

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

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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/cm³. 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.^{1,2} In the fabrication of multilayer microwave devices, low-firing microwave dielectric materials with high dielectric constant (ϵ_r), low dielectric loss, and near-zero temperature coefficient of resonant frequency (τ_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.^{3,4} In Bi_2O_3 - Nb_2O_5 systems, BiNbO_4 has attracted much attention because of its good sintering behavior (could be well densified below 960°C with a small amount of CuO , WO_3 , or V_2O_5 additives) and excellent microwave dielectric properties with dielectric constant (ϵ_r) about 43, $Q \times f$ value about 5000–20 000 GHz, and TCF value about -20 to +20 ppm/°C.^{5–9} Considering the similar ion radii and characteristics of Ta^{5+} , Sb^{5+} , and Nb^{5+} , Wang *et al.* used Ta^{5+} and Sb^{5+} to substitute for Nb^{5+} in BiNbO_4 and pure orthorhombic phase of $\text{BiNb}_{1-x}(\text{Ta},\text{Sb})_x\text{O}_4$ could be obtained at $0 \leq x \leq 0.4$.^{10,11} In our previous work, pure 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 BiSbO_4 ceramics were not likely to react with silver and that they might be good candidates for LTCC application.¹² BiSbO_4 was also reported in detail by Lin *et al.*¹³ 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 BiSbO_4 , it is necessary and meaningful to carry out some initial study to modify its physical and chemical properties. In this work, Ta^{5+} was used to substitute for Sb^{5+} in 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 Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Cheng Du, China), Ta_2O_5 , and Sb_2O_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 Sb_2O_3 to Sb_2O_5 , the mixed oxides were calcined at 600° and 800°C for 4 h, respectively. After being crushed and remilled for 5 h using 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

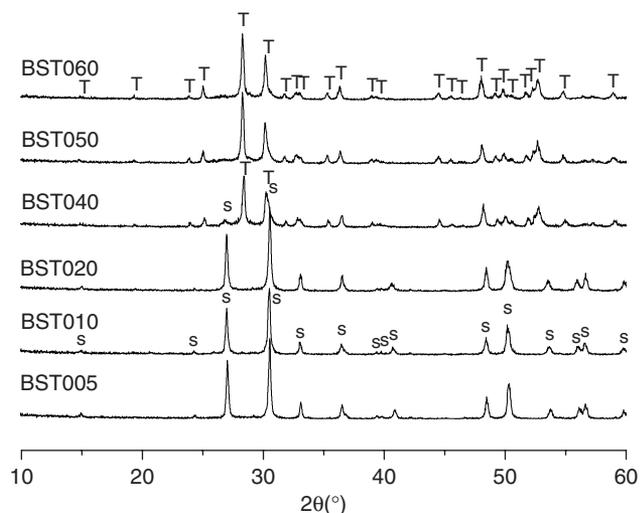


Fig. 1. XRD patterns of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ ceramics sintered at 1020°C for 2 h (s—monoclinic phase of $\text{Bi}(\text{SbTa})\text{O}_4$, T—orthorhombic phase of $\text{Bi}(\text{TaSb})\text{O}_4$).

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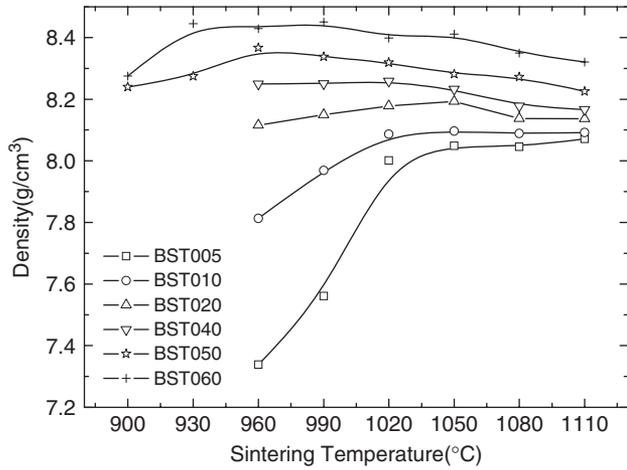


Fig. 2. Density of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ ceramics after being sintered for 2 h as a function of sintering temperature.

diameter and 4 mm in height) in a steel die under a uniaxial pressure of 20 kN/cm^2 with PVA binder addition. Samples were sintered at a temperature range from 900° to 1200°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 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 (τ_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 TE_{018} resonant frequencies at 85° and 25°C , respectively.

