

# Microwave dielectric properties and co-firing of BiNbO<sub>4</sub> ceramics with CuO substitution

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## Abstract

The effect of CuO substitution on the sintering behavior and the microwave dielectric properties of BiNbO<sub>4</sub> ceramics were studied. The sintering temperatures of (Bi<sub>1-2x</sub>Cu<sub>2x</sub>)NbO<sub>4-x</sub> and (Bi<sub>1-2x</sub>Cu<sub>3x</sub>)NbO<sub>4</sub> ceramics decrease from 930 to 850 °C with  $x$  value increasing. The size of grains increased with the sintering temperature increasing and decreased with the substitution amount increasing. The dielectric constant  $\epsilon_r$  changes between 40 and 45 and the Qf values lie between 4000 and 8000 GHz at about frequency 5.2 GHz. The  $\tau_f$  values changes between 0 and -20 ppm °C<sup>-1</sup> and decreases with the increasing of  $x$  value. Copper electrode was found not to penetrate the ceramic from the SEM and EDS results of the broken surface of co-fired samples.

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*Keywords:* BiNbO<sub>4</sub> ceramics; Microwave dielectrics; Quality value; Co-firing; Polarizability

## 1. Introduction

Recently, low-temperature co-fired ceramic (LTCC) technology has played a more and more important role in advanced packaging and multilayered integrated circuits [1]. In order to use low-melting point conductors, low-firing-microwave dielectric materials with high dielectric constants  $\epsilon_r$ , high Qf values and small temperature coefficients of the resonant frequency  $\tau_f$  are needed. Three methods are commonly used for reducing the sintering temperature of dielectric ceramics: low-melting glass or oxides addition [2,3], chemical processing [4] and using starting materials with smaller particle sizes [5]. And the first method was more popular in practice, and the addition of low-melting point oxides have been used broadly to lower sintering temperature of dielectric ceramics [6,7].

Bismuth-based dielectric ceramics are suitable candidates as low-firing temperature materials and have been studied for application as piezoelectric materials and in multilayer ceramic capacitors [8]. The microwave properties of BiNbO<sub>4</sub> were first reported by Kagata et al. [9]. They found BiNbO<sub>4</sub> ceramics was difficult to be densified without addition of low-melting

oxide. With V<sub>2</sub>O<sub>5</sub> or CuO addition, the ceramics could be sintered well and had  $\epsilon_r$  of about 43, while Qf varied between 10,000 and 17,000 GHz. Later, some researchers [10–13] studied the relationship between microwave dielectric properties of BiNbO<sub>4</sub> ceramics and the addition amount of V<sub>2</sub>O<sub>5</sub>, CuO, etc. In Tzou's work [14,15], the addition of CuO, V<sub>2</sub>O<sub>5</sub>, or CuO–V<sub>2</sub>O<sub>5</sub> to BiNbO<sub>4</sub> ceramics were studied in detail. In their studies, the sintering temperature could be lowered below 960 °C to form  $\alpha$ -BiNbO<sub>4</sub> with the dielectric constant being stabled between 43 and 44 with different addition and sintering temperatures. The  $\tau_f$  was positive with V<sub>2</sub>O<sub>5</sub> addition and negative with CuO addition while  $\tau_f$  near to zero could be obtained by CuO–V<sub>2</sub>O<sub>5</sub> addition together. Excessive amounts of additions would result in the appearance of abnormal grain growth, which will decrease the microwave dielectric properties including the quality factor  $Q$  and the temperature coefficient of resonant frequency. The study on the equivalent substitution for A site Bi<sup>3+</sup> [16–18] and B site Nb<sup>5+</sup> [19–21] also have been carried out to modify the densified temperature and the temperature coefficient of resonant frequency.

However, the reaction between BiNbO<sub>4</sub> ceramics and the silver electrode have limited its further application in LTCC [22,23]. Some modification of composition and different kinds of electrodes are used to avoid the reaction between ceramic and electrode. In order to study the influence of using copper

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electrode in further work, a small amount of Cu was introduced to the BiNbO<sub>4</sub> substituting Bi<sup>3+</sup> and the (Bi<sub>1–2x</sub>Cu<sub>2x</sub>)NbO<sub>4–x</sub> and (Bi<sub>1–2x</sub>Cu<sub>3x</sub>)NbO<sub>4</sub> compositions were designed with different *x* values considering the electrovalence balance and ionic radii. In this paper, the sintering properties, microstructure and microwave dielectric properties of the samples were studied in detail, and the relationship between microstructure and dielectric properties was also investigated. Some simple theoretical calculations were compared to the measured results. The co-firing between ceramics and copper electrode under N<sub>2</sub> atmosphere was also carried out and characterized.

