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Improvements in the sintering and microwave properties of $BiNbO_4$ microwave ceramics by V_2O_5 addition

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

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

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Abstract

The effects of V_2O_5 on the phase formation and the microwave dielectric properties of $BiNbO_4$ ceramics were investigated as a function of the amount of V_2O_5. As the amount of V_2O_5 addition increased from 0.125 to 1 wt%, the densification temperatures of $BiNbO_4$ ceramics decreased from 960 to 900°C. For densified $BiNbO_4$ ceramics, as the amount of V_2O_5 increased from 0.125 to 1 wt% V_2O_5 added, the dielectric constants decreased from 43.7 to 43.4 and the temperature coefficients (τ_f) increased from +2.8 to +19.5 ppm/°C. The quality values (Q) of V_2O_5-doped $BiNbO_4$ ceramics first increased, reached a maximum at 0.5 wt% V_2O_5, and then decreased with the further increase amount of V_2O_5 addition. The 0.5 wt%-V_2O_5-doped $BiNbO_4$ ceramics sintered at 960°C had the optimum microwave dielectric properties: $\varepsilon_r = 43.6$, $\tau_f = +13.8$ ppm/°C, and $Q = 3410$.

Keywords: $BiNbO_4$; Dielectric properties; Microstructure-final; Sintering; V_2O_5

1. Introduction

Multilayer microwave devices had been investigated to miniaturize devices of band-pass filters and antenna duplexers for portable phone.[1] These microwave dielectrics with low sintering temperatures were needed to cofire with low loss conductors and melting-point electrode such as silver and gold. Furthermore, these ceramics were desirable to have a high dielectric constant (ε_r), a high quality value (Q value), and a small temperature coefficient of resonant frequency (τ_f). $Ba_2Ti_9O_{20}$,[2] $BaMg_{1/3}(Ta,Nb)_{2/3}O_3$,[3,4] $(Zr,Sn)TiO_4$,[5] BaO–$(Nd,Sm)_2O_3$–TiO_2[6,7] systems were the most common materials suitable for use in dielectric resonators at microwave frequency. These ceramics had a high dielectric constant with a low dielectric loss (or high quality value) and a low temperature coefficient. $Ba_2Ti_9O_{20}$ required a sintering temperature of ≈1400°C to achieve densification of the ceramics. Alkoxide hydrolysis has been used to produce $(Zr,Sn)TiO_4$ and $BaMg_{1/3}(Ta,Nb)_{2/3}O_3$, but their sintering temperature were about 1500 and 1550°C. The BaO–$(Nd,Sm)_2O_3$–TiO_2 system could be densified at about 1350°C. The sintering temperatures for those microwave dielectrics were too high to use the low melting point electrode. It was imperative to lower the sintering temperature of those microwave ceramics in order to use silver and gold electrode.

In the past, low-melting-point glass additions, chemical processing, and smaller particle sizes of starting materials were three of the methods used to reduce the sintering temperature of a dielectric. Bismuth-based dielectric ceramics were known as low-fire materials and had been studied for multilayer ceramic capacitors.[8] However, $BiNbO_4$ ceramic with practical dielectric properties at microwave frequency was only developed by Kagata et al.[9] They used V_2O_5 and CuO to densify the $BiNbO_4$ ceramics, but the influences of V_2O_5 amount on the sintering and dielectric properties were not presented. In this study, the microwave dielectric based on the $BiNbO_4$ was chosen as the host material. We used V_2O_5 as the sintering aid to lower the sintering temperature of $BiNbO_4$ ceramics and to discuss the sintering and microwave dielectric properties of $BiNbO_4$ ceramics with different amount of V_2O_5 addition. Relationships among crystalline phase and both of the sintering temperature and amount of V_2O_5 addition were also developed.

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[*] Corresponding author.

