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Microwave dielectric characteristics of $(Bi_{1-x}Sm_x)NbO_4$ ceramics

Wen-Cheng Tzou[a,*], Cheng-Fu Yang[b], Ying-Chung Chen[a], Ping-Shou Cheng[a]

[a]*Department of Electrical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, ROC*
[b]*Department of Electronic Engineering, Chinese Air Force Academy, PO Box 90277-4, Kangshan, Kaohsiung, Taiwan 82012, ROC*

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Abstract

The effect of sintering temperature on the microwave characteristics of $(Bi_{1-x}Sm_x)NbO_4$ ceramics was investigated. As the sintering temperature increased from 940 to 1060 °C, the amount of the α-form of $(Bi_{1-x}Sm_x)NbO_4$ first increased, reached a saturation value, and then decreased. The high temperature form of the $(Bi_{1-x}Sm_x)NbO_4$ (β-form, triclinic) started to appear at 960 °C for $x=0.1$, and then its amount increased with the increase of the sintering temperature. The dielectric constant (ε_r) did not apparently change with the increase of Sm content and saturated at 41.5–42.5. The quality factor ($Q\times f$) reached a maximum value in samples sintered at 1000–1020 °C and then rapidly decreased with the increase of the sintering temperature for $x\geqslant 0.1$. In samples sintered at >1000 °C, the negative temperature coefficient of the resonant frequency (τ_f) critically increased with the increase of sintering temperature for all compositions. $(Bi_{1-x}Sm_x)NbO_4$ ceramics sintered at 960 °C and $x=0.1$ had a minimum τ_f value of 1.5 ppm/ °C. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: $(Bi_{1-x}Sm_x)NbO_4$; Microwave characteristics; Sm_2O_3; α-Form; β-Form

1. Introduction

Recent development in microwave telecommunication systems, demand the miniaturization of the size and weight of multilayer microwave devices [1]. In multilayer structures, low sintering temperatures are needed to cofire with low loss and low melting point electrode such as silver (melting point = 961 °C) and gold (1065 °C). $Ba_2Ti_9O_{20}$ [2], $(Zr,Sn)TiO_4$ [3], $BaMg_{1/3}(Ta,Nb)_{2/3}O_3$ [4] and $BaO–(Nd,Sm)_2O_3–TiO_2$ [5] systems were the most common ceramic materials suitable for use in dielectric resonators at microwave frequency. These ceramics possessed a high dielectric constant (ε_r) with a high quality value (Q), and a small temperature coefficient of resonant frequency (τ_f). The temperatures needed to densify $Ba_2Ti_9O_{20}$, $(Zr,Sn)TiO_4$, $BaMg_{1/3}(Ta,Nb)_{2/3}O_3$ and $BaO–(Nd,Sm)_2O_3–TiO_2$ systems were about 1350, 1500, 1550 and 1350 °C, respectively. The sintering temperatures for those microwave materials were too high to use the low melting point silver and gold electrode. Addition of the low-melting-point glasses, chemical processing, and smaller particle size of the starting materials were three different methods used to reduce the sintering temperature of a dielectric. However, the sintering temperatures for these compositions using the methods mentioned above were still too high to cofire with low melting point electrode. Therefore, it was imperative to find microwave ceramics with low sintering temperatures and excellent dielectric properties in order to use the silver and gold electrode.

In the past, bismuth-based dielectric ceramics were known as low-fire materials and had been studied for multilayer ceramic capacitors [6]. However, the $BiNbO_4$ ceramic with practical dielectric properties at microwave frequency was first developed by Kagata et al. [7]. They prefered $BiNbO_4$ ceramics with high Q values and low sintering temperature, but the τ_f values were too high for practical application. In order to lower the τ_f values, several researchers attempted to modify the microwave dielectric properties of $BiNbO_4$ ceramics using different chemical elements. $(Bi_{1-x}Nd_x)NbO_4$ compositions were developed by Choi et al. [8] and $Bi(Nb_{1-x}Ta_x)O_4$ compositions were developed by Weng et al. [9]. Both compositions possessed high $Q\times f$ values and low τ_f values. In this study, $BiNbO_4$ was used as the host material and Sm_2O_3 was used to substitute for Bi_2O_3. Being $BiNbO_4$-

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[*] Corresponding author. Tel. +886-922-702-157; fax: +886-945-834-460.
E-mail address: twj.b826@msa.hinet.net (W.-C. Tzou).