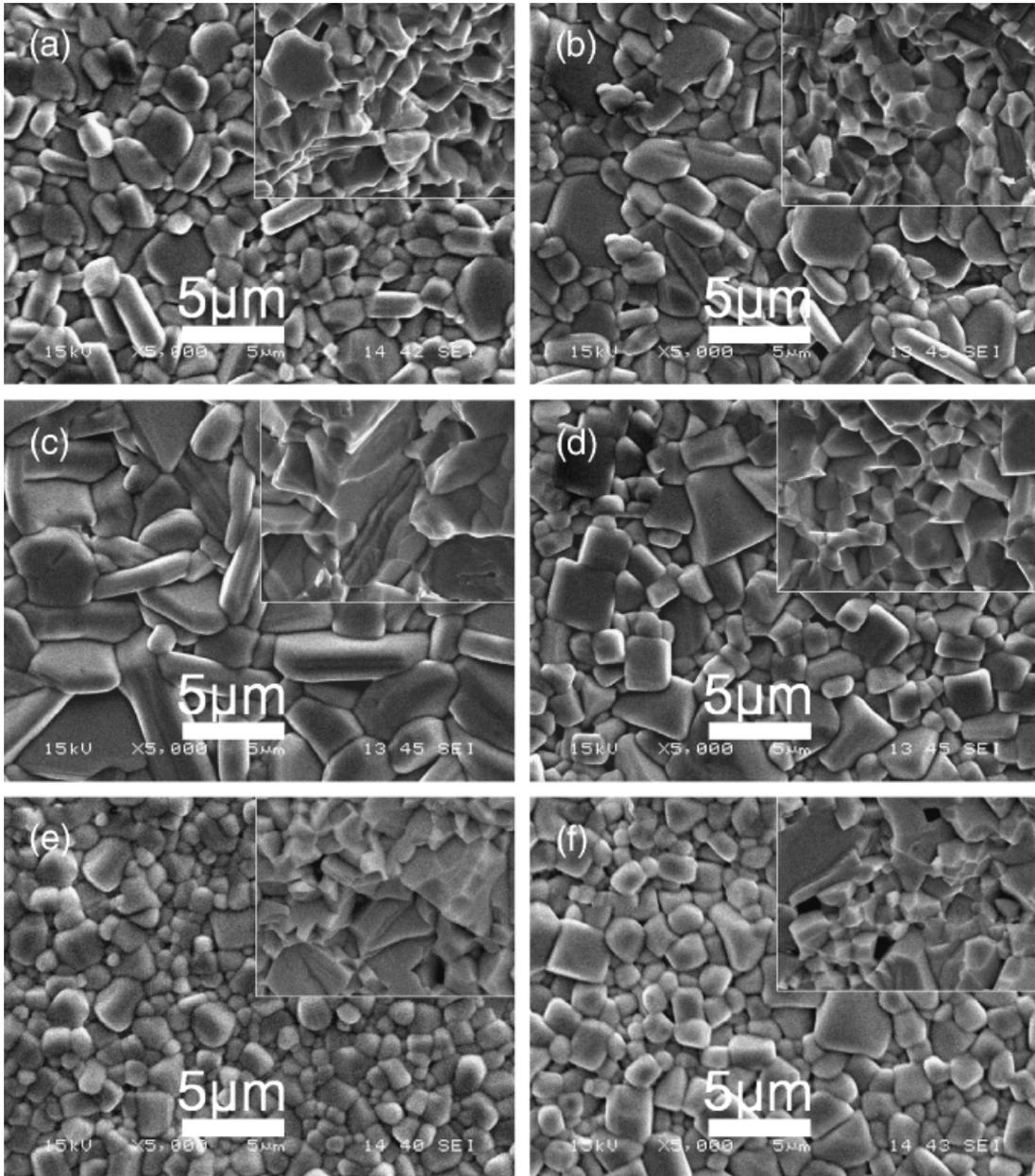


Fig. 3. Scanning electron microscopy micrographs of natural surface and fraction surface (top right corner) of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ ceramics sintered at 1050°C for 2 h: (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.20$, (d) $x = 0.40$, (e) $x = 0.50$, and (f) $x = 0.60$.