## 2. Experimental

Proportionate amounts of reagent-grade starting materials of Bi<sub>2</sub>O<sub>3</sub> (>99%, Shu-Du Powders Co. Ltd., China), Nb<sub>2</sub>O<sub>5</sub> and CuO (>99%, Zhu-Zhou Harden Alloys Co., Ltd., China) were mixed according to the composition (Bi<sub>1–2x</sub>Cu<sub>2x</sub>)NbO<sub>4–x</sub> (*x*=0.002, 0.004, 0.008) and (Bi<sub>1–2x</sub>Cu<sub>3x</sub>)NbO<sub>4</sub> (*x*=0.008), which were defined as Cu1, Cu2, Cu3 and Cu4, respectively, in this paper. The mixtures were ball-milled for 4 h with alcohol in a nylon container with ZrO<sub>2</sub> balls. The mixtures were dried and calcined at 700 °C for 4 h. Then the mixtures were re-milled, and after drying, the powder with 5 wt.% PVA binder was uniaxially pressed into pellets and cylinder in a steel die. The pellets and cylinders were sintered from 850 to 910 °C for 2 h. Copper paste was screen-printed on the surface of green pellets. Green pellets of Cu3 samples were co-fired with copper electrode at 850 °C for half an hour under N<sub>2</sub> atmosphere.

After the surface was polished, the crystalline structures of the BiNbO<sub>4</sub> substituted by CuO ceramics were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). To investigate the morphology of the samples, the natural surface (polished and annealed at 600 °C) of the sintered specimens were observed by scanning electron microscopy (SEM) (JEOL JSM-6460, Japan). The broken surface of co-fired sample was observed by SEM and EDS to observe the boundary.

Dielectric behaviors at microwave frequency were measured by Hakki–Coleman's dielectric resonator method improved by Kobayashi and Katoh (method I) [24], and shielded cavity method (method II) improved by Krupka [25]. A 8720ES network analyzer (8720ES, Agilent, USA) was used in both the above methods for the microwave measurement.

The temperature coefficients  $\tau_f$  of resonant frequencies were measured with the 8720ES network analyzer and a DELTA 9023 Chamber using the shielded cavity method. The  $\tau_f$  value was calculated by the formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \quad (1)$$

where  $f_{85}$  and  $f_{25}$  were the TE<sub>018</sub> resonant frequencies at the measuring temperature 85 °C and at RT (25 °C), respectively.

## 3. Results and discussion

As known to all, BiNbO<sub>4</sub> has two polymorph phases, low-temperature orthorhombic  $\alpha$ -phase and high temperature triclinic  $\beta$ -phase. Pure  $\alpha$ -BiNbO<sub>4</sub> has a crystal structure of the orthorhombic-SbTaO<sub>4</sub> type below 1020 °C, and transform to  $\beta$ -phase when the temperature increases [26]. As shown in Fig. 1, both  $\alpha$ -phase and  $\beta$ -phase of BiNbO<sub>4</sub> were observed in the XRD patterns of samples sintered at 910 °C. It is evident that the substitution of Cu<sup>2+</sup> for Bi<sup>3+</sup> lowered the phase transition temperature efficiently. Cu<sup>2+</sup> has an ionic radius of 0.73 Å while it is 1.03 Å for Bi<sup>3+</sup>. The cell volume (330.66 Å<sup>3</sup>) of  $\alpha$ -BiNbO<sub>4</sub> is larger than that of  $\beta$ -BiNbO<sub>4</sub> (325.44 Å<sup>3</sup>) [27,28]. The lower electrovalency and smaller ionic radius of Cu<sup>2+</sup> than that of Bi<sup>3+</sup> caused the lattice distortion and accelerated the formation of  $\beta$ -

