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Journal of the European Ceramic Society 29 (2009) 1543–1546
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Technical note

Low temperature firing of $BiSbO_4$ microwave dielectric ceramic with B_2O_3–CuO addition

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Received 9 July 2008; received in revised form 17 August 2008; accepted 21 August 2008
Available online 27 September 2008

Abstract

The influence of B_2O_3–CuO addition on the sintering behavior, phase composition, microstructure and microwave dielectric properties of $BiSbO_4$ ceramic have been investigated. The $BiSbO_4$ ceramics can be well densified to approach above 95% theoretical density in the sintering temperature range from 840 to 960 °C as the addition amount of B_2O_3–CuO increases from 0.6 to 1.2 wt.%. Sintered ceramic samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The microwave permittivity ε_r saturated at 19–20 and Qf values varied between 33,000 and 46,000 GHz while temperature coefficient of resonant frequency shifting between −70 and −60 ppm/°C at sintering temperature around 930 °C. Lowering sintering temperature of $BiSbO_4$ ceramics makes it possible for application in low temperature co-fired ceramic technology.

Keywords: Firing; Dielectric properties; $BiSbO_4$

1. Introduction

Production of multilayer or chip devices in wireless communications requires the miniaturization of microwave dielectrics and co-firing of dielectrics with internal electrodes. To meet this requirement, low temperature-cofired ceramics (LTCC) technology has been widely investigated.[1–5] To co-fire with the most common internal electrode silver (melting point = 960 °C), the sintering temperature of microwave dielectrics must be lowered to below 960 °C.

Recently, bismuth-based dielectric ceramics have been broadly studied for its relatively low sintering temperature (less than 1000 °C), high dielectric constant and have been investigated for the application as multilayer capacitors.[6,7] Many single phase of bismuth-based dielectric ceramics have been explored for LTCC application, such as orthorhombic phase of $Bi(Nb,Ta)O_4$,[8,9] fluorite phase of $Bi_3(Nb,Ta)O_7$,[10–12] monoclinic phase of $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ and $Bi_2(Zn_{2/3}Ta_{4/3})O_7$,[13,14] tetragonal phase of $Bi_{18}Ca_8Nb_{12}O_{65}$,[8] orthorhombic of $Bi_2W_2O_9$[15], sillenite phase of $Bi_{12}MO_{20}$ (M=Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$)[16] and $BiPO_4$,[17] etc. In our recent work, a new kind of bismuth-based microwave dielectric $BiSbO_4$ ceramic has been reported.[18] Single crystal of $BiSbO_4$ was ever synthesized by Popolitov et al.[19] and the X-ray powder diffraction of $BiSbO_4$ was studied by Kennedy.[20] $BiSbO_4$ was found to crystalline with monoclinic structure [*I*2/*c* space group, $a = 5.4690(2)$, $b = 4.8847(3)$, $c = 11.8252(6)$ Å, and $\beta = 101.131(3)°$]. In our work $BiSbO_4$ ceramic was found to be sintered above 990 °C and exhibit dielectric constant about 19, Qf values about 70,000 GHz and TCF about −62 ppm/°C at around 1080 °C. Its firing temperature is a little higher and this limits its application in LTCC.

In present work, different amounts of B_2O_3–CuO mixtures were chosen as sintering aids to lower the sintering temperature of $BiSbO_4$ ceramics. The influences of sintering temperature and the addition of B_2O_3–CuO mixtures on the sintering behavior, crystalline phases, microstructure and the microwave dielectric properties of $BiSbO_4$ ceramics are studied.

2. Experimental

Appropriate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China) and Sb_2O_3 (>99%, Guo-Yao Co., Ltd., Shanghai, China) were mixed, according to the composition of $BiSbO_4$, and ball-milled for 4 h using a planetary mill (Nanjing Machine Factory, China) by setting the running speed at 150 rpm with the Zirconia balls

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0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2008.08.024

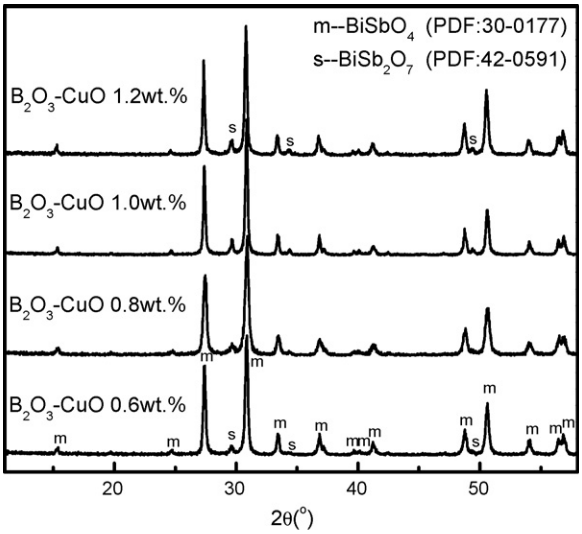

Fig. 1. XRD patterns of $BiSbO_4$ ceramics sintered at 930 °C for 2 h with different B_2O_3–CuO additions.