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based ceramics hard to be densified, CuO was used as sintering aid. The microwave dielectric properties of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics were investigated, and the relationship between the crystalline phase and the microwave properties was discussed.

2. Experimental procedures

Reagent-grade starting materials of Bi_2O_3, Sm_2O_3, and Nb_2O_5 were mixed, according to the composition $(Bi_{1-x}Sm_x)NbO_4$, ($x=0.05$, 0.1, and 0.15) and ball-milled for 5 h with deionized water. After drying, the powder was ground and calcined at 800 °C for 2 h. Then the $(Bi_{1-x}Sm_x)NbO_4$ powder was mixed with 0.5 wt.% CuO by ball milling with deionized water. After drying, the mixed powder was uniaxially pressed into pellets in a steel die. Sintering of these pellets was carried out at temperatures between 940 and 1060 °C under ambient conditions for 4 h.

The crystalline phases were analyzed by X-ray powder diffraction using Cu-K_α radiation.

The densities of the sintered specimens, as a function of sintering temperature, were measured by the liquid displacement method using deionized water as the liquid (Archimedes method). To investigate the internal morphology of the samples, the sintered surfaces of the specimens were observed by SEM. Dielectric characteristics at microwave frequency were measured with the Hakki and Coleman's dielectric resonator method [10], which was improved by Courtney [11]. An HP8510B network analyzer and an HP8340A sweeper were used for the microwave characteristic measurements. The dielectric constant can be accurately determined by measuring the resonant frequency of the TE_{011} mode and verified by the $TE_{01\delta}$ resonant modes. The temperature coefficient of resonant frequency (τ_f) was defined as follows.

$$\tau_f = (f_{80} - f_{20})/(f_{20} \times 60) \quad (1)$$

where f_{20} and f_{80} were the resonant frequency at 20 and 80 °C, respectively.

3. Results and discussion

Typical X-ray diffraction patterns of $(Bi_{0.9}Sm_{0.1})NbO_4$ are shown in Fig. 1. For compositions calcined at 800 °C, the low temperature form of $(Bi_{1-x}Sm_x)NbO_4$ (α-form, orthorhombic structure, which is stable below 1020 °C) was revealed as major crystalline phase. The satellite crystalline phases, $(Bi,Sm)_8Nb_{18}O_{57}$, $(Bi,Sm)_5Nb_3O_{15}$ and $(Bi,Sm)_2Nb_{10}O_{28}$ could also be found in the calcined $(Bi_{1-x}Sm_x)NbO_4$ powder, as shown in Fig. 1(a). For the 940 °C-sintered $(Bi_{0.9}Sm_{0.1})NbO_4$ ceramics, Fig.1(b), only the α-form of $(Bi_{1-x}Sm_x)NbO_4$ was revealed. As the sintering temperature increased, the intensity of the α-form of $(Bi_{1-x}Sm_x)NbO_4$ first increased, reached a maximum at 960 °C, then decreased with the increase of the sintering temperature and disappeared at 1040 °C (Fig. 1). The high temperature form of the $(Bi_{1-x}Sm_x)NbO_4$ (β-form, triclinic structure) started to appear in the 960 °C-sintered $(Bi_{0.9}Sm_{0.1})NbO_4$ ceramics [Fig. 1(c)]. The crystalline intensity of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ increased with the increase of the sintering temperature and saturated at 1040 °C. The phase transition temperature for $(Bi_{1-x}Sm_x)NbO_4$ ceramics studied are listed in Table 1. It was reported that $BiNbO_4$ had a crystal structure similar to orthorhombic-$SbTaO_4$ type

