

Low-temperature sintering and microwave dielectric properties of TiO₂-based LTCC materials

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Abstract Temperature stable high-K LTCC material was prepared. The influence of fabrication process on the crystalline phases, microstructures and microwave dielectric properties of TiO₂-Bi₂O₃-CuO ceramics were investigated. The crystalline phases and microstructures of TiO₂-Bi₂O₃-CuO ceramics were investigated by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. It was found that rutile TiO₂ phase and Bi₂Ti₄O₁₁ phase co-existed in the TiO₂-Bi₂O₃-CuO ceramics. Separate TiO₂ grains and Bi₂Ti₄O₁₁ grains distributed uniformly in the ceramic matrix. The composition 0.92TiO₂-0.08Bi₂Ti₄O₁₁ with 2 wt% CuO addition that was sintered at 900 °C for 2 h showed high dielectric constant ($\epsilon_r \sim 81$), high quality factor ($Q \times f \sim 3,500$ GHz) and near zero temperature coefficient of resonant frequency ($\tau_f \sim -5.1$ ppm/°C), meanwhile the compatibility test showed that it could co-fire with silver electrode. The processing-microstructure-property interrelationship was also studied.

1 Introduction

For the last 40 years, integration of active electronic components progressed at a rapid rate and has been the engine driving many aspects of the electronics industry, particularly in the computer market. Transitioning from

surface mount discrete components to integrated components into the substrate can result in enhanced reliability, better electrical performance and miniaturization [1].

Recently, a new technologies based on the use of ceramic multilayer have been developed. By applying low-temperature cofired ceramics (LTCC) technology, passive elements can be integrated in monolithic, highly reliable, and robust LTCC modules that consist of several layers of ceramic substrates with integrated elements (inductors, capacitors, resonators), which are interconnected with 3-D strip-line circuitry [2]. From the view of electronics industry, new materials suited for microwave applications compatible with LTCC technologies are required. One of the highly desirable requirements is the development of a cofirable capacitor structure with NP0 (± 15 ppm/°C temperature coefficient of capacitance (TCC) [3]. This is because some of the key elements integrated within the dielectric in the high frequency circuit such as filters and resonators need to be very stable against temperature fluctuation. There are additional requirements that these new dielectric materials should exhibit that are critical for the successful integration into LTCC technology. In addition to the evident low sintering temperature (below 960 °C, in order to use Ag conductors) materials with NP0 characteristics should also have k values between 60 and 100, quality factor Q ($1/\tan\delta$) values above 1,000, and silver electrode compatibility [3]. The conductor loss typically dominates the total loss of microstrip resonator devices, therefore high conductivity metals are more useful than refractory metals such as tungsten and platinum.

As high-K microwave dielectric ceramics, BaO-Ln₂O₃-TiO₂ system (Ln: Rare earth) has been widely studied for their typical properties for microwave resonators of $\epsilon_r = 80$ –100, $Qf = 1,800$ –10,000 GHz and small τ_f [4]. However, the sintering temperature of BaO-Ln₂O₃-TiO₂ system

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was too high (above 1350 °C) and it was difficult to lower the sintering temperature of BaO-Ln₂O₃-TiO₂ to below 900 °C for LTCC application [5].

