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The effect of CuO on the sintering and properties of $BiNbO_4$ microwave ceramics

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Abstract

Even if 960°C is used as sintering temperature, the undoped $BiNbO_4$ ceramics are difficult to be densified. The addition of CuO will improve the densification process of $BiNbO_4$ ceramics. As the amount of CuO addition increases from 0.125 to 1.5 wt%, the dielectric constants (ε_r) of densified $BiNbO_4$ ceramics decrease from 43.9 to 42.8 and the temperature coefficients (τ_f) change from −4.5 to −31.2 ppm/°C. The quality values (Q) first increase, reach a maximum at 0.5wt% CuO, and then decrease with the increase of CuO amount. In CuO-doped $BiNbO_4$ system, $BiNbO_4$ ceramics with 0.5wt% CuO added and sintered at 920°C have the optimum microwave dielectric properties: ($\varepsilon_r = 43.6$, $\tau_f = -20.8$ ppm/°C, and $Q = 1610$ ($Q \times f = 10\,070$)

Keywords: $BiNbO_4$; Microwave dielectric properties; Quality value

1. Intrduction

In producing miniaturized devices, multilayer structures with low sintering temperatures are needed to cofire with low melting-point electrode such as silver and gold. $Ba_2Ti_9O_{20}$ [1], $Ba(Zn,Mg)_{1/3}Ta_{2/3}O_3$ [2,3], $(Zr,Sn)TiO_4$ [4], BaO-$(Nd,Sm)_2O_3$-TiO_2 [5,6] system were the most common low loss (high Q, Q is given by $1/\tan\delta$) and low temperature coefficient of resonant frequency (τ_f) ceramic materials suitable for use in dielectric resonators at microwave frequency. The BaO-$(Nd,Sm)_2O_3$-TiO_2 system could be densified at about 1350°C. $Ba_2Ti_9O_{20}$ required a sintering temperature of (1380–1400°C to achieve densification of the ceramics. Alkoxide hydrolysis had been used to produce $(Zr,Sn)TiO_4$ and $BaMg_{1/3}(Ta,Nb)_{2/3}O_3$, but they required a very high sintering temperature of 1550–1600°C. The sintering temperatures for those microwave dielectrics were too high to use the low melting point silver and gold electrodes. It was imperative to lower the sintering temperature of those microwave ceramics in order to use low melting point electrodes.

Addition of low-melting-point glasses, chemical processing, and smaller particle size of starting materials were three of the methods used to reduce the sintering temperature of a dielectric. Bismuth-based dielectric ceramics are known as low-fire materials and had been studied for multilayer ceramic capacitors [7]. However, $BiNbO_4$ ceramic with practical dielectric properties at microwave frequency was only developed by Kagata et al. [8] They used CuO and V_2O_5 as sintering additives because the $BiNbO_4$ ceramics could not be densified without additives. In this study, we also used $BiNbO_4$ and CuO as the host materials and sintering aid. It is found that the amount of CuO addition needed to lower the sintering temperature of $BiNbO_4$ dielectric is more than that reported by Kagata et al. [8] The influence of CuO addition on the sintering temperature, crystalline phase evolution, and the dielectric properties of $BiNbO_4$ ceramics are presented.

2. Experimental procedure

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

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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, then the powder was calcined at 800°C for 3 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% CuO by ball milling with deionized water. After drying, the powder was uniaxially pressed into pellets in a steel die. Sintering of these pellets was carried out at temperatures between 880 and 960°C under ambient conditions during 4 h. Crystallization of the CuO-doped $BiNbO_4$ ceramics was also investigated using X-ray diffraction patterns. The densities of the sintered specimens, as a function of sintering temperature, was measured by the liquid Archimedes method using deionized water as the liquid. To investigate the internal morphology of the samples, the surfaces of the sintered specimens were observed, by using SEM. Dielectric characteristics at microwave frequency were measured by Hakki and Coleman's dielectric resonator method [9], as modified and improved by Courtney and Kobayashi et al. [10,11]. A cylindrical shaped dielectric resonators were positioned between two plates. An HP8510B network analyzer and an HP8340A sweeper were used for the microwave property measurements. The dielectric constant can be accurately determined by measuring the resonant frequency of the TE011 mode and verified by $TE_{01\sigma}$ resonant modes. The temperature change of the resonant frequency $\Delta f_o/f_o$ and temperature coefficient of resonant frequency τ_f are defined as follows.

$$\Delta f_o/f_o = (f_T - f_o)/f_o \quad (1)$$

where f_T and f_o are the resonant frequencies at 85 and 0°C, respectively.

