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Effects of $CaTiO_3$ addition on the densification and microwave dielectric properties of $BiSbO_4$ ceramics

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Abstract

In this study, the effects of $CaTiO_3$ addition on the sintering characteristics and microwave dielectric properties of $BiSbO_4$ were investigated. Pure $BiSbO_4$ achieved a sintered density of 8.46 g/cm^3 at 1100 °C. The value of sintered density decreased with increasing $CaTiO_3$, and sintering at a temperature higher than 1100 °C led to a large weight loss (>2 wt%) caused by the volatile nature of the compound. Samples either sintered above 1100 °C or with a $CaTiO_3$ content exceeding 3 wt% showed poor densification. SEM micrographs revealed microstructures with bimodal grain size distribution. The size of the smaller grains ranged from 0.5 to 1.2 μm and that of the larger grains between 3 and 7 μm. The microwave dielectric properties of the $(1-x)$ $BiSbO_{4-x}$ $CaTiO_3$ ceramics are dependent both on the x value and on the sintering temperature. The 99.0 wt% $BiSbO_4$–1.0 wt% $CaTiO_3$ ceramic sintered at 1100 °C reported overall microwave dielectric properties that can be summarized as $\varepsilon_r \approx 21.8$, $Q \times f \approx 61{,}150$ GHz, and $\tau_f \approx -40.1$ ppm/°C, all superior to those of the $BiSbO_4$ ceramics sintered with other additives.

Keywords: B. Microstructure; Microwave properties; Densification; $BiSbO_4$

1. Introduction

In response to the rapid development of mobile communication devices like cellular phones, global positioning systems, and personal communication systems, dielectric ceramics for use in resonators at microwave frequency have continued to elicit substantial R&D endeavors. Dielectric materials with a high dielectric constant and dielectric loss quality ($Q > 2000$) plus a near zero temperature coefficient of resonant frequency τ_f are generally required for use in microwave devices. A high dielectric constant helps trim down the size of the material by a factor of $1/\varepsilon_r^{1/2}$ to facilitate considerable reduction in circuit size. A high Q value, on the other hand, enables low insertion loss and low bandwidth of resonance frequency, both essential for achieving high frequency selectivity and stability in microwave transmitter components. A near-zero τ_f is further required for stabilizing frequency against temperature.

Most microwave dielectric ceramics need to be sintered at temperatures ranging from 1200 to 1500 °C to obtain sufficient densification. For instance, the sintering temperatures of the $Ba_2Ti_9O_{20}$, $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$, and $(Zr,Sn)TiO_4$ systems are respectively 1300 °C, 1350 °C and 1400 °C [1–3]. Several approaches have been explored to lower the sintering temperature of the materials. One involves investigating the effects of glass-forming additives on the properties of established microwave materials [4]. Another way is the use of new material systems with a lower sintering temperature [5,6]. Recent studies have shown that bismuth-based ceramics, including the binary systems of Bi_2O_3-$(Nb,Ta)_2O_5$ and Bi_2O_3-$(Sb,Ta)_2O_5$ [7–9], the ternary systems of Bi_2O_3–CaO–Nb_2O_5 and Bi_2O_3–ZnO–$(Nb,Ta)_2O_5$ [7,10,11], possess low sintering temperatures ranging from 900 to 1100 °C and excellent microwave dielectric characteristics.

Examining the microwave dielectric properties of $BiSbO_4$ ceramic, the study of Wang and colleagues [12] reported a dielectric constant (ε_r) of 19, a Qf value of 70,000 GHz, and a

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temperature coefficient of resonant frequency (τ_f) of -62 ppm/°C at a sintering temperature of 1080 °C. $BiSbO_4$ ceramic sintered with 1 wt% of V_2O_5–CuO and 0.6 wt% of B_2O_3–CuO at 930 °C demonstrated respectively the following microwave dielectric properties: $\varepsilon_r \approx 19$, $Qf \approx 40{,}000$ GHz, and $\tau_f \approx -71.5$ ppm/°C, and $\varepsilon_r \approx 19.47$, $Qf \approx 45{,}405$ GHz, and $\tau_f \approx -66.2$ ppm/°C [13,14]. Though $BiSbO_4$ ceramic exhibits dielectric properties approaching the criteria necessary for use in microwave devices, the present paper aimed to improve its dielectric constant and temperature coefficient of resonant frequency by modifying the composition with $CaTiO_3$ reported to possess a high ε_r of 162 and a high Q of 8700 at a microwave frequency of 1.49 GHz [15]. The effects of $CaTiO_3$ addition on the sintering characteristics and microwave dielectric properties of $BiSbO_4$ are discussed based on the results of X-ray diffraction (XRD), scanning electron microscopy (SEM), and dielectric characterization.