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2. Experimental procedures

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 and Nb_2O_5 were mixed, according to the composition $BiNbO_4$, and ball-milled for 5 h with deionized water using an agate ball mill in an Al_2O_3 bottle. After drying, the reagent was ground with an agate mortar for 1 h and filtered through a 100-mesh screen. Then the powder was calcined at 800°C for 2 h. The crystal structure of calcined powder was examined using an X-ray powder diffractometer. After calcining, the $BiNbO_4$ ceramic powder was mixed with 0.125~1.5 wt% V_2O_5 (−200 mesh, purity high than 99.9%) by ball milling with deionized water for ≈1 h. After drying, the powder was uniaxially pressed into pellets in a steel die. Typical dimensions of the pellets were 15 mm in diameter and 1.5 mm in thickness. Sintering of these pellets was carried out at temperatures between 880 and 960°C under ambient conditions for duration of 4 h. After surface published, the crystalline structures of the V_2O_5-doped $BiNbO_4$ ceramics were investigated using X-ray diffraction patterns. X-ray diffraction patterns were taken at $2\theta = 4°$ per min using CuK_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, using SEM. Dielectric characteristics at microwave frequency were measured by Hakki–Coleman's dielectric resonator method, as modified and improved by Courtney and Kobayashi et al.[10] A cylindrically shaped resonator was positioned between two brass plates. An HP8510B network analyzer and an HP8340A sweeper were used for the microwave measurement system. The dielectric constant of a cylindrical dielectric resonator could be accurately determined by measuring the resonant frequency (5.7~6.2 GHz) of the TE_{011} mode and verified by $TE_{01\delta}$ resonant modes. The temperature change of the resonant frequency $\Delta f_0/f_0$ and temperature coefficient of resonant frequency τ_f were defined as follows.

$$\frac{\Delta f_0}{f_0} = \frac{f_T - f_0}{f_0} \tag{1}$$

where f_T and f_0 were the resonant frequency at 85 and 0°C (ΔT), respectively.

$$\tau_f = \frac{\Delta f_0}{f_0 {*} \Delta T} = . \tag{2}$$

3. Results and discussion

It was well known that in the Bi_2O_3–Nb_2O_5 system numerous phases, e.g. $Bi_8Nb_{18}O_{57}$, $BiNbO_4$, and $Bi_5Nb_3O_{15}$ coexisted. It was also reported that pure $BiNbO_4$ had a crystal structure similar to $SbTaO_4$ type below 1020°C. According to the XRD results, the Bi_2O_3–Nb_2O_5 powder after calcination leaded to the formation of the $Bi_8Nb_{18}O_{57}$ as major crystalline phase and consisted of α-$BiNbO_4$ and $Bi_5Nb_3O_{15}$ as minor phases [Fig. 1(a)]. When V_2O_5 was used as sintering aid, phase control was expected to be extremely important in such a system. For undoped $BiNbO_4$ ceramics sintered at 900°C [Fig. 1(b)], the main crystalline phase was α-$BiNbO_4$, the $Bi_8Nb_{18}O_{57}$ and $Bi_5Nb_3O_{15}$ phases were also residual. When 960°C was used as sintering temperature the only crystalline phase was α-$BiNbO_4$ [Fig. 1(c)]. For $BiNbO_4$ ceramics added with 0.25 wt% [Fig. 1(d)], 1 wt% [Fig. 1(e)] V_2O_5 and sintered at 900°C, the only crystalline phase was α-$BiNbO_4$. The $Bi_8Nb_{18}O_{57}$ and $Bi_5Nb_3O_{15}$ phases did not appear in the V_2O_5-doped $BiNbO_4$ ceramics. These results suggest that V_2O_5 does improve the satellite phases of $Bi_8Nb_{18}O_{57}$ and $Bi_5Nb_3O_{15}$ to form $BiNbO_4$ phase, and thus V_2O_5 can be used as a sintering aid of $BiNbO_4$ ceramics.

