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Low temperature sintering and microwave dielectric properties of $7NiNb_2O_6$–$9TiO_2$ ceramics with CuO addition

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Abstract The effects of CuO additive on sintering temperature and microwave dielectric properties of $7NiNb_2O_6$–$9TiO_2$ ceramics prepared by solid-state reaction method have been investigated. The phases and microstructure have also been evaluated using X-ray diffraction and scanning electron microscopy. The pure $7NiNb_2O_6$–$9TiO_2$ ceramics show a high sintering temperature of about 1,200 °C. However, the addition of CuO lowered the sintering temperature of $7NiNb_2O_6$–$9TiO_2$ ceramics from 1,200 to 935 °C due to the CuO liquid-phase. The results showed that the microwave dielectric properties were strongly dependent on densification, crystalline phases and grain size. The $7NiNb_2O_6$–$9TiO_2$ ceramics with the addition of 3.2 wt% CuO sintered at 935 °C afforded excellent dielectric properties of $\varepsilon_r = 60.5$, $Q \times f = 10{,}039$ GHz (at 3.8 GHz) and $\tau_f = 62$ ppm/°C, which represented very promising candidates for LTCC dielectric materials.

1 Introduction

Low-temperature Co-fired Ceramic (LTCC) technology has received increasing attention by component manufacturers [1, 2]. A great advantage of LTCC technology is allowing integration of passive components such as resistors, capacitors, inductors, and other functional parts into the co-fired substrates, which leads to highly integrated and multi-functional LTCC modules [3]. In order to increase the density of integration and obtain higher processing accuracy, much more efforts should be put into the research in the field of component miniaturization. Since the size of the dielectric component is inversely related to the $\varepsilon_r^{1/2}$, higher dielectric permittivity ($\varepsilon_r > 20$) of microwave dielectric materials is required to meet the requirement of reducing the size of the device [4, 5]. In order to minimize dielectric losses, high quality factor ($Q \times f > 10{,}000$) is needed. Meanwhile, low temperature coefficient of resonant frequency (τ_f) and low sintering temperature are required. In the case of Ag (Cu) electrodes, the processing temperature of the microwave dielectric ceramics must be below 950 °C (≤950 °C) [1, 4]. However, the sintering temperature of conventional dielectric ceramics used for wireless communication systems usually ranges from 1,200 to 1,500 °C [1]. For instance, the sintering temperature of microwave dielectric ceramics $7NiNb_2O_6$–$9TiO_2$ is about 1,200 °C [6], which is too high to be applicable to LTCC. Nevertheless, $7NiNb_2O_6$–$9TiO_2$ ceramics exhibit high dielectric permittivity of 68.7, a $Q \times f$ of 19,300, and acceptable τ_f of 56.6 ppm/°C, which are deemed to be suitable for the application of component miniaturization [6]. So it is of great significance for LTCC if we can decrease the sintering temperature of $7NiNb_2O_6$–$9TiO_2$ dielectric ceramics to 950 °C. Many researchers have adopted several approaches to lower the sintering temperature of the ceramics: (1) the usage of smaller particle size of starting materials synthesized by chemical processes and (2) the addition of low-melting glasses, oxides or mixed-oxides. Chemical synthesis is often time consuming and expensive. In contrast, the most popular and cheapest method for achieving densified ceramics is the addition of low-melting glasses, oxide or mixed-oxide additives such as B_2O_3, V_2O_5, CuO [7]. CuO is one of the most popular sintering fluxes. Kim et al. have observed that the addition of CuO reduced the

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sintering temperature of $ZnNb_2O_6$ ceramics from 1,150 to 900 °C, and good microwave dielectric characteristics ($Q \times f = 59{,}500$, $\varepsilon_r = 22.1$, $\tau_f = -66$ ppm/°C) were obtained from the low-fired $ZnNb_2O_6$ with 5 wt% CuO addition [8]. Besides, Chien-Min Cheng et al. reported that the $BiNbO_4$ ceramics, which could not be densified without additives, was dense at 900–920 °C by using the CuO addition [9].

In this work, CuO was chosen as a sintering aid to lower the firing temperature of $7NiNb_2O_6$–$9TiO_2$ ceramics. The influence of CuO addition on the densification, microstructure and microwave dielectric properties of $7NiNb_2O_6$–$9TiO_2$ ceramics was investigated. We have found that the addition of CuO significantly lowers the sintering temperature from 1,200 to 935 °C. Moreover, stable microwave dielectric properties were obtained in $7NiNb_2O_6$–$9TiO_2$ ceramics doped with 3.2 wt% CuO sintered at the temperature from 935 to 1,005 °C.