2. Experimental procedure

In this study, $BiSbO_4$ ceramics with various amounts of $CaTiO_3$ (ranging from 0 to 3 wt%) were prepared using the solid-state reaction technique. $BiSbO_4$ and $CaTiO_3$ compounds were pre-calcined from highly pure (>99.9% purity) raw materials, including Bi_2O_3 (Acros, Reagent grade), Sb_2O_3 (STREM, Reagent grade), TiO_2 (SHOWA, Reagent grade) and $CaCO_3$ (Alfa, Reagent grade) at 850 and 1100 °C respectively. Subsequently, $BiSbO_4$ and various amounts of $CaTiO_3$ were mixed and milled in methyl alcohol solution using polyethylene jars and zirconia balls for 24 h and then oven-dried at 80 °C for overnight. After drying, the powders were calcined at 850 °C for 4 h at a heating rate of 5 °C/min and re-milled in methyl alcohol for 24 h. The powders were added with 5 wt% of 15%-PVA solution and pressed into disc-shaped compacts under a uniaxial pressure of 140 MPa. The samples were then heat treated at 550 °C for 4 h to eliminate PVA, followed by sintering at 1050–1150 °C for 4 h (heating rate = 5 °C/min). Densities of the sintered samples were measured using the Archimedes method with de-ionized water. Phase identification of the calcined powders as well as the sintered bulk ceramics was performed using X-ray diffraction (XRD, Simens D5000) to identify the resultant phases. The samples used for SEM observation were thermally etched, and the microstructures were observed by scanning electron microscopy (SEM, JEOL 6500F) with an energy-dispersive spectroscope (EDS). The densified cylindrical samples were polished to achieve an exact thickness of 5 mm for measuring microwave properties. The dielectric constants and unloaded Q values at microwave frequencies were measured in the $TE_{01\delta}$ mode using the Hakki and Colleman method [16] and a network analyzer (HP 8722ES). Measurements of the temperature coefficient of the resonant frequency τ_f in the temperature range of 25–85 °C were performed in a Delta Design box furnace. The τ_f was defined by $(f_T - f_{25})/f_{25}(T - 25°C)$.

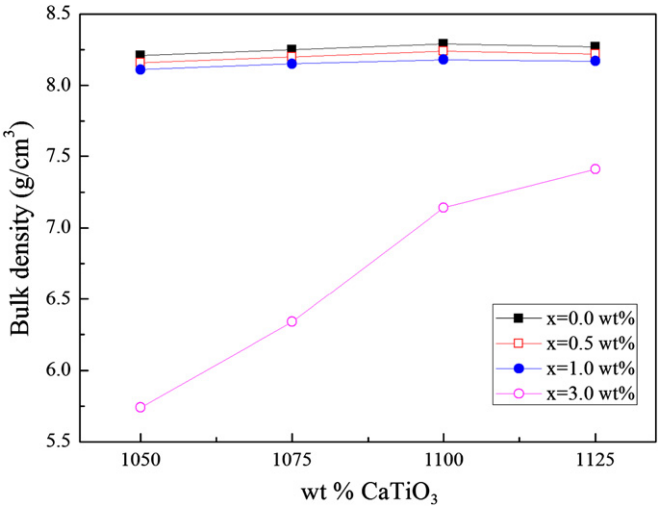

Fig. 1. Sintered densities of $(100-x)$ wt% $BiSbO_4 + x$ wt% $CaTiO_3$ ceramics sintered at different temperatures for 2 h.