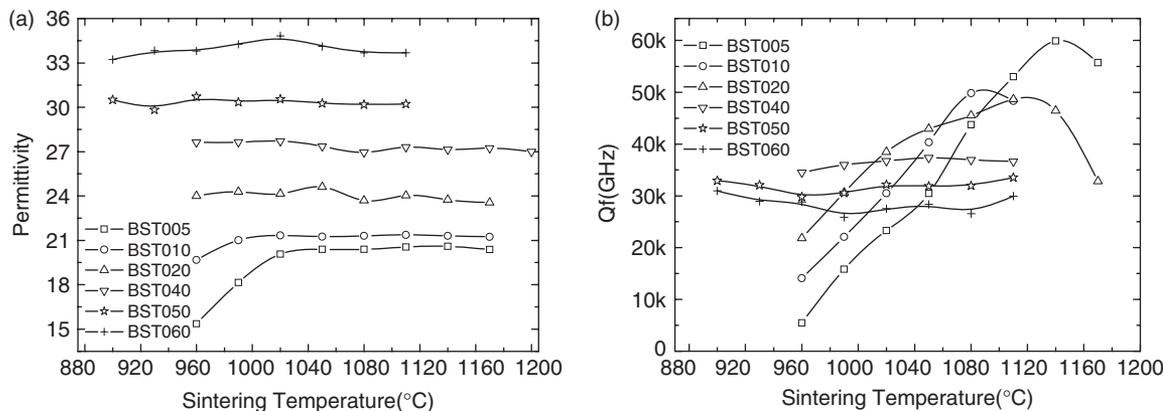


Fig. 4. Microwave dielectric constant (a) and $Q \times f$ values (b) of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ ceramics as a function of sintering temperature.

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°C for 2 h. When $x \leq 0.2$, Sb^{5+} could be completely substituted by 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°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 Ta^{5+} as compared with Sb^{5+} , and the densified temperatures decreased to about 960°C when the x value was >0.2 . It was not easy to obtain dense ceramics of both pure BiSbO_4 and BiTaO_4 ceramics below 1050°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 BiSbO_4 and orthorhombic BiTaO_4 were 8.459 and 9.179 g/cm^3 , respectively.^{14,15} 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°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 μm to about 4–6 μm 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 μm 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 μm .

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 (ϵ_r) of pure BiSbO_4 was about 19, as reported in our previous work,¹² and ϵ_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 Ta^{5+} was greater than that of Sb^{5+} , as reported by Shannon,¹⁶ and the ϵ_r of BiTaO_4 ceramic with a little CuO addition was about 40.¹⁷ 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°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°C . This result agreed well with that of density discussed above. $Q \times f$ values of BiSbO_4 and 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.).¹⁸ 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.¹⁹ Considering that Ta^{5+} has larger polarizability than Sb^{5+} , it could be concluded that contribution to microwave permittivity from ionic displacement polarization of Ta^{5+} was greater than that of Sb^{5+} and the oscillation of Ta^{5+} was stronger than that of 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 Ta^{5+} were larger than those introduced by

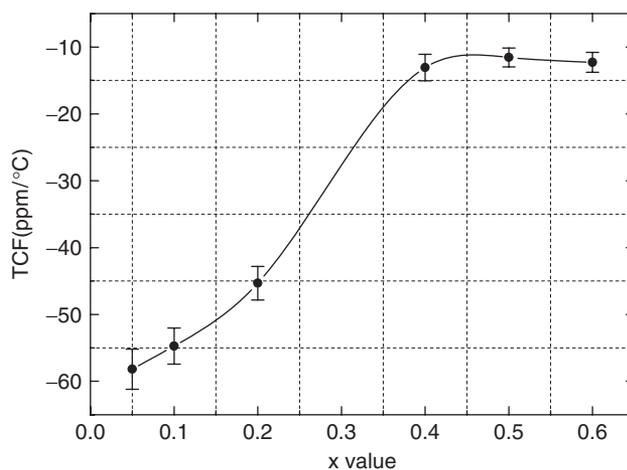


Fig. 5. Temperature coefficient of resonant frequency (TCF) of $\text{Bi}(\text{Sb}_{1-x}\text{Ta}_x)\text{O}_4$ ceramics as a function of x values.

Sb^{5+} . Hence substitution of 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 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° and 1120°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 Ta^{5+} for 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.

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