Phase evolution and microwave dielectric properties of Bi_3SbO_7 ceramic

Li-Xia Pang [a,*], Di Zhou [b], Hong Wang [b], Ying Wu [b], Jing Guo [b], Yue-Hua Chen [b]

[a] *Laboratory of Thin Film Techniques and Optical Test, Xi'an Technological University, No. 4, Jin Hua North Road, Xi'an 710032, China*
[b] *Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China*

ABSTRACT

The Bi_3SbO_7 ceramic was prepared by the solid state reaction method and its phase evolution at different temperatures was studied. Low temperature phase α-Bi_3SbO_7 was formed at about 890 °C and it started to transform to high temperature phase β-Bi_3SbO_7 at about 960 °C. Microwave dielectric constants of α-Bi_3SbO_7 ceramic and β-Bi_3SbO_7 ceramic were 43.2 and 37.6, Qf value were 2080 and 5080 GHz, respectively. TCF of α-Bi_3SbO_7 ceramic was near zero and TCF of β-Bi_3SbO_7 ceramic was about −120 ppm/°C. The Bi_3SbO_7 ceramic is a promising candidate for low temperature co-fired ceramic (LTCC) technology due to its large dielectric constant, low dielectric loss at microwave region, low sintering temperature and simple composition.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The development of multilayer microwave chips and devices demands dielectric materials with large dielectric constant (ε_r), high quality value (Q), near zero temperature coefficient of resonant frequency (TCF) and sintering temperatures (T_s) lower than the melting point of common metal electrode materials, such as Ag, Cu, Al, etc., in order to use low temperature co-fired ceramic (LTCC) technology to produce chips with internal electrodes. Most dielectric ceramics with good microwave dielectric properties have relative high sintering temperature. Addition of sintering aids with low melting temperatures is an effective method to lower the firing temperature of ceramics. Recently many new simple binary or ternary compounds with low densification temperature have been found to possess good microwave dielectric properties and they have attracted more and more attention [1–4].

Bismuth-based dielectric ceramics are well-known as low-fired materials and have been investigated for the application as multi-layer capacitors [5–9]. Besides Bi_2O_3–Nb_2O_5 binary system and Bi_2O_3–(Zn,Ca)O–Nb_2O_5 ternary system, monoclinic $BiSbO_4$ in Bi_2O_3–Sb_2O_3 system was also found to be a promising candidate for LTCC and some modifications of $BiSbO_4$ ceramic have been done [10,11] and being done in our recent work. In fact as early as about twenty years ago, many works have investigated the solid state reactions and phase diagram of the binary system of Bi_2O_3–Sb_2O_3 [12–18]. In this binary system, some original

stoichiometric compounds such as $BiSbO_4$, $(Bi,Sb)SbO_4$, $Bi_5Sb_2O_{12.5}$, Bi_3SbO_7 and Sb_3BiO_7 are known to occur, in which $BiSbO_4$ and Bi_3SbO_7 compositions have been studied more broadly than others for their potential application in photocatalyst and dielectric resonator fields [10,11,19–22]. $BiSbO_4$ is known to crystallize in monoclinic symmetry and Bi_3SbO_7 exists in two polymorphs: the low-temperature polymorph (α) has a triclinic structure, and the high-temperature one (β) has an orthorhombic structure. According to Tairi et al. [17] and Manier et al. [21] the polymorphic transformation occurs at about 1030 °C. As shown by X-ray photoelectron spectroscopy (XPS) [20], the antimony in Bi_3SbO_7 is in its highest oxidation state, 5^+. The XPS data reported by Schuhl et al. [23] and the isomorphism of $BiSbO_4$ and β-Sb_2O_4, a mixed oxide of Sb^{3+} and Sb^{5+} [24–26], give grounds to expect that the antimony in $BiSbO_4$ is also presented in the form of Sb^{5+}. Bi_3SbO_7 melts congruently at a temperature close to about 1120 °C. Its high temperature β phase can be stabilized in the metastable state by quenching. Manier et al. [21] studied the microwave dielectric properties of Bi_3SbO_7 ceramics (relative density between 93.7% and 94.8%) prepared by solid state reaction method and co-precipitate method in detail. Their results showed that the low-temperature polymorph α-Bi_3SbO_7 ceramic was a good candidate for dielectric resonator having a dielectric constant between 34.6 and 42.1 and microwave dielectric losses lied between 5×10^{-4} and 7×10^{-4} while temperature coefficient of resonant frequency shifting between −31.3 and −88 ppm/°C (at resonant frequency about 6.6–7.3 GHz). In the present study, phase evolution of Bi_3SbO_7 composition versus sintering temperature under air atmosphere and the relationship between phase and microwave dielectric properties have been studied.