(2 mm in diameter) as milling media. After drying, mixed powders were calcined at 600 and 750 °C for 4 h respectively. The calcined $BiSbO_4$ powder was mixed with x wt.% B_2O_3–CuO mixtures (mass ratio of B_2O_3 to CuO was 1:1 and x = 0.6, 0.8, 1.0 and 1.2, samples were named BC06, BC08, BC10 and BC12, respectively). After being milled for 5 h again by setting the running speed at 200 rpm and dried, powders were uniaxially pressed into pellets of 10 mm diameter and 5 mm thickness with proper PVA addition. The pellets then were sintered at temperatures between 840 and 990 °C for 2 h in air.

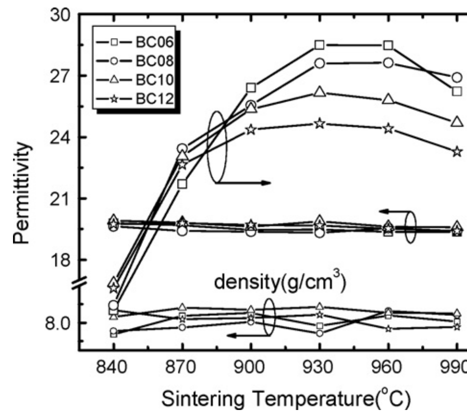

Fig. 3. Bulk densities and microwave dielectric properties of $BiSbO_4$ ceramics with different B_2O_3–CuO additions as a function of sintering temperature.

Crystalline structures of ceramics were investigated using an X-ray diffractometry with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Apparent densities of ceramics were measured using Archimedes' method. The fracture surfaces of ceramics were investigated by scanning electron microscopy (JSM-6460, JEOL, Tokyo, Japan). Microwave dielectric behaviors were measured by the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficients of resonant frequency TCF were calculated by the following formula:

$$\mathrm{TCF} = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (1)$$

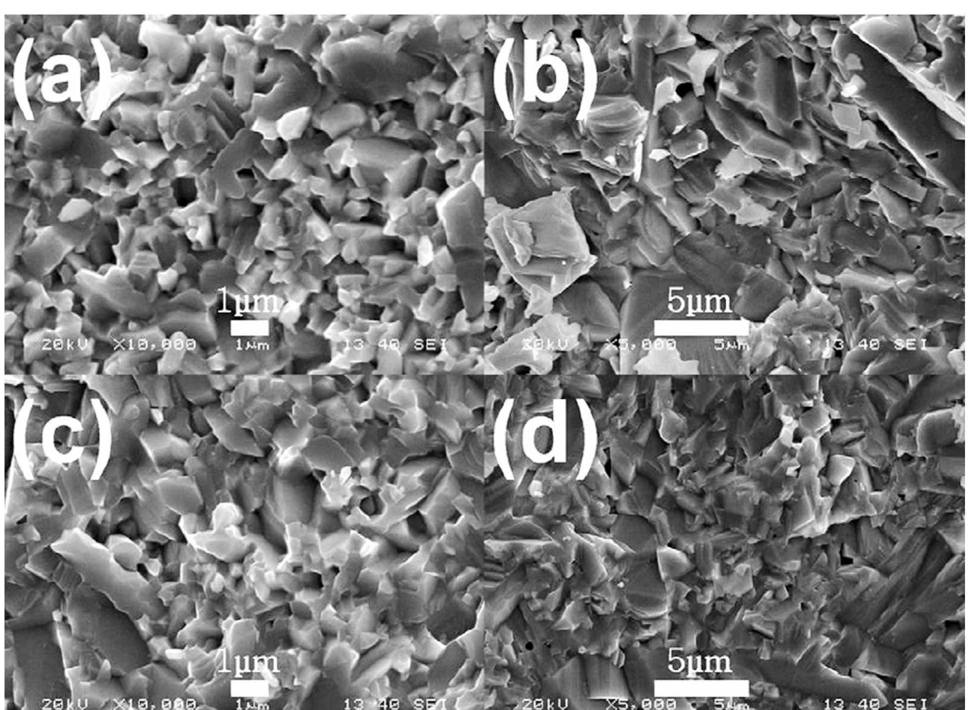

Fig. 2. SEM micrographs of fractured surface of BC06 ceramics sintered at 840 °C/2 h (a), 930 °C/2 h (b) and BC12 ceramics sintered at 840 °C/2 h (c), 930 °C/2 h (d).

