

Low-firing of BiSbO₄ microwave dielectric ceramic with V₂O₅–CuO addition

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

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

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ABSTRACT

Effects of 1.0 wt.% V₂O₅–CuO mixture addition on the sintering behavior, phase composition and microwave dielectric properties of BiSbO₄ ceramics have been investigated. BiSbO₄ ceramics can be well densified below temperature about 930 °C with 1.0 wt.% V₂O₅–CuO mixtures addition with different ratios of CuO to V₂O₅. The formation of BiVO₄ phase and substitution of Cu²⁺ can explain the decrease of sintering temperature. Dense BiSbO₄ ceramics sintered at 930 °C for 2 h exhibited good microwave dielectric properties with permittivity between 19 and 20.5, Qf values between 19,000 and 40,000 GHz and temperature coefficient of resonant frequency shifting between –71.5 ppm °C⁻¹ and –77.8 ppm °C⁻¹. BiSbO₄ ceramics could be a candidate for microwave application and low temperature co-fired ceramics technology.

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1. Introduction

In order to enable the fabrication of multilayer microwave devices in mobile communications, the co-firing of microwave dielectric ceramics with an internal electrode is highly desirable. To reach this requirement, low temperature co-fired ceramics (LTCC) technology has been widely investigated [1–5]. To use the cheap metal Ag (melting point = 960 °C) as the internal electrode, the co-firing temperature must be lower than 960 °C.

Bismuth-based dielectric ceramics are well known as low-fired materials and have been investigated in multilayer capacitors application [6,7]. In Bi₂O₃–(Nb,Ta)₂O₅ binary systems, Bi(Nb,Ta)O₄ [8–12] and Bi₃(Nb,Ta)O₇ [13–16] ceramics have attracted much attention because of their good microwave dielectric properties and low sintering temperatures (well densified below 960 °C with a little CuO, WO₃ or V₂O₅ addition for Bi(Nb,Ta)O₄). In Bi₂O₃–ZnO–(Nb,Ta)₂O₅ and Bi₂O₃–CaO–Nb₂O₅ ternary systems, some compounds with single-phase, such as Bi₂(Zn_{2/3}Nb_{4/3})O₇, Bi₂(Zn_{2/3}Ta_{4/3})O₇ and Bi₁₈Ca₈Nb₁₂O₆₅ [8,17–20], also have good microwave dielectric properties. Wang et al. studied the microwave dielectric properties of Bi(Nb,Sb)O₄ ceramic in the orthorhombic solid solution region in 2004 [21]. Recently, we have reported the microwave dielectric behaviors of pure monoclinic BiSbO₄ [22]. BiSbO₄ ceramic can be sintered well at around 1080 °C and exhibits dielectric constant about 19, Qf values about 70,000 GHz and temperature coefficient of resonant frequency (TCF) about –62 ppm °C⁻¹. Ta⁵⁺ is ever used to substitute for Sb⁵⁺ in BiSbO₄

to modify its sintering and dielectric behaviors. Although both single-phases of BiSbO₄ and BiTaO₄ ceramics can not be well densified below 1050 °C, the sintering temperatures for Bi(Sb_{1–x}Ta_x)O₄ (0.2 < x ≤ 0.6) ceramics can be lowered to around 960 °C, which could be attributed to the formation of solid solution [23].

Addition of low melting point oxides is an often used method to lower the sintering temperature of microwave dielectric ceramics. In our recent work [24], we used B₂O₃–CuO mixture addition to lower the sintering temperature of BiSbO₄ ceramic to below 960 °C. In fact, a small amount of CuO, V₂O₅ and V₂O₅–CuO additions are effective to lower the sintering temperature of BiNbO₄ system [25,26]. Sometimes, in the case of mixture addition of V₂O₅–CuO, the Cu₂V₂O₇ and Cu₃(VO₄)₂ with very low melting point could be formed and the liquid sintering could effectively lower the sintering temperature [27]. In the present work, different V₂O₅–CuO mixtures were chosen as the sintering aids to lower the sintering temperature of BiSbO₄ ceramics. The influences of sintering temperature and V₂O₅–CuO addition on the crystalline phases, sintering behavior, microstructures and microwave dielectric properties of BiSbO₄ ceramic are investigated.