2 Experimental procedure

The general formula of the materials studied was $7NiNb_2O_6$–$9TiO_2$ + y wt% CuO, where y = 2.8, 3.2, 3.6, 4.0, respectively. The samples were synthesized by conventional solid-state reaction method from high-purity oxide powders of NiO (99.9%), Nb_2O_5 (99.5%), TiO_2 (99.6%) and CuO (97.5%). The powders were weighed according to the compositions of $NiNb_2O_6$ and milled with ZrO_2 balls in distilled water for 3.5 h by Planet-Ball-Grinding machine. After drying and sieving, the milled powders were calcined at 900 °C for 3 h to obtain the single phase of $NiNb_2O_6$ powder. Next, these calcined powders were mixed according to the formula of $7NiNb_2O_6$–$9TiO_2$ and the mixtures were re-calcined at 1,100 °C for 3 h. Then, different weight percentages (2.8–4.0 wt%) of CuO additive were added to $7NiNb_2O_6$–$9TiO_2$ compounds. After ball-milling for 3.5 h, the powders were dried, granulated and then pellets of 15 mm diameter were formed by double-action pressing. These pellets were sintered at 900 °C to 1,050 °C for 3.5 h in air with the heating rate of 5 °C/min, then furnace cooled to room temperature.

The sintered pellets were analyzed by X-ray diffraction (XRD: PANalytical B.V., X'Pert PRO) to identify the flections of various phases. Microstructures were characterized by scanning electron microscopy (SEM: Philip, XL30TM) and energy-dispersive X-ray spectrometer (EDS: EDAX, PHOENIX). The apparent densities of the sintered specimens were measured by the liquid Archimedes method using distilled water as the liquid. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method by Advantest network analyzer (E5071C) [10].

The temperature coefficient of resonant frequency (τ_f) was also measured by the method associated with Eq. (1):

$$\tau_f(ppm/^\circ C) = \frac{(f_{80} - f_{25}) \times 10^6}{55 f_{25}} \qquad (1)$$

where f_{80} and f_{25} represent the resonant frequencies at 80 and 25 °C, respectively.

3 Result and discussion

3.1 Microstructure evolution of compounds

Figure 1 illustrates the XRD patterns of 3.2 wt% CuO-doped $7NiNb_2O_6$–$9TiO_2$ ceramics sintered at 900–1,025 °C for 3.5 h. Figure 2 illustrates the XRD patterns of the $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at 935 °C for 3.5 h. It is observed that all the samples exhibited tetragonal tri-rutile structure. A phase with the same structure as that of a $Ni_{0.5}Ti_{0.5}NbO_4$ (NTN) phase (ICDD #00-052-1875) was identified as the major phase. In addition, three other phases were also detected: $Ni_4Nb_2O_9$ phase (JCPDS file no. 46-0525), $NiNb_2O_6$ phase (JCPDS file no. 31-0906) and the fourth phase. Unfortunately, the fourth phase has not been identified. It was noted that the $NiNb_2O_6$ phase could be detected easily in the pellets doped with 3.2 wt% of CuO addition sintered at 900 °C shown in Fig. 1, as well as the pellets doped with 2.8 wt% of CuO additions sintered at 935 °C shown in Fig. 2. However, with the increase of the sintering temperature and CuO content, the residual $NiNb_2O_6$ phase decreased remarkably. Figure 1 shows that the $NiNb_2O_6$ phase could hardly be detected and solid

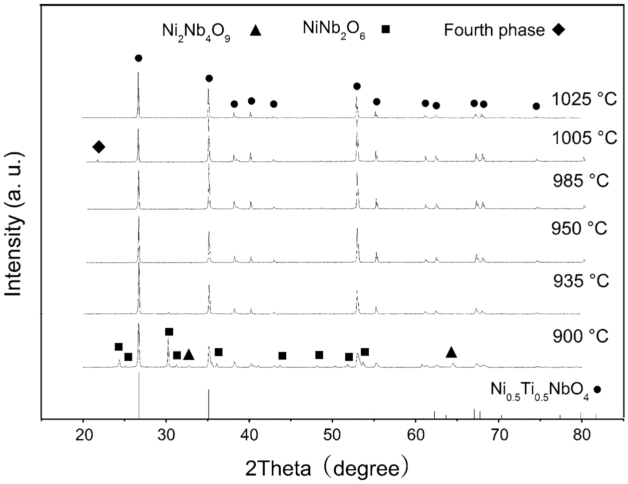


Fig. 1 XRD patterns of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with 3.2 wt% CuO addition sintered at 900–1,025 °C for 3.5 h

