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Microwave dielectric properties and co-firing with copper of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics

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Abstract

Effect of substitution of CuO and WO_3 on the microwave dielectric properties of $BiNbO_4$ ceramics and the co-firing between ceramics and copper electrode were investigated. The $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ($x = 0.005, 0.01, 0.015, 0.02$) composition can be densified between 900 and 990 °C. The microwave dielectric constants lie between 36 and 45 and the pores in ceramics were found to be the main influence. The Q values changes between 1400 and 2900 with different x values and sintering temperatures while Q_f values lie between 6000 and 16,000 GHz. The microwave dielectric losses, mainly affected by the grain size, pores, and the secondary phase, are discussed. The $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics and copper electrode was co-fired under N_2 atmosphere at 850 °C and the EDS analysis showed no reaction between the dielectrics and copper electrodes. This result presented the $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ dielectric materials to be good candidates for LTCC applications with copper electrode.

Keywords: A. Sintering; C. Dielectric properties; D. Niobates; E. Electrodes

1. Introduction

In order to reduce the size of microwave devices in mobile radio communication systems, the multilayer microwave devices have been well developed in recent years. The microwave dielectrics with low sintering temperatures are needed to co-fire with low melting point electrode such as silver and copper. Adding low melting point oxides is popularly adopted to reduce the sintering temperature of dielectric materials [1]. Bismuth-based dielectric ceramics have been found to have low-firing temperature and have been studied for piezoelectric materials or multiplayer ceramic capacitors [2]. Especially Bi–Nb systems have recently received increasing attention.

The microwave dielectric properties of $BiNbO_4$ ceramics were first reported by Kagata et al. [3]. Yang [4] and Huang et al. [5] studied the influence of CuO, V_2O_5 and CuO–V_2O_5 additions. Based on their studies, the sintering temperature could be lower below 960 °C to form α-$BiNbO_4$ with the dielectric constant being stable between 43 and 44 and Q_f lying between 10,000 and 17,000 GHz. The τ_f was positive with V_2O_5 addition and negative with CuO addition while τ_f near to zero could be obtained by adding CuO–V_2O_5 together. Wang et al. [6] reported $BiNbO_4$ ceramics sintered under N_2 atmosphere had better dielectric properties than those under air atmosphere. Some researchers modified the microwave dielectric properties of $BiNbO_4$ ceramics using different amounts of Nd^{3+}, Sm^{3+}, Y^{3+} substituting for Bi^{3+} and Ta^{5+}, Sb^{5+}, V^{5+} substituting for Nb^{5+} [7–10]. Some promising results were obtained in their studies and especially the very small τ_f near to zero could be obtained.

But the reaction between $BiNbO_4$ ceramics and the silver electrode limits its further application in LTCC [11]. 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 electrode, small amounts of CuO and WO_3 were introduced into $BiNbO_4$. The $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ composition was designed in this work considering the electroneutrality and ionic radii. The sintering properties, microstructure and microwave dielectric properties of the $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics were studied in details. The relationship between microstructure and dielectric properties was also discussed. Work on the co-firing of copper electrode and $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$

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ceramics was studied and some simple qualitative decisions were obtained.

2. Experimental procedure

The $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics, with $x = 0.005$, 0.010, 0.015, 0.020, were prepared via traditional mixed oxides method using reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., China), Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd., China), CuO and WO_3. The copper slurry was screen-printed on the surface of green pellets, then the samples were sintered at 850 °C for half an hour under N_2 atmosphere.

The crystal structures of ceramics were investigated by X-ray diffractometry with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). The surfaces of the sintered specimens and broken surfaces of co-fired sample were observed by SEM and EDS (JEOL JSM-6460, Japan). The densities of sintered specimens were measured by the Archimedes method.

Dielectric behavior at microwave frequency was measured by the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, USA) and a temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficient of resonant frequency τ_f value was calculated by the formula:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_T, f_0 were the resonant frequencies at the measuring temperature T and RT (25 °C), respectively.

3. Results and discussion

Fig. 1 shows the bulk densities of the $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics sintered at various temperatures. With increasing sintering temperature (ST), the porosity decreased and the relative densities increased. The densities reached their saturated values at different ST for different x values. With increasing substitution amounts of CuO and WO_3, the relative densities also increased efficiently and the densified temperatures decreased from 990 °C at $x = 0.005$ to 890 °C at $x = 0.02$. The addition of CuO and WO_3 lowered the densified temperature and increased the relative densities efficiently.