2. Experimental

Appropriate amounts of reagent-grade starting materials of Bi₂O₃ (>99%, Shu-Du Powders Co. Ltd, China) and Sb₂O₃ (>99%, Guo-Yao Co. Ltd, China) were mixed, according to the composition of BiSbO₄, and ball-milled for 4 h with ZrO₂ balls using ethanol nylon bottle. After drying, mixed powders were calcined at 600 °C and 750 °C for 4 h respectively. Then the calcined BiSbO₄ powder was mixed with 1 wt.% V₂O₅–CuO mixtures (V1C0–V₂O₅ only, V3C1–V₂O₅:CuO = 3:1 mass ratio, V1C1–V₂O₅:CuO = 1:1 mass ratio). After milling for 5 h again and drying, powders were granulated with PVA binder and then uniaxially pressed into cylinders with diameter 10 mm and thickness 5 mm. The samples were sintered at 840–930 °C for 2 h in air.

* Corresponding author. Fax: +86 029 82668794.

E-mail addresses: zhoudi1220@gmail.com (D. Zhou), hwang@mail.xjtu.edu.cn (H. Wang).

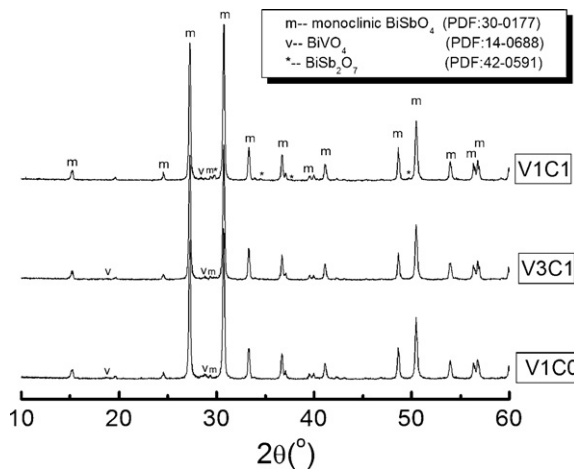


Fig. 1. XRD patterns of BiSbO₄ ceramics with V₂O₅-CuO addition sintered at 900 °C for 2 h.

After being ground, crystalline structures of ceramics were investigated using an X-ray diffractometry with CuK α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). Apparent densities of ceramics were measured using Archimedes' method. The as-fired surfaces and fractured surfaces of ceramics were investigated by scanning electron microscopy (JEOLJSM-6460, Japan). The precipitated phases in

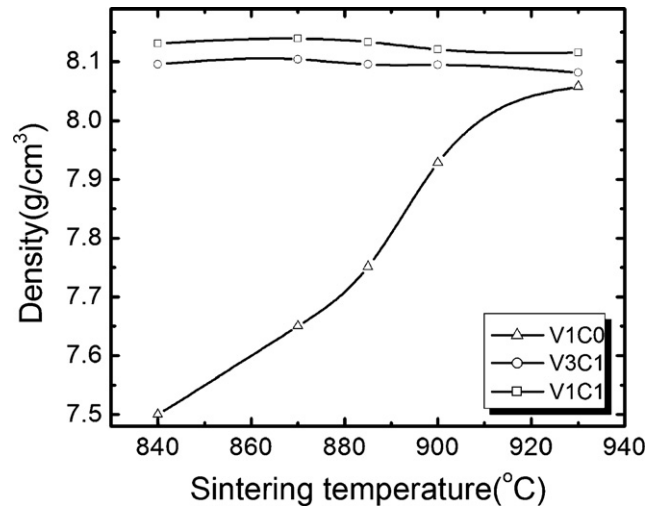


Fig. 2. Apparent density of BiSbO₄ ceramics with V₂O₅-CuO addition as a function of sintering temperature.

ceramics were studied using energy-dispersive X-ray spectrometer (EDS) analysis. Microwave dielectric behaviors were measured by the TE₀₁₈ shielded cavity method using a network analyzer (8720ES, Agilent, U.S.A.) and a temperature chamber (Delta Design 9023, U.S.A.). The temperature coefficients of resonant frequency τ_f /TCF were