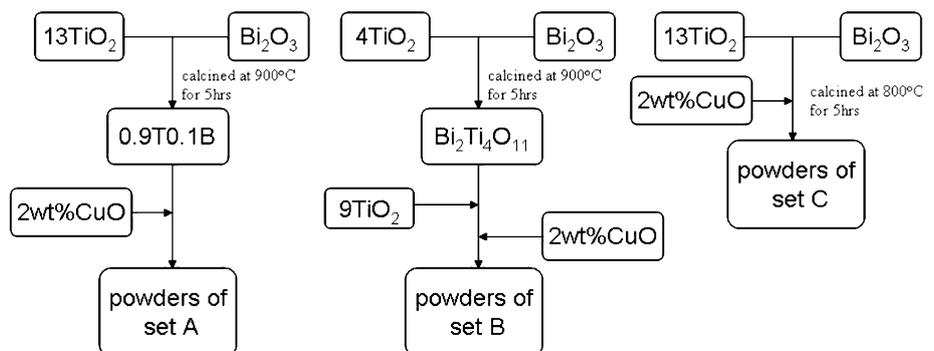
Another high-K microwave dielectric ceramics was TiO₂-based ceramics. TiO₂ has three polymorphs of brookite, anatase and rutile. The brookite and anatase would transform into the rutile phase between 400 and 1,000 °C [6]. Rutile TiO₂ possesses a high dielectric constant (105) and high quality factor (Q) (9,200 at 5 GHz), but unfortunately the τ_f value of TiO₂ was too large (+465 ppm/°C) to be used for LTCC application [7]. TiO₂-Bi₂O₃ binary ceramics was studied by Alford et al. [7, 8] The 0.88TiO₂-0.12Bi₂Ti₄O₁₁ ceramics possessed a microwave dielectric properties of $\epsilon_r = 81$, Qf = 6,500–8,500 GHz and $\tau_f = 8$ –15 ppm/°C [7]. A near zero τ_f value was obtained in TiO₂-Bi₂O₃ binary ceramics because of the fact that Bi₂Ti₄O₁₁ possessed a negative τ_f value (–520 to –550 ppm/°C) [8]. Although the TiO₂-Bi₂O₃ binary ceramics possessed a perfect microwave dielectric property, their sintering temperature was above 1,150 °C, too high to be used for LTCC application. Three approaches are usually used to develop low-firing microwave dielectric ceramics: (a) addition of oxides or glass with low melting temperature; (b) utilization of ultra-fine particles for raw materials; (c) development of novel glass-free low-firing dielectric ceramics. CuO is a low melting point oxide. Previous works showed that the sintering temperature of TiO₂ could be lowered from 1,250–900 °C by 2 wt% CuO addition [9, 10]. In present work, TiO₂-Bi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition were prepared to obtain TiO₂-based microwave dielectric materials with high dielectric constant that were suitable for LTCC application. TiO₂-Bi₂Ti₄O₁₁ is inorganic/inorganic composite material. For this kind of material, when fabricated by conventional solid state reaction method, the two phases could be fabricated separately and then mixed together [11] or be fabricated by one step calcination [12]. Recently, a novel preparation process named reaction-sintering process was successfully used to prepare some ceramic materials such as Ba₅Nb₄O₁₅ and Sr₅Nb₄O₁₅ [13]. In present work, 0.9TiO₂-0.1Bi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition were

prepared with three different fabrication procedures. Influence of fabrication procedures on the crystalline phases, microstructures and microwave dielectric properties of the samples was studied to select a proper fabrication process. Then the microwave dielectric properties were tailored by changing the ratio of the TiO₂ phase to the Bi₂Ti₄O₁₁ phase. The processing-microstructure-property interrelationship was investigated.

2 Experimental procedure

The TiO₂-Bi₂O₃ composition with 2 wt% CuO addition were prepared by conventional solid state reaction method using high purity anatase TiO₂ (>99%, Guo-Yao Co. Ltd., Shanghai, China), Bi₂O₃ (>99%, Shu-Du Powders Co. Ltd., Chengdu, China) and CuO (>99%, Guo-Yao Co. Ltd., Shanghai, China). Three different sets of powders were prepared to investigate the influence of fabrication process on the crystalline phase, microstructure and microwave dielectric properties of the final sintered samples. Figure 1 presents the flow chart for preparing the three sets of 0.9TiO₂-0.1Bi₂Ti₄O₁₁ + 2 wt% CuO powders. Set A: the starting powders of TiO₂ and Bi₂O₃ were weighted according to the composition 0.9TiO₂-0.1Bi₂Ti₄O₁₁ and then milled with ZrO₂ balls (2 mm in diameter) for 4 h in ethanol. The mixtures were dried and calcined at 900 °C for 5 h. 2 wt% CuO was added into the mixtures and they were milled again for 5 h with ZrO₂ balls in ethanol. This set of samples was marked as 0.9T0.1B + 2 wt% CuO for short; Set B: composition Bi₂Ti₄O₁₁ was firstly prepared by conventional solid state reaction method (calcined at 900 °C for 5 h). The calcined Bi₂Ti₄O₁₁ powders and TiO₂ powders were then weighted according to 0.9TiO₂-0.1Bi₂Ti₄O₁₁ and 2 wt% CuO was added at the same time. The mixtures were also milled with ZrO₂ balls for 5 h in ethanol. This set of samples was marked as 0.9T0.1BT + 2 wt% CuO; Set C: the starting powders of TiO₂ and Bi₂O₃ were weighted according to 0.9TiO₂-0.1Bi₂Ti₄O₁₁ and 2 wt% CuO was added at the same time. The mixtures were milled with ZrO₂ balls for 4 h in ethanol. Then the

Fig. 1 Flow charts of preparing procedures of the three sets of 0.9TiO₂-0.1Bi₂Ti₄O₁₁ + 2 wt% CuO powders



mixtures were dried and calcined at 800 °C for 5 h. The calcined powders were re-milled with ZrO₂ balls for 5 h in deionized water. This set of samples was marked as 0.9TiO₂.1Bi₂Ti₄O₁₁.02Cu. These three sets of mixtures were dried, mixed with an appropriate amount of PVA (5 wt%) as a binder and then uniaxially pressed into disks of 8 mm in diameter and 4 mm in thickness and pellets of 10 mm in diameter and 1 mm in thickness. The disks were sintered in air at 870–960 °C for 2 h. Samples of TiO₂ ceramics with 2 wt% CuO addition were also fabricated in present work. To check the chemical compatibility of the ceramic oxide compound and the silver electrode, compatibility test was performed with the method reported by Valant et al. [14]. 20 wt% of powdered silver was mixed and homogenized with the ceramic powder, and then the mixture was pressed into pellets and fired at a temperature of 900 °C for 0.5–4 h to achieve equilibrium.