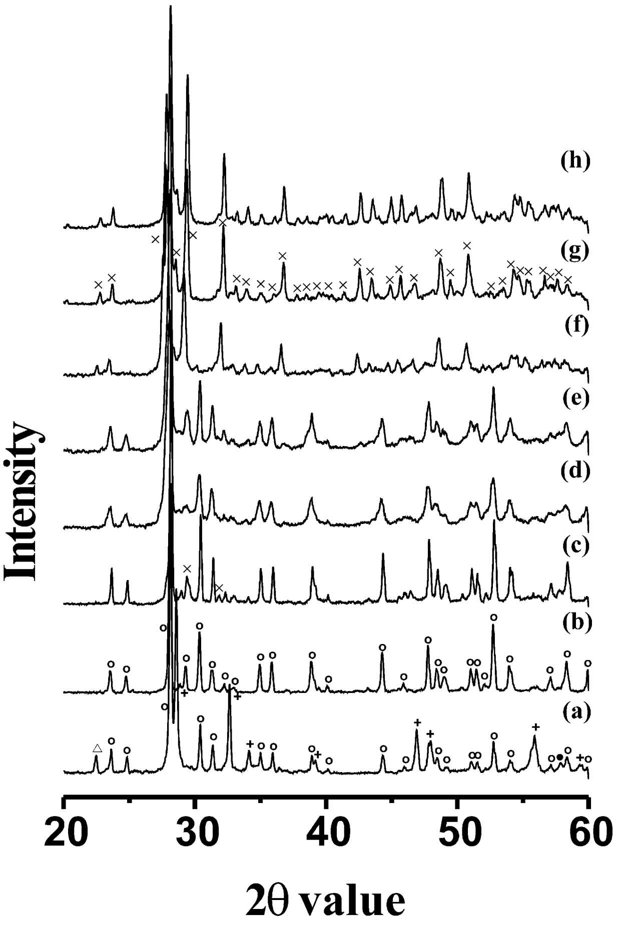

Fig. 1. X-ray patterns for (a) $(Bi_{0.9}Sm_{0.1})NbO_4$ powder calcined at 800 °C for 2 h, and 0.5 wt.%-CuO-doped $(Bi_{0.9}Sm_{0.1})NbO_4$ ceramics sintered at (b) 940 °C, (c) 960 °C, (d) 980 °C, (e) 1000 °C, (f) 1020 °C, (g) 1040 °C and (h) 1060 °C, respectively. [○: α-(Bi,Sm)NbO_4, ×: β-(Bi,Sm)NbO_4, △: $(Bi,Sm)_2Nb_{10}O_{28}$, +: $(Bi,Sm)_5Nb_3O_{15}$, ●: $(Bi,Sm)_8Nb_{18}O_{57}$].

Table 1
Phase transition temperature for $(Bi_{1-x}Sm_x)NbO_4$ ceramics

Composition, x	Temperature (°C)
0.05	980
0.1	960
0.15	960

below 1020 °C, and then transformed to the triclinic phase as the temperature was increased [12]. According to this experimental result, the phase transition temperature of $(Bi_{1-x}Sm_x)NbO_4$ ceramics can be lowered as Bi^{3+} is substituted by Sm^{3+}.

SEM observations revealed the changes in the morphology of the $(Bi_{1-x}Sm_x)$ NbO_4 ceramics in the samples subjected to different sintering temperature and with different Sm_2O_3 content. The changes in the density and grain size can be seen in the SEM photographs of