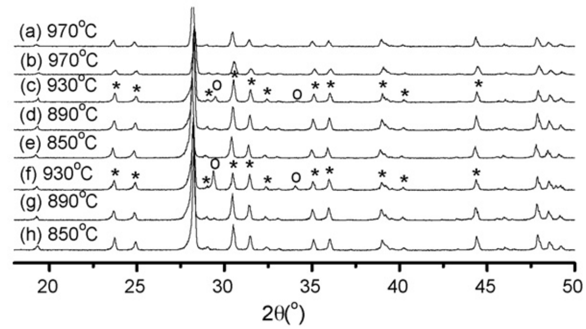

Fig. 2. XRD patterns of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics for $x = 0.005$ (a), $x = 0.010$ (b), $x = 0.015$ (c–e) and $x = 0.020$ (f–h) at different sintering temperature (*: α-phase; o: β-phase).

The XRD patterns of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics at different sintering temperatures are shown in Fig. 2. The α-$BiNbO_4$ was the main phase in all the sintered samples. The β-$BiNbO_4$ occurred in samples sintered at 890 °C both for $x = 0.015$ and 0.02. It is known that α-$BiNbO_4$ would gradually transform to β-$BiNbO_4$ as the sintering temperature increased [12]. So it is clear that the transformation temperature was lowered by the substitution. The amount of β-$BiNbO_4$ increased as both the sintering temperature and substitution amount were increased as shown in Fig. 2.

Fig. 3 shows the SEM micrographs of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics. When $x = 0.005$ and 0.01, the ceramics could be densified at high sintering temperature. But the bar shape grains and secondary growth were observed. These abnormalities might cause the low relative density as shown in Fig. 1. When the substitution amounts reached $x = 0.015$ and 0.02, the ceramics could be densified at lower sintering temperatures and small size grains could be obtained. Although some pores could be found in the SEM micrographs,

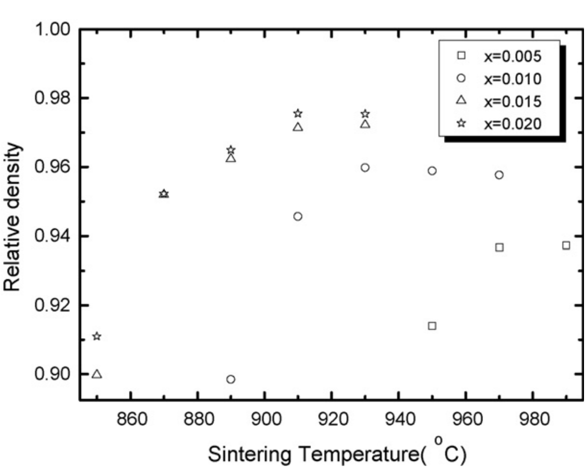

Fig. 1. The density of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics as a function of sintering temperature.

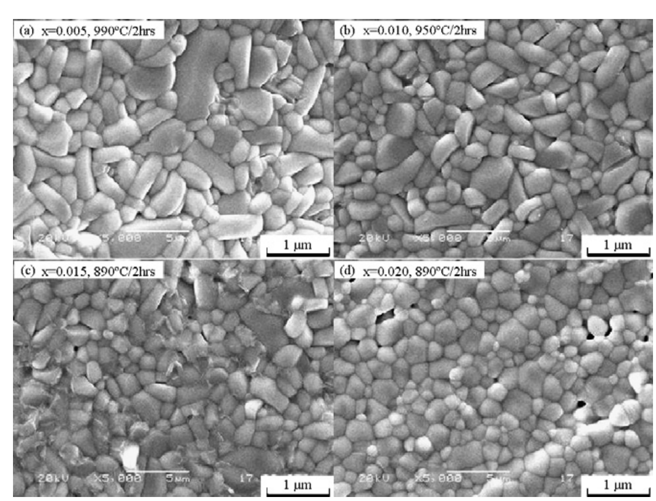

Fig. 3. SEM micrographs of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics.

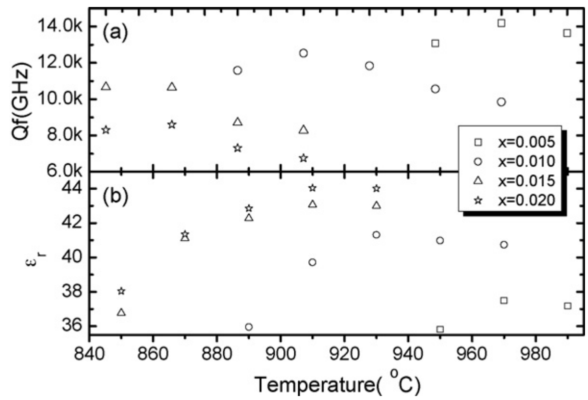

Fig. 4. Microwave dielectric properties as a function of sintering temperature for $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics.