The crystalline phases of the samples were investigated using X-ray diffractometry with CuK α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). These specimens were ground with SiC sandpaper and polished using 1/4 μ m diamond paste. The microstructures of the sintered samples were observed on the polished surfaces, after thermal etching at 750 °C for 30 min, with scanning electron microscopy (SEM) (JEOL JSM-6460, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS). The densities of the sintered specimens, as a function of sintering temperature, were measured by Archimedes method. Dielectric behaviors at microwave frequency were measured at a frequency of 4–6 GHz by the TE_{01 δ} shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, USA) and a DELTA 9023 temperature chamber (Delta Design, Poway, USA). Temperature coefficient of resonant frequency τ_f was calculated from the following equation:

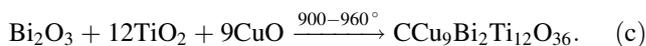
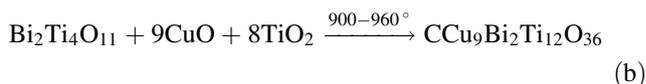
$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \quad (1)$$

where f_{85} and f_{25} are the resonant frequencies of dielectric resonator at 85 and 25 °C, respectively.

3 Results and discussion

Figure 2 shows the XRD patterns of sintered TiO₂ ceramic with 2 wt% CuO addition, Bi₂Ti₄O₁₁ ceramic and three sets of 0.9TiO₂-0.1Bi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition. It was observed that the XRD pattern of TiO₂ ceramic with 2 wt% CuO addition can be identified as single rutile TiO₂ phase (PDF Number 21-1276), and the result was in agreement with that reported by Kim [9] and Shin [10]. For Bi₂Ti₄O₁₁ ceramic, most of the diffraction peaks were indexed as Bi₂Ti₄O₁₁ phase (PDF Number

15-0325), but a residual rutile TiO₂ phase was also observed. It indicates that the reaction between TiO₂ and Bi₂O₃ in Bi₂Ti₄O₁₁ ceramic was not a thorough reaction process when they were mixed in the ratio of 4–1. XRD patterns in Fig. 2 also showed that the main crystalline phases of the three sets of 0.9TiO₂-0.1Bi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition were Bi₂Ti₄O₁₁ phase and rutile TiO₂ phase, however the diffraction peaks of Bi₂Ti₄O₁₁ phase in 0.9TiO₂.1B + 2 wt% CuO ceramic (Set A) and 0.9TiO₂.1Bi0.02Cu ceramic (Set C) were a bit sharper than that in 0.9TiO₂.1BT + 2 wt% CuO ceramic (Set B). It indicates that an excess TiO₂ was propitious to the formation of Bi₂Ti₄O₁₁ phase. Cubic Cu₉Bi₂Ti₁₂O₃₆ phase (PDF Number 46-0725) also existed in the three sets of samples. It was also observed that an unknown phase also existed in the ceramic of Set C. The following solid state reaction might occur during the calcination process and sintering process:



Calcination is an important section of fabrication process of ceramics, although some ceramic systems could be fabricated by reaction-sintering process without calcination process. The solid state reaction occurred mainly in calcination process. In 0.9TiO₂-0.1Bi₂Ti₄O₁₁ ceramic with 2 wt% CuO addition of Set A, the mol ratio of TiO₂ to Bi₂O₃ was 13:1 during the calcination process, which was