The density curves of the V_2O_5-doped $BiNbO_4$ ceramics are shown in Fig. 2. The density of undoped $BiNbO_4$ ceramics steadily increased from 54 to 83.6% of theoretical density (TD, TD = 7.28 ± 0.08 g/cm^3, estimated from the XRD pattern of 960°C-sintered ceramics) with

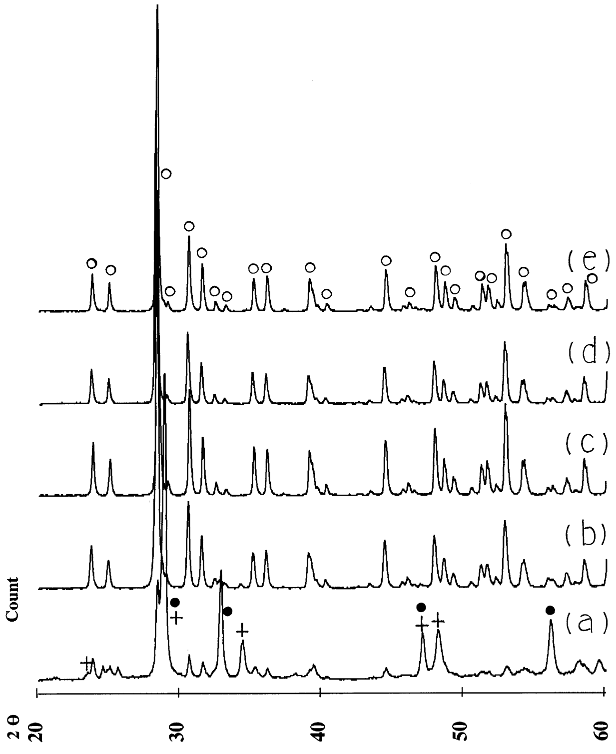

Fig. 1. The X-ray patterns for (a) $BiNbO_4$ powder calcined at 800°C for 2 h; (b) and (c) undoped-$BiNbO_4$ sintered at 900 and 960°C; (d) and (e) $BiNbO_4$ sintered at 900°C with 0.25 and 1 wt% V_2O_5 addition (○, $BiNbO_4$; ●, $Bi_8Nb_{18}O_{57}$; +, $Bi_5Nb_3O_{15}$).

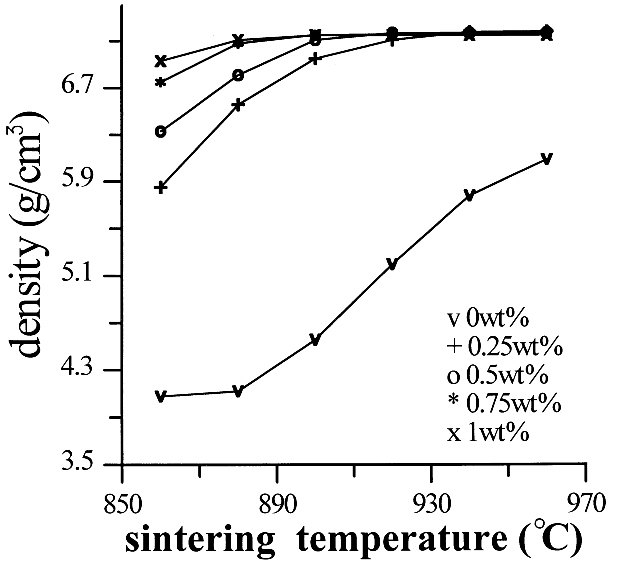

Fig. 2. The densities of $BiNbO_4$ ceramics as a function of sintering temperature and amount of V_2O_5 addition.

increasing temperature from 860 to 960°C. Even only the $BiNbO_4$ phase was revealed in the sintered ceramics, the $BiNbO_4$ ceramics were difficult to be densified without sintering aids. As V_2O_5 was added as sintering aid, the saturation densities of $BiNbO_4$ ceramics were obtained at a temperature decreased with the increase amount of V_2O_5 addition. For $BiNbO_4$ with 0.125, 0.25, and 0.5 wt% V_2O_5 addition, a bulk density over 98% of the TD were obtained with ease at 960, 940 and 920°C, respectively. As the V_2O_5 addition was in the range of 0.75~1 wt%, the $BiNbO_4$ ceramics could be densified at about 900°C.

