



Sintering behavior, phase evolution and microwave dielectric properties of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics

Di Zhou, Hong Wang*, Xi Yao, Li-Xia Pang, Yue-Hua Chen

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:

Received 2 April 2008

Received in revised form 5 July 2008

Accepted 17 July 2008

Keywords:

BiSbO_4

BiNbO_4

Microwave dielectric

ABSTRACT

$\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ compositions were designed with $0.05 \leq x \leq 0.4$ and ceramics were prepared using solid state reaction method. All ceramics were well densified when sintering temperature was above 960°C . Single monoclinic phase was obtained when x value was less than 0.2 and $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramic was composed of both monoclinic phase and orthorhombic phase. As x value increased from 0.05 to 0.2, microwave dielectric constant of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics increased from 22.1 to 31.4 while Q_f value decreasing from 41000 GHz to 8000 GHz and TCF shifting from $-54.4 \text{ ppm } ^\circ\text{C}^{-1}$ to $+8 \text{ ppm } ^\circ\text{C}^{-1}$. $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramic has also good microwave dielectric properties with dielectric constant about 34.7, Q_f value about 16000 GHz and TCF about $+16.1 \text{ ppm } ^\circ\text{C}^{-1}$. This kind of ceramics might be a good candidate for LTCC application.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Microwave dielectric materials have to possess dielectric characteristics [1–3] such as high dielectric constant (ϵ_r), high quality factor (Q), and stable temperature coefficient of the resonant frequency ($\text{TCF}/\tau_f \approx 0 \text{ ppm } ^\circ\text{C}^{-1}$). Recently, varieties of low-temperature sintered microwave dielectric ceramics which could be co-fired with high conductivity metals such as Ag or Cu have been studied for the fabrication of multilayer microwave devices. Therefore, much attention has been paid to develop the low-temperature co-fired ceramics (LTCC). Generally speaking, high dielectric constant (ϵ_r), high quality factor (Q), near zero TCF and low sintering temperature were strongly required for LTCC application [4–7].

Bismuth-based dielectric ceramics are well-known as low-fired materials and have been investigated for the application as multilayer capacitors [8,9]. In $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ systems BiNbO_4 has attracted much attention because of its good sintering behavior (well densified below 960°C with a small amount of CuO , WO_3 or V_2O_5 addition) and excellent microwave dielectric properties with dielectric constant ϵ_r about 43, Q_f value about 5000–20000 GHz and TCF value about -20 to $+20 \text{ ppm } ^\circ\text{C}^{-1}$ [4,7,10–13]. Considering the similar ion radii and characteristic of Ta^{5+} , Sb^{5+} and Nb^{5+} , Wang et al. ever used Ta^{5+} and Sb^{5+} to substitute Nb^{5+} in BiNbO_4 and pure orthorhombic phase of $\text{BiNb}_{1-x}(\text{Ta,Sb})_x\text{O}_4$ could be obtained

at $0 \leq x \leq 0.4$ [14,15]. In our previous work, pure BiSbO_4 ceramics with monoclinic structure were synthesized via solid state reaction method and good microwave dielectric properties were obtained in ceramics sintered at 1080°C with dielectric constant about 19, Q_f values about 70000 GHz and TCF about $-62 \text{ ppm } ^\circ\text{C}^{-1}$. It was found that after co-firing with 20 wt.% Ag at 900°C for 5 h only very little unknown phase consisting of a little Ag was formed, and most Ag was scattered in the grain boundaries. BiSbO_4 ceramics might be a good candidate for LTCC application [16]. BiSbO_4 has also been reported in detail as novel p-block metal oxide, possessing a visible light response for the photocatalytic degradation of methylene blue, by Lin et al. [17]. Considering potential value in various application of monoclinic phase of BiSbO_4 , it is necessary and meaningful to do some initial study to modify its physical and chemical properties. In this work, Nb^{5+} was used to substitute Sb^{5+} in monoclinic BiSbO_4 . Considering that substitution of V_2O_5 could lower sintering temperature efficiently [4,7,18], $\text{Bi}(\text{Nb}_{0.992}\text{V}_{0.008})\text{O}_4$ composition was used as the starting material to mix with BiSbO_4 . $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ compositions were designed with $0.05 \leq x \leq 0.4$. Sintering behavior, phase evolution and microwave dielectric properties of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics were studied and their relationship was also discussed in detail.