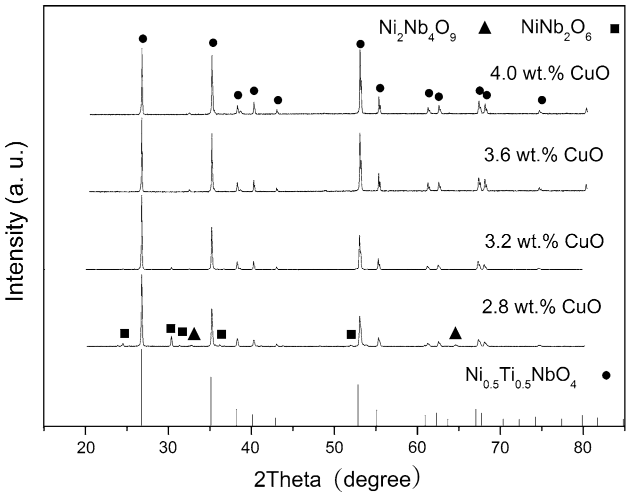


Fig. 2 XRD patterns of the $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at 935 °C for 3.5 h

solutions with almost entirely tetragonal rutile structure were confirmed through the $7NiNb_2O_6$–$9TiO_2$ ceramics sintering at 950 °C-1,025 °C. This could be also observed at the 3.6-4.0 wt% level of CuO addition shown in Fig. 2. That's one of the reasons why stable microwave dielectric properties were obtained in pellets sintered at a large range of temperature. The diminution of $NiNb_2O_6$ phase means the formation of $Ni_{0.5}Ti_{0.5}NbO_4$ (NTN) phase is easier than $NiNb_2O_6$ phase when the sintering temperature and/or CuO content increased. Yi-Cheng Liou and co-workers had also observed the morphotropic phase transition of columbite $NiNb_2O_6$ to $Ni_{0.5}Ti_{0.5}NbO_4$ (NTN) for $(1 - x)NiNb_2O_6$-$xTiO_2$ occurred at a lower TiO_2 content <30 mol% [11].