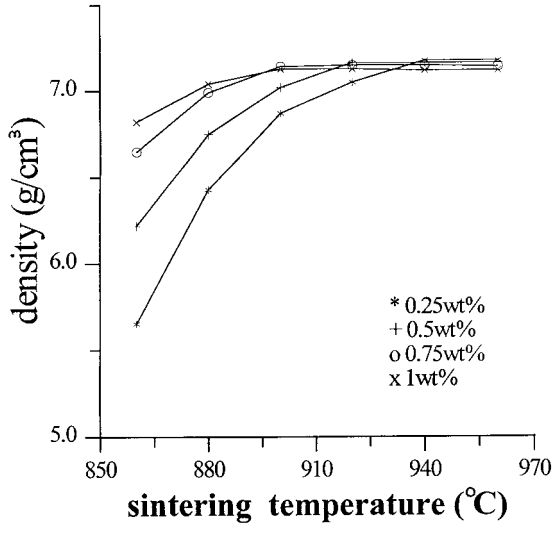

Fig. 1. Densities of CuO-doped $BiNbO_4$ dielectric as a function of sintering temperature.

$$\tau_f = \frac{\Delta f_o}{(f_o \times \Delta T)} \quad (2)$$

3. Results and discussion

Even if 960°C is used as the sintering temperature, the undoped $BiNbO_4$ ceramics are difficult to be densified. The bulk densities of around 83.5% of the theoretical density (TD, 7.28 g/cm^3) are obtained [12], and the microwave dielectric characteristics are poor. The effects of CuO on the densification of $BiNbO_4$ dielectrics sintered at different temperatures are shown in Fig. 1. Normally, CuO consisted in the densification of $BiNbO_4$ dielectrics by liquid-phase sintering. The densities of $BiNbO_4$ ceramics, with addition of CuO, increase steadily with firing temperatures, as shown in Fig. 1. The densities reach a maximum at a certain temperature and then start to fall slightly. The temperatures at which the maximum densities were achieved depend on the CuO content. The larger amount of CuO addition is used, the lower the temperatures are. For $BiNbO_4$ ceramics with 0.125 and 0.25 wt% CuO addition, a bulk density of around 96.6 and 98.6% of the theoretical density can be obtained at 960 and 940°C, respectively. As the CuO amount is in the range of 0.5–1.0 wt%, the $BiNbO_4$ ceramics could be densified at 900–920°C. Therefore, added CuO is thought to act as a sintering aid for the $BiNbO_4$ ceramics.