3. Results and discussion

Fig. 1 shows the sintered densities of the $BiSbO_4$ ceramics with various amounts of $CaTiO_3$ addition. Pure $BiSbO_4$ reached the highest densification at 1100 °C, and a sintered density exceeding 98% theoretical density (8.46 g/cm^3) [17] was achieved. With the addition of 0.5 and 1 wt% $CaTiO_3$, the sintered density versus sintered temperature followed a similar path while the density value decreased with increasing $CaTiO_3$. The sintered densities of the $BiSbO_4$ ceramic with 3 wt% $CaTiO_3$ were significantly degraded and a sintered density of 7.66 g/cm^3 was obtained at 1150 °C. The density value declined dramatically with the increase in the $CaTiO_3$ content due to the relatively low theoretical density of $CaTiO_3$ (3.98 g/cm^3) and the hindered sintering caused by $CaTiO_3$ addition. With further increase in the $CaTiO_3$ content, a higher sintering temperature is required to densify the ceramic, which is detrimental to stoichiometric control because of the high volatile nature of Bi_2O_3. Less than 1 wt% weight loss was observed for the $BiSbO_4$–$CaTiO_3$ compounds sintered at 1100 °C while the weight loss rapidly rose beyond 2 wt% as the sintering temperature went up above 1100 °C. Therefore, no further characterization was performed for samples sintered at temperatures exceeding 1100 °C or with a $CaTiO_3$ content greater than 3 wt% due to their poor densification.

Fig. 2 reveals the XRD patterns of $BiSbO_4$ with various amounts of $CaTiO_3$ addition and sintered at 1100 °C. Without $CaTiO_3$ addition, pure $BiSbO_4$ phase with space group $P2_1/c$ (No 14) monoclinic structure was obtained after sintering. Trace amount of second phases of antimony oxides, Sb_2O_3 and Sb_6O_{13}, and an unknown phase was identified for the $BiSbO_4$ ceramic sintered with various amount of $CaTiO_3$ additions. It was also observed in this study that the intensities of the Sb_2O_3 and unknown phase diminished while that of Sb_6O_{13} escalated as the sintering

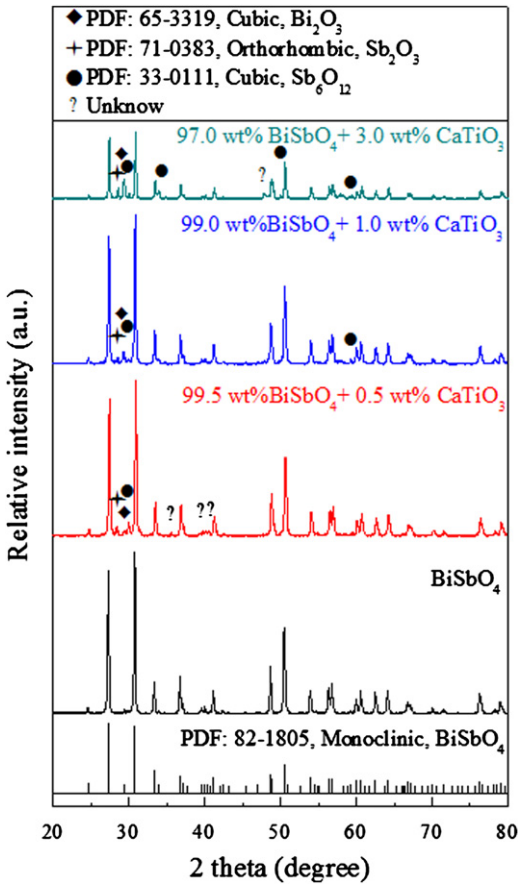

Fig. 2. XRD patterns of $(100-x)$ wt% $BiSbO_4+x$ wt% $CaTiO_3$ ceramics sintered at different temperatures.

temperature increased to 1125 °C. There is no visible variation in the XRD intensity of the $BiSbO_4$ phase associated with sintering temperature.

