

# Sintering Behavior, Phase Evolution, and Microwave Dielectric Properties of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ Ceramics

Di Zhou, Hong Wang,<sup>†</sup> Xi Yao, and Li-Xia Pang

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

**Sintering behavior, phase evolution, and microwave dielectric properties of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics ( $0.05 \leq x \leq 0.60$ ) were studied and their relationships were discussed in detail. Phase studies revealed that a pure monoclinic phase could be formed when  $x \leq 0.20$  and a pure orthorhombic phase could be obtained when  $x \geq 0.50$ . As the  $x$  value increased from 0.05 to 0.60, the densified temperature of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics decreased from 1050° to about 960°C whereas the density increased from 8.07 to 8.41 g/cm<sup>3</sup>. The microwave dielectric constant increased from 20.5 to 34 whereas the  $Q \times f$  value decreased from 60 000 to 29 000 GHz. In the monoclinic phase region, the temperature coefficients of resonant frequency shifted linearly from -58 to -45 ppm/°C as the  $x$  value increased from 0.05 to 0.2 and then remained constant at about -12 ppm/°C when  $x \geq 0.40$ . The  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics are promising for application of low-temperature cofired ceramics technology.**

## I. Introduction

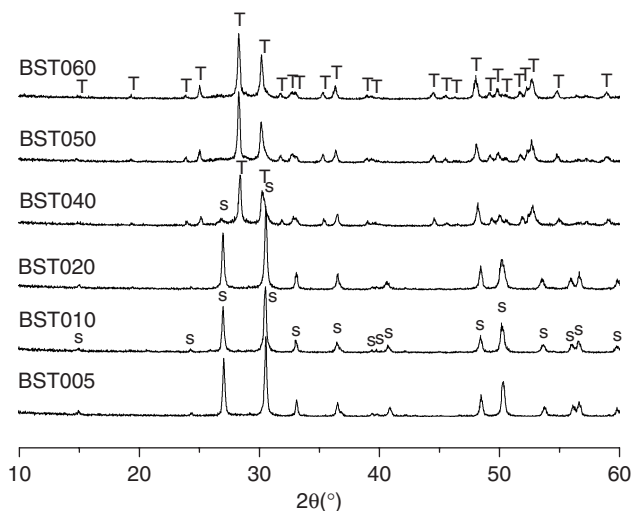
THE recent rapid progress in communications in microwave frequencies, such as portable phones and car telephones, has increased demand for the miniaturization of components such as band pass filters and local oscillators. Low-temperature cofired ceramic (LTCC) technology offers significant benefits over other established packaging technologies for high-density, high-RF, and fast digital applications requiring hermetical packaging and good thermal management.<sup>1,2</sup> In the fabrication of multilayer microwave devices, low-firing microwave dielectric materials with high dielectric constant ( $\epsilon_r$ ), low dielectric loss, and near-zero temperature coefficient of resonant frequency ( $\tau_f$ /TCF) are needed to cofire with low-loss, low-melting-point conductors such as Ag (melting point = 961°C) or Cu (1064°C).

Bismuth-based dielectric ceramics are well known as low-firing materials and have been investigated for their application as multilayer capacitors.<sup>3,4</sup> In  $\text{Bi}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$  systems,  $\text{BiNbO}_4$  has attracted much attention because of its good sintering behavior (could be well densified below 960°C with a small amount of  $\text{CuO}$ ,  $\text{WO}_3$ , or  $\text{V}_2\text{O}_5$  additives) and excellent microwave dielectric properties with dielectric constant ( $\epsilon_r$ ) about 43,  $Q \times f$  value about 5000–20 000 GHz, and TCF value about -20 to +20 ppm/°C.<sup>5–9</sup> Considering the similar ion radii and characteristics of  $\text{Ta}^{5+}$ ,  $\text{Sb}^{5+}$ , and  $\text{Nb}^{5+}$ , Wang *et al.* used  $\text{Ta}^{5+}$  and  $\text{Sb}^{5+}$  to substitute for  $\text{Nb}^{5+}$  in  $\text{BiNbO}_4$  and pure orthorhombic phase of  $\text{BiNb}_{1-x}(\text{Ta},\text{Sb})_x\text{O}_4$  could be obtained at  $0 \leq x \leq 0.4$ .<sup>10,11</sup> In our previous work, pure  $\text{BiSbO}_4$  ceramics with monoclinic structure were synthesized via solid-state reaction method, and good microwave dielectric properties with dielectric constant about 19,