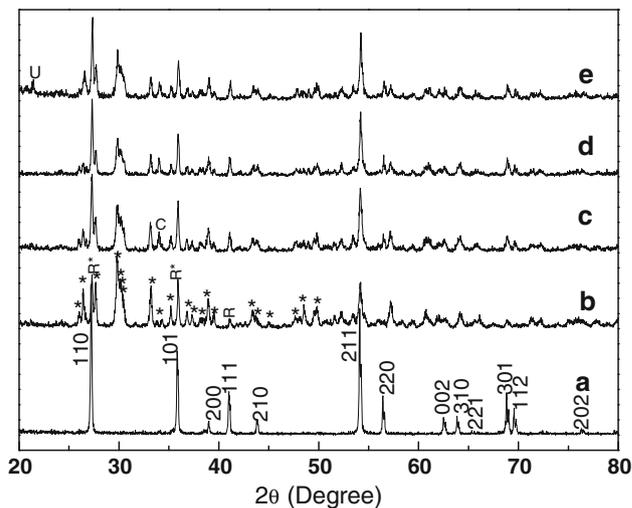


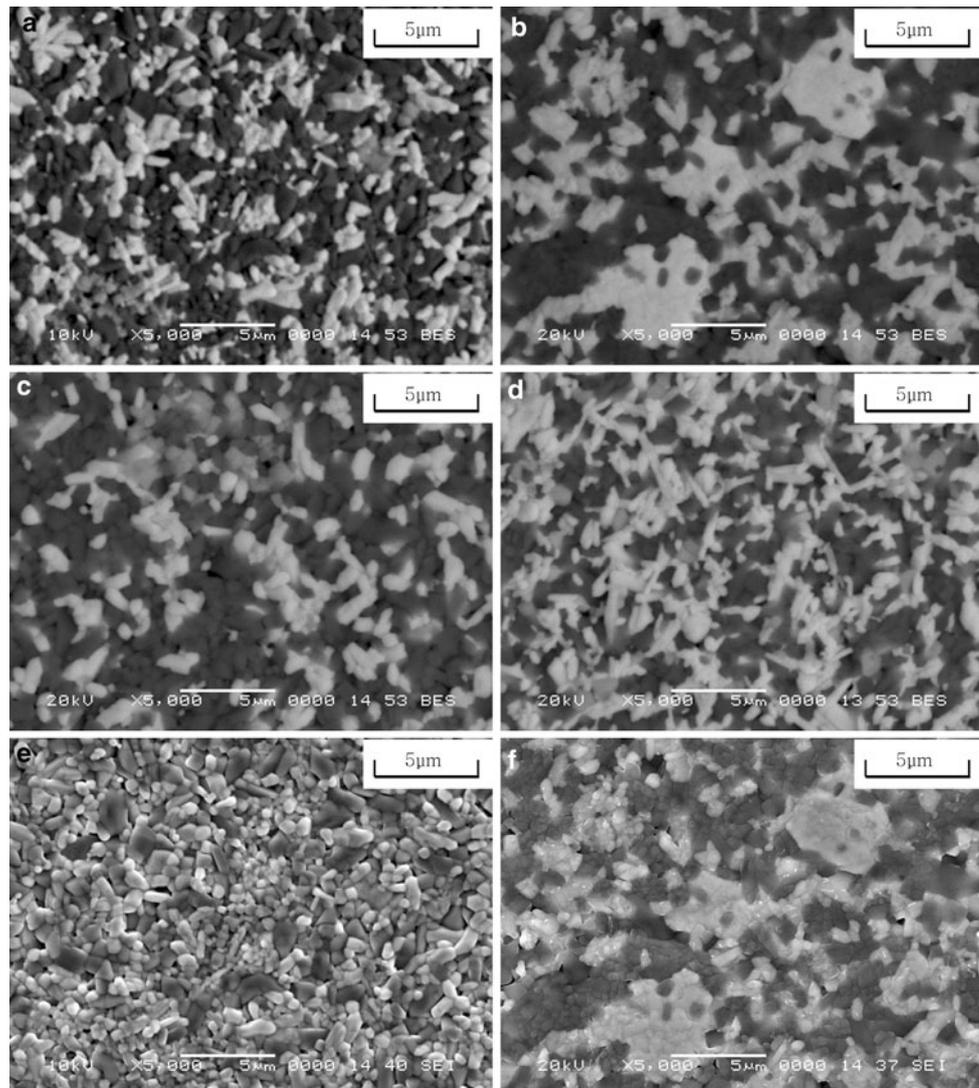
Fig. 2 XRD patterns of ceramics: **a** TiO₂ + 2 wt% CuO; **b** Bi₂Ti₄O₁₁; 0.9TiO₂-0.1Bi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition of **c** Set A; **d** Set B; **e** Set C (R: rutile phase; *: Bi₂Ti₄O₁₁ phase; C: cubic Cu₉Bi₂Ti₁₂O₃₆ phase; U: unknown phase)

propitious to the formation of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase in function (a) because of the excess of TiO_2 . Thus the content of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase in the sample of Set A was a little higher than that in the ceramic of Set B, although they were of the same composition. All the solid state reactions occurred during the sintering process for ceramic of Set C. Although the reaction between TiO_2 and Bi_2O_3 was thorough in ceramic of Set C during the sintering process, the solid state reactions might be difficult to be controlled because there is no calcination process. Thus an unknown phase was detected only in sample of Set C. Thus on the view of crystalline phases, the fabrication procedures of Set A and Set B were more proper than that of Set C.