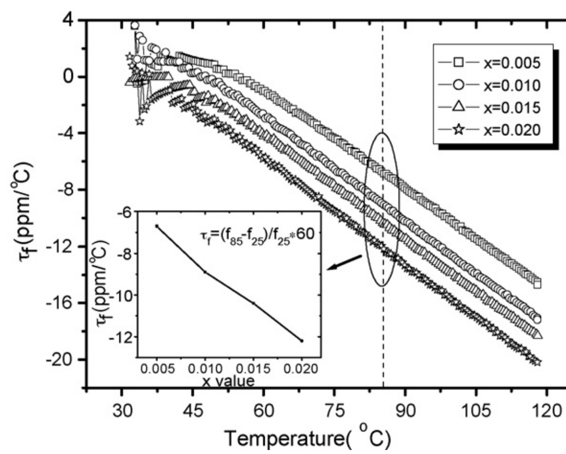

Fig. 5. The temperature coefficients of resonant frequency of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics.

the small size of grains and no abnormity might explain the high relative densities.

The dielectric constants ε_r of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics as a function of sintering temperature and x value are shown in Fig. 4(a). The ε_r values exhibit a similar trend as that for the bulk densities as demonstrated in Fig. 1. It implies that the increase and saturation for ε_r values of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics with increasing sintering temperature are due to the increase and saturation of density. The main influences on ε_r should be attributed to the pores in ceramics (ε_r of air is about 1).

The Q_f values of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics with various x values at different sintering temperatures are plotted in Fig. 4(b). It is known that there are intrinsic and extrinsic losses for dielectric ceramics at the microwave region [13]. The extrinsic loss, caused by the defects in ceramics, e.g., intrinsic crystal defects, pores, substitution or doping, grain boundaries, secondary phase etc, dominates the trend of a change in Q_f value as a function of ST at microwave region. As shown in Fig. 4(b), when the sintering temperature was increased, all the Q_f values firstly increased and then decreased. With increasing the substitution amounts, the Q_f values decreased quickly. These changes could be attributed to grain size, pores, and secondary phase present. With increasing the sintering temperature, firstly the pores shrank and the grains grew larger resulting in the increase of Q_f values. Then at high temperature, the secondary growth deteriorates the Q_f values seriously. As the substitution amounts increase, the further decrease of Q_f values for samples at $x = 0.015$ and 0.02 could be attributed to the smaller grain size (as shown in Fig. 3) and the existence of β-$BiNbO_4$. The total number of the grain boundaries would increase with a decrease in the average grain size and this would contribute significantly to extrinsic dielectric loss. Kim and Choi [14] gave the calculated results $\varepsilon_r = 30$ and $Q_f = 8900$ GHz extrapolated from IR down to MW range. As the sintering temperature and substitution amounts increased, the amounts of β-$BiNbO_4$ increased and the Q_f values decreased quickly as shown in Fig. 4(b).

The temperature coefficient τ_f as a function of measuring temperature and substitution amounts of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics is shown in Fig. 5. It is obvious that the τ_f decreased inversely proportional to an increase in measuring temperature and x value as shown in Fig. 5. The τ_f of ceramics at the same measuring temperature $T = 85$ °C changed from −6.6 to −8.9, −10.3 and −12.4 ppm/°C as the x value increased from 0.005 to 0.010, 0.015 and 0.020.

The co-firing between copper electrode and green samples was performed at 850 °C for half an hour under N_2 atmosphere and the SEM and EDS results are shown in Fig. 6. The boundary between copper electrode and ceramic is clearly distinguished. The Cu remains in the electrode mostly and the Cu diffusion into the ceramic region was not observed by the recent SEM and EDS results. On the contrary, Bi and Nb are hardly observed in the electrode region but concentrated in the ceramic one. The distribution of O is different from other elements in that it exists both in the regions of electrode and ceramic. The Cu element was expected to exist in the form of either CuO or Cu_2O dependent upon the impurity of N_2 atmospheres. The co-firing and reaction mechanism between copper electrode and

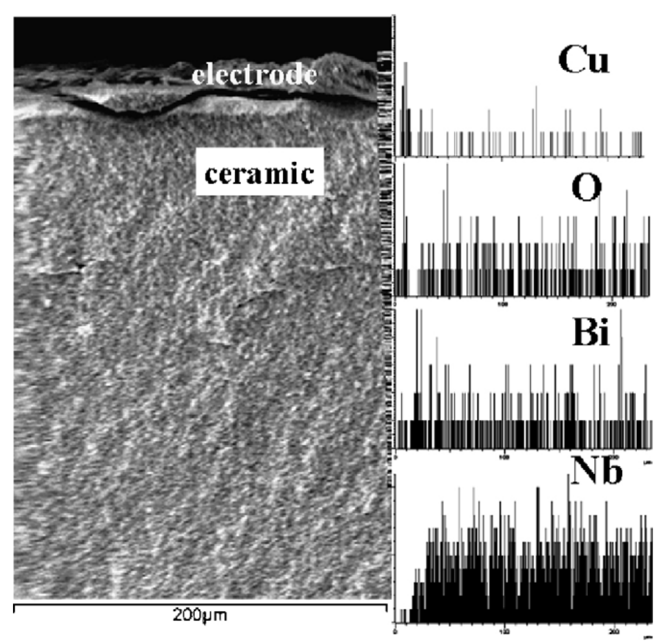

Fig. 6. EDS analysis of $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ceramics.

ceramic are very important for its application for LTCC and this work needs to be studied further.