$Q \times f$  values about 70 000 GHz, and TCF about -62 ppm/°C were obtained in ceramics sintered at 1080°C. It was found that  $\text{BiSbO}_4$  ceramics were not likely to react with silver and that they might be good candidates for LTCC application.<sup>12</sup>  $\text{BiSbO}_4$  was also reported in detail by Lin *et al.*<sup>13</sup> as a novel p-block metal oxide, possessing a visible-light response for the photocatalytic degradation of methylene blue. Considering the potential value in various applications of the monoclinic phase of  $\text{BiSbO}_4$ , it is necessary and meaningful to carry out some initial study to modify its physical and chemical properties. In this work,  $\text{Ta}^{5+}$  was used to substitute for  $\text{Sb}^{5+}$  in  $\text{BiSbO}_4$  and  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  compositions were designed with  $0.05 \leq x \leq 0.6$ . Sintering behavior, phase evolution, and microwave dielectric properties of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics were studied and their relationships were also discussed in detail.

## II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of  $\text{Bi}_2\text{O}_3$  (>99%, Shu-Du Powders Co. Ltd., Cheng Du, China),  $\text{Ta}_2\text{O}_5$ , and  $\text{Sb}_2\text{O}_3$  (>99%, Guo-Yao Co. Ltd., Shanghai, China) were prepared according to the composition  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ( $x = 0.05, 0.1, 0.2, 0.4, 0.5,$  and  $0.6$ ; samples were named BST005, BST010, BST020, BST040, BST050, and BST060, respectively). Powders were mixed and milled for 4.5 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with zirconia balls (2 mm in diameter) as milling media. Considering thorough oxidation of  $\text{Sb}_2\text{O}_3$  to  $\text{Sb}_2\text{O}_5$ , the mixed oxides were calcined at 600° and 800°C for 4 h, respectively. After being crushed and remilled for 5 h using  $\text{ZrO}_2$  balls and deionized water, powders were pressed into pellets (8 mm in diameter and 1 mm in height) and cylinders (8 mm in



**Fig. 1.** XRD patterns of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics sintered at 1020°C for 2 h (s—monoclinic phase of  $\text{Bi}(\text{SbTa})\text{O}_4$ , T—orthorhombic phase of  $\text{Bi}(\text{TaSb})\text{O}_4$ ).

N. Alford—contributing editor

Manuscript No. 24131. Received December 20, 2007; approved March 21, 2008.

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

<sup>†</sup>Author to whom correspondence should be addressed. e-mail: hwang@mail.xjtu.edu.cn

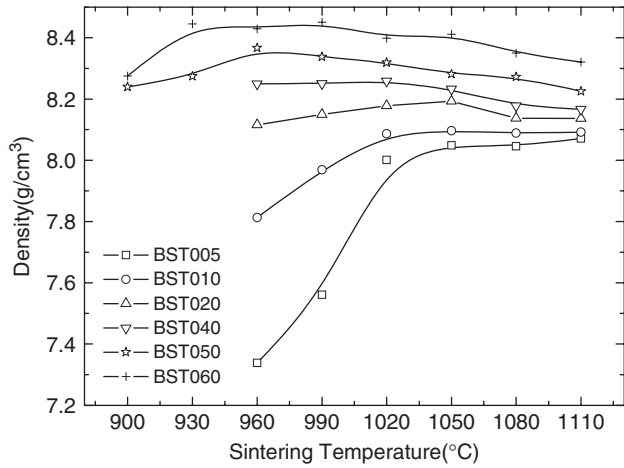


Fig. 2. Density of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics after being sintered for 2 h as a function of sintering temperature.

diameter and 4 mm in height) in a steel die under a uniaxial pressure of  $20 \text{ kN/cm}^2$  with PVA binder addition. Samples were sintered at a temperature range from  $900^\circ$  to  $1200^\circ\text{C}$  for 2 h.