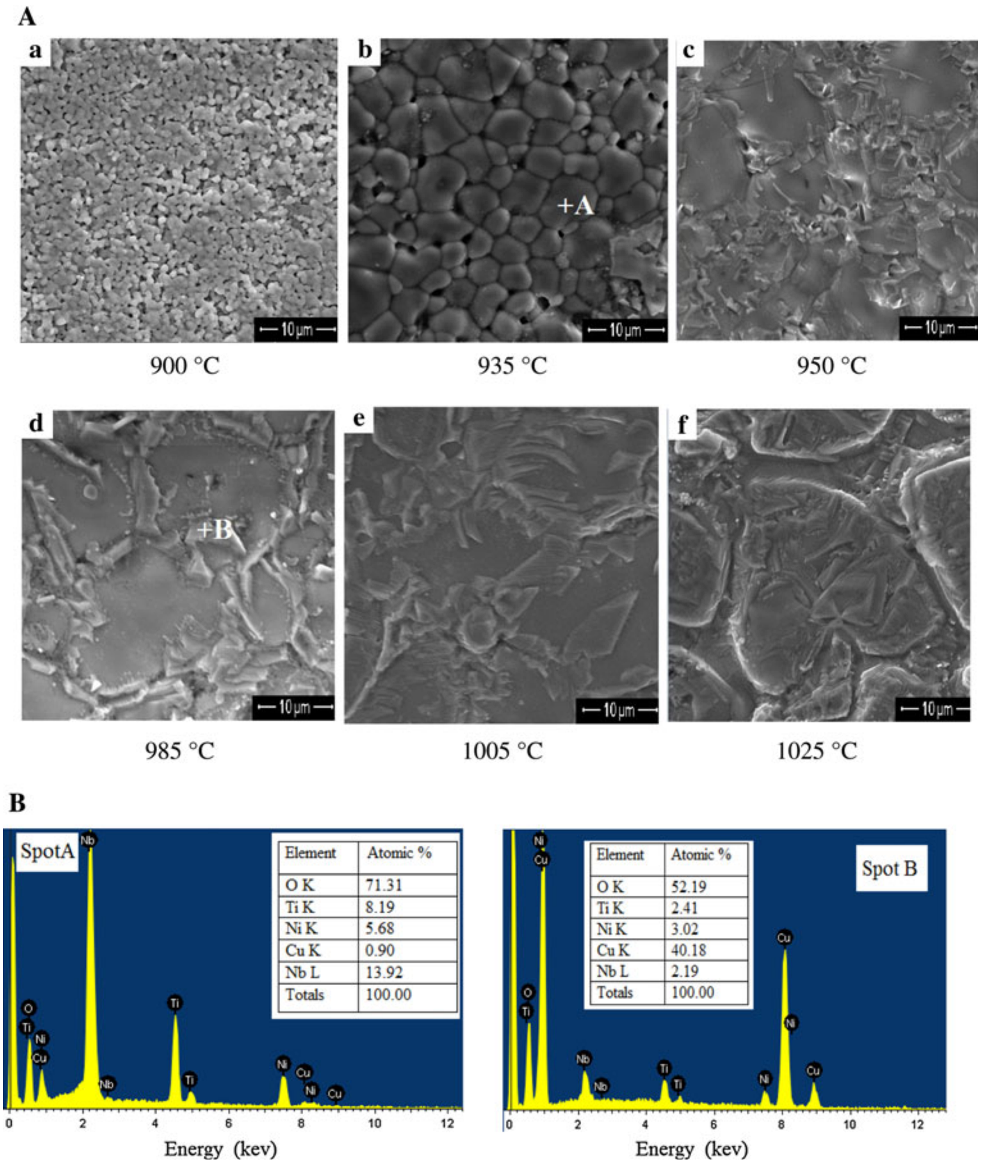
The SEM micrographs of 3.2 wt% CuO-doped $7NiNb_2O_6$–$9TiO_2$ ceramics sintered at different temperature are shown in Fig. 3A. For the $7NiNb_2O_6$–$9TiO_2$ ceramics sintered at 900 °C, many distinct pores were easily observed. However, pores decreased significantly and much larger grains were found in pellets sintered at 935 °C shown in Fig. 3Ab. The grain size increased rapidly with the increasing of sintering temperature, which can be attributed partly to the presence of liquid phase. Figure 3Af shows the liquid-phase of CuO was overproduced in the pellets sintered at 1,025 °C. Because of the excess liquid-phase, gases in the pellets couldn't be evacuated in time, so that the microwave dielectric properties became worse at 1,025 °C. Figure 4 shows the SEM micrographs of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at 935 °C. The size of grains of these ceramics increased significantly with the increasing of CuO from 2.8 to 4.0 wt%. Besides, more liquid-phase of CuO could be observed with the increase of CuO content. It can be concluded that the introduction of CuO additive into $7NiNb_2O_6$–$9TiO_2$ ceramics increased the size of grains and promoted the densification at a lower temperature. However, it should be noted that excess CuO-liquid phase might also lead to a degradation in the microwave dielectric properties of the ceramics.

To reveal the element distribution of grains and the location of CuO in sintered ceramics, the EDX datum of spots A and B measured by EDS equipped on SEM are shown in Fig. 3B. The grain morphology of $7NiNb_2O_6$–$9TiO_2$ ceramics exhibited only one type of grain, which is a synthesis of $Ni_{0.5}Ti_{0.5}NbO_4$ and $Cu_{0.5}Ti_{0.5}NbO_4$ shown in Fig. 3B (spot A). EDS analysis has confirmed that Cu and O ions were detected at a ratio of approximately 1:1 of spot B. This may suggest that the grain boundary is rich in a liquid-phase of CuO.

The bulk densities of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at different temperatures for 3.5 h are shown in Fig. 5. The density of the specimen sintered below 935 °C was low, but increased with increasing sintering temperature to a maximum and slightly declined thereafter. The increase in density is attributed to the reduction in porosity and uniform grain growth. The decrease in density can be attributed to the liquid-phase effect induced by the over-sintering, which is clearly observed from the microstructure of the sample shown above. Therefore, the addition of CuO improved the sinter ability of $7NiNb_2O_6$–$9TiO_2$ ceramics and reduced their sintering temperature by more than 250 °C. When the sintering temperature was above 935 °C ($T \geq 935$ °C), the density of the samples with the CuO content more than 3.2 wt% reached above 4.65 g/cm^3, indicating that the samples sintered above 935 °C ($T \geq 935$ °C) were very dense as shown in Fig. 3Ab–f).