---

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (> 99%, Cheng Du of China) and Sb_2O_3 (three kinds of starting materials were used to repeat all the experimental results, > 99%, Guo-Yao Co. Ltd., Shanghai, China; > 99%, Xi'an Chemical Reagent, Xi'an, China; > 99%, Fuchen Chemical Reagents, Tianjin, China) were prepared according to the composition Bi_3SbO_7. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the zirconia balls (2 mm in diameter) as milling media. To investigate the phase evolution, some of the mixed powders were calcined at different temperatures in the range from 500 to 1070 °C for 2 h, respectively. In order to investigate the microwave dielectric properties of Bi_3SbO_7 ceramics, other powders were calcined at 600 and 700 °C for 4 h, respectively, first to fulfill thorough oxidation from Sb_2O_3 to Sb_2O_5. After being crushed and re-milled for 5 h using ZrO_2 balls and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die under uniaxial pressure of 20 kN/cm^2 with PVA binder addition. Then samples were sintered from 860 to 1070 °C for 2 h and naturally cooled down to room temperature under air atmosphere (the natural cooling rate of the furnace used here was about 10 °C/min when temperature is above 800 °C. When temperature is below 800 °C, the cooling rate becomes very slow about lower than 5 °C/min).

The crystalline structures of samples (ground powders of the sintered ceramics) were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan) and using ground powders. The apparent densities of sintered ceramics were measured by Archimedes' method. Dielectric behaviors at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, Poway, U.S.A.). The temperature coefficient of resonant frequency (TCF) was calculated by the following formula:

$$TCF = \frac{f_{85} - f_{25}}{f_{25}(85-25)} \times 10^6 (ppm/°C) \tag{1}$$

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

3. Results and discussion

Fig. 1 shows the XRD patterns of $3Bi_2O_3$–Sb_2O_3 samples calcined and sintered at different temperatures for 2 h. After calcined at 500 °C for 2 h, Sb_2O_3 was first oxygenized to Sb_2O_4. Then a new single phase seemed to be formed at 600 °C. Peaks of this phase were similar to that of cubic Bi_3NbO_7 and Bi_3TaO_7 [27,28]. It was not stable and easy to transform to other phases when temperature increased. Low temperature phase of Bi_3SbO_7 was formed at about 890 °C and strong peaks could be observed in well crystalloid ceramic sintered at 920 °C as shown in Fig. 1. When sintering temperature was above 960 °C, low temperature phase α-Bi_3SbO_7 began to transform to high temperature phase β-Bi_3SbO_7 gradually. At around 1020 °C, pure high temperature phase β-Bi_3SbO_7 was obtained. This result was similar to that reported by Tairi et al. [17], Manier et al. [21] and Dinnebier et al. [24]. The clear course of phase transformation in Bi_3SbO_7 ceramic were first shown in this work. Different starting materials had a little influence on the phase transformation temperature but the trend was always the same.

Apparent densities of Bi_3SbO_7 ceramics as a function of sintering temperature are shown in Fig. 2. As sintering temperature increased from 900 to about 980 °C, apparent density increased from about 8.37 to 8.65 g/cm^3 because of both
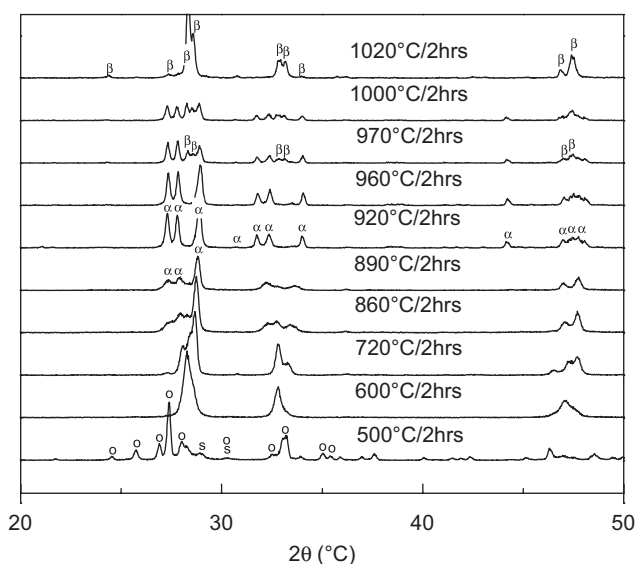