Observations with SEM revealed changes in the morphology of the $BiNbO_4$ ceramics in the samples with different amount of V_2O_5 addition as the sintering aid. The changes in the density and grain size can be seen in the SEM photographs of selected V_2O_5-added $BiNbO_4$ ceramics and the results are shown in Fig. 3. With no addition of V_2O_5, isolated $BiNbO_4$ particles and pores were easily observed, even after sintering at 960°C (not shown here). For 0.25 wt%–V_2O_5-doped $BiNbO_4$ ceramics, the size of pores decreased and became less numerous than that of undoped $BiNbO_4$ ceramics after sintering at 920°C [Fig. 3(a)], but the pores were still residual. Further increasing the amount of V_2O_5 addition, 0.5- and 1 wt%-V_2O_5-doped $BiNbO_4$ ceramics [Fig. 3(b) and (c)], the homogeneously fine microstructures with almost no pores were observed. Compared the sintered surfaces of 0.5- and 1 wt%-V_2O_5-doped $BiNbO_4$ ceramics, the grain size of $BiNbO_4$ ceramics did not increase with the amount of V_2O_5 addition. The pores of all samples decreased [compare Fig. 3(a) with (d)] and the grain size of all samples increased continuously [compare Fig. 3(b) with (e) or (c) with (f)] with sintering temperatures independent of V_2O_5 amount. Using 960°C as sintering temperature, the 0.5 wt%-V_2O_5-added $BiNbO_4$ ceramics revealed a larger grain size than 0.25- and 1 wt%-V_2O_5-added $BiNbO_4$ ceramics did.

Fig. 4 shows the average grain size (G_0) of $BiNbO_4$ ceramics as a function of sintering temperature and amount of V_2O_5 addition. The temperature to present normal grain growth decreased with the increase amount of V_2O_5 addition. The temperatures for 0.25-, 0.5-, 0.75- and 1 wt%-V_2O_5-added $BiNbO_4$ ceramics to reveal the normal grain growth were 940, 920, 900 and 900°C, respectively. Because the melting point of V_2O_5 is about 678°C,[11] more liquid phase engaged in grain growth may cause above results. At higher sintering temperature ($\geqslant$940°C) the G_0 first increased with the amount of V_2O_5, reached a maximum at 0.5 wt% V_2O_5 addition, then decreased with the amount of V_2O_5 addition. These results suggest that too much sintering aid is not necessary. Because as the amount of V_2O_5 increases, the grain boundary inclusions increase and the energy necessary for the movement of a grain boundary increases, and that will cause that the grain growth decreases.[12]

The effects of V_2O_5 content on the microwave dielectric properties of $BiNbO_4$ ceramics sintered at different temperatures are shown in Figs. 5–7. As Fig. 5 shows, the relationships between ε_r values and sintering temperatures are shown the same trend with those between densities and sintering temperatures. The ε_r values increased with the increase of sintering temperature and then reached a saturation value. Those results maybe caused by the increases of the sintered density with the sintering temperature. The saturation values were shifted to lower temperatures as the amount of V_2O_5 increased and they were decreased slightly with the increase of V_2O_5 amount. However, as V_2O_5 was used as a sintering agent, the sintering temperatures of $BiNbO_4$ ceramics could be reduced to 900~920°C without apparent degradation of ε_r.

The Q values of $BiNbO_4$ ceramics are strongly dependent on the sintering temperature and amount of V_2O_5 addition and the results are shown in Fig. 6. The Q values of $BiNbO_4+x$ wt% V_2O_5 ceramics firstly increased with increasing sintering temperatures for all x values, the increases in densities and grain growth were the reasons to cause this result. The Q values reached a saturation value at a certain temperature dependent on the amount of V_2O_5 addition. As the amount of V_2O_5 addition was less than 0.5 wt% for all sintering temperatures, the increase in Q values was also caused by the increase in densities and grain growth [compare Fig. 3(a) and (b) or (d) and (e)]. As the sintering temperature was $\geqslant$900°C, even the 0.5 wt%-V_2O_5-doped $BiNbO_4$ ceramics did not own the maximum grain size, but it revealed the maximum Q values. Kucheiko et al. reported that the Q values increased with the average grain size.[13] Because as the grain size increased, the