3.2 Microwave dielectric property of compounds

Figure 6 shows the dielectric constant of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at different temperatures for 3.5 h. The variation of ε_r value was consistent with that of density. The dielectric constant of the pellets sintered below 935 °C was low. As the sintering temperature increased, the dielectric constant of all the samples increased, followed by a slight decrease. Moreover, it is observed that the dielectric constant of $7NiNb_2O_6$–$9TiO_2$ ceramics increased with the increase of CuO content. Two reasons are thought to cause the increase in dielectric constant: (1) larger grains, less porosity, and the more dense pellets were obtained as the sintering temperature and/or CuO content increased, (2) a structural change from columbite to rutile structure with the increasing of the sintering temperature and/or CuO content: the formation of the $Ni_{0.5}Ti_{0.5}NbO_4$ (NTN)-like phase in the $7NiNb_2O_6$–$9TiO_2$ ceramics was considered to increase the value of ε_r. Similar phenomenon was observed



Element	Atomic %
O K	71.31
Ti K	8.19
Ni K	5.68
Cu K	0.90
Nb L	13.92
Totals	100.00

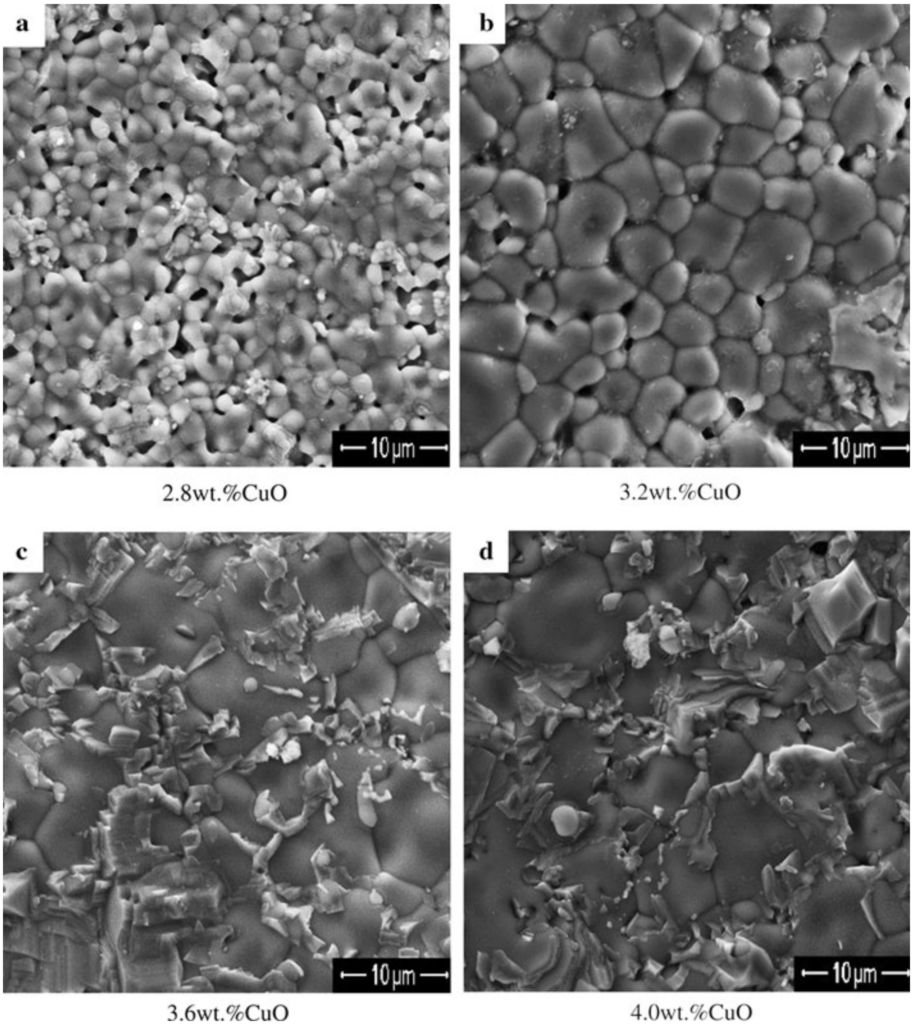
Element	Atomic %
O K	52.19
Ti K	2.41
Ni K	3.02
Cu K	40.18
Nb L	2.19
Totals	100.00