Fig. 1. XRD patterns of $3Bi_2O_3$–Sb_2O_3 samples calcined and sintered at different temperatures for 2 h (α-Bi_3SbO_7 (PDF: 45-0925), β-Bi_3SbO_7 (PDF: 39-0979), o-Bi_2O_3, s-Sb_2O_4).
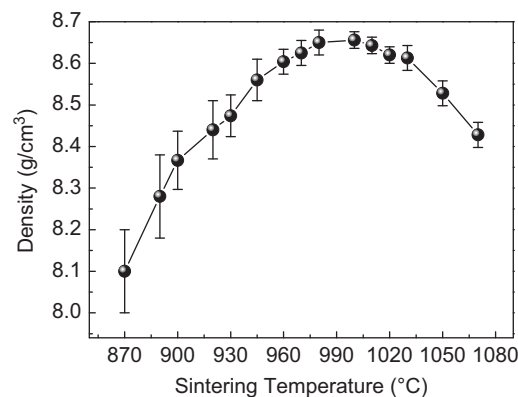

Fig. 2. Apparent density of Bi_3SbO_7 ceramics as a function of sintering temperature.

pores being eliminated and phase transformation from α-Bi_3SbO_7 to β-Bi_3SbO_7 gradually. Theoretical density of pure α-Bi_3SbO_7 and β-Bi_3SbO_7 are 8.738 and 8.958 g/cm^3, respectively [17]. Measured density of α-Bi_3SbO_7 ceramic sintered at 960 °C was about 8.60 g/cm^3, which is equivalent to a relative density of about 98% of the theoretical density. Measured density of β-Bi_3SbO_7 ceramic sintered at 1020 °C was about 8.61 g/cm^3 and its relative density of about 96%. When sintering temperature increased above 1000 °C, bismuth volatilization should be accounted to the decrease of density. It must be pointed out that different starting materials would affect the Bi-loss very much and serious volatilization of bismuth at high temperature would cause the nonstoichiometry in samples. Microstructures of Bi_3SbO_7 ceramics sintered at different temperatures are shown in Fig. 3. It is seen that dense microstructure can be observed for Bi_3SbO_7 ceramics sintered in the temperature range 960–1000 °C with almost no pores. In this temperature range, the Bi_3SbO_7 ceramics are composites of both α and β phases. Unfortunately, although it seems that there are more than one kind of shape for the grains, the different grains cannot be separated from the back scattering electron images due to the same composition. It is clear that the grain size increases with the sintering temperature.
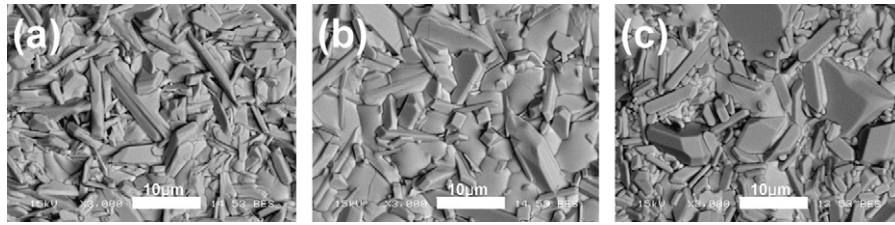
Fig. 3. BEI of Bi_3SbO_7 ceramics sintered at 960 °C/2 h (a), 980 °C/2 h (b) and 1000 °C/2 h (c).