2. Experimental procedure

BiSbO_4 and $\text{Bi}(\text{Nb}_{0.992}\text{V}_{0.008})\text{O}_4$ powder compositions were prepared using solid state reaction method, respectively. The starting materials were Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., China), Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co., Ltd., China), Sb_2O_3 and V_2O_5 (>99%, Guo-Yao Co., Ltd., China). After being milled for 4.5 h with ZrO_2 balls using ethanol, mixed powders were calcined at 500°C and 750°C for 4 h continuously. According to the compositions $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ($x=0.05$,

* Corresponding author. Fax: +86 29 82668794.

E-mail address: hwang@mail.xjtu.edu.cn (H. Wang).

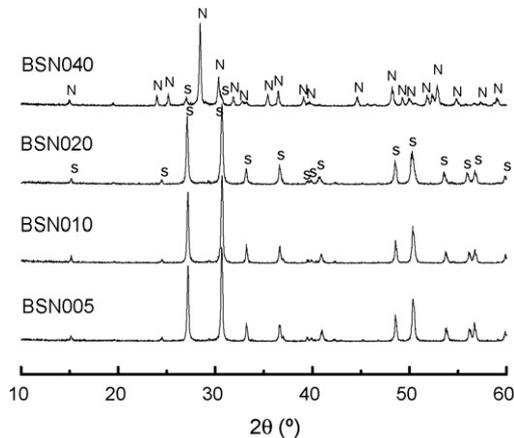


Fig. 1. XRD patterns of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics sintered at 990°C for 2 h (S-monoclinic phase of $\text{Bi}(\text{Sb,Nb})\text{O}_4$, N-orthorhombic phase of $\text{Bi}(\text{Nb,Sb})\text{O}_4$).

0.1, 0.2, 0.4; samples were named BSN005, BSN010, BSN020 and BSN040, respectively), BiSbO_4 and $\text{Bi}(\text{Nb}_{0.992}\text{V}_{0.008})\text{O}_4$ powders were mixed and ball-milled for 5 h again. Final mixed 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 960°C and 1050°C for 2 h in air.

After surface polished, crystalline structures of samples were investigated using an X-ray diffractometry with $\text{Cu K}\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). Apparent densities of ceramics were measured using Archimedes' method. The polished surfaces of ceramics were investigated by scanning electron microscopy (JEOL JSM-6460, Japan) after thermal etching at 850°C for 30 min in air. Dielectric behaviors at microwave frequency were measured by the TE_{018} shielded cavity method with a network analyzer (8720ES, Agilent, USA) and a temperature chamber (Delta Design 9023, USA). The temperature coefficients of resonant frequency TCF was calculated by the following formula:

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

where f_{85} and f_{25} were the TE_{018} resonant frequencies at 85°C and 25°C , respectively.

3. Results and discussions

XRD patterns of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics sintered at 990°C for 2 h were illustrated in Fig. 1. When x value was smaller than 0.4, Nb^{5+} could absolutely substitute Sb^{5+} in monoclinic phase BiSbO_4 and form the solid solution $\text{Bi}(\text{Sb,Nb})\text{O}_4$. When x increased to 0.4, main phase was indexed as orthorhombic phase of $\text{Bi}(\text{Nb,Sb})\text{O}_4$ and only very weak peaks of monoclinic phase could be observed. As reported by Wang [14], when x increased to 0.6, $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ would appear as pure orthorhombic phase. It indicates that orthorhombic phase has broader tolerance region than monoclinic phase in BiSbO_4 – BiNbO_4 binary system.