Fig. 3 **A** SEM micrographs of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with 3.2 wt% CuO addition sintered at different temperature: a 900 °C, b 935 °C, c 950 °C, d 985 °C, e 1,005 °C, f 1,025 °C; **B** EDX datum of $7NiNb_2O_6$–$9TiO_2$ ceramics for spots A and B

by Yi-Cheng Liou and his co-workers that ε_r value of $(1-x)$ $NiNb_2O_6$–$xTiO_2$ ceramics decreased as the NTN-like phase decreased [12]. The decrease in dielectric constant was caused by the decrease in density, which was closely linked to the overproduction of the CuO-liquid phase. The maximum ε_r value of 64.1 was obtained for the specimen doped with 4.0 wt% CuO sintered at 950 °C. Furthermore, stable ε_r values ranging from 60.5 to 63.5 were obtained in pellets doped with 3.2 wt% CuO sintered at the temperature from 935 to 1,005 °C.

The $Q \times f$ value of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at 900–1,050 °C for 3.5 h are demonstrated in Fig. 7. With the increasing sintering temperature, the $Q \times f$ value of pellets increased to a maximum value and decreased thereafter, which showed a similar trend with that of density. It is also observed that the $Q \times f$ value increased with the increase in concentration of CuO up to 3.2 wt%, and decreased when the CuO content more than 3.2 wt%. The dramatically increase of $Q \times f$ values can be attributed partly to a structural change from columbite to rutile structure with the increasing sintering temperature and/or CuO content. Moreover, $Q \times f$ values are known to be affected by the morphology of the samples, such as grain size, porosity, and density. A noteworthy fact is that the $Q \times f$ value of the sample may also decrease with an oversize grain, which can be related to the presence of liquid-phase of CuO in grain boundary [7, 13]. So the $Q \times f$ value increased with the increase of CuO addition first and then decreased when the CuO content more than 3.2 wt%. It is observed that stable $Q \times f$ values from 9,200 to 10,544 GHz can be obtained in the pellets doped with 3.2 wt% CuO sintered at the temperature from 935 to 1,005 °C.

Fig. 4 SEM micrographs of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at 935 °C: **a** 2.8 wt% CuO, **b** 3.2 wt% CuO, **c** 3.6 wt% CuO, and **d** 4.0 wt% CuO for 3.5 h



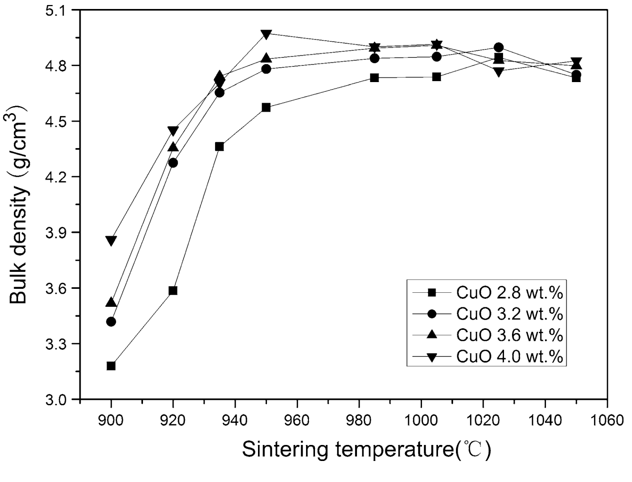


Fig. 5 The relative density of $7NiNb_2O_6$–$9TiO_2$ ceramics with (*y*) wt% CuO addition as a function of sintering temperature

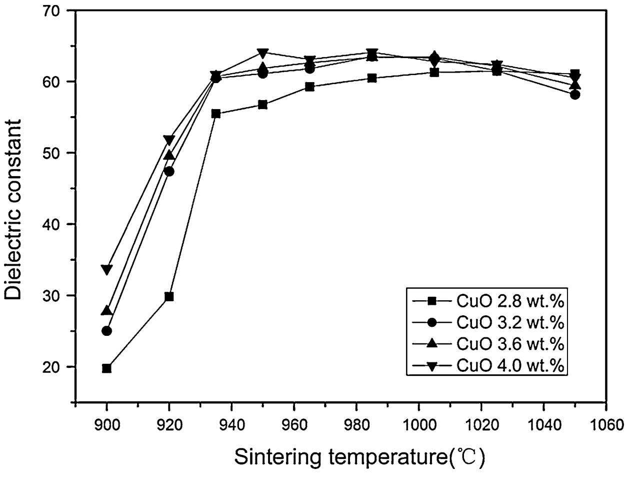


Fig. 6 The dielectric constant of $7NiNb_2O_6$–$9TiO_2$ ceramics with (*y*) wt% CuO addition as a function of sintering temperature