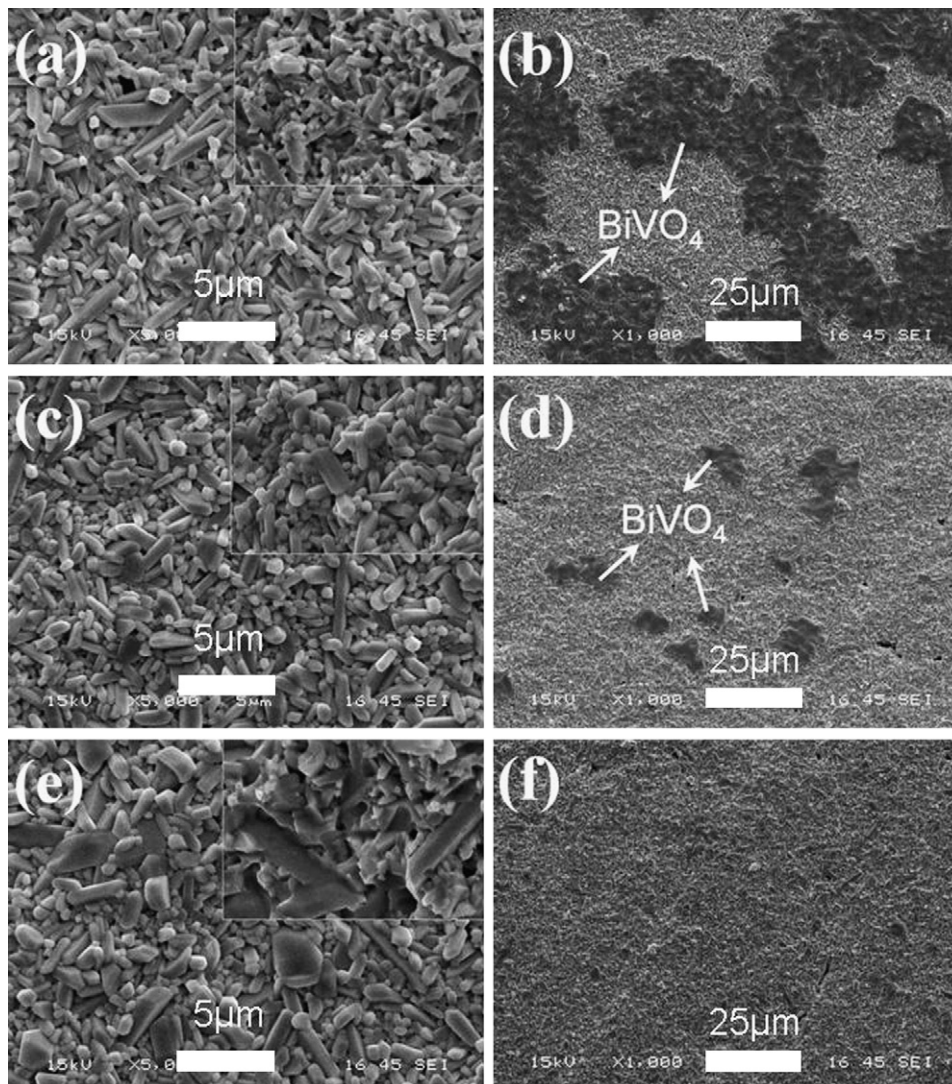


Fig. 3. SEM micrographs of as-fired surface and fractured surface of V1C0 sample (a and b), V3C1 sample (c and d) and V1C1 sample (e and f) sintered at 900 °C for 2 h.

calculated by the following formula:

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

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 BiSbO_4 ceramics with V_2O_5 – CuO additions sintered at 900 °C for 2 h are shown in Fig. 1. The main phases of all samples were monoclinic BiSbO_4 phase. For V1C0 sample, two weak peaks were observed and indexed as BiVO_4 phase. The peaks of BiVO_4 phase became weaker as CuO amount increased and V_2O_5 amount decreased. Although it is not very clear from the XRD analysis due to the weakness of the secondary phase peaks, this phenomenon would be affirmed by the following EDS results. Meanwhile, a new phase which might be indexed as BiSb_2O_7 (PDF: 42-0591) appeared in V1C1 sample as shown in Fig. 1. Its peaks were so weak that it was difficult to be indexed thoroughly. This phenomenon needed further experimental study. Although the addition amount was very little, the following reactions might occur during the sintering process, which could improve the sinterability of BiSbO_4 ceramics.