Fig. 2 shows the apparent density of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics as a function of sintering temperature. Ceramics got their saturated density when sintering temperature was above 990°C for $x = 0.05$ and $x = 0.1$. $\text{Bi}\{\text{Sb}_{0.8}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.2}\}\text{O}_4$ ceramic could be well densified at temperature of 960°C . As x value increased from 0.05 to 0.20, density of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics decreased from about 8.15 g cm^{-3} to 8.00 g cm^{-3} because of the smaller atom weight of $(\text{Nb}_{0.992}\text{V}_{0.008})^{5+}$ than Sb^{5+} . $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramic could also be well densified at temperature of 960°C but its density sharply decreased to about 7.65 g cm^{-3} due to both the substitution of Nb^{5+} for Sb^{5+} and the appearance of orthorhombic phase (pure orthorhombic BiNbO_4 has a density of 7.345 g cm^{-3}). All the relative densities of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics were above 96% (density of pure BiSbO_4 is 8.459 g cm^{-3}) [19].

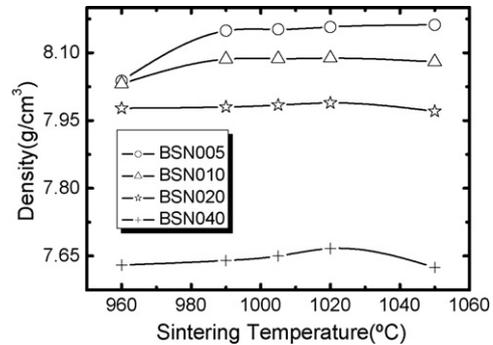


Fig. 2. Apparent density of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics as a function of sintering temperature.

SEM micrographs of polished surface (after thermal etching) of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics sintered at 990°C for 2 h are shown in Fig. 3. Grains sizes of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics at $x = 0.05$ and $x = 0.10$ scattered evenly between $0.75 \mu\text{m}$ and $2 \mu\text{m}$. When x value increased to 0.20, many very small grains could be observed and the average grains sizes became smaller than $1 \mu\text{m}$. The size distribution of grains was broadened. $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramic was composed of both orthorhombic phase and monoclinic phase. Because of the similar composition of these two phases, no evident difference could be observed in SEM photos as shown in Fig. 3(d). Grain size of $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramic lied between $1.5 \mu\text{m}$ and $2 \mu\text{m}$.

Microwave dielectric properties of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics as a function of x value are shown in Fig. 4. Pure BiSbO_4 has the ϵ_r of about 19 as reported in our previous work [16]. Dielectric constant of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics increased from about 22.1 to 34.7 as x value increased from 0.05 to 0.4. Considering that $(\text{Nb}_{0.992}\text{V}_{0.008})^{5+}$ had larger polarizability [20] than Sb^{5+} [21] and orthorhombic $\text{Bi}(\text{Nb}_{0.992}\text{V}_{0.008})\text{O}_4$ had a permittivity [4,18] about 43, the increase of ϵ_r versus x value could be attributed to both the substitution and structure transformation. Q_f values of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics first decreased from 41000 GHz to 8000 GHz as x value increased from 0.05 to 0.2 in the region of monoclinic phase. Main origin of dielectric loss is the anharmonic terms in the crystal's potential energy. Substitution of $(\text{Nb}_{0.992}\text{V}_{0.008})^{5+}$ increased the polarizability of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$, meanwhile the stronger oscillation of $(\text{Nb}_{0.992}\text{V}_{0.008})^{5+}$ than Sb^{5+} would introduce more intrinsic dielectric loss due to the contribution of increasing anharmonic terms [22]. This might be the main reason for the decrease of Q_f values as x value increase. Orthorhombic $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramics had the Q_f value about 16000 GHz, which was similar with that of orthorhombic BiNbO_4 [4,14].

The molecular dielectric polarizability α_x , which contains both ionic and electronic components, could be calculated from the dielectric constant and the molar volume, V_x in \AA^3 , using the Clausius–Mossotti relation:

$$\alpha_x = \frac{V_x \times (\epsilon_x - 1)}{b \times (\epsilon_x + 2)} \quad (2)$$

where b is assumed to be $4\pi/3$ for a cubic material and ϵ_x is the calculated dielectric constant of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$. Shannon, Subramanian et al. [20,23–27] pointed out that while this equation is strictly valid only for compounds where the molecule has cubic symmetry, it can also be used as a good approximation to many non-cubic materials.