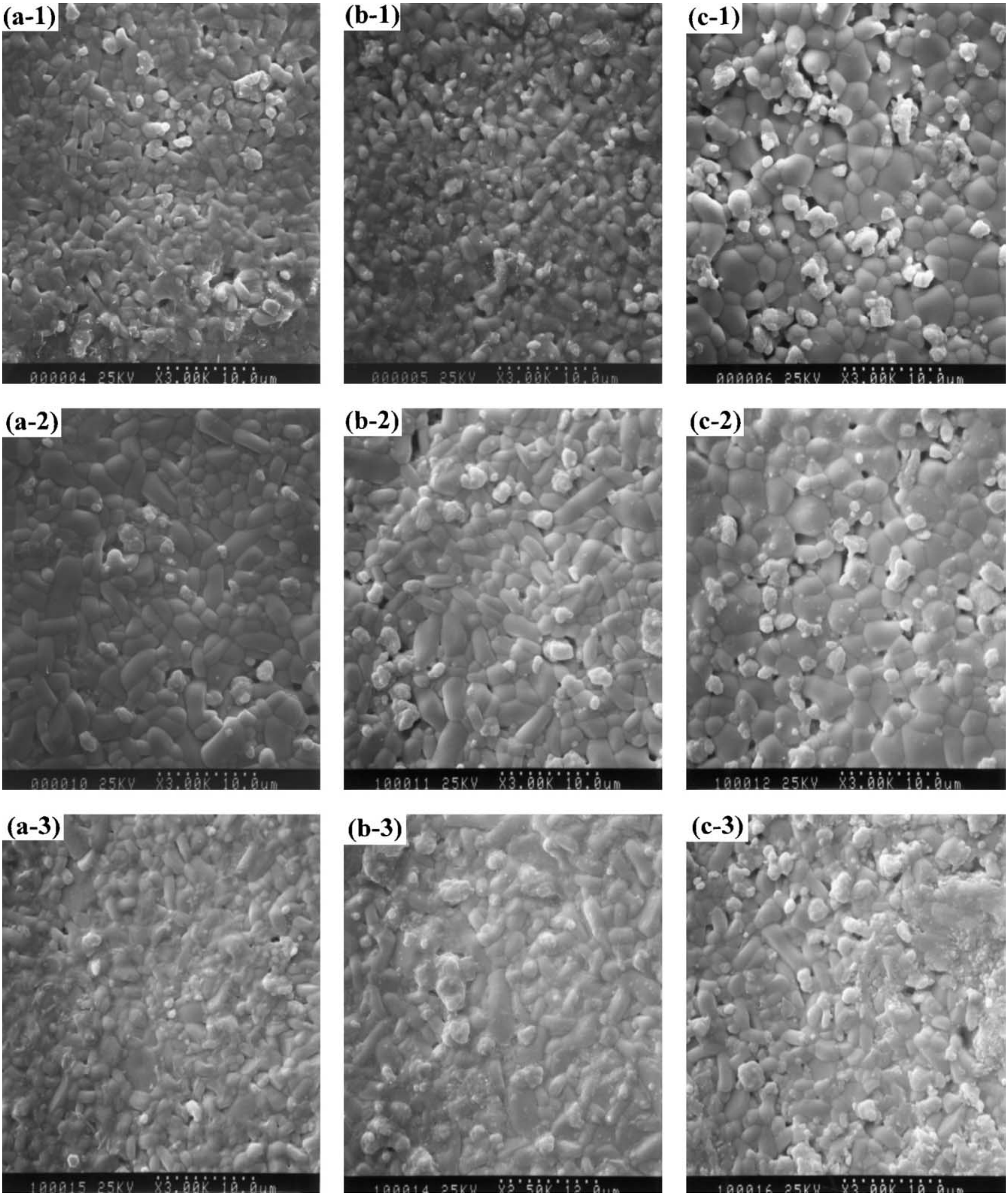

Fig. 2. Micrographs of $(Bi_{1-x}Sm_x)NbO_4$ ceramics. For $x = 0.05$ and sintered at (a-1) 940 °C, (a-2) 960 °C and (a-3) 980 °C. For $x = 0.1$ and sintered at (b-1) 940 °C, (b-2) 960 °C and (b-3) 980 °C. For $x = 0.15$ and sintered at (c-1) 940 °C, (c-2) 960 °C and (c-3) 980 °C.