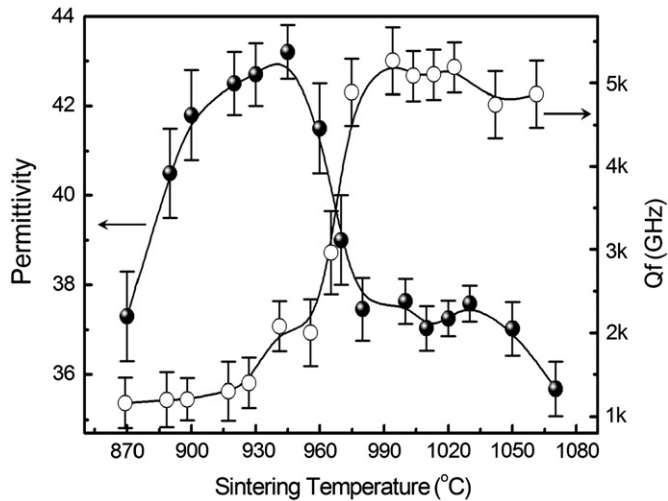**Fig. 4.** Microwave permittivity and Qf values of Bi_3SbO_7 ceramics as a function of sintering temperature (several samples prepared by different starting Sb_2O_3 and sintered at the same temperature were measured to calculate the error bar).

Fig. 5. Temperature coefficient of resonant frequency (TCF) of Bi_3SbO_7 ceramics as a function of sintering temperature.

Table 1
Comparison of microwave dielectric properties of Bi_3SbO_7 ceramics reported in this work and Manier et al.'s work.

Phase composition	Resonant frequency (GHz)	Dielectric permittivity	Q value	Qf value (GHz)	TCF (ppm/°C)	Reference
–	6.6457	42.1	1426	9480	−31.3	[21]
–	6.618	41.6	1426	9440	−32	[21]
α-Bi_3SbO_7	5.625	43.2	370	2078	0	This work
β-Bi_3SbO_7	5.914	37.6	860	5080	−120	This work

Microwave dielectric properties of Bi_3SbO_7 ceramics as a function of sintering temperature are shown in Fig. 4. Resonant frequency lied between 5.6 and 6.4 GHz. Microwave permittivity first reached saturated value about 43.2 at 945 °C and at this temperature only pure α-Bi_3SbO_7 was revealed from XRD analysis. Qf value of α-Bi_3SbO_7 ceramic was about 2080 GHz. After α-Bi_3SbO_7 transformed to β-Bi_3SbO_7, permittivity decreased to about 37.6 and Qf values increased to about 5080 GHz for ceramics sintered around 1020 °C. To the best of our knowledge, this is the first time to distinguish the microwave dielectric properties of α-Bi_3SbO_7 and β-Bi_3SbO_7. Permittivity reported here had the similar value to that reported by Manier et al. [21] but the Qf values were a little smaller than their results (dielectric loss between 5×10^{-4} and 7×10^{-4}, resonant frequency between 6.6 and 7.3 GHz) as shown in Table 1. Temperature coefficients of resonant frequency TCF of Bi_3SbO_7 ceramics as a function of sintering temperature are shown in Fig. 5. When sintering temperature was lower than 960 °C, TCF values of α-Bi_3SbO_7 were shifting between +4 and −22 ppm/°C and the absolute
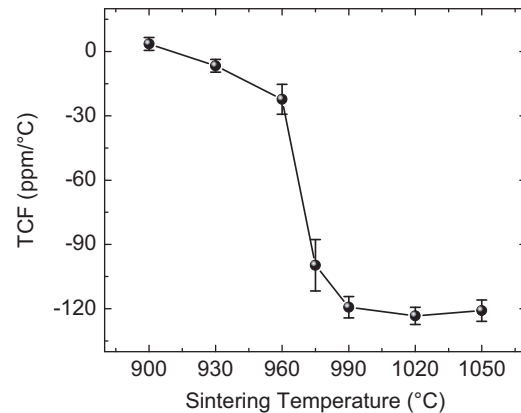
values were not very large. When sintering temperature was above 960 °C, β-Bi_3SbO_7 occurred and TCF values sharply decreased to near −120 ppm/°C and became stable as temperature increased further.