BiVO_4 could be formed by solid-state reaction method at a low temperature as reported by Valant and Suvorov [28]. In this work BiVO_4 phase seemed to be formed firstly when V_2O_5 addition was enough. Then main phase BiSbO_4 were secondarily formed. Since the radius of V^{5+} (0.54 Å) and Cu^{2+} (0.73 Å) are smaller than that of Sb^{5+} (0.6 Å) and Bi^{3+} (0.76 Å) respectively and considering the electrovalence balance, V^{5+} and Cu^{2+} might partially substitute for the A site and B site in BiSbO_4 structure respectively and form solid solution of $(\text{Bi,Cu})(\text{Sb,V})\text{O}_4$. This assumption might explain where the Cu^{2+} existed within the crystalline lattice either solid solution or ion substitution, which could both lower the sintering temperatures of many systems [12,23,29].

Bulk densities of BiSbO_4 ceramics with V_2O_5 – CuO addition as a function of sintering temperature are shown in Fig. 2. For V1C0 samples, density increased sharply from 7.5 g cm^{-3} to 8.06 g cm^{-3} as sintering temperature increased from 840 °C to 930 °C. For V3C1 and V1C1 samples, densities stabilized at about 8.10 – 8.14 g cm^{-3} in the sintering temperature range from 840 °C to 930 °C. This indicates that mixtures of CuO and V_2O_5 were more effective to lower the sintering temperature of BiSbO_4 ceramics than pure V_2O_5 addition. The BiVO_4 additive was ever used lower the firing temperatures of ZnNb_2O_6 and MgTiO_3 ceramics, etc. [30,31] because of its low densification temperature [28]. In this work, it seemed that addition of CuO or substitution of Cu^{2+} was more effective on BiSbO_4 ceramic than BiVO_4 addition. The density of BiSbO_4 is about 8.459 g cm^{-3} as reported by Kennedy [32]. Ignoring the weak influence of second phase and addition, the densities of all the samples have relative densities above 95%.

SEM micrographs of both as-fired and fractured surfaces of BiSbO_4 ceramics with V_2O_5 – CuO addition sintered at 900 °C for 2 h are shown in Fig. 3. Dense and fine microstructures with almost no pores were revealed for V1C0 and V3C1 samples as shown in Fig. 3(a)–(d) with different magnifications. From the SEM photos with $1000\times$ magnification, it is clear that big grains of BiVO_4 could be observed as shown in Fig. 3(b) and (d) according to EDS analysis. It is seen from Fig. 3 that BiVO_4 amount decreased obviously as V_2O_5 amount decreased and CuO amount increased, which supports the XRD analysis above. In V1C1 ceramic, there are almost

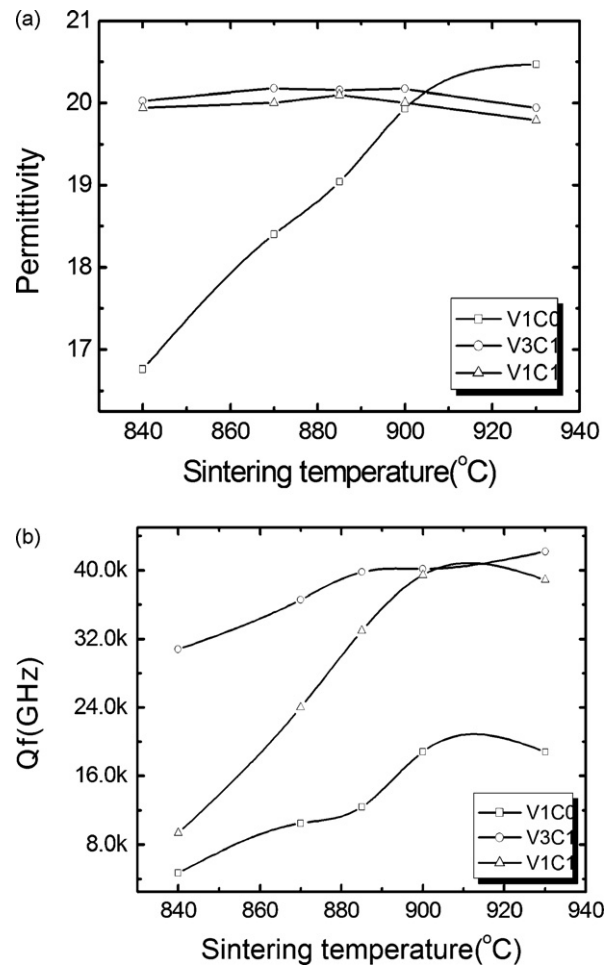


Fig. 4. Microwave dielectric constant (a) and Qf values (b) BiSbO_4 ceramics with V_2O_5 – CuO addition as a function of sintering temperature.

no BiVO_4 grains revealed as shown in Fig. 3(e) and (f). However, BiSb_2O_7 grains could not be observed in V1C1 sample. This might be attributed to the small BiSb_2O_7 amount and its similar chemical composition to BiSbO_4 .