Fig. 3 presents the SEM micrographs of the $BiSbO_4$ ceramic sintered with 0–3.0 wt% $CaTiO_3$ at 1100 °C for 2 h. Grains with bimodal distribution were obviously observed in the microstructure. The size of the smaller grains fell in the range of 0.5–1.2 μm and that of the larger grains between 3 and 7 μm. It was further observed that, as the $CaTiO_3$ content rose, the number of smaller grains in the microstructure escalated and their grain size slightly shrunk; on the other hand, the number of the larger grains decreased while their size showed no visible change. In terms of porosity, the content increased and the size grew larger in consistency with the sintered densities presented in Fig. 1. The change in microstructure was observed to become more remarkable as the $CaTiO_3$ content exceeded 0.5 wt%. EDS results indicated that most Ca and Ti elements were distributed in the smaller grains but not detectable in the larger grains. Study results further revealed that the larger grains experienced a rapid growth in size by consuming the smaller grains, which underwent virtually no change in size with increasing sintering temperature. It can be inferred that $CaTiO_3$ addition is capable of inhibiting the grain growth of the $BiSbO_4$ ceramic.

The microwave dielectric properties, including dielectric constant (ε_r), quality factor ($Q\times f$), and temperature coefficient of resonant frequency (τ_f), of the $BiSbO_4$ ceramic sintered with 0–3.0 wt% $CaTiO_3$ at different temperatures are listed in Table 1, and the results corresponding to the

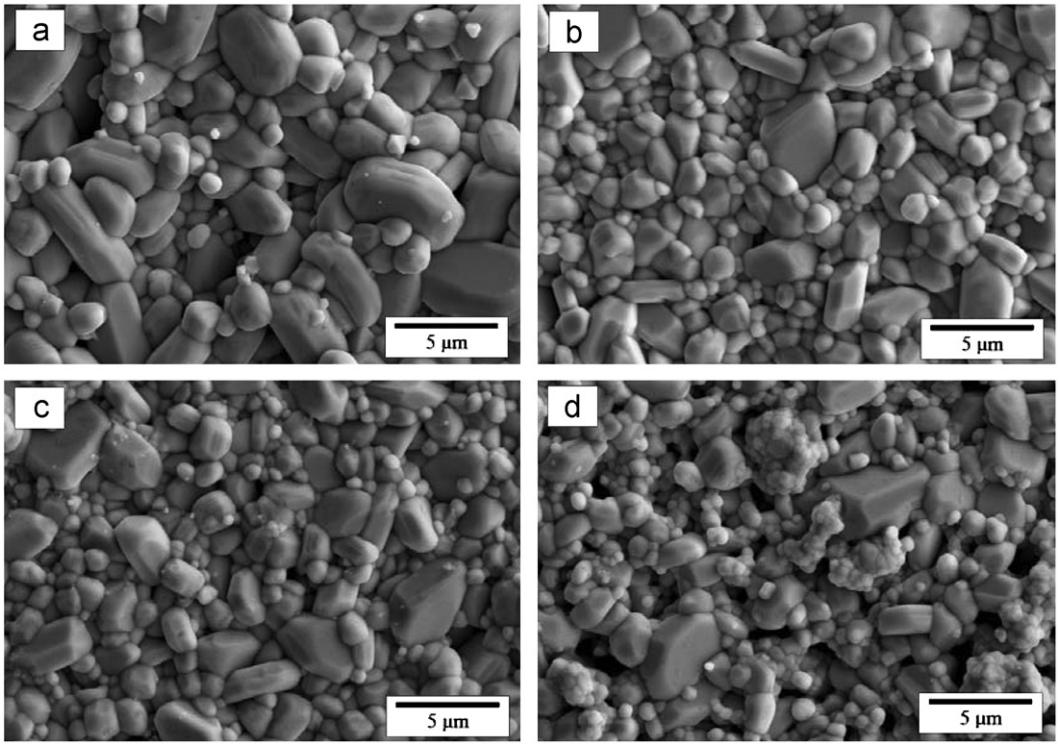

Fig. 3. SEM micrographs of $(100-x)$ wt% $BiSbO_4+x$ wt% $CaTiO_3$ ceramics: (a) $x=0$ wt%, (b) $x=0.5$ wt%, (c) $x=1.0$ wt%, and (d) $x=3.0$ wt% sintered at 1100 °C for 2 h.

Table 1
Microwave dielectric properties of $(100-x)$ wt% $BiSbO_4+x$ wt% $CaTiO_3$ ceramics, sintered at 1100 °C for 2 h.

