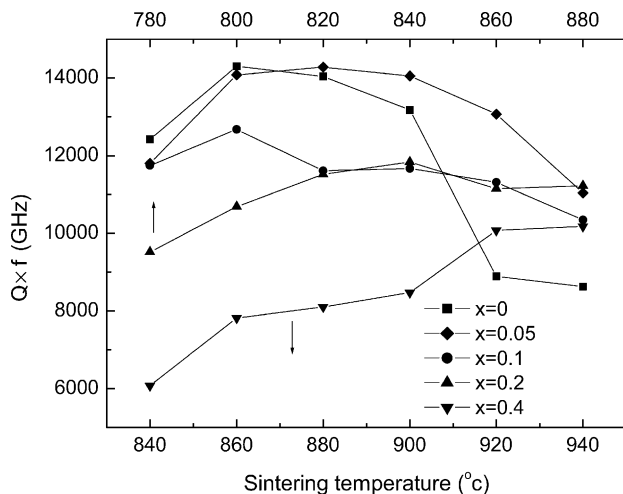


Fig. 6. $Q \times f$ values of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with $x = 0\text{--}0.4$ as a function of sintering temperature.

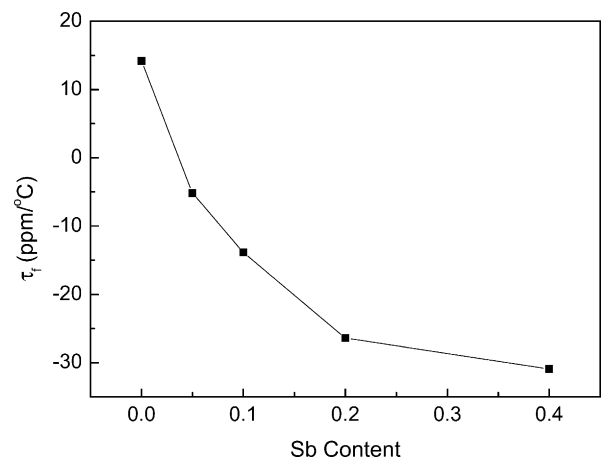


Fig. 7. τ_f values of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics as a function of Sb content.

trinsic losses are caused by crystal defects, grain boundaries, second phases, and pores [26]. The densities and grain sizes of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics increased with increasing of sintering temperature and then the pores and grain boundary areas decreased, which meant less lattice imperfections and lower dielectric loss. The abnormal grain growth occurred in sintered $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with further increasing in sintering temperatures above the densified temperatures, which led to the increase in the crystal defects and the decrease in the $Q \times f$ values. The saturated $Q \times f$ values of the $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics were strongly dependent on the Sb content. The $Q \times f$ value decreased from 14296 to 10174 GHz with x value increasing from 0 to 0.4. Such a significant decrease might arise from substitutional impurity effects in $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ solid solutions, which increase the anharmonicity of phonon vibrations [27–29].

The τ_f values of dense $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with various x values are shown in Fig. 7. It was found that the τ_f decreased to negative values with increasing of Sb content. Compared with Figs. 2 and 7, the change in τ_f value with Sb content was in accord with that in unit cell volume with Sb content. Lee et al. [30,31] reported that τ_f , which may depend on the lattice energy of $\text{M}'\text{Nb}_2\text{O}_6$ compounds, is correlated to the unit cell volume of $\text{M}'\text{Nb}_2\text{O}_6$. They suggested that the unit cell volume is inversely proportional to the lattice energy if compounds are same structure. The τ_f values of dense $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics linearly decreased with increasing of x value. This might also be attributed to the corresponding decrease in unit cell volume as shown in Fig. 2. The τ_f value changed from 14.19 ppm/°C for BiNbO_4 to a negative value of -13.86 ppm/°C for $\text{BiNb}_{0.9}\text{Sb}_{0.1}\text{O}_4$ ceramics. An extra point with $x = 0.05$ was examined to further confirm the trend of the τ_f value with various amounts of the Sb content. It was found that the $\text{BiNb}_{0.95}\text{Sb}_{0.05}\text{O}_4$ ceramics sintered at 820 °C had the optimum τ_f value of -5.19 ppm/°C. This implies that the τ_f can be adjusted to near zero by substituting suitable amount of Nb by Sb between $x = 0$ and $x = 0.05$ in BiNbO_4 ceramics.

4. Conclusion

The solid solutions could be formed in sintered $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with x value being no more than 0.4. The phase transition temperature of BiNbO_4 ceramics was lowered by the substitution of Sb for Nb but the degree of triclinic phase transition was far smaller than that of Ln (Ln = La, Nd, Sm) substitution for Bi in BiNbO_4 ceramics. The unit cell volume of orthorhombic phase $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ decreased with increasing of Sb content. The densified temperatures increased from 800 to 940 °C with x value increasing from 0 to 0.4. The microwave dielectric properties of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics were found to be affected by the substitution of Sb for Nb and the sintering temperature. The saturated ϵ_r values first increased from 44.00 to 44.61 with x increasing from 0 to 0.1 and then decreased to 40.69 with x to 0.4. The saturated $Q \times f$ values decreased with increasing of x value due to substitutional impurity effects. The τ_f values were correlated to the unit cell volume of $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ and continuously decreased from positive (14.19 ppm/°C for $x = 0$) to negative (−30.94 ppm/°C for $x = 0.4$). A near zero τ_f value could be obtained by carefully adjusting the Sb content. The $\text{BiNb}_{(1-x)}\text{Sb}_x\text{O}_4$ ceramics with $x = 0.05$ sintered at 820 °C showed good microwave dielectric properties of $\epsilon_r \sim 44.49$, $Q \times f \sim 14278$ GHz, and $\tau_f \sim -5.19$ ppm/°C.

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