Table 1
Microwave dielectric properties and densities of $BiSbO_4$ ceramics with B_2O_3–CuO addition sintered at 930 °C and pure $BiSbO_4$ ceramics[18] sintered at 1080 °C

B_2O_3–CuO (wt.%)	Density (g/cm^3)	Permittivity	Qf values (GHz)	TCF (ppm/°C)
0	–	19.3	70,000	−62
0.6	8.04	19.47	45,405	−66.2
0.8	8.04	19.32	42,674	−64.9
1.0	8.09	19.87	38,303	−65.5
1.2	8.04	19.67	33,717	−66.1

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

3. Results and discussions

X-ray diffraction (XRD) patterns of $BiSbO_4$ ceramics sintered at 930 °C for 2 h with different B_2O_3–CuO additions are shown in Fig. 1. The main phase in all samples was indexed as a single-phase of monoclinic $BiSbO_4$ (PDF: 30-0177). Several weak peaks of second phase could also be found in XRD patterns. The second phase might be $BiSb_2O_7$ (PDF: 42-0591) and its amount increased as the addition amount of B_2O_3–CuO increased.

The scanning electron microscopy (SEM) micrographs of fractured surface of $BiSbO_4$ ceramics with different B_2O_3–CuO additions are shown in Fig. 2. Fine dense microstructures could be observed in all $BiSbO_4$ ceramics. Grains sizes of $BiSbO_4$ ceramics sintered at 840 °C/2 h were all around 1–2 μm. Grains sizes increased to about 2–5 μm when sintering temperature increased to 930 °C. It was obvious that grain size of BC12 ceramics was smaller than that of BC06 ceramics as shown in Fig. 2(b) and (d). This indicated more addition of B_2O_3–CuO can restrain the further growth of grain. Although second phase was revealed by XRD analysis, grains of second phase could not be observed clearly because that its amount was too little.

Fig. 3 shows the bulk densities and microwave dielectric properties of $BiSbO_4$ ceramics with different B_2O_3–CuO additions as a function of sintering temperature. Pure $BiSbO_4$ can be well densified above 990 °C and its best microwave dielectric properties can be obtained in ceramic sintered at around 1050 °C according to our previous work.[18] Its theoretical density was 8.459 g/cm^3 as reported by Kennedy.[20] For all samples in this work sintered in the temperature range from 840 to 990 °C, densities always maintained between 7.96 and 8.08 g/cm^3 and this means all the samples reached dense. This result indicated that small amount of B_2O_3–CuO additions can efficiently lower the sintering temperature of $BiSbO_4$ ceramic to below 990 °C.

For all samples, in the whole temperature range from 840 to 99 °C, the microwave dielectric constant kept about 19.5 which were similar to that of pure $BiSbO_4$ ceramic. Qf values of samples increased remarkably as the sintering temperature increased first and then reached their saturated values at about 930 °C. The dielectric loss at microwave frequency is mainly caused by the anharmonic terms from various kinds of defects. It is known that the grain boundaries act as two-dimensional defects and may contribute significantly into the extrinsic dielectric loss.[21] When sintering temperature increased, grains size increased remarkably as shown in Fig. 2 and the total number of the grain boundaries decreases. Then Qf values would increase because of a reduction in the number of grain boundaries per unit volume. As B_2O_3–CuO additions increased from 0.6 to 1.2 wt.%, Qf values of $BiSbO_4$ ceramic sintered at 930 °C for 2 h decreased from 45,405 to 33,717 GHz (at around 8.3 GHz) and this might be attributed to both the increase of second phase and smaller grains mentioned above. The best microwave dielectric properties of $BiSbO_4$ ceramics sintered at 930 °C and their densities are listed in Table 1. This result indicates that while efficiently lowering sintering temperature of $BiSbO_4$ ceramic, B_2O_3–CuO additions did not deteriorate the microwave dielectric properties seriously and made $BiSbO_4$ ceramic possible for LTCC technology.

4. Conclusion

Additions of B_2O_3–CuO can efficiently lower the sintering temperature of $BiSbO_4$ ceramic from about 1050 °C to below 960 °C. Microwave dielectric constant of $BiSbO_4$ ceramics with x wt.% B_2O_3–CuO (x = 0.6, 0.8, 1.0, 1.2) addition kept between 19.3 and 19.7 in the temperature range from 840 to 990 °C. Qf values were influenced remarkably by the sintering temperature because of the numbers of grain boundaries decreased as temperature increased. As addition amount of B_2O_3–CuO increased from 0.6 to 1.2 wt.%, Qf values decreased from 45,405 to 33,717 GHz because of the increase of second phase. The best microwave dielectric properties were obtained in the $BiSbO_4$ ceramic with 0.6 wt.% addition sintered at 930 °C for 2 h with permittivity about 19.47, Qf value about 45,405 GHz and TCF value about −66.2 ppm/°C.

Acknowledgements

This work was supported by the National 973-project of China (2002CB613302), National 863-project of China (2006AA03Z0429), NSFC project of China (50572085) and NCET-05-0840.

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