The crystalline structures of samples (ground powders) were investigated using X-ray diffraction with  $\text{CuK}\alpha$  radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Microstructures of natural surfaces and fracture surfaces (pellets) were observed using scanning electron microscopy (SEM) (JEOL JSM-6460, Tokyo, Japan). The apparent densities of ceramics (cylinders) were measured by Archimedes' method. Dielectric behaviors of cylinder samples (about 6.8 mm in diameter and 3.5 mm in height after sintering) at microwave frequency were measured by the  $\text{TE}_{018}$  shielded-cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA). TCF ( $\tau_f$ ) was calculated by the following formula:

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

where  $f_{85}$  and  $f_{25}$  are the  $\text{TE}_{018}$  resonant frequencies at  $85^\circ$  and  $25^\circ\text{C}$ , respectively.

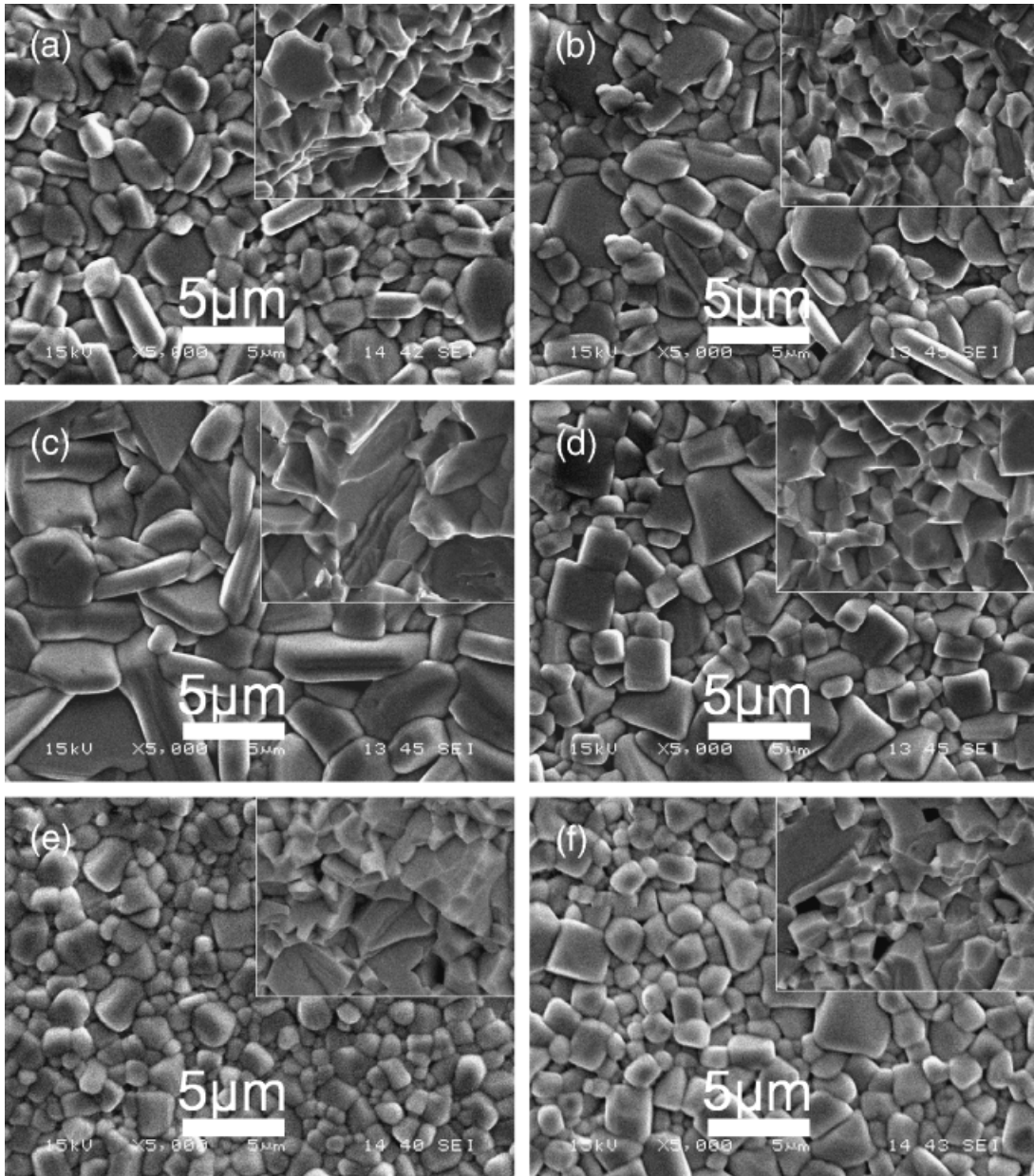


Fig. 3. Scanning electron microscopy micrographs of natural surface and fraction surface (top right corner) of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics sintered at  $1050^\circ\text{C}$  for 2 h: (a)  $x = 0.05$ , (b)  $x = 0.10$ , (c)  $x = 0.20$ , (d)  $x = 0.40$ , (e)  $x = 0.50$ , and (f)  $x = 0.60$ .

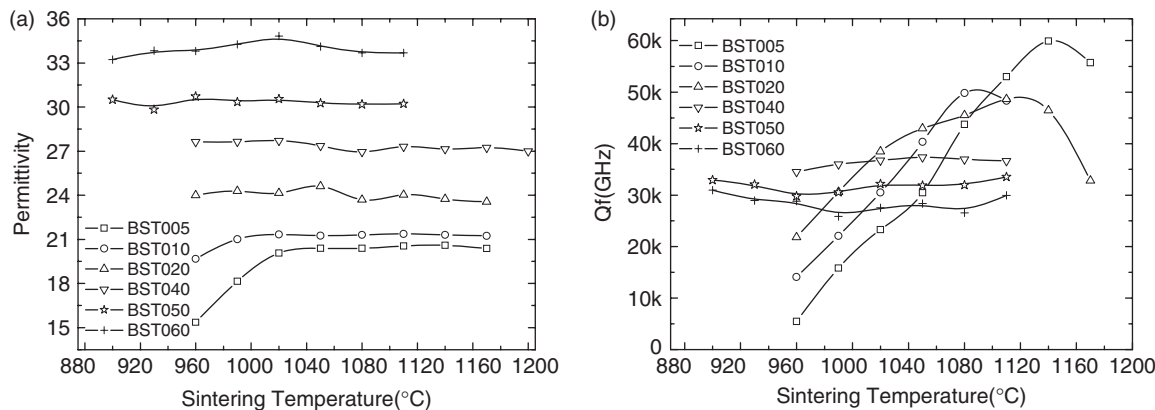


Fig. 4. Microwave dielectric constant (a) and  $Q \times f$  values (b) of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics as a function of sintering temperature.

### III. Results and Discussions

Figure 1 shows the XRD patterns of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics sintered at  $1020^\circ\text{C}$  for 2 h. When  $x \leq 0.2$ ,  $\text{Sb}^{5+}$  could be completely substituted by  $\text{Ta}^{5+}$  and a solid solution of monoclinic  $\text{Bi}(\text{Sb,Ta})\text{O}_4$  was obtained. When  $x$  value increased to 0.4, orthorhombic