selected CuO-added $(Bi_{1-x}Sm_x)NbO_4$ ceramics (Fig. 2). For 940 °C-sintered $(Bi_{0.95}Sm_{0.05})NbO_4$ ceramics, isolated $(Bi_{1-x}Sm_x)NbO_4$ particles and pores were also observed, as shown in Fig. 2(a-1), (b-1) and (c-1). Further increasing the sintering temperature, homogeneously fine microstructures with less pores were observed for all compositions. This implies that the pores of all $(Bi_{1-x}Sm_x)$ NbO_4 ceramics decrease and the grain sizes increase with sintering temperatures independent of Sm_2O_3 content. For a given sintering temperature, the pores were more for samples with larger Sm content [compare Fig. 2(a-2), (b-2) and (c-2)]. Inhibited grain growth, due to the reduction of sinterability, is caused by the substitution of Sm^{3+} for Bi^{3+}.

The densities of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics were investigated at sintering temperature of 940–1060 °C, and the results are shown in Fig. 3. As the sintering temperature increased, from 940 to 960–980 °C, the densities of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics critically increased. According to the results in Fig. 2, the decrease of the pores will account for this result. As the sintering temperature was higher than 1000 °C, the densities of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics slightly increased with the increase of the sintering temperature. By comparing the results shown in Figs. 1 and 2, the intensity increase of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ may account for the unobvious increase. At sintering temperatures higher than 980 °C, the $(Bi_{1-x}Sm_x)NbO_4$ ceramics revealed a densified bulk, and the intensity of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ ceramics increased with the sintering temperature. (The theoretical densities of the β-form of $BiNbO_4$-based ceramics are higher than for the α-form of $BiNbO_4$-based ceramics. The theoretical density of the α-form of $BiNbO_4$ ceramic is 7.345 g/cm^3 while that of the β-form of $BiNbO_4$ ceramic is 7.5 g/cm^3 [12,13]. The theoretical density of the α-form of $BiTaO_4$ ceramic is 9.179 g/cm^3 while that of the β-form of $BiTaO_4$ ceramic is 9.332 g/cm^3 [14].) The relative densities of all $(Bi_{1-x}Sm_x)NbO_4$ ceramics exhibited a value higher than 97% at a sintering temperature of 980 °C. These results imply that the crystalline phase has a large effect on the density values of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics, and that Sm_2O_3 has a beneficial influence on the densification of $(Bi_{1-x}Sm_x)$ NbO_4 ceramics. However, the saturation density values of $(Bi_{1-x}Sm_x)NbO_4$ ceramics should be decreased with larger x value because of the substitution of heavier Bi atoms by lighter Sm atoms [15] and the increase of pores in $(Bi_{1-x}Sm_x)NbO_4$ ceramics.

The ε_r values of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics were investigated as a function of sintering temperature and Sm_2O_3 content, and the results are shown in Fig. 4. At first, the ε_r values of all $(Bi_{1-x}Sm_x)NbO_4$ ceramics increased with sintering temperatures and saturated at 960–1000 °C dependent on the Sm_2O_3 content. The relationships between ε_r values and sintering temperatures revealed the same trend as that between densities and sintering temperatures. The increase in the ε_r value with sintering temperature may result from the increase of density and grain growth. The maximum ε_r values of $(Bi_{1-x}Sm_x)NbO_4$ ceramics increased from 41.5 to 42.5 nonlinearly as x was changed from 0.05 to 0.15. On the other hand, as the sintering temperature increased from 960 to 1060 °C, the ε_r values had an unobvious change with the increase of the sintering temperature. These results indicate that the Sm_2O_3 content and the crystalline phase have no apparent influence on the ε_r values of $(Bi_{1-x}Sm_x)NbO_4$ ceramics.