The microstructures the three sets of 0.9TiO_2 - $0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition were observed by SEM (Fig. 3) and micro-analyzed by EDS (Fig. 4). Figure 3 shows the micrographs of backscattered electron images and second electron images of the surfaces of the

0.9TiO_2 - $0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition. Separate dark grains and light grains distributed uniformly in the ceramic matrix of all the samples sintered at 900°C , as shown in Fig. 3a, c, d. A small amount of grey grains were observed, too. EDS analysis showed that the dark grains were TiO_2 grains, the light ones and the grey ones were $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ and $\text{Cu}_9\text{Bi}_2\text{Ti}_{12}\text{O}_{36}$ respectively, as shown in Fig. 4. The SEM and EDS analysis here well supports the result of XRD analysis in Fig. 2. It was also observed that the grain sizes of the three sets of samples sintered at 900°C were in the range of 0.5 – $2\ \mu\text{m}$. Comparing with the micrograph of ceramic of Set B (Fig. 3c) showing a microstructure with a small amount of pores in the grain boundaries, the micrograph of ceramics of Set A and Set C showed that the grain boundaries were narrow and clean in the dense microstructures, as shown in Fig. 3a, d, e. It indicates that 0.9TiO_2 - $0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition of Set A and Set C had been well densified at

Fig. 3 SEM images for the surfaces of 0.9TiO_2 - $0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition: backscattered electron images of **a** ceramic of Set A sintered at 900°C ; **b** ceramic of Set A sintered at 960°C ; **c** ceramic of Set B sintered at 900°C ; **d** ceramic of Set C sintered at 900°C ; second electron images of ceramics of Set A sintered at **e** 900°C and **f** 960°C



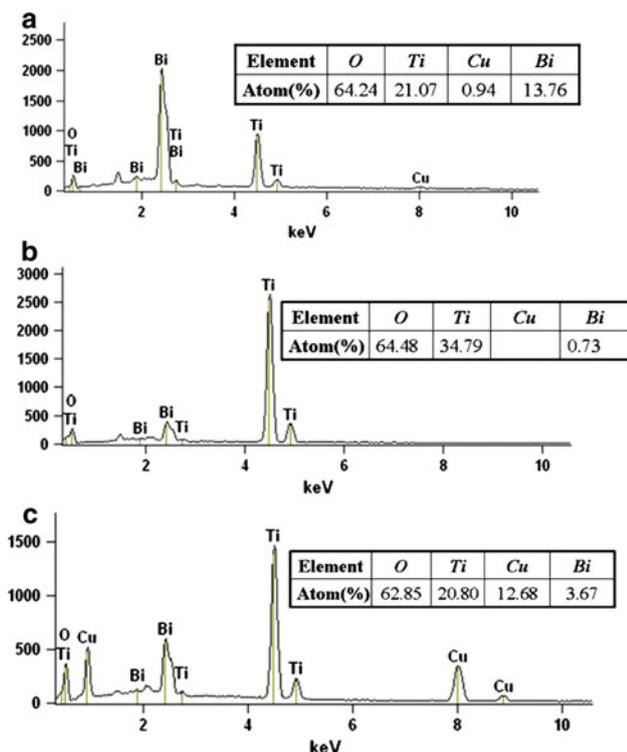


Fig. 4 EDS spectrum of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition: **a** the light grains; **b** the dark grains; and **c** the grey grains

about 900 °C, while ceramic of Set B could not. The grains agglomerated and the grain boundaries were dying away in the ceramic of Set A sintered at 960 °C for 2 h, as shown in Fig. 3b, f. It indicates a strong tendency of abnormal grain growth in ceramic of Set A when the sintering temperature was as high as 960 °C.

Figure 5 illustrates the bulk densities of the three sets of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition as a function of sintering temperature. The bulk densities of all the three sets ceramics increased with the sintering temperature because of the decrease of pores. The bulk densities of ceramics of Set A and Set C sintered at 900–960 °C were 4.72–4.98 g/cm³. Associating with the result from SEM micrographs, it indicates that ceramics of Set A and Set C were densified well at 900–960 °C. For ceramics of Set B, the relative density of ceramic of Set B sintered at 900 °C was less than 86%. Thus it was believed that the sintering temperature of ceramic of Set B was 930–960 °C. On the view of low-temperature sintering, the fabrication procedures of Set A and Set C were more proper than that of Set B.

The microwave dielectric properties of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition as a function of sintering temperature were shown in Fig. 6 and Table 1. The dielectric constant of the three sets of ceramics increased as the sintering temperature increasing. The dielectric constants of ceramics of Set A and Set B increased

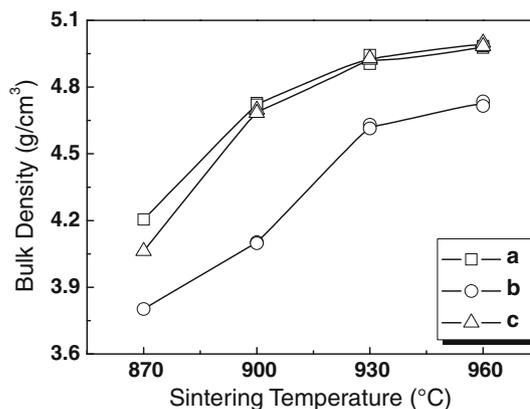


Fig. 5 Bulk densities of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition as a function of sintering temperature: **a** ceramics of Set A; **b** ceramics of Set B; **c** ceramics of Set C