phase became the major phase and a small amount of monoclinic phase also existed in  $\text{Bi}(\text{Sb}_{0.6}\text{Ta}_{0.4})\text{O}_4$  ceramics. As  $x$  value further increased to 0.5 or 0.6, the monoclinic phase disappeared and a single orthorhombic phase of  $\text{Bi}(\text{Sb,Ta})\text{O}_4$  was revealed. This indicates that the tolerance region of the orthorhombic phase of  $\text{Bi}(\text{Sb,Ta})\text{O}_4$  ceramics was larger than that of the monoclinic phase.

Densities of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics as a function of sintering temperature are shown in Fig. 2. As sintering temperature increased, grains grew bigger and pores shrank, and most of the pores could be eliminated from ceramics. After being sintered at  $1050^\circ\text{C}$  for 2 h, the density of the  $\text{Bi}(\text{Sb}_{0.95}\text{Ta}_{0.05})\text{O}_4$  ceramic got its saturated value. As  $x$  value increased, the saturated density of the  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramic increased because of the larger atomic weight of  $\text{Ta}^{5+}$  as compared with  $\text{Sb}^{5+}$ , and the densified temperatures decreased to about  $960^\circ\text{C}$  when the  $x$  value was  $>0.2$ . It was not easy to obtain dense ceramics of both pure  $\text{BiSbO}_4$  and  $\text{BiTaO}_4$  ceramics below  $1050^\circ\text{C}$ . The formation of a solid solution of monoclinic or orthorhombic phases or their coexistence accelerated low-temperature densification of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics without any addition. Theoretical densities of pure monoclinic  $\text{BiSbO}_4$  and orthorhombic  $\text{BiTaO}_4$  were 8.459 and 9.179  $\text{g}/\text{cm}^3$ , respectively.<sup>14,15</sup> All the relative densities of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics in this work were  $>96\%$ .