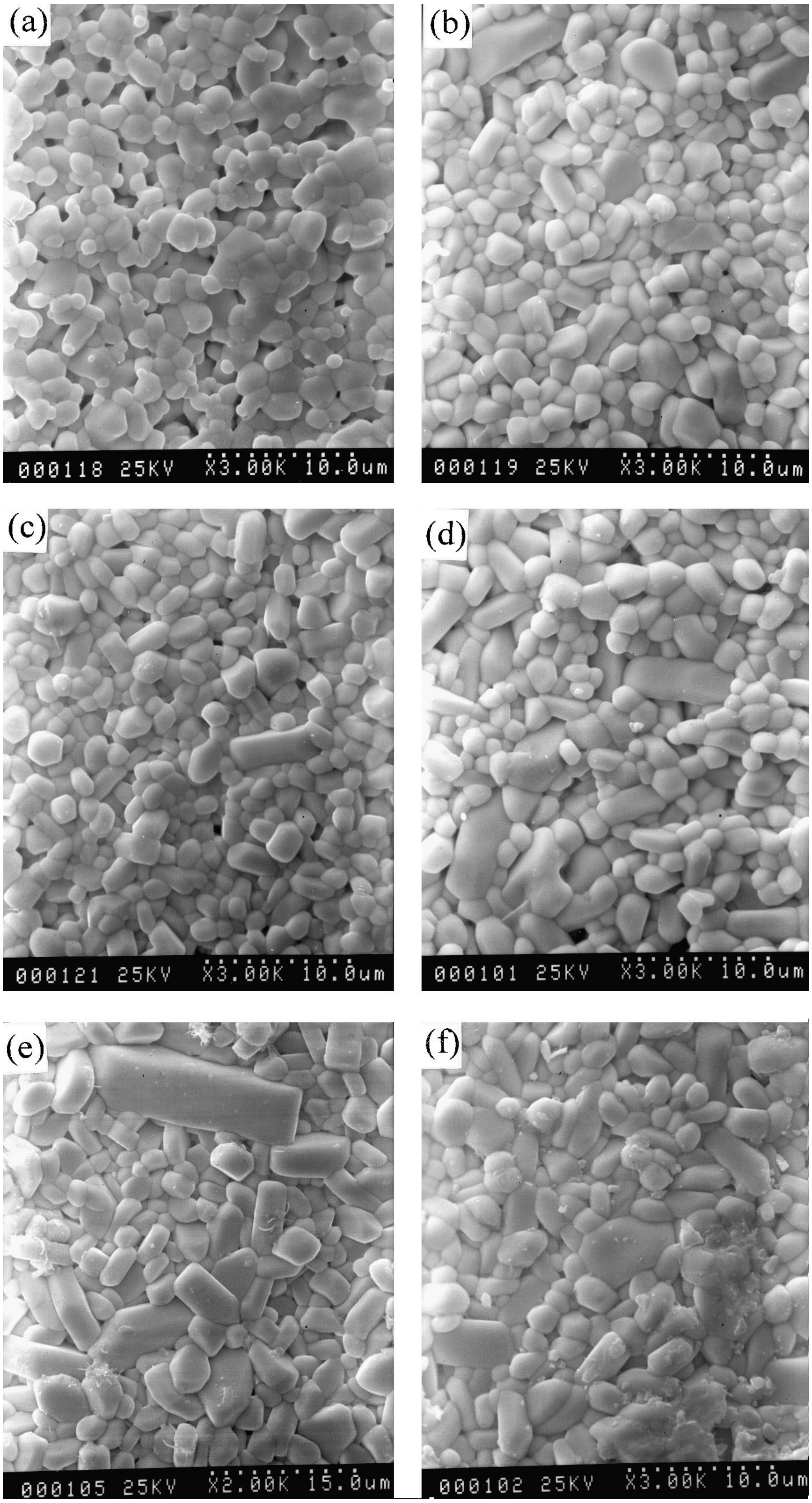

Fig. 3. The micrographs of $BiNbO_4$ ceramics sintered at 920°C with (a) 0.25 wt%, (b) 0.5 wt%, (c) 1 wt% V_2O_5 added and sintered at 960°C with (d) 0.25 wt%, (e) 0.5 wt%, (f) 1 wt% V_2O_5 added.

pores and grain boundary area decreased, thus reducing the lattice imperfections and increasing the *Q* value.[14] Yang et al. reported that the $\tan\delta$ ($Q = 1 \tan\delta$) increased with the increasing of sintering aid.[15] Because as the sintering aid increased, the pores and the boundary inclusions increased and caused that the $\tan\delta$ increased. The larger maximum *Q* values in 0.5 wt%-V_2O_5-doped $BiNbO_4$ ceramics maybe caused by the larger grain growth and the less boundary inclusions. However, such significant changes in dielectric losses were hardly explained only by the lattice imperfection or boundary defects.