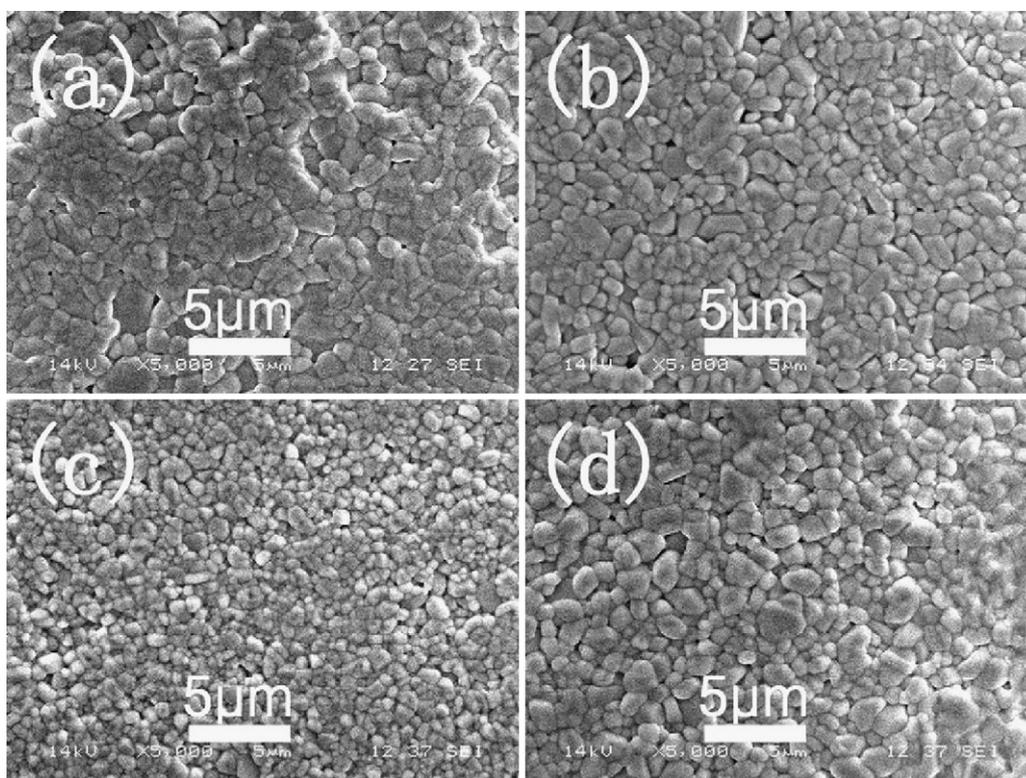


Fig. 3. SEM micrographs of polished surface (after thermal etching) of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics sintered at 990°C for 2 h ((a) $x=0.05$, (b) $x=0.10$, (c) $x=0.20$, and (d) $x=0.40$).

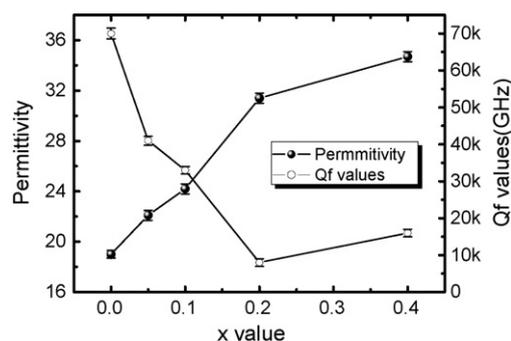


Fig. 4. Microwave dielectric constant ϵ_r and Q_f values of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics as a function of x value.