SEM micrographs of both natural surfaces and fracture surfaces of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics sintered at  $1050^\circ\text{C}$  for 2 h are shown in Fig. 3. Homogeneously fine microstructures with almost no pores were revealed for  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics. When  $x \leq 0.2$ , grains of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics showed a disc shape and the grain size increased from 1–3  $\mu\text{m}$  to about 4–6  $\mu\text{m}$  as the  $x$  value increased from 0.05 to 0.20 in the monoclinic phase region. When  $x$  was 0.4, grain size decreased to about 1–3  $\mu\text{m}$  abruptly, and most grains showed a quadrate shape because of the formation of orthorhombic phase. As  $x$  increased further, a pure orthorhombic phase was obtained and grain size remained about 1–3  $\mu\text{m}$ .

Microwave dielectric properties of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics as a function of sintering temperature are shown in Fig. 4. Microwave permittivity ( $\epsilon_r$ ) of pure  $\text{BiSbO}_4$  was about 19, as reported in our previous work,<sup>12</sup> and  $\epsilon_r$  of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics increased from about 20.5 to 34 as  $x$  increased from 0.05 to 0.6. The polarizability of  $\text{Ta}^{5+}$  was greater than that of  $\text{Sb}^{5+}$ , as reported by Shannon,<sup>16</sup> and the  $\epsilon_r$  of  $\text{BiTaO}_4$  ceramic with a little  $\text{CuO}$  addition was about 40.<sup>17</sup> This could explain why permittivity increased as  $x$  value increased here. The permittivity at the microwave region was affected severely by pores in the ceramics. The permittivity of  $\text{Bi}(\text{Sb}_{0.95}\text{Ta}_{0.05})\text{O}_4$  and

$\text{Bi}(\text{Sb}_{0.9}\text{Ta}_{0.1})\text{O}_4$  ceramics obtained their saturated values when the sintering temperature was above  $1020^\circ\text{C}$ . When the  $x$  value was  $>0.2$ , the permittivity of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics became stable while the sintering temperature was above  $960^\circ\text{C}$ . This result agreed well with that of density discussed above.  $Q \times f$  values of  $\text{BiSbO}_4$  and  $\text{BiTaO}_4$  were about 70 000 and 12 000 GHz, respectively.  $Q \times f$  values of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics decreased from about 60 000 to 29 000 GHz as  $x$  value increased from 0.05 to 0.6. When  $x \leq 0.2$ ,  $Q \times f$  values of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics reached their maximums in a very narrow range of sintering temperatures. When  $x$  was  $>0.2$ , the range of sintering temperatures broadened remarkably as shown in Fig. 4(b). Microwave dielectric loss includes two parts: intrinsic loss and extrinsic loss. Intrinsic losses were caused by absorptions of phonon oscillation and extrinsic losses were caused by lattice defect (impurity, cavity, substitution, grain boundaries, size and shapes of grains, second phase, pores etc.).<sup>18</sup> In fact the origins of dielectric losses at microwave frequency have not been understood well and are still the main subject for discussions by researchers. The main origin of dielectric loss is the anharmonic terms in the crystal's potential energy. For most dielectrics, material with a larger permittivity has a smaller  $Q \times f$  value because of the contribution of increasing anharmonic terms.<sup>19</sup> Considering that  $\text{Ta}^{5+}$  has larger polarizability than  $\text{Sb}^{5+}$ , it could be concluded that contribution to microwave permittivity from ionic displacement polarization of  $\text{Ta}^{5+}$  was greater than that of  $\text{Sb}^{5+}$  and the oscillation of  $\text{Ta}^{5+}$  was stronger than that of  $\text{Sb}^{5+}$  in the same structure and the same atomic position. It meant that in  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics, intrinsic losses caused by oscillation of  $\text{Ta}^{5+}$  were larger than those introduced by