4. Conclusions

Low temperature phase α-Bi_3SbO_7 could be formed at about 890 °C. It gradually transformed to the high temperature phase β-Bi_3SbO_7 when temperature was above 960 °C and pure β-Bi_3SbO_7 could be obtained at around 1020 °C. Microwave dielectric constants of α-Bi_3SbO_7 ceramic and β-Bi_3SbO_7 ceramic were 43.2 and 37.6, Qf values were 2078 and 5080 GHz, respectively. TCF of α-Bi_3SbO_7 ceramic was near zero and TCF of β-Bi_3SbO_7 ceramic was about −120 ppm/°C. The Bi_3SbO_7 ceramic might be a candidate for LTCC technology.

References

[1] M.T. Sebastian, H. Jantunen, Int. Mater. Rev. 53 (2008) 57.
[2] M. Valant, D. Suvorov, R.C. Pullar, K. Sarma, N.M. Alford, J. Eur. Ceram. Soc. 26 (2006) 2777.
[3] R.R. Tummala, J. Am. Ceram. Soc. 74 (1991) 895.
[4] H. Jantunen, T. Kangasvieri, J. Vähäkangas, S. Leppävuori, J. Eur. Ceram. Soc. 23 (2003) 2541.
[5] H.C. Ling, M.F. Yan, W.W. Rhodes, J. Mater. Res. 5 (1990) 1752.
[6] M.A.L. Nobre, S. Lanfredi, J. Phys. Chem. Solids 64 (2003) 2457.
[7] D.H. Liu, Y. Liu, S.Q. Huang, X. Yao, J. Am. Ceram. Soc. 76 (1993) 2129.
[8] H.L Du, X. Yao, J. Phys. Chem. Solids 63 (2002) 2123.
[9] H. Kagata, T. Inoue, J. Kato, I. Kameyama, Jpn. J. Appl. Phys. 31 (1992) 3152.
[10] D. Zhou, H. Wang, X. Yao, L.X. Pang, J. Am. Ceram. Soc. 91 (2008) 1380.
[11] D. Zhou, H. Wang, X. Yao, L.X. Pang, J. Am. Ceram. Soc. 91 (2008) 2228.

[12] H.T. Cahen, T.G.M. Van Den Belt, J.H.W. De Wit, G.H.J. Broers, Solid State Ionics 1 (1980) 411.
[13] V.B. Chernogorenko, I.G. Donets, A.A. Semenov-Kobzar, I.V. Kursenko, L.V. Doncheva, Ukr. Khimiski Zh. 43 (1977) 1058.
[14] B.J. Kennedy, Powder Diffr. 9 (1994) 164.
[15] O. Türkoğlu, M. Soylak, N. Külcü, Kuwait J. Sci. Eng. 26 (1999) 289.
[16] B. Aurivillius, Ark. Kemi 3 (1951) 153.
[17] A. Tairi, J.C. Champarnaud-Mesjard, D. Mercurio, B. Frit, Rev. Chim. Miner. 22 (1985) 699.
[18] J.K. Liang, Y.L. Zhang, X. Fang, Diwen Wuli Xuebao 14 (1992) 161.
[19] X.P. Lin, F.Q. Huang, W.D. Wang, K.L. Zhang, Appl. Catal. A: Gen. 307 (2006) 257.
[20] X.P. Lin, F.Q. Huang, W.D. Wang, Z.C. Shan, J.L. Shi, Dyes Pigm. 78 (2008) 39.
[21] M. Manier, J.P. Mercurio, D. Mercurio, B. Frit, J. Phys. Colloq. 47 (1986) Cl. 907.
[22] H.L. Du, X. Yao, J. Phys. Chem. Solids 63 (2002) 2123.
[23] Y. Schuhl, H. Baussart, R. Delobel, J. Chem. Soc. Faraday Trans. 1 (79) (1983) 2055.
[24] R.E. Dinnebier, R.M. Ibberson, H. Ehrenberg, M. Jansen, J. Solid State Chem. 163 (2002) 332.
[25] D. Stewart, O. Knop, C. Ayasse, Can. J. Chem. 50 (1972) 690.
[26] R. Izquierdo, E. Sacher, A. Yelon, Appl. Surf. Sci. 40 (1989) 175.
[27] C.D. Ling, M. Johnson, J. Solid State Chem. 177 (2004) 1838.
[28] D. Zhou, H. Wang, X. Yao, L.X. Pang, Mater. Chem. Phys. 110 (2008) 212.