The dielectric polarizability for $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ follows the oxide additivity rule [28]:

$$\alpha_x = \alpha_{\text{Bi}^{3+}} + (1-x) \times \alpha_{\text{Sb}^{5+}} + x \times (0.992\alpha_{\text{Nb}^{5+}} + 0.008\alpha_{\text{V}^{5+}}) + 4\alpha_{\text{O}^{2-}} \quad (3)$$

where α_x is the total dielectric polarizability for the $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$, and $\alpha_{\text{Bi}^{3+}}$, $\alpha_{\text{Sb}^{5+}}$, $\alpha_{\text{Nb}^{5+}}$, $\alpha_{\text{V}^{5+}}$ and $\alpha_{\text{O}^{2-}}$ are the polarizabilities of Bi^{3+} , Sb^{5+} , Nb^{5+} , V^{5+} and O^{2-} , respectively. Using the Clausius–Mossotti relationship, polariz-

abilities as given by Shannon [20] ($\alpha_{\text{Bi}^{3+}} = 6.12 \text{ \AA}^3$, $\alpha_{\text{Nb}^{5+}} = 3.97 \text{ \AA}^3$, $\alpha_{\text{V}^{5+}} = 2.92 \text{ \AA}^3$ and $\alpha_{\text{O}^{2-}} = 2.01 \text{ \AA}^3$) and Tidrow [21] ($\alpha_{\text{Sb}^{5+}} = 1.18 \pm 0.49 \text{ \AA}^3$) and the cell volumes, the dielectric constant ϵ_{cal} of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ could be calculated and listed in Table 1 with measured microwave dielectric properties and relative density. The deviations from measured dielectric constant might be caused by the following possible reasons: 1, measurement errors; 2, influence of pores and phase compositions; 3, permanent dipole moments (ferroelectric or antiferroelectric materials) or “rattling” or “compressed” cations [20,27]. The influence of rattling cation was described by Dunitz et al. as a progressive “loosening of the central cation at the center of its surrounding octahedron to off-center displacements characteristic of ferroelectric and antiferroelectric substances” as the size of the central cation in an octahedron decreases [20,29]. Orthorhombic BiNbO_4 was believed to be antiferroelectric in the temperature range from 20°C to 360°C [30]. Its specific crystalline structure determined that its polarizability did not obey the oxide additivity rule. This could explain the large relative errors for orthorhombic $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ sample. In addition, the ionic polarizability used here are all empirical calculated from many series of oxides. High dielectric constant of many oxides must be attributed to their specific crystalline structure and atom positions. The work on the dielectric constant of ABO_4 systems will be studied further.

Table 1
Relative density and calculated dielectric constant of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics

x value	Density (g cm^{-3})	Relative density	ϵ_{meas}	ϵ_{cal}	Q_f (GHz)	TCF ($\text{ppm } ^\circ\text{C}^{-1}$)
0.05	8.15	0.970	22.1	19.33	41000	-54.4
0.10	8.09	0.966	24.2	20.13	33000	-46.2
0.20	8.00	0.968	31.4	21.69	8000	+8.0
0.40	7.65	0.984	34.7	19.00	16000	+16.1

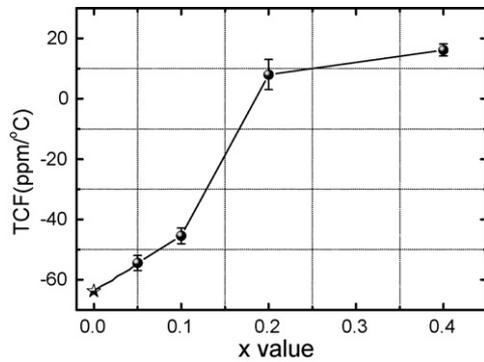


Fig. 5. Temperature coefficient of resonant frequency (TCF) of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics as a function of x values.

Fig. 5 shows the temperature coefficient of resonant frequency (TCF) of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics as a function of x values. The TCF of pure monoclinic BiSbO_4 was about $-62 \text{ ppm } ^\circ\text{C}^{-1}$ as reported in our previous work [16]. The TCF of $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics shifted from $-54.4 \text{ ppm } ^\circ\text{C}^{-1}$ to $+8 \text{ ppm } ^\circ\text{C}^{-1}$ as x value increased from 0.05 to 0.2 in the range of monoclinic solid solution. The TCF of $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ was about $+16.1 \text{ ppm } ^\circ\text{C}^{-1}$ because of its main phase was orthorhombic phase.