Fig. 5 shows the $Q \times f$ values of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics as a function of sintering temperature and Sm_2O_3 content. It was observed that the Q×f values of

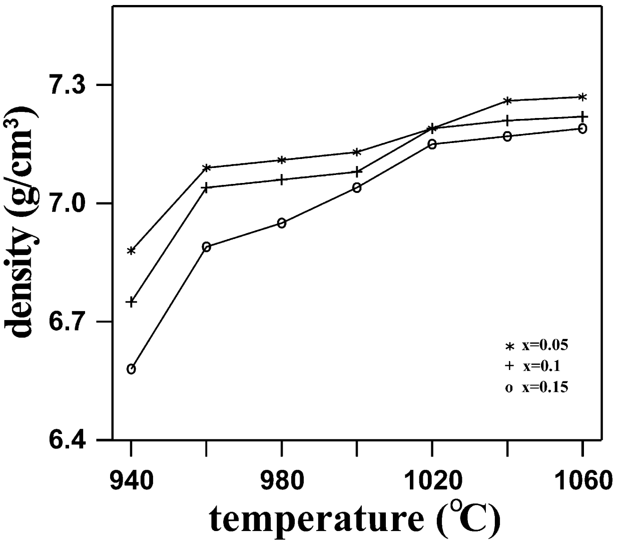

Fig. 3. Densities of $(Bi_{1-x}Sm_x)NbO_4$ ceramics as a function of sintering temperature and Sm_2O_3 content.

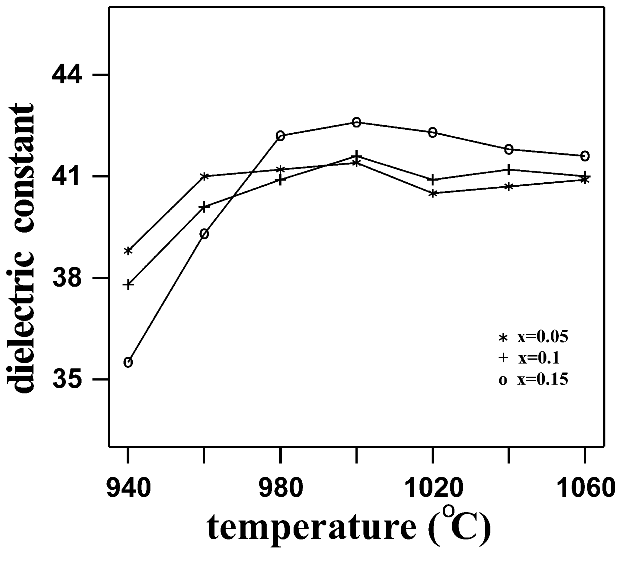

Fig. 4. Dielectric constants of $(Bi_{1-x}Sm_x)NbO_4$ ceramics as a function of sintering temperature and Sm_2O_3 content.

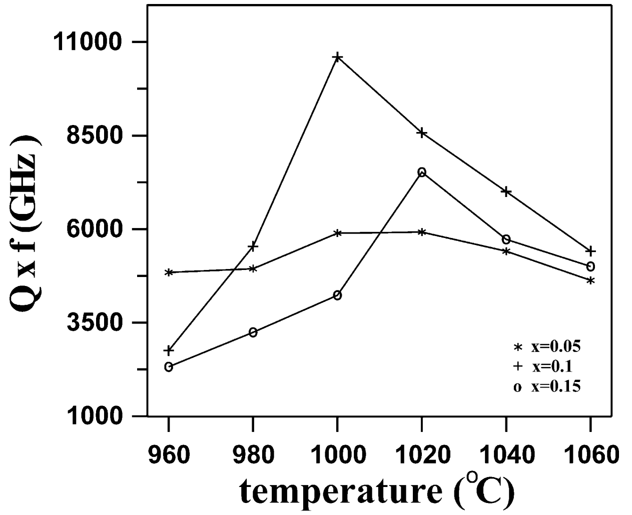

Fig. 5. Quality value of $(Bi_{1-x}Sm_x)NbO_4$ ceramics as a function of sintering temperature.

the $(Bi_{1-x}Sm_x)NbO_4$ ceramics were strongly dependent on the amount of Sm_2O_3. For $x \geqslant 0.1$, the $Q \times f$ values increased with the increase of sintering temperature. After reaching a maximum value, the $Q \times f$ values decreased rapidly, which might be related with the intensity increase of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ ceramics. A maximum $Q \times f$ value of 10656 GHz appeared for the $(Bi_{0.9}Sm_{0.1})NbO_4$ composition sintered at 1000 °C.