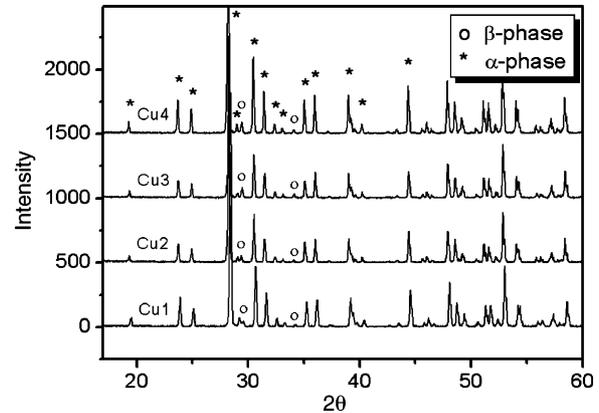


Fig. 1. XRD patterns of samples sintered at 910 °C.

BiNbO<sub>4</sub>. With the amount of Cu<sup>2+</sup> increasing, the  $\beta$ -BiNbO<sub>4</sub> phase was easy to form and its amount increased as shown in Fig. 1 for Cu1, Cu2 and Cu3 samples.

The SEM micrographs of samples sintered at 870 and 910 °C are illustrated in Fig. 2. The grains size was distributed from 1–2 μm for samples sintered at 870 °C. The grain size decreased with the amount of Cu increasing, as shown in Fig. 2(a)–(c), while the grain size of Cu4 lying between Cu2 and Cu3. The pores were observed for samples sintered at 870 °C. Homogeneously fine microstructures with almost no pores were revealed for samples sintered at 910 °C, the grain size of which lied between 1 and 5 μm. With the sintering temperature increasing, the grain size increased greatly for samples with small amounts of substitution, but less for samples with large amount substitution. This suggested that the substitution of Cu suppressed the grain growth while it lowering the densified temperature of BiNbO<sub>4</sub> ceramics. Relative density of ceramics as a function of sintering temperature was shown in Fig. 3. The densities of ceramics increased with the sintering temperature and substitution amount increasing and reached their saturated values at about 900 °C. This result corresponded well with that of SEM photos for Cu3 and Cu4, but did not match for Cu1 and Cu2 samples. The fine microstructures shown in Fig. 2(a) and (b) might be caused by the annealing course. For Cu3 and Cu4 samples, the grain growth was suppressed during the annealing course by the substitution of Cu.

Fig. 4 shows the dielectric properties of samples at microwave frequency region by the shielded cavity method and parallel-plate resonant method. The dielectric constant of samples increased with the sintering temperature increasing, because with the sintering temperature increasing, the pores (whose  $\epsilon_r$  near to 1) decreased and the relative density increased as shown in Fig. 3, so the  $\epsilon_r$  of samples increased.

At microwave region, the polarizability is the sum of both ionic and electronic components [29]. Shannon [30] suggested that molecular polarizabilities of complex substances can be estimated by summing the polarizabilities of constituent ions. Then the polarizabilities  $\epsilon_s$  could be got as follows:

$$\alpha[(\text{Bi}_{1-2x}\text{Cu}_{2x})\text{NbO}_{4-x}] = (1 - 2x)\alpha(\text{Bi}^{3+}) + 2x\alpha(\text{Cu}^{2+}) + \alpha(\text{Nb}^{5+}) + (4 - x)\alpha(\text{O}^{2-}) \quad (2)$$