4. Conclusions

$\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics with $0.05 \leq x \leq 0.4$ were well prepared using solid state reaction method. All the ceramics could be well densified at the temperature above $990 \text{ } ^\circ\text{C}$. As x value increased from 0.05 to 0.2, single monoclinic phase was obtained and microwave dielectric constant increased from 22.1 to 31.4 while Q_f value decreasing from 41 kGHz to 8 kGHz and TCF shifting from $-54.4 \text{ ppm } ^\circ\text{C}^{-1}$ to $+8 \text{ ppm } ^\circ\text{C}^{-1}$. $\text{Bi}\{\text{Sb}_{0.6}(\text{Nb}_{0.992}\text{V}_{0.008})_{0.4}\}\text{O}_4$ ceramic was found to composed of both monoclinic phase and orthorhombic phase. It also had good microwave dielectric properties with dielectric constant about 34.7, Q_f value about 16 kGHz and TCF about $+16.1 \text{ ppm } ^\circ\text{C}^{-1}$. $\text{Bi}\{\text{Sb}_{1-x}(\text{Nb}_{0.992}\text{V}_{0.008})_x\}\text{O}_4$ ceramics might be a good candidate for LTCC application.

Acknowledgements

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

References

- [1] W. Wersing, High Frequency ceramic dielectrics and their application for microwave components, in: B.C.H. Steele (Ed.), *Electronic Ceramics*, Elsevier Applied Science, London, UK, 1991, pp. 67–119.
- [2] S. Nomura, Ceramics for microwave dielectric resonator, *Ferroelectrics* 49 (1983) 61–70.
- [3] H.M. O'Bryan Jr., J. Thomson Jr., J.K. Plourde, A new BaO-TiO_2 compound with temperature-stable high permittivity and low microwave loss, *J. Am. Ceram. Soc.* 57 (1974) 450–453.