The τ_f values of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics with various x values at different sintering temperatures are shown in Fig. 6. The Sm_2O_3 content had no apparent effect but the sintering temperature had large effect on the τ_f values. As the sintering temperature increased, the τ_f values changed steadily to the larger negative values. The τ_f values of $(Bi_{0.9}Sm_{0.1})NbO_4$ shifted from positive to negative between 1000 and 1020 °C. According to the X-ray patterns, as shown in Fig. 1, the α-form of $(Bi_{1-x}Sm_x)NbO_4$ and the β-form of $(Bi_{1-x}Sm_x)NbO_4$ co-existed within the sintering temperature range of 1000–1020 °C. If the $(Bi_{1-x}Sm_x)NbO_4$ ceramics were thought as heterogeneous phases, the apparent change of τ_f values of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics could be thought as the influence of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ ceramics.

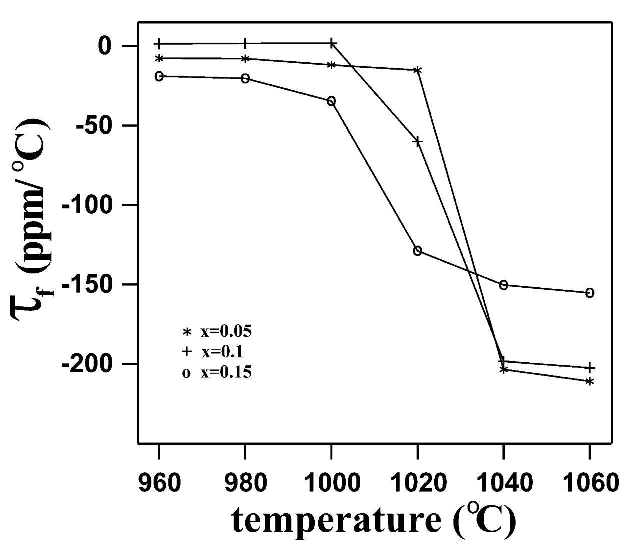

Fig. 6. Temperature coefficient of resonant frequency of $(Bi_{1-x}Sm_x)NbO_4$ ceramics as a function of sintering temperature.

4. Conclusions

The microwave dielectric properties and the microstructure of $(Bi_{1-x}Sm_x)NbO_4$ ceramics have been found to be affected by the substitution of Sm for Bi and by the sintering temperature. The phase transition temperature of $(Bi_{1-x}Sm_x)NbO_4$ ceramics can be lowered below 1000 °C with the increase of Sm_2O_3 content. For sintering temperatures higher than 960 °C, the α-form and the β-form of $(Bi_{1-x}Sm_x)NbO_4$ coexist or only the β-form $(Bi_{1-x}Sm_x)NbO_4$ exists. The presence of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ has large effect on the sintering and microwave dielectric characteristics of the $(Bi_{1-x}Sm_x)NbO_4$ ceramics, including grain growth, density, $Q \times f$ values and τ_f values. Furthermore, the density decreases with increasing Sm content, and the $Q \times f$ values are also influenced by the Sm content. Nevertheless the ε_r values are not affected by the existence of the β-form of $(Bi_{1-x}Sm_x)NbO_4$ and the Sm content. In this study, the best microwave dielectric properties of $(Bi_{1-x}Sm_x)NbO_4$ ceramics appear at 1000 °C and $x = 0.1$, where the $(Bi_{0.9}Sm_{0.1})NbO_4$ ceramic has the higher $Q \times f$ value of 10656 GHz and the lower τ_f value of 1.9 ppm/°C.

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