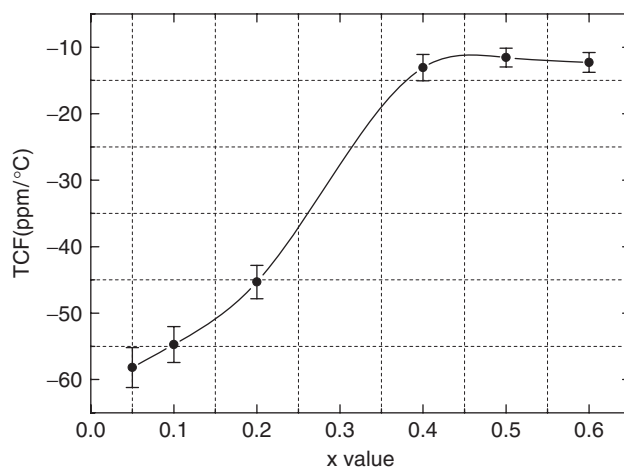


Fig. 5. Temperature coefficient of resonant frequency (TCF) of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics as a function of  $x$  values.

$\text{Sb}^{5+}$ . Hence substitution of  $\text{Ta}^{5+}$  decreased the  $Q \times f$  values of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics.

TCF of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics as a function of  $x$  values are shown in Fig. 5 (at least three samples were used for error bars). The TCF of pure monoclinic  $\text{BiSbO}_4$  was about  $-62 \text{ ppm}/^\circ\text{C}$  as reported in our previous work. The TCF of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics shifted from  $-58 \text{ ppm}/^\circ\text{C}$  to  $-45 \text{ ppm}/^\circ\text{C}$  as  $x$  increased from 0.05 to 0.2 in the range of monoclinic solid solution. When  $x$  increased to 0.4, TCF sharply shifted to about  $-12 \text{ ppm}/^\circ\text{C}$  because of the formation of an orthorhombic solid solution in  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics. The TCF of orthorhombic  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  remained stable (about  $-12 \text{ ppm}/^\circ\text{C}$ ) and did not change as  $x$  increased further. The near-zero TCF of orthorhombic  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics would be suitable for LTCC technology.

#### IV. Conclusion

Dense ceramics of monoclinic and orthorhombic solid solutions of  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ( $0.05 \leq x \leq 0.60$ ) can be prepared at a sintering temperature range between  $960^\circ$  and  $1120^\circ\text{C}$ , and they exhibit adjustable permittivity (between 20.5 and 34) and high  $Q \times f$  values (between 29 000~60 000 GHz) at the microwave region and room temperature. A pure monoclinic solid solution can be formed when  $x \leq 0.20$ , and when  $x \geq 0.50$  a pure orthorhombic phase can be obtained. Both dielectric constant and loss depended highly on the content of the substitution of  $\text{Ta}^{5+}$  for  $\text{Sb}^{5+}$  and on the phase structure. TCFs increased linearly from  $-58$  to  $-45 \text{ ppm}/^\circ\text{C}$  as  $x$  value increased from 0.05 to 0.2 in the range of monoclinic solid solution and then remained at a constant of about  $-12 \text{ ppm}/^\circ\text{C}$  when  $x \geq 0.40$ . The  $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$  ceramics would be good candidates for LTCC technology.

#### References

<sup>1</sup>Y. Higuchi and H. Tamura, "Recent Progress on the Dielectric Properties of Dielectric Resonator Materials with Their Applications from Microwave to Optical Frequencies," *J. Eur. Ceram. Soc.*, **23**, 2683–8 (2003).

<sup>2</sup>H. Shimoda, N. Ishitobi, K. Kawamura, and M. Kobayashi, "Development of a High-Q Multilayer Ceramic Resonator," *Jpn. J. Appl. Phys.*, **31**, 3160–3 (1992).

<sup>3</sup>H. C. Ling, M. F. Yan, and W. W. Rhodes, "High Dielectric Constant and Small Temperature Coefficient Bismuth-Based Dielectric Compositions," *J. Mater. Res.*, **5**, 1752–62 (1990).