The V_2O_5 amounts of dependence of temperature coefficient τ_f are shown in Fig. 7. For $BiNbO_4 + x$ wt% V_2O_5 composition and sintered at 960°C, the τ_f values changed from +2.9 ppm/°C for 0.125 wt%-doped $BiNbO_4$ dielectric to larger positive values with increasing *x* values. The τ_f values for $BiNbO_4$ ceramics with 0.5, 0.75 and 1 wt%-V_2O_5-added were +13.8, +16 and +19.5 ppm/°C, respectively. According to the X-ray patterns, the crystalline phase of V_2O_5-doped $BiNbO_4$ ceramics was the low temperature phase of α-$BiNbO_4$. Therefore, the changes of the τ_f values were considered to be due to the effects of V_2O_5.

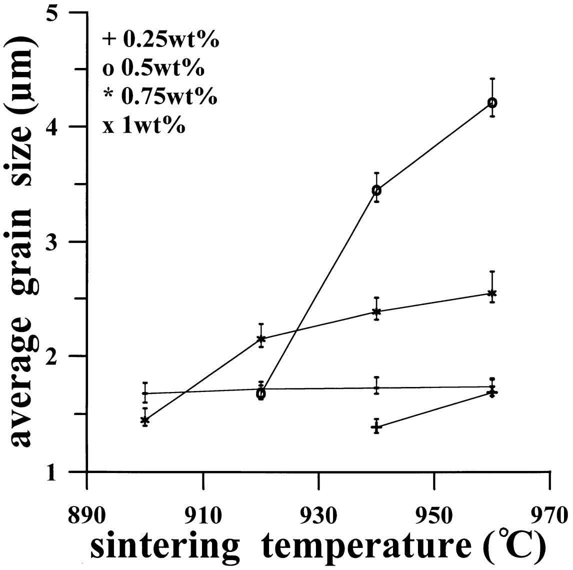

Fig. 4. The average grain size of $BiNbO_4$ ceramics as a function of sintering temperature and amount of V_2O_5 addition.

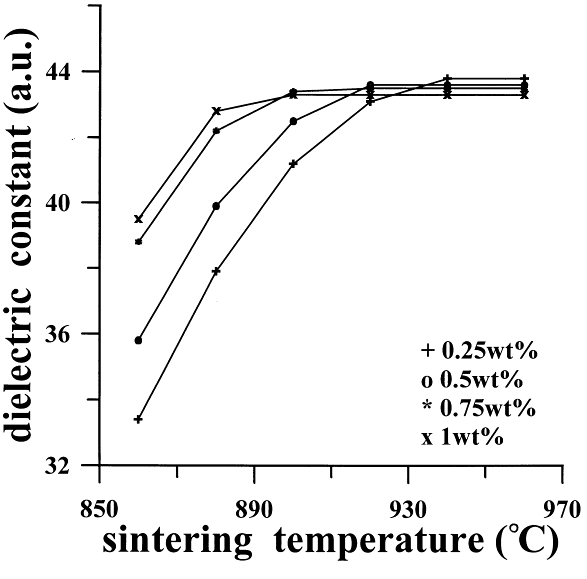

Fig. 5. The dielectric constants of $BiNbO_4$ ceramics as a function of sintering temperature and amount of V_2O_5 addition.