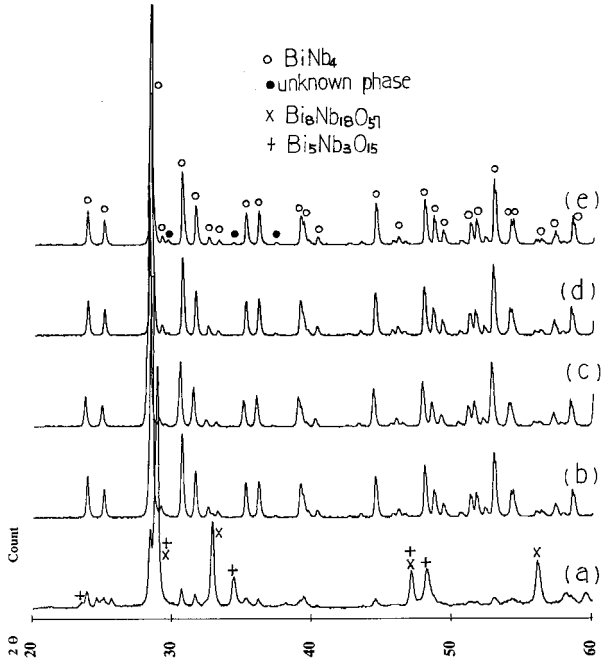

Fig. 2. X-ray patterns for (a) $BiNbO_4$ powder calcined at 800°C for 2h, (b), (c), (d), and (e) $BiNbO_4$ sintered at 920°C, $BiNbO_4$ with 0, 0.25, 0.5, and 1wt% CuO addition. (o:$BiNbO_4$, x:$Bi_8Nb_{18}O_{57}$, +:$Bi_5Nb_3O_{15}$, (•:unknown phase).

According to the XRD results, the $BiNbO_4$ powder after calcining leads to the formation of the $Bi_8Nb_{18}O_{57}$ as major crystalline phase and consists of $BiNbO_4$ and $Bi_5Nb_3O_{15}$ as minor phases, as shown in Fig. 2(a). For the $BiNbO_4$ ceramics sintered at 920°C and with different amount of CuO addition, the X-ray diffraction patterns from the as-sintered surfaces are also shown in Fig. 2. The $Bi_8Nb_{18}O_{57}$ and $Bi_5Nb_3O_{15}$ phases are eliminated, and only the low temperature phase $BiNbO_4$ stable below 1020°C is revealed in the doped and undoped $BiNbO_4$ ceramics, as shown in Fig. 2(b)–(e). As the amount of CuO addition is less or equal than 0.5 wt%, the XRD diffraction patterns indicate no crystalline phase difference between the ceramics undoped and doped with CuO. As the amount of CuO addition is more than 0.5 wt%, some unknown phases are revealed in the CuO-doped $BiNbO_4$ ceramics. On the basis of Fig. 2(c)–(e), the diffraction intensity of $BiNbO_4$ phase decreases apparently as the amount of CuO addition increases. These results suggest that CuO may form eutectic with the calcining powder and does improve the satellite phases of $Bi_8Nb_{18}O_{57}$ and $Bi_5Nb_3O_{15}$ to form $BiNbO_4$ phase, and thus CuO can be used as a sintering aid of $BiNbO_4$ ceramics. But excess of CuO addition can inhibit the crystallization of $BiNbO_4$ phase.

SEM micrographs of CuO-doped $BiNbO_4$ ceramics are shown in Fig. 3. With the addition of CuO, a much easier densification of $BiNbO_4$ ceramics is evident, as shown in Fig. 3. The size distribution of the $BiNbO_4$ grain is mainly determined by the amount of CuO addition and sintering temperature. For 0.25 wt%-CuO-doped $BiNbO_4$ ceramics, isolated $BiNbO_4$ particles and pores are easily observed, even after sintering at 920°C, as shown in Fig. 3(a). For 0.5 and 1 wt%-CuO-doped $BiNbO_4$ ceramics, the size of pores can be easily eliminated after sintering at 920°C [Fig. 3(b) and (c)]. For 0.25 wt%-CuO additive concentration, the homogeneously fine microstructures with almost no pores, as shown in Fig. 3(d), is observed for the $BiNbO_4$ ceramics sintered at 940°C.