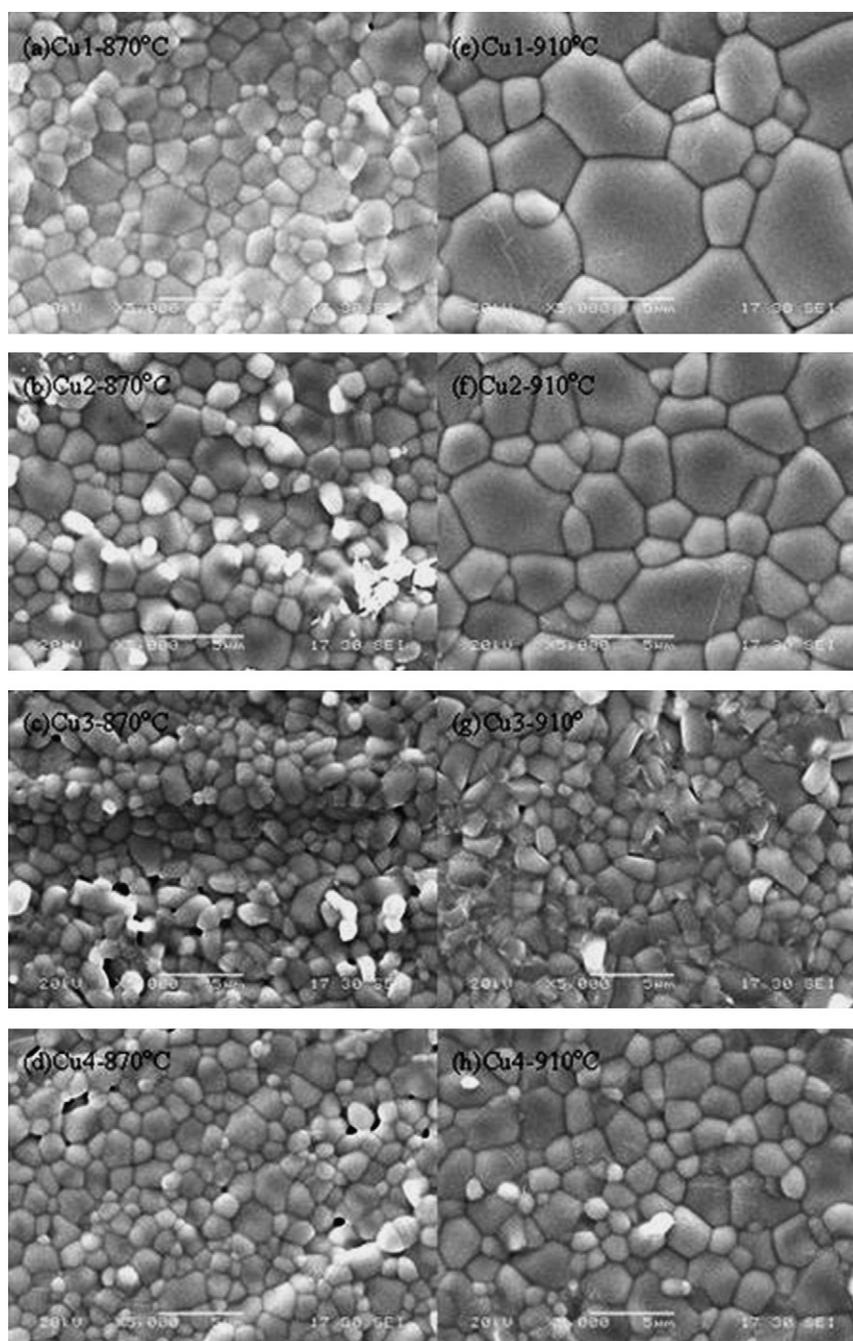


Fig. 2. SEM micrographs of samples sintered at 870 and 910 °C.

$$\alpha[(\text{Bi}_{1-2x}\text{Cu}_{3x})\text{NbO}_4] = (1 - 2x)\alpha(\text{Bi}^{3+}) + 3x\alpha(\text{Cu}^{2+}) + \alpha(\text{Nb}^{5+}) + 4\alpha(\text{O}^{2-}) \quad (3)$$

where  $\alpha$  is the polarizability. The experiential data of ionic polarizabilities could be obtained from Shannon's paper [30], as shown in Table 1. With the Clausius–Mossotti relation shown in Eq. (4), the calculated dielectric constants of the composition could be obtained as shown in Table 2. The calculated dielectric constant decreases from 32.144 to 31.049 with  $x$  increasing from 0.002 to 0.008 and the trend goes well with the measured results by the two methods. Shannon's summing theory the polarizabilities is only an approximate method for the dielec-

tric constant calculating and for most high dielectric constant materials ( $\epsilon_r > 25$ ) the accurate absolute value of  $\epsilon_r$  could not be obtained. In  $\alpha$ -BiNbO<sub>4</sub> phase, the NbO<sub>6</sub> octahedra are linked over four corners and the structure could be viewed as con-

Table 1  
Ionic polarizabilities of O<sup>2-</sup>, Cu<sup>2+</sup>, Bi<sup>3+</sup> and Nb<sup>5+</sup> obtained from literature [26]

Ionic kinds	Ionic polarizability (Å <sup>3</sup> )
O <sup>2-</sup>	2.0–2.01
Cu <sup>2+</sup>	2.11–2.11
Bi <sup>3+</sup>	6.04–6.12
Nb <sup>5+</sup>	3.98–3.97