Composition	Sintering condition	ε_r	Qf (GHz)	τ_f (ppm/°C)
$BiSbO_4$	1050 °C/2 h	21.0	53,336	−47.2
	1075 °C/2 h	21.0	54,340	−48.7
	1100 °C/2 h	21.0	54,518	−50.3
	1125 °C/2 h	21.1	54,506	−51.4
99.5 wt% $BiSbO_4$–0.5 wt% $CaTiO_3$	1000 °C/2 h	21.2	46,372	−45.2
	1075 °C/2 h	21.1	57,437	−44.6
	1100 °C/2 h	21.1	63,412	−43.5
	1125 °C/2 h	21.2	52,048	−42.7
99.0 wt% $BiSbO_4$–1.0 wt% $CaTiO_3$	1050 °C/2 h	21.9	38,724	−43.1
	1075 °C/2 h	21.8	53,938	−42.0
	1100 °C/2 h	21.8	61,150	−40.1
	1125 °C/2 h	21.8	48,327	−39.1
97.0 wt% $BiSbO_4$–3.0 wt% $CaTiO_3$	1050 °C/2 h	23.1	24,428	−38.5
	1075 °C/2 h	22.9	30,272	−37.3
	1100 °C/2 h	22.9	29,423	−36.4
	1125 °C/2 h	22.9	25,155	−35.7

sintering temperature of 1100 °C versus $CaTiO_3$ content are plotted in Figs. 4 and 5. The dielectric constants of the $BiSbO_4$ ceramics escalated from 21.0 to 22.9 with the addition of $CaTiO_3$; their porosities, on the other hand, revealed a tendency of exaggeration. The $Q\times f$ values of the $BiSbO_4$ ceramics experienced a drastic variation with $CaTiO_3$ addition; the pure $BiSbO_4$, for example, reported a $Q\times f$ value 54,218 while that of 97.0 wt% $BiSbO_4$–3.0 wt% $CaTiO_3$ counterpart read 29,423. A maximum $Q\times f$ value of 63,412 occurred in the 99.5 wt% $BiSbO_4$–0.5 wt% $CaTiO_3$ ceramic. The τ_f value varied from −50.25 to −36.43 ppm/°C as the $CaTiO_3$ content rose from 0 wt% to 3.0 wt%.

The microwave dielectric properties of the $(1-x)$ $BiSbO_{4-x}$ $CaTiO_3$ ceramics are dependent both on the x value and on the sintering temperature. The dielectric constant of the $(1-x)$ $BiSbO_{4-x}$ $CaTiO_3$ systems seemed to experience no significant change at various sintering temperatures but did register a slight increase with the $CaTiO_3$ content, due to the fact that $CaTiO_3$ reports a dielectric constant of 170 which is larger than that of $BiSbO_4$ (21.0) and partially offset by the effect of the increased porosity. The change in $Q\times f$ values of the $(1-x)$ $BiSbO_{4-x}$ $CaTiO_3$ ceramics associated with the variation in the x value and sintering temperature was closely correlated to those of grain size and porosity content in the microstructure. In light of the facts that the smaller grains retained a similar grain size while the larger grains grew bigger as the sintering temperature escalated, it can be inferred that the number of grain boundary decreased with sintering temperature. Therefore, the $Q\times f$ values rose with sintering temperature until traded off by the trapped porosity which was significantly intensified as the sintering temperature exceeded 1100 °C. For instance, the $Q\times f$ values of the

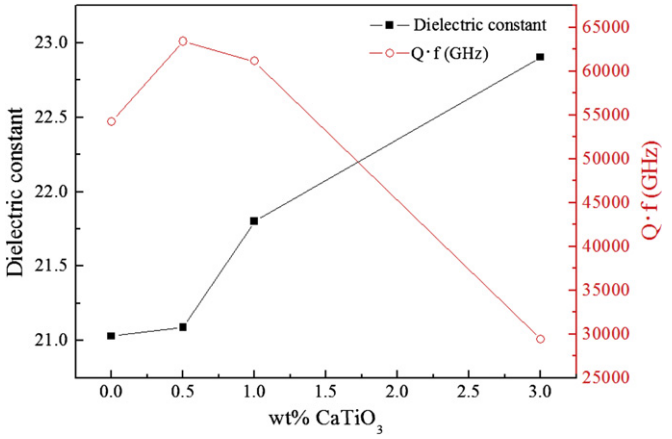

Fig. 4. Dielectric constants and quality factors of $(100-x)$ wt% $BiSbO_4+x$ wt% $CaTiO_3$ ceramics, sintered at 1100 °C for 2 h.