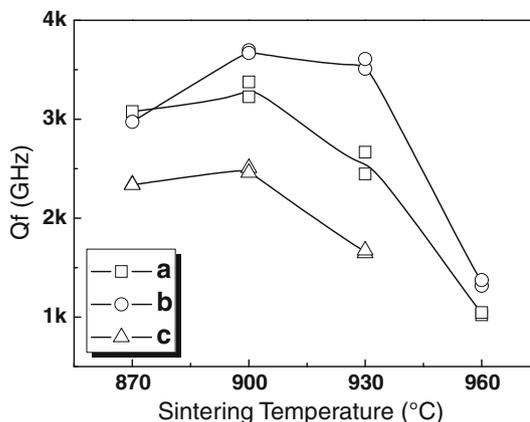
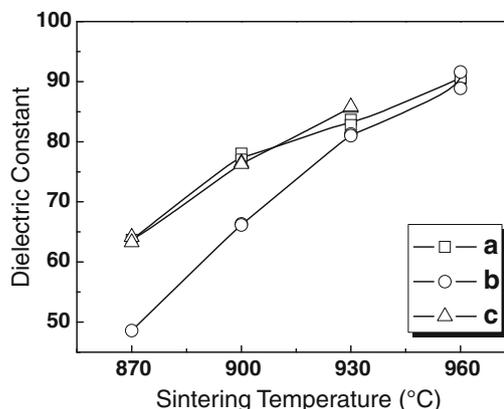


Fig. 6 Microwave dielectric properties of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition as a function of sintering temperature: **a** ceramics of Set A; **b** ceramics of Set B; **c** ceramics of Set C

from 80 to 90 when the sintering temperature increased from 930 to 960 °C (the microwave dielectric properties of ceramic of Set C sintered at 960 °C could not be measured because of its high dielectric loss). The trace of dielectric constant versus sintering temperature does not agree with

Table 1 Sintering behavior and microwave dielectric properties for the three sets of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition and the series of $(1-x)\text{TiO}_2\text{-}x\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition

Set	Sample	T_s^*	ρ (g/cm ³)	ϵ_r	Qf (GHz)	τ_f (ppm/°C)
–	TiO_2^7	–	4.2	105.0	46,000	+465
–	$\text{TiO}_2 + 2 \text{ wt\% CuO}$	930/2 h	3.96	84–86	12,000–13,000	+430
–	$\text{Bi}_2\text{Ti}_4\text{O}_{11}$	1,070/2 h	5.85	68.5	2,900	–632
A	$0.9\text{TiO}_2.1\text{B} + 2 \text{ wt\% CuO}$	900/2 h	4.73	77–79	3,350	–84.1
B	$0.9\text{TiO}_2.1\text{BT} + 2 \text{ wt\% Cu}$	900/2 h	4.10	66–67	3,700	–
B	$0.9\text{TiO}_2.1\text{BT} + 2 \text{ wt\% Cu}$	930/2 h	4.63	81	3,500–3,600	25.1
C	$0.9\text{TiO}_2.1\text{B}0.02\text{Cu}$	900/2 h	4.70	76–77	2,500	–107
A	$x = 0.05$	900/2 h	4.40	82–84	3950–4,000	+141
A	$x = 0.08$	900/2 h	4.66	81.5	3,500	–5.1
A	$x = 0.10$	900/2 h	4.73	77–79	3,350	–84.1
A	$x = 0.12$	900/2 h	4.88	75	3,050	–150

T_s^* sintering temperature

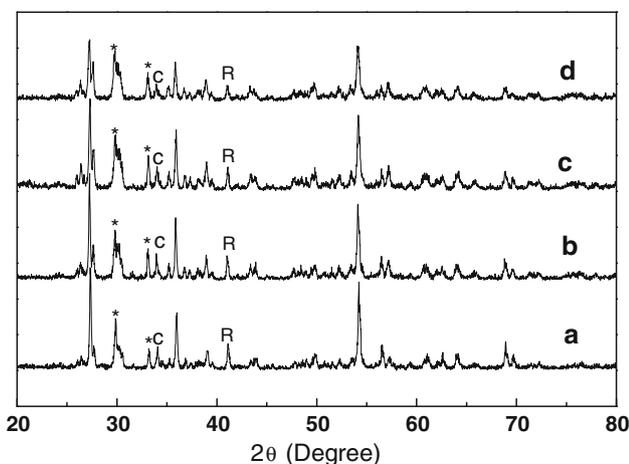


Fig. 7 XRD patterns for the series of $(1-x)\text{TiO}_2\text{-}x\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition: **a** $x = 0.05$; **b** $x = 0.08$; **c** $x = 0.10$; **d** $x = 0.12$ (R: rutile TiO_2 phase; * $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase; C: cubic $\text{Cu}_9\text{Bi}_2\text{Ti}_{12}\text{O}_{36}$ phase)