4. Conclusions

The $(Bi_{1-x}Cu_x)(Nb_{1-x}W_x)O_4$ ($x = 0.005$, 0.01, 0.015, 0.02) composition can be densified at 900–990 °C. The microwave dielectric constants lie between 36 and 45 while Q_f values are between 6000 and 16,000 GHz. The microwave dielectric losses are mainly affected by the grain size, pores, and the secondary phase as discussed. The increase of substitution contents inversely caused a decrease of temperature coefficient τ_f of resonant frequency. And the τ_f also decreased as the measuring temperature was increased. The co-firing between copper electrode and green samples was performed at 850 °C for half an hour under N_2 atmosphere. The EDS results showed no diffusion of Cu element into the ceramic and this result might accelerate the practical application of $BiNbO_4$ in LTCC field.

Acknowledgements

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References

[1] T. Takada, S.F. Wang, S. Yoshikawa, S.J. Jang, R.E. Newnham, Effect of glass additions on $BaO–TiO_2–WO_3$ microwave ceramics, J. Am. Ceram. Soc. 77 (1994) 1909–1916.

[2] D. Liu, Y. Liu, S.Q. Huang, X. Yao, Phase structure and dielectric properties of $Bi_2O_3–ZnO–Nb_2O_5$-based dielectric ceramics, J. Am. Ceram. Soc. 76 (1993) 2129–2132.

[3] H. Kagata, T. Inoue, J. Kato, I. Kameyama, Low-fire bismuth-based dielectric ceramics for microwave use, Jpn. J. Appl. Phys. 31 (1992) 3152–3155.

[4] C.F. Yang, Improvement of the dielectric properties of $BiNbO_4$ ceramics by the addition of $CuO–V_2O_5$ mixtures, J. Mater. Sci. Lett. 18 (1999) 805–807.

[5] C.L. Huang, M.H. Weng, G.M. Shan, Effect of V_2O_5 and CuO additives on sintering behavior and microwave dielectric properties of $BiNbO_4$ ceramics, J. Mater. Sci. 35 (2000) 5443–5447.

[6] Zh.W. Wang, X. Yao, L.Y. Zhang, The effect of sintering atmosphere on the microwave dielectric properties of V_2O_5 doped $BiNbO_4$ ceramics, Ceram. Int. 30 (2004) 1929–1933.

[7] W. Choi, K.Y. Kim, Effect of Nd_2O_3 on the microwave dielectric properties of $BiNbO_4$ ceramics, J. Mater. Res. 13 (1998) 2945–2949.

[8] Y.Ch. Chen, W.Ch. Tzou, Ch.F. Yang, P.Sh. Cheng, The effect of the crystalline phase on the sintering and microwave dielectric properties of Cu-doped $(Bi_{0.95}Sm_{0.05})NbO_4$ ceramics, Jpn. J. Appl. Phys. 40 (2001) 3225–3255.

[9] Ch.L. Huang, M.H. Weng, The microwave dielectric properties and the microstructures of $Bi(Nb,Ta)O_4$ ceramics, Jpn. J. Appl. Phys. 38 (1999) 5949–5952.

[10] N. Wang, M.Y. Zhao, W. Li, Zh.W. Yin, The sintering behavior and microwave dielectric properties of $Bi(Nb,Sb)O_4$ ceramics, Ceram. Int. 30 (2004) 1017–1022.

[11] S.Y. Cho, H.J. Youn, D.W. Kim, T.G. Kim, K.S. Hong, Interaction of $BiNbO_4$-based low-firing ceramics with silver electrodes, J. Am. Ceram. Soc. 81 (1998) 3038–3040.

[12] M.A. Subramanian, J.C. Calabrese, Crystal structure of the low temperature form of bismuth niobium oxide, Mater. Res. Bull. 28 (1993) 523–529.

[13] H. Tamura, Microwave loss quality of $(Zr_{0.8}Sn_{0.2})TiO_4$, Am. Ceram. Soc. Bull. 73 (1994) 92–95.

[14] E.S. Kim, W. Choi, Effect of phase transition on the microwave dielectric properties of $BiNbO_4$, J. Eur. Ceram. Soc. 26 (2006) 1761–1766.