- [4] 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.
- [5] J.H. Lee, Y.I. Jang, H.J. Youn, J.W. Jang, B.K. Kim, Low-firing and microwave dielectric properties of $\text{Ba}[(\text{Ni}_{0.6}\text{Zn}_{0.4})_{0.33}\text{Nb}_{0.67}\text{O}_3]$ ceramics doped with Sb_2O_5 and B_2O_3 , *J. Mater. Sci.* 34 (1999) 625–628.
- [6] C.L. Huang, R.J. Lin, J.J. Wang, Effect of B_2O_3 additives on sintering and microwave dielectric behaviors of CuO -doped ZnNb_2O_6 ceramics, *Jpn. J. Appl. Phys.* 41 (2002) 758–762.
- [7] W.C. Tzou, C.F. Yang, Y.C. Chen, P.S. Cheng, Improvements in the sintering and microwave properties of BiNbO_4 microwave ceramics by V_2O_5 addition, *J. Eur. Ceram. Soc.* 20 (2000) 991–996.
- [8] H.C. Ling, M.F. Yan, W.W. Rhodes, High dielectric constant and small temperature coefficient bismuth-based dielectric compositions, *J. Mater. Res.* 5 (1990) 1752–1762.
- [9] D.H. Liu, Y. Liu, S.Q. Huang, X. Yao, Phase structure and dielectric properties of $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ -based dielectric ceramics, *J. Am. Ceram. Soc.* 76 (1993) 2129–2132.
- [10] D. Zhou, H. Wang, X. Yao, Microwave dielectric properties and co-firing of BiNbO_4 ceramics with CuO substitution, *Mater. Chem. Phys.* 104 (2007) 397–402.
- [11] Ch.F. Yang, Improvement of quality value and shift of τ_f value of BiNbO_4 ceramics with addition of $\text{CuO-V}_2\text{O}_5$ mixtures, *Jpn. J. Appl. Phys.* 38 (1999) 6797–6800.
- [12] Ch.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.
- [13] D. Zhou, H. Wang, X. Yao, L.X. Pang, Microwave dielectric properties and co-firing of BiNbO_4 ceramics with CuO-WO_3 substitution, *Mater. Sci. Eng. B* 142 (2007) 106–111.
- [14] N. Wang, M.Y. Zhao, Z.W. Yin, The sintering behavior and microwave dielectric properties of $\text{Bi}(\text{Nb,Sb})\text{O}_4$ ceramics, *Ceram. Int.* 30 (2004) 1017–1022.
- [15] N. Wang, M.Y. Zhao, Z.W. Yin, Effects of Ta_2O_5 on microwave dielectric properties of BiNbO_4 ceramics, *Mater. Sci. Eng. B* 99 (2003) 238–242.
- [16] D. Zhou, H. Wang, X. Yao, L.X. Pang, Dielectric behavior and co-firing with silver of monoclinic BiSbO_4 ceramic, *J. Am. Ceram. Soc.* 91 (2008) 1380–1383.
- [17] X.P. Lin, F.Q. Huang, W.D. Wang, K.L. Zhang, A novel photocatalyst BiSbO_4 for degradation of methylene blue, *Appl. Catal. A: Gen.* 307 (2006) 257–262.
- [18] D. Zhou, H. Wang, X. Yao, Y. Liu, Microwave dielectric properties of low-firing BiNbO_4 ceramics with V_2O_5 substitution, *J. Electroceram.* doi:10.1007/s10832-007-9223-2.
- [19] B. Kennedy, X-ray powder diffraction study of BiSbO_4 , *Powder Diffraction* 9 (1994) 164–167.
- [20] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, *J. Appl. Phys.* 73 (1993) 348–366.
- [21] S.C. Tidrow, A. Tauber, W.D. Wilber, R.D. Finnegan, D.W. Eckart, W.C. Drach, Dielectric properties of perovskite antimonates, *IEEE Trans. Appl. Supercond.* 7 (2) (1997) 1769–1771.
- [22] H. Tamura, Microwave dielectric losses caused by lattice defects, *J. Eur. Ceram. Soc.* 26 (2006) 1775–1780.
- [23] R.D. Shannon, R.A. Oswald, T.H. All, J.P. Damen, D. Mateika, B.A. Wechsler, G.R. Rossman, Dielectric constants of YVO_4 , Fe-, Ge-, and V-containing garnets, the polarizabilities of Fe_2O_3 , GeO_2 , and V_2O_5 , and the oxide additivity rule, *J. Solid State Chem.* 95 (1991) 313–318.
- [24] M.A. Subramanian, Dielectric constant of Y-stabilized zirconia, the polarizability of zirconia and the oxide additivity rule, *Mater. Res. Bull.* 24 (1989) 1477–1483.
- [25] R.D. Shannon, G.R. Rossman, Dielectric constants of apatite, epidote, vesuvianite, and zoisite, and the oxide additivity rule, *Phys. Chem. Miner.* 19 (1992) 157–165.
- [26] R.D. Shannon, R.A. Oswald, J.B. Parise, B.H.T. Chai, P. Byszewski, A. Pajaczowska, R. Sobolewski, Dielectric constants and crystal structures of CaYAlO_4 , CaNdAlO_4 , and SrLaAlO_4 , and deviations from the oxide additivity rule, *J. Solid State Chem.* 98 (1992) 90–98.
- [27] V.J. Fratello, C.D. Brandle, Calculation of dielectric polarizabilities of perovskite substrate materials for high-temperature superconductors, *J. Mater. Res.* 9 (10) (1994) 2554–2560.
- [28] A. Heydweiller, Dichte, Dielektrizitätskonstante und Refraktion fester Salze, *Z. Phys.* 3 (1920) 308–317.
- [29] J.D. Dunitz, L.E. Orgel, Stereochemistry of ionic solids, *Adv. Inorg. Chem. Radiochem.* 2 (1960) 1.
- [30] V.I. Popolitov, A.N. Lobachev, V.F. Peskin, Antiferroelectrics, ferroelectrics and pyroelectrics of a stibiotantalite structure, *Ferroelectrics* 40 (1982) 9–16.