the trace of bulk density versus sintering temperature. $\text{Cu}_9\text{Bi}_2\text{Ti}_{12}\text{O}_{36}$ ceramic is giant dielectric constant material [15, 16]. Our work showed that the dielectric constant (at 1 MHz) of $\text{Cu}_9\text{Bi}_2\text{Ti}_{12}\text{O}_{36}$ ceramic sintered at 930 °C was just 344, while it increased to 3,900 and 7,750 when sintered at 960 and 990 °C respectively. The abnormal increase of dielectric constant of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition might be caused by the interesting behavior of dielectric constant of $\text{Cu}_9\text{Bi}_2\text{Ti}_{12}\text{O}_{36}$ phase. The Qf value of the three sets of $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition reached their maximums at 900 °C, and then decreased when the sintering temperature increased further due to the agglomeration of grains [17] (as shown in Fig. 3) and oxygen vacancies [6, 18]. The maximum Qf value of ceramic of Set A was 3,350 GHz, higher than that of ceramic of Set C

(2,500 GHz) and a bit lower than that of ceramic of Set B (3,700 GHz). Ceramics of Set C were synthesized by reaction-sintering process without the calcination process, and an unknown phase existed in the sintered samples. That might be partially responsible for the low Qf value for ceramics of Set C. Comparing with the ceramic of Set B sintered at 930 °C for 2 h with a temperature coefficient of resonant frequency (τ_f value) of 25.1 ppm/°C, ceramic of Set A and Set C sintered at 900 °C possessed a τ_f value of –84.1 and –107 ppm/°C (Table 1).

On all accounts, the fabrication procedures of Set C (reaction-sintering process) will be obviated to fabricate the $0.9\text{TiO}_2\text{-}0.1\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition, and in point of low temperature sintering behavior, fabrication procedures of Set A outbalanced that of Set B. For Both ceramic of Set A and ceramic of Set B, there were three phases. They were TiO_2 phase, $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase and $\text{Cu}_9\text{Bi}_2\text{Ti}_{12}\text{O}_{36}$ phase. The dielectric constant, Qf value and τ_f value for TiO_2 ceramics and $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics were $\epsilon_r \sim 105$, $Qf \sim 46,000$ GHz, $\tau_f \sim 465$ ppm/°C and $\epsilon_r \sim 68.5$, $Qf \sim 2,900$ GHz, $\tau_f \sim -632$ ppm/°C (as shown in Table 1). According to the mixing rule of dielectric constant [19] and τ_f value [20] for composite dielectrics, the ratio of TiO_2 phase to $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase was very important to the microwave dielectric properties of $\text{TiO}_2\text{-}\text{Bi}_2\text{Ti}_4\text{O}_{11}$ ceramics with 2 wt% CuO addition. As analyzed before, the fabrication process influenced the ratio of TiO_2 phase to $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase in ceramics of Set A and Set B. The ratio of TiO_2 phase to $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ phase in ceramics of Set A was a little smaller than that in ceramics of Set B, as shown in Fig. 2. Thus the dielectric constant of ceramics of Set A was smaller than that of ceramics of Set B, and comparing with ceramics of Set B possessing a positive τ_f value, ceramics of Set A showed a negative τ_f value (Table 1).

The microwave dielectric properties can be tailored by changing the ratio of the TiO₂ phase to the Bi₂Ti₄O₁₁ phase, and a series of (1 - x)TiO₂-xBi₂O₃ compositions with 2 wt% CuO addition (x = 0.05, 0.08, 0.10, 0.12) were prepared following the fabrication process of Set A to obtain temperature stable LTCC material. Figure 7 presents the XRD patterns of (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition sintered at 900 °C for 2 h. The crystalline phases of all the samples could be indexed as tetragonal rutile phase, Bi₂Ti₄O₁₁ phase and a small amount of cubic Cu₉Bi₂Ti₁₂O₃₆ phase. As the x value increased from 0.05 to 0.12, the ratio of Bi₂Ti₄O₁₁ phase to rutile TiO₂ phase increased while the amount of Cu₉Bi₂Ti₁₂O₃₆ phase maintaining stable. Table 1 shows the sintering behavior and microwave dielectric properties for the (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramics with 2 wt% CuO addition. All the samples could be densified well at 900 °C. The dielectric constant decreased from 82–84 to 75 and the temperature coefficient of resonant frequency (τ_f) shifted from +141 to -150 ppm/°C by changing the x value from 0.05 to 0.12. Temperature stable high-K microwave dielectric ceramic were obtained when x = 0.08.