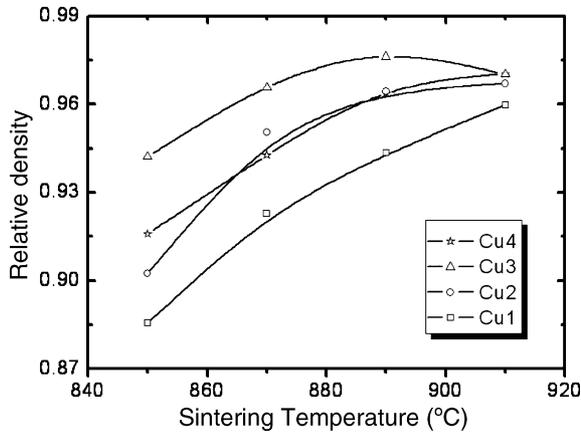


Fig. 3. Relative density of BiNbO<sub>4</sub> ceramics as a function of sintering temperature.

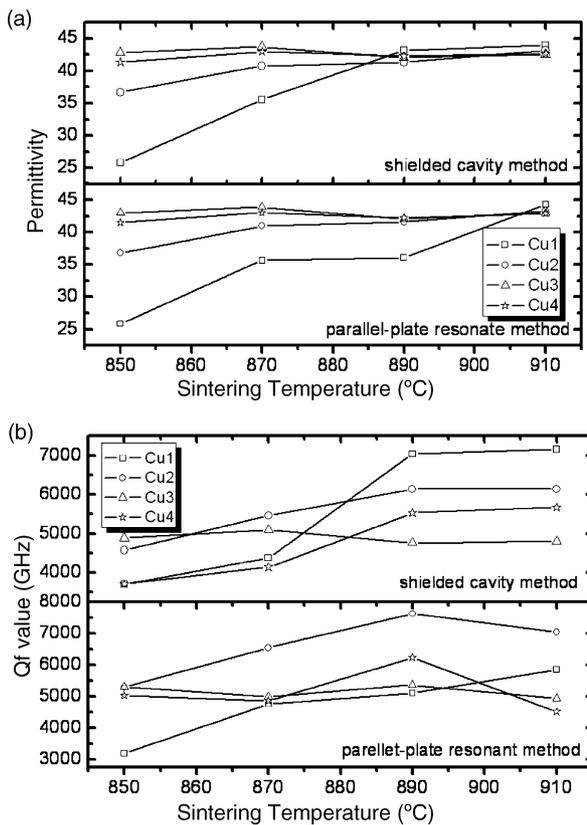


Fig. 4. Dielectric properties of samples as a function of sintering temperature.

Table 2

The calculated  $\alpha_D$  (polarizabilities) and  $\epsilon_s$  (permittivity) from the dielectric polarizability of ions and the measured  $\epsilon_{m1}$  by method I,  $\epsilon_{m2}$  by method II of samples

Samples	$x$	$\alpha_D$ ( $\text{\AA}^3$ )	$\epsilon_s$	$\epsilon_{m1}$ (910 °C)	$\epsilon_{m2}$ (910 °C)
Cu1	0.002	18.000	32.144	44.262	43.965
Cu2	0.004	17.981	31.771	43.331	43.209
Cu3	0.008	17.941	31.049	42.932	42.545
Cu4	0.008	17.974	31.667	42.876	42.633

sisting of sheets of  $[\text{NbO}_4]^{3-}$  units separated by  $\text{Bi}^{3+}$  cations [27]. The  $\text{Bi}^{3+}$  ions have relative broad space surroundings and the presences of “rattling”  $\text{Bi}^{3+}$  ions could have unusually large polarizability. If the  $\epsilon_r$  was assumed as 43 and the polarizability of  $\text{Bi}^{3+}$  could be calculated contrarily equal to  $6.43 \text{ \AA}^3$ , which is a little bigger than  $6.12 \text{ \AA}^3$ :

$$\epsilon_s = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \quad (4)$$

where  $V_m$  is the molar volume and  $\alpha_D$  is the polarizability. Considering the co-existing of both  $\alpha$  and  $\beta$  phases of  $\text{BiNbO}_4$ , the equivalent  $V_m$  was defined as follows:

$$V_m = V_m(\alpha)(1 - x) + V_m(\beta)x \quad (5)$$

where the  $V_m(\alpha) = 82.665 \text{ \AA}^3$  is the volume of  $\alpha$ - $\text{BiNbO}_4$ , and the  $V_m(\beta) = 81.36 \text{ \AA}^3$  is the volume of  $\beta$ - $\text{BiNbO}_4$ .