Microwave dielectric properties of BiSbO_4 ceramics with V_2O_5 – CuO addition as a function of sintering temperature are presented in Fig. 4. Microwave permittivity of V1C1 and V3C1 samples kept saturated values about 20 at the sintering temperature range from 840 °C to 930 °C and it agreed well with the result of density. Qf values of V1C1 and V3C1 samples increased as sintering temperature increased and got maximum value of about 40,000 GHz at 900 °C. When temperature increased, grain grew big and grain boundaries decreased. Then the extrinsic dielectric loss caused by grain boundaries reduced. This could explain the Qf values curve versus sintering temperature for V1C1 and V3C1 samples. For V1C0 sample, BiVO_4 phase affected microwave dielectric properties seriously. Pure BiVO_4 ceramic possessed microwave dielectric properties of $\epsilon_r = 68$, $Qf = 8000 \text{ GHz}$ and $\text{TCF} = -243 \text{ ppm } ^\circ\text{C}^{-1}$ as reported by both Valant and Suvorov [28] and Wee et al. [30]. It is obvious that the existence of BiVO_4 phase increased permittivity of BiSbO_4 from 19 to about 20.5 but deteriorated its Qf values seriously. Generally speaking, excess BiVO_4 phase would have many detrimental effects on the microwave dielectric properties of BiSbO_4 ceramic.

Temperature coefficients of resonant frequency of three kinds BiSbO_4 ceramics are shown in Fig. 5. As V_2O_5 amount increased, TCF values shifted from $-71.5 \text{ ppm } ^\circ\text{C}^{-1}$ for C1V1 sample to

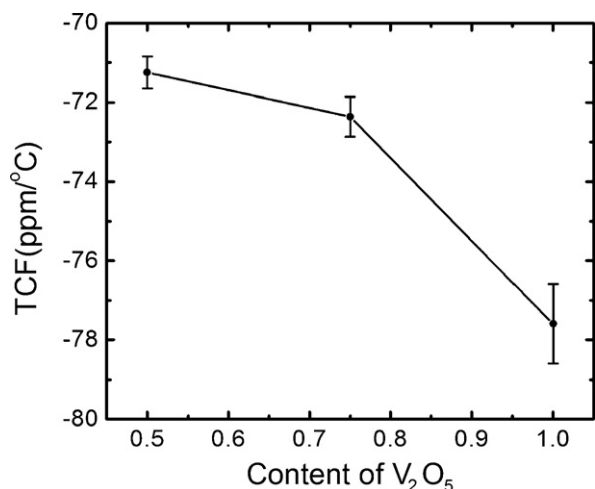


Fig. 5. TCF of BiSbO₄ ceramics as a function of content of V₂O₅.

−77.8 ppm °C^{−1} for C1V0 sample. This is caused by the increase of BiVO₄ phase (TCF = −243 ppm °C^{−1} [28]). As discussed above, although the sintering temperatures of BiSbO₄ ceramics were lowered to below 960 °C successfully by V₂O₅–CuO addition, the TCF value is still a big negative value and it must be modified to near zero before it could be applied in LTCC technology. Adding a small amount of TiO₂ is the often used method to modify the TCF of systems with negative values [33,34]. Therefore the BiSbO₄ ceramic could be used as a potential material for fabrication of ceramic composites with positive TCF ceramics.

4. Conclusions

Additions of 1.0 wt.% V₂O₅–CuO mixtures can effectively lower the sintering temperature of BiSbO₄ ceramic from above 1050 °C to around 930 °C because of the formation of BiVO₄ phase and substitution of Cu²⁺. Microwave permittivity of BiSbO₄ ceramic with V₂O₅–CuO addition is about 20 and a little bigger than that of pure BiSbO₄ ceramic because of the existence of BiVO₄. Good microwave

dielectric properties and low sintering temperatures were obtained in V3C1 and V1C1 samples and this will extend the application for BiSbO₄ ceramics.

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