Figure 8 depicts the τ_f of $7NiNb_2O_6$–$9TiO_2$ ceramics doped with different amount of CuO addition sintered at different temperatures for 3.5 h. It was observed that the τ_f values did not show a significant change with the change of CuO content as well as the sintering temperature, because the addition of CuO did not cause a secondary phase.

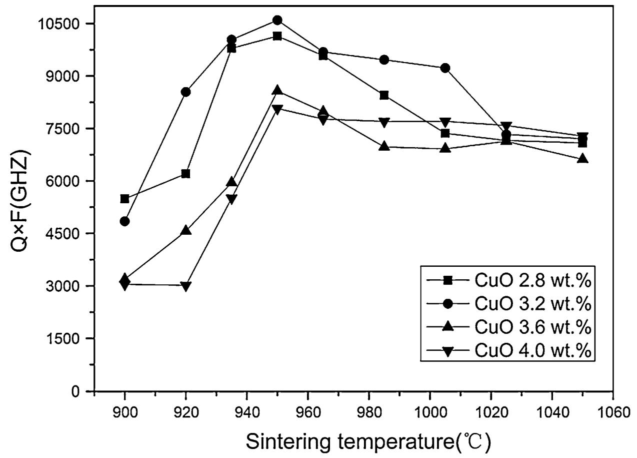


Fig. 7 $Q \times f$ values of $7NiNb_2O_6$–$9TiO_2$ ceramics with (y) wt% CuO addition sintered at 900–1,050 °C for 3.5 h

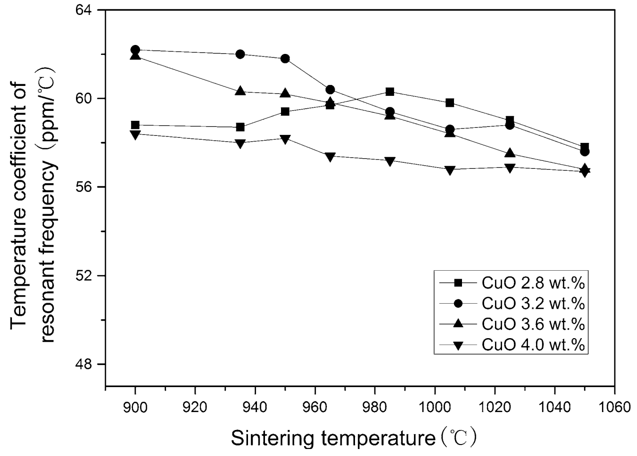


Fig. 8 The τ_f of $7NiNb_2O_6$–$9TiO_2$ ceramics with (y) wt% CuO addition sintered at 900–1,050 °C for 3.5 h

In conclusion, high dielectric constant and stable $Q \times f$ values were obtained for the sample doped with 3.2 wt% CuO sintered at the temperature from 935 to 1,005 °C. The temperature coefficient of resonant frequencies (τ_f) of the sample with 3.2 wt% CuO sintered at 935 °C was about 62 ppm/°C.

4 Conclusions

The effects of CuO additive on sintering temperature and microwave dielectric properties of $7NiNb_2O_6$–$9TiO_2$ ceramics have been investigated. The phases and microstructure have also been evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the microwave dielectric properties were strongly dependent on densification, crystalline phases and grain size, which were all influenced by the sintering temperature and the amount of CuO. The addition of CuO lowered the sintering temperature of $7NiNb_2O_6$–$9TiO_2$ ceramics from 1,200 to 935 °C due to the CuO liquid-phase. The $7NiNb_2O_6$–$9TiO_2$ ceramics with the addition of 3.2 wt% CuO sintered at 935 °C afforded excellent dielectric properties of $\varepsilon_r = 60.5$, $Q \times f =$ 10,039 GHz (at 3.8 GHz) and $\tau_f = 62$ ppm/°C, which represented very promising candidates for LTCC dielectric materials.

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