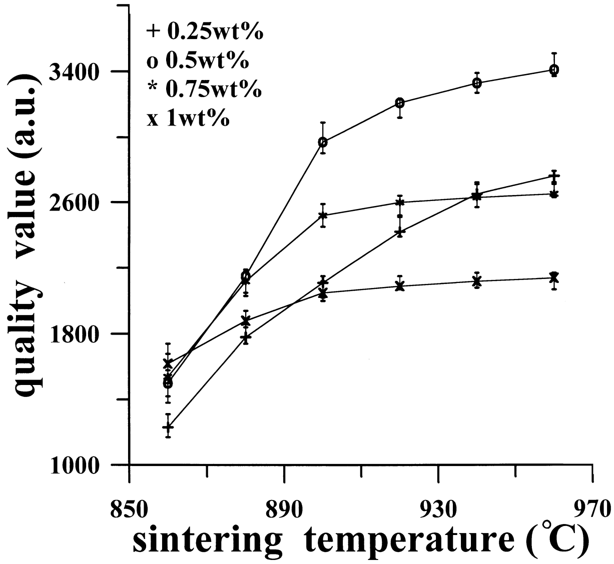

Fig. 6. The quality values (*Q*) of $BiNbO_4$ ceramics as a function of sintering temperature and amount of V_2O_5 addition.

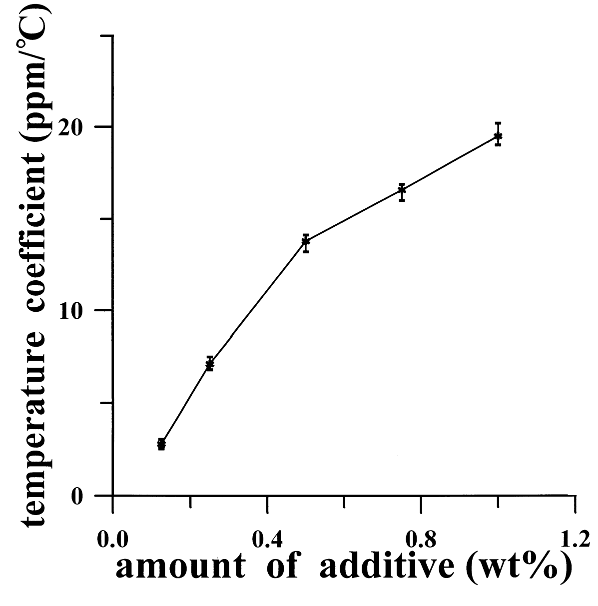

Fig. 7. The temperature coefficients of $BiNbO_4$ ceramics as a function of amount of V_2O_5 addition.

4. Conclusions

The sintering characteristics of $BiNbO_4$ ceramics with different amounts of V_2O_5 addition have been investigated in this study. The sintering temperatures of $BiNbO_4$ ceramics decrease with the increase amount of V_2O_5 addition. The temperatures revealed the saturation dielectric constants decrease with the increase amount of V_2O_5 addition. The dielectric constants of $BiNbO_4$ ceramics decrease slightly and the temperature coefficients of $BiNbO_4$ ceramics increase with the increase amount of V_2O_5 addition, but the quality values reveal a maximum at 0.5 wt%-V_2O_5-added $BiNbO_4$ ceramics. However, these results suggest that a large amount of V_2O_5 is unnecessary, because as the amount of V_2O_5 addition is more than 0.5 wt%, the Q values decrease critically and the τ_f values reveal a larger positive value.

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