At microwave region, the dielectric constant of the ceramics is closely related to the sum of electronic and ionic polarizabilities of components. According to the ionic polarizabilities reported by Shannon [30], the polarizability of  $\text{Cu}^{2+}$  ( $2.11 \text{ \AA}^3$ ) is smaller than that of  $\text{Bi}^{3+}$  ( $6.12 \text{ \AA}^3$ ), so the dielectric constant of samples would decrease with the substitution amount of Cu increasing. And this corresponded well to the results as shown in Fig. 4(a) for samples well densified at sintering temperature 910 °C. Besides the intrinsic influence, pores, grains size and grain boundaries also influenced the microwave permittivity.

The Qf values as a function of sintering temperature were shown in Fig. 4(b). At the sintering temperature range 870–910 °C, the Qf lied between 4000 and 7200 GHz (resonant frequencies between 4 and 5 GHz) measured by the shielded cavity method. And the results are similar to each other measured by the two methods. As the sintering temperature increasing, the Qf increased firstly and then reached to their saturated values. Many factors are believed to affect Qf of samples. Besides the intrinsic loss, the crystal defects, grain boundaries, second phases and pores are thought to the most important factors. With the sintering temperature increasing, the grains grew bigger and loss caused by grain boundaries decreased whiles the pores decreased. These all increased the Qf. The amount of  $\beta$ -

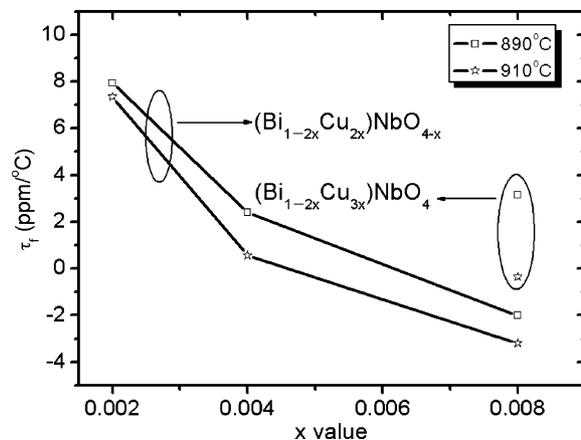


Fig. 5. The temperature coefficient of resonant frequency  $\tau_f$  as a function of substitution amount  $x$ .

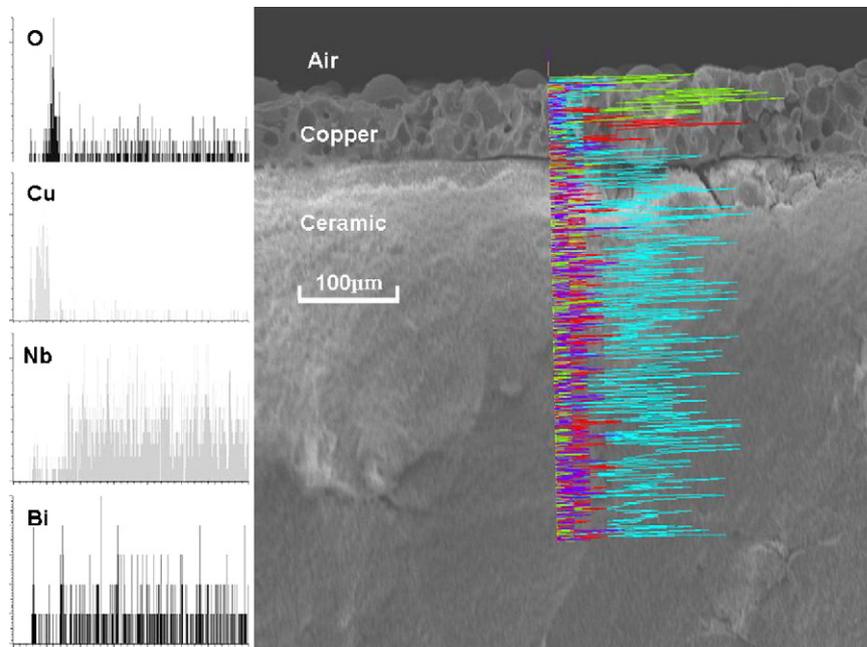


Fig. 6. SEM and ESD photos of co-fired sample.