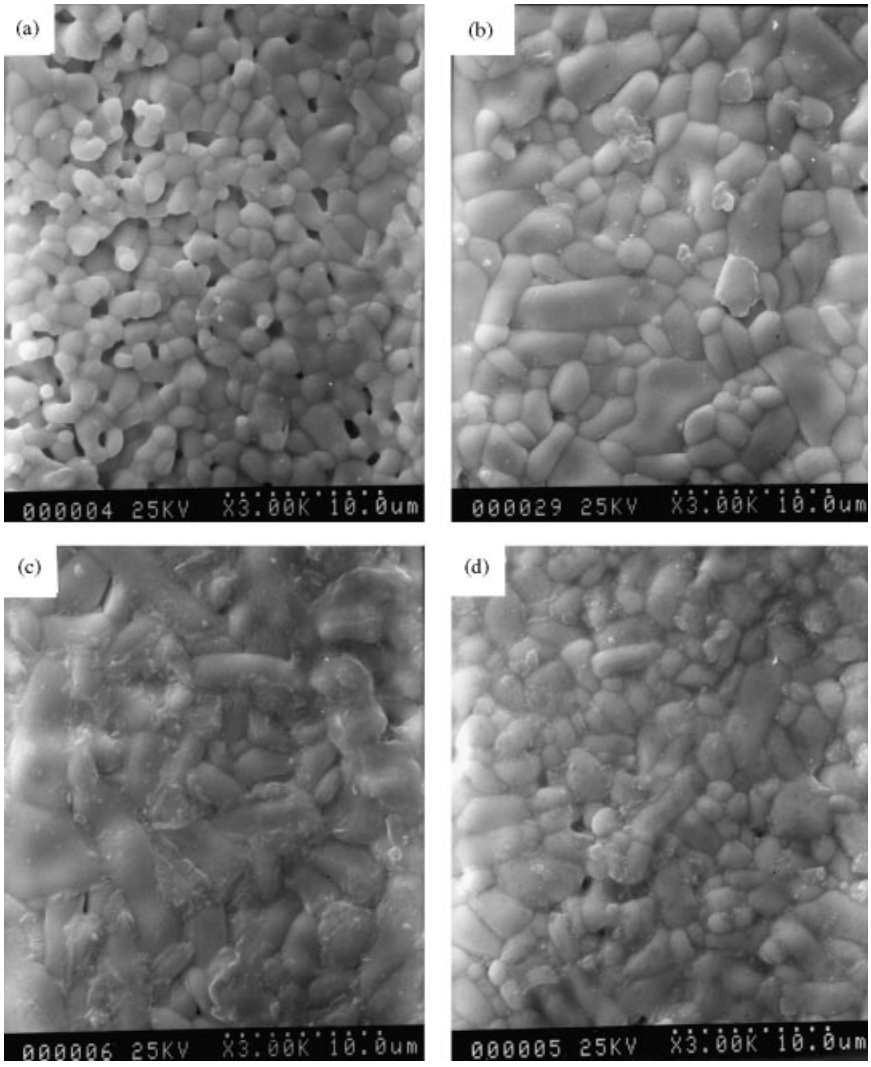

Fig. 3. Micrographs of CuO-doped $BiNbO_4$ dielectric: (a) 920°C, 0.25 wt%, (b) 0.5 wt%, 920°C, (c) 1 wt%, 920°C, (d) 0.25 wt%, 940°C.

The microwave dielectric constants of the $BiNbO_4$ ceramics under various sintering temperatures and amount of CuO addition were measured, and the results are shown in Fig. 4. With the addition of CuO in the $BiNbO_4$ composition, the quality factor values (Q) and temperature coefficients (τ_f) are found to be sensitive to amount of CuO addition, but the dielectric constants ε_r are not. As Fig. 4 shows, the relationships between sintering temperature and ε_r values reveal the same trend with those between sintering temperature and density. The ε_r values of $BiNbO_4$ ceramics increase with the increase of sintering temperature and then reach a saturation value. The saturation values are shifted to lower temperatures as the amount of CuO increases, and those results may be caused by the increases of the sintered density with the sintering temperature. However, as the amount of CuO addition is more than 0.5 wt%, the sintering temperature could be reduced to 900–920°C without apparent degeneration of dielectric constant.