<sup>4</sup>D. H. Liu, Y. Liu, S. Q. Huang, and X. Yao, "Phase Structure and Dielectric Properties of  $\text{Bi}_2\text{O}_3$ - $\text{ZnO}$ - $\text{Nb}_2\text{O}_5$ -Based Dielectric Ceramics," *J. Am. Ceram. Soc.*, **76**, 2129–32 (1993).

<sup>5</sup>H. Kagata, T. Inoue, J. Kato, and I. Kameyama, "Low-Fire Bismuth-Based Dielectric Ceramics for Microwave Use," *Jpn. J. Appl. Phys.*, **31**, 3152–5 (1992).

<sup>6</sup>D. Zhou, H. Wang, and X. Yao, "Microwave Dielectric Properties and Co-Firing of  $\text{BiNbO}_4$  Ceramics with  $\text{CuO}$  Substitution," *Mater. Chem. Phys.*, **104**, 397–402 (2007).

<sup>7</sup>Ch. F. Yang, "Improvement of Quality Value and Shift of  $\tau_f$  Value of  $\text{BiNbO}_4$  Ceramics with Addition of  $\text{CuO}$ - $\text{V}_2\text{O}_5$  Mixtures," *Jpn. J. Appl. Phys.*, **38**, 6797–800 (1999).

<sup>8</sup>Ch. L. Huang, M. H. Weng, and G. M. Shan, "Effect of  $\text{V}_2\text{O}_5$  and  $\text{CuO}$  Additives on Sintering Behavior and Microwave Dielectric Properties of  $\text{BiNbO}_4$  Ceramics," *J. Mater. Sci.*, **35**, 5443–7 (2000).

<sup>9</sup>D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Microwave Dielectric Properties and Co-Firing of  $\text{BiNbO}_4$  Ceramics with  $\text{CuO}$ - $\text{WO}_3$  Substitution," *Mater. Sci. Eng.*, **142**, 106–11 (2007).

<sup>10</sup>N. Wang, M. Y. Zhao, and Zh. W. Yin, "The Sintering Behavior and Microwave Dielectric Properties of  $\text{Bi}(\text{Nb},\text{Sb})\text{O}_4$  Ceramics," *Ceram. Int.*, **30**, 1017–22 (2004).

<sup>11</sup>N. Wang, M. Y. Zhao, and Zh. W. Yin, "Effects of  $\text{Ta}_2\text{O}_5$  on Microwave Dielectric Properties of  $\text{BiNbO}_4$  Ceramics," *Mater. Sci. Eng. B*, **99**, 238–42 (2003).

<sup>12</sup>D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Dielectric Behavior and Co-Firing with Silver of Monoclinic  $\text{BiSbO}_4$  Ceramic," *J. Am. Ceram. Soc.*, **91** [4], 1380–3 (2008).

<sup>13</sup>X. P. Lin, F. Q. Huang, W. D. Wang, and K. L. Zhang, "A Novel Photocatalyst  $\text{BiSbO}_4$  for Degradation of Methylene Blue," *Appl. Catal. A: Gen.*, **307**, 257–62 (2006).

<sup>14</sup>B. Kennedy, "X-Ray Powder Diffraction Study of  $\text{BiSbO}_4$ ," *Powder Diffr.*, **9**, 164–7 (1994).

<sup>15</sup>R. S. Roth and J. L. Waring, "Synthesis and Stability of Bismutotantalite, Stibiotantalite and Chemically Similar  $\text{ABO}_4$  Compounds," *Am. Mineral.*, **48**, 1348–56 (1963).

<sup>16</sup>R. D. Shannon, "Dielectric Polarizabilities of Ions in Oxides and Fluorides," *J. Appl. Phys.*, **73**, 348–66 (1993).

<sup>17</sup>C. L. Huang and M. H. Weng, "Low-Fire  $\text{BiTaO}_4$  Dielectric Ceramics for Microwave Applications," *Mater. Lett.*, **43**, 32–5 (2000).

<sup>18</sup>H. Tamura, "Microwave Loss Quality of  $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$ ," *Am. Ceram. Soc. Bull.*, **73**, 92–5 (1994).

<sup>19</sup>H. Tamura, "Microwave Dielectric Losses Caused by Lattice Defects," *J. Eur. Ceram. Soc.*, **26**, 1775–80 (2006). □