The bulk densities and microwave dielectric properties of (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramics (x = 0.08) with 2 wt% CuO addition as a function of sintering temperature and the typical backscattered electron images were shown in Fig. 8. The (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramic (x = 0.08) with 2 wt% CuO addition sintered at 900 °C for 2 h presented a densified microstructure, and showed excellent microwave dielectric properties (ε_r = 81.5, Qf = 3,500 GHz and τ_f = -5.1 ppm/°C). The XRD patterns and backscattered electron image in Fig. 9 shows that the (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramic (x = 0.08) with 2 wt% CuO addition co-exists with

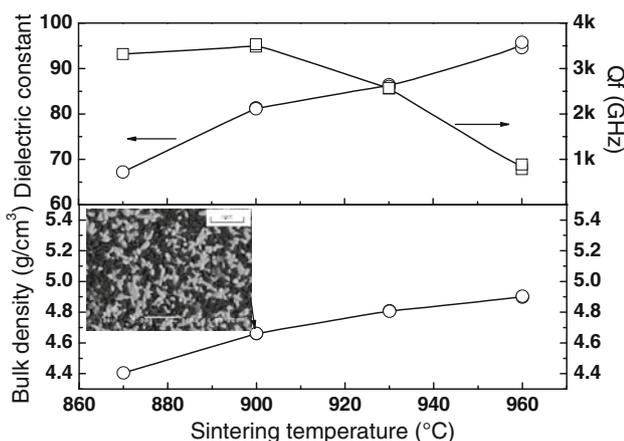


Fig. 8 Bulk densities and microwave dielectric properties of (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramics (x = 0.08) with 2 wt% CuO addition as a function of sintering temperature; backscattered electron images of (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramic (x = 0.08) with 2 wt% CuO addition sintered at 900 °C for 2 h

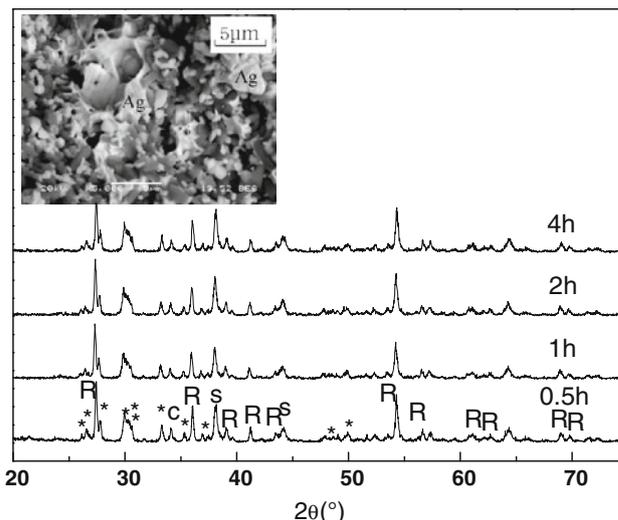


Fig. 9 XRD patterns and backscattered electron image of (1 - x)TiO₂-xBi₂Ti₄O₁₁ ceramics (x = 0.08) with 2 wt% CuO addition after firing with 20 wt% silver for 0.5–4 h at 900 °C

silver powders after co-firing at 900 °C, which indicates that the 0.92T0.08B + 2 wt% CuO ceramic could co-fire with silver electrode. It could be a good candidate for LTCC application.

4 Conclusions

Three sets of TiO₂-Bi₂O₃-CuO powders were prepared by conventional solid state reaction method with different fabrication process. The influences from fabrication process on the crystalline phase, microstructure and microwave dielectric properties of TiO₂-Bi₂O₃-CuO ceramics were investigated. It was found that the rutile TiO₂ phase and Bi₂Ti₄O₁₁ phase co-existed in the TiO₂-Bi₂O₃-CuO ceramics. Separate grains of TiO₂ and Bi₂Ti₄O₁₁ distributed uniformly in the ceramic matrix. The fabrication process influenced the ratio of TiO₂ phase to Bi₂Ti₄O₁₁ phase in TiO₂-Bi₂O₃-CuO ceramics with the same composition, thus influenced the sintering behavior and microwave dielectric properties of TiO₂-Bi₂O₃-CuO ceramics. Bi₂O₃ powders reacted well with TiO₂ powders during the calcination process in set A. Thus the ratio of TiO₂ phase to Bi₂Ti₄O₁₁ phase in the sintered samples of set A was near to that was designed, and that was important for electronics industry. That is to say the fabrication process as set A in preparing TiO₂-Bi₂O₃-CuO ceramics is more suitable for electronics industry. The 0.92T0.08B + 2 wt%Cu ceramics (Set A) sintered at 900 °C for 2 h showed a high dielectric constant (ε_r ~ 81), high quality factor (Q × f ~ 3,500 GHz) and near zero temperature coefficient of resonant frequency (τ_f ~ -5.1 ppm/°C), meanwhile it could co-fire with

silver electrode. It could be a good candidate for LTCC application.

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