The temperatures to reveal the maximum Q values or quality values×frequency ($Q \times f$) of the $BiNbO_4$ ceramics and the temperature coefficients revealed at the maximum Q values are also measured under different amount of CuO addition, and the results are shown in Table 1. According to the X-ray patterns, the crystalline phase of CuO-doped $BiNbO_4$ ceramics are the low temperature phase of $BiNbO_4$ stable below 1020°C. Therefore, the changes of the Q and τ_f values is considered to be due to the effects of CuO. For $BiNbO_4$ ceramics, the temperatures to reveal the optimum Q values are controlled by the amount of CuO addition. As the amount of CuO addition increases, the Q and $Q \times f$ values first increase, reach a maximum for 0.5 wt% CuO, and then decrease apparently with the further increase of CuO addition. As the amount of CuO addition is less than 0.5 wt%, the increase in Q values maybe caused by the increase in densities and grain growth. As the density and grain size increase [compare Fig. 3(a) and (b)], the pores and grain boundary area decrease, thus reducing the lattice imperfections and dielectric losses and increasing the Q values [13]. As the amount of CuO addition is more than 0.5 wt%, the Q values decrease apparently [compare Fig. 3(b) and (c)]. However when larger amount of sintering aid is used, the grain boundary phase increases, which will cause that the loss tangent increases [14]. However, such significant changes in dielectric losses is hardly explained only by the lattice imperfection or boundary defects.

Table 1
The maximum quality values (quality value×frequency) and the temperature coefficient of CuO-doped $BiNbO_4$ ceramics

Amount of CuO addition and sintering temperature (wt%, °C)	Quality value	Quality value× frequency	Temperature coefficient (ppm/°C)
0.125, 960	980	6180	−6.2
0.25, 940	1380	8650	−13.6
0.5, 920	1610	10,070	−20.8
0.75, 920	1350	8430	−24.2
1, 920	920	5770	−27.1
1.25, 900	860	5420	−29.5
1.5, 900	820	5150	−31.2

As the amount of CuO addition increase, the τ_f values change to large negative value steadily. Table 1 shows that the amount of CuO addition change from 0.125 to 1.5 wt%, the τ_f values change from −6.2 to −31.5 ppm/°C. These results also suggest that a large amount of CuO is unnecessary since CuO concentrations larger than 0.5 wt% leads to decrease in Q values and higher negative τ_f values.

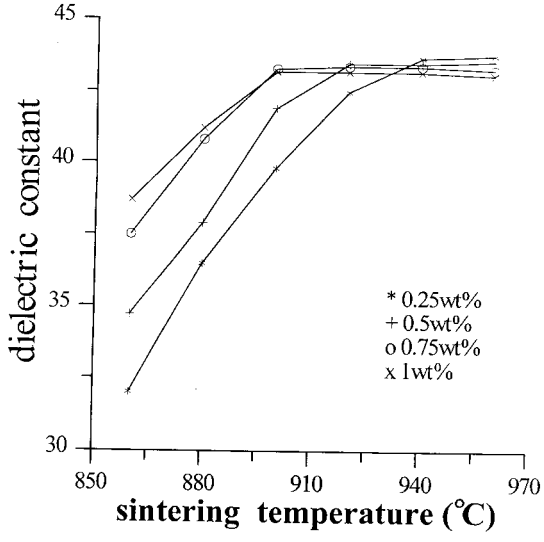

Fig. 4. Dielectric constants of CuO-doped $BiNbO_4$ ceramics as a function of sintering temperature.

4. Conclusions

1. $BiNbO_4$ ceramics can be densified to 98% TD at 920°C when 0.5wt% CuO is used as sintering aid. For CuO concentrations higher than 0.75wt% the $BiNbO_4$ ceramics can be densified at 900°C.
2. As the amount of CuO addition is increased from 0.125wt% to 1.5 wt%, the τ_f values of densified $BiNbO_4$ ceramics change from −6.2 to −31.2 ppm/°C, steadily.
3. $BiNbO_4$ ceramics with 0.5wt% CuO added and sintered at 920°C own the optimum dielectric characteristics: $Q = 1610$ and $\tau_f = -20.8$ppm/°C. Because the sintering temperatures of $BiNbO_4$ ceramics with 0.25–0.75 wt% CuO added are lower than 940°C and the Q values are higher than 1350, for that those compositions can be developed as the multilayer filter material.

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