99.5 wt% $BiSbO_4$−0.5 wt% $CaTiO_3$ ceramics sintered at 1050, 1075, 1100, 1125 °C read respectively 46,372, 57,437, 63,412, and 52,048. As the $CaTiO_3$ content increased, the number of smaller grains in the microstructure escalated and their grain size grew smaller while the number of the larger grains declined and their size showed no visible change. With respect to porosity, the content was observed to rise and the size exaggerated. The $Q\times f$ values rose slightly at the beginning of $CaTiO_3$ addition but proceeded to drop significantly with increased $CaTiO_3$ content.

Other than that for the pure $BiSbO_4$, the τ_f value appeared to slightly decrease with increasing sintering temperature; 99.5 wt% $BiSbO_4$–0.5 wt% $CaTiO_3$ ceramics, for example, revealed τ_f values of −45.2, −44.6, −43.5, and −42.1 ppm/°C when sintered respectively at 1050, 1075,

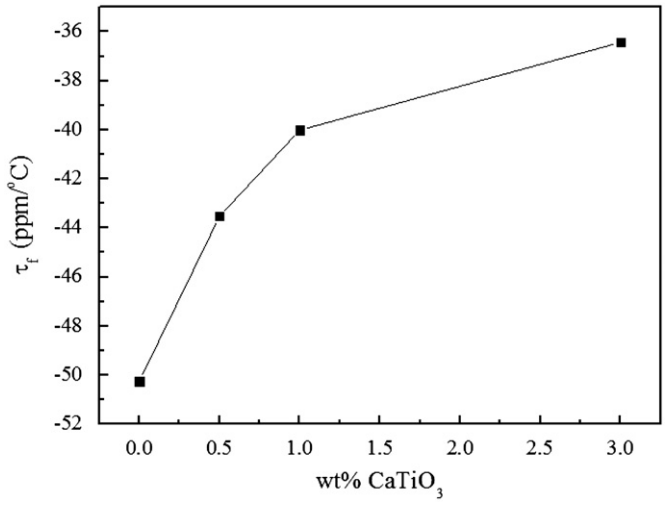

Fig. 5. Temperature coefficients of resonance frequency of $(100-x)$ wt% $BiSbO_4+x$ wt% $CaTiO_3$ ceramics, sintered at 1100 °C for 2 h.

1100, 1125 °C. The τ_f values of the $(1-x)$ $BiSbO_{4-x}$ $CaTiO_3$ ceramics underwent a change toward the positive direction due to the large positive τ_f value of $CaTiO_3$ (800 ppm/°C). The overall microwave dielectric properties of the 99.0 wt% $BiSbO_4$–1.0 wt% $CaTiO_3$ ceramic sintered at 1100 °C can be summarized as follows: $\varepsilon_r \approx 21.8$, $Q \times f \approx 61{,}150$ GHz, and $\tau_f \approx -40.1$ ppm/°C, all of which are superior to those of the $BiSbO_4$ ceramics sintered with other additives [13,14].

4. Conclusion

Based on the results reported above, the sintering characteristics and microwave dielectric properties of $BiSbO_4$ appeared to be dependent on both the $CaTiO_3$ content and the sintering temperature. It was observed that samples sintered at temperatures over 1100 °C or added with a $CaTiO_3$ content greater than 3 wt% resulted in poor densification. Microstructures with bimodal grain size distribution were obtained, in which one fell in the range of 0.5–1.2 μm and the other between 3 and 7 μm. The 99.0 wt% $BiSbO_4$–1.0 wt% $CaTiO_3$ ceramic sintered at 1100 °C was found to report the following microwave dielectric properties: $\varepsilon_r \approx 21.8$, $Q \times f \approx 61{,}150$ GHz, and $\tau_f \approx -40.1$ ppm/°C.

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