$\text{BiNbO}_4$  is believed to increase with sintering temperature, but whether it increased the Qf or not is not very clear in the reported literature [16,31]. With the substitution amount of Cu increasing, the grain size was suppressed as shown in SEM photos and this caused increased loss from grain boundaries. The results shown in Fig. 4(b) of samples sintered at  $910^\circ\text{C}$  also validated it. And the results measured by the paralleled-plate have the same trend as shown in Fig. 4(b). The Qf values of ceramics obtained here were a little smaller than that of pure  $\text{BiNbO}_4$  reported by Kagatan et al. [9]. The substitution of Cu deteriorate the Qf while it could lower the sintering temperature efficiently and both  $(\text{Bi}_{1-2x}\text{Cu}_{2x})\text{NbO}_{4-x}$  and  $(\text{Bi}_{1-2x}\text{Cu}_{3x})\text{NbO}_4$  compositions had the similar results.

The temperature coefficient of resonant frequency  $\tau_f$  of samples as a function of substitution amount  $x$  value is shown in Fig. 5. With the  $x$  value increased from 0.002 to 0.008 for  $(\text{Bi}_{1-2x}\text{Cu}_{2x})\text{NbO}_{4-x}$  ceramics, the  $\tau_f$  decreased from +8 to  $-2 \text{ ppm } ^\circ\text{C}^{-1}$  for samples sintered at  $870^\circ\text{C}$  and the values of  $\tau_f$  moved to the negative direction when sintering temperature increased to  $910^\circ\text{C}$ . The  $\tau_f$  values of  $(\text{Bi}_{1-2x}\text{Cu}_{3x})\text{NbO}_4$  ceramics ( $x=0.008$ ) sintered at 870 and  $910^\circ\text{C}$  were shown in Fig. 5. It is similar to that of  $(\text{Bi}_{1-2x}\text{Cu}_{2x})\text{NbO}_{4-x}$  ceramics with  $x=0.004$  because their wt.% of CuO is similar. The substitution of CuO could modify the  $\tau_f$  efficiently and the  $0 \text{ ppm } ^\circ\text{C}^{-1}$  of  $\tau_f$  could be got if the proper  $x$  valued was chosen.

The co-firing between copper electrode and green samples was well performed at  $850^\circ\text{C}$  for half an hour under  $\text{N}_2$  atmosphere and the SEM and EDS results are shown in Fig. 6. The boundary between copper electrode and ceramic is clear and the ceramic has also been sintered well. The Cu element is centralized in the electrode mostly and the pervasion into the ceramic was hardly observed in the SEM and EDS results. Furthermore, Bi and Nb elements are hardly to be observed in the electrode and concentrate in the ceramic. The distribution of O element is dif-

ferent from the other elements and it exists both in the electrode and ceramic. The Cu element could be thought to exist in CuO or  $\text{Cu}_2\text{O}$  and this might be caused by the low purity of  $\text{N}_2$  atmospheres. The co-firing and reaction mechanism between copper electrode and ceramic are very important for its application for LTCC and this work needs to be studied furthermore.

#### 4. Conclusions

Considering both  $(\text{Bi}_{1-2x}\text{Cu}_{2x})\text{NbO}_{4-x}$  and  $(\text{Bi}_{1-2x}\text{Cu}_{3x})\text{NbO}_4$  compositions, influence to the sintering behavior and microwave dielectric properties of  $\text{BiNbO}_4$  ceramics by substitution of CuO was studied. As the increase amount of CuO substitution, the sintering temperatures decreased efficiently and microwave permittivity decreased slightly. Qf values were relative large when substitution amount was small and excess substitution of CuO would deteriorate Qf values seriously. Temperature coefficient of resonant frequency changed from +8 to  $-2 \text{ ppm } ^\circ\text{C}^{-1}$  as the increase of substitution amount of CuO. The co-firing between  $\text{BiNbO}_4$  green pellets and copper paste was studied. Cu element was found not to penetrate into the ceramics but it was easy to be oxygenated into CuO or  $\text{Cu}_2\text{O}$ .

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