

# Low-firing of BiSbO<sub>4</sub> microwave dielectric ceramic with V<sub>2</sub>O<sub>5</sub>–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.% V<sub>2</sub>O<sub>5</sub>–CuO mixture addition on the sintering behavior, phase composition and microwave dielectric properties of BiSbO<sub>4</sub> ceramics have been investigated. BiSbO<sub>4</sub> ceramics can be well densified below temperature about 930 °C with 1.0 wt.% V<sub>2</sub>O<sub>5</sub>–CuO mixtures addition with different ratios of CuO to V<sub>2</sub>O<sub>5</sub>. The formation of BiVO<sub>4</sub> phase and substitution of Cu<sup>2+</sup> can explain the decrease of sintering temperature. Dense BiSbO<sub>4</sub> 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<sup>-1</sup> and –77.8 ppm °C<sup>-1</sup>. BiSbO<sub>4</sub> 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 Bi<sub>2</sub>O<sub>3</sub>–(Nb,Ta)<sub>2</sub>O<sub>5</sub> binary systems, Bi(Nb,Ta)O<sub>4</sub> [8–12] and Bi<sub>3</sub>(Nb,Ta)O<sub>7</sub> [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, WO<sub>3</sub> or V<sub>2</sub>O<sub>5</sub> addition for Bi(Nb,Ta)O<sub>4</sub>). In Bi<sub>2</sub>O<sub>3</sub>–ZnO–(Nb,Ta)<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>3</sub>–CaO–Nb<sub>2</sub>O<sub>5</sub> ternary systems, some compounds with single-phase, such as Bi<sub>2</sub>(Zn<sub>2/3</sub>Nb<sub>4/3</sub>)O<sub>7</sub>, Bi<sub>2</sub>(Zn<sub>2/3</sub>Ta<sub>4/3</sub>)O<sub>7</sub> and Bi<sub>18</sub>Ca<sub>8</sub>Nb<sub>12</sub>O<sub>65</sub> [8,17–20], also have good microwave dielectric properties. Wang et al. studied the microwave dielectric properties of Bi(Nb,Sb)O<sub>4</sub> ceramic in the orthorhombic solid solution region in 2004 [21]. Recently, we have reported the microwave dielectric behaviors of pure monoclinic BiSbO<sub>4</sub> [22]. BiSbO<sub>4</sub> 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<sup>-1</sup>. Ta<sup>5+</sup> is ever used to substitute for Sb<sup>5+</sup> in BiSbO<sub>4</sub>

to modify its sintering and dielectric behaviors. Although both single-phases of BiSbO<sub>4</sub> and BiTaO<sub>4</sub> ceramics can not be well densified below 1050 °C, the sintering temperatures for Bi(Sb<sub>1–x</sub>Ta<sub>x</sub>)O<sub>4</sub> (0.2 < x ≤ 0.6) ceramics can be lowered to around 960 °C, which could be attributed to the formation of solid solution [23].

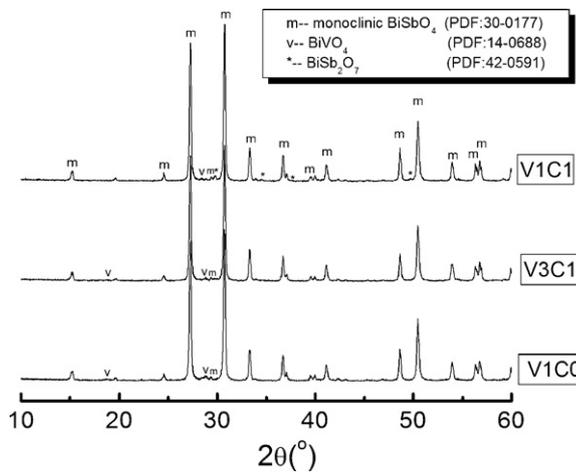
Addition of low melting point oxides is an often used method to lower the sintering temperature of microwave dielectric ceramics. In our recent work [24], we used B<sub>2</sub>O<sub>3</sub>–CuO mixture addition to lower the sintering temperature of BiSbO<sub>4</sub> ceramic to below 960 °C. In fact, a small amount of CuO, V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>–CuO additions are effective to lower the sintering temperature of BiNbO<sub>4</sub> system [25,26]. Sometimes, in the case of mixture addition of V<sub>2</sub>O<sub>5</sub>–CuO, the Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Cu<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> with very low melting point could be formed and the liquid sintering could effectively lower the sintering temperature [27]. In the present work, different V<sub>2</sub>O<sub>5</sub>–CuO mixtures were chosen as the sintering aids to lower the sintering temperature of BiSbO<sub>4</sub> ceramics. The influences of sintering temperature and V<sub>2</sub>O<sub>5</sub>–CuO addition on the crystalline phases, sintering behavior, microstructures and microwave dielectric properties of BiSbO<sub>4</sub> ceramic are investigated.

## 2. Experimental

Appropriate amounts of reagent-grade starting materials of Bi<sub>2</sub>O<sub>3</sub> (>99%, Shu-Du Powders Co. Ltd, China) and Sb<sub>2</sub>O<sub>3</sub> (>99%, Guo-Yao Co. Ltd, China) were mixed, according to the composition of BiSbO<sub>4</sub>, and ball-milled for 4 h with ZrO<sub>2</sub> balls using ethanol nylon bottle. After drying, mixed powders were calcined at 600 °C and 750 °C for 4 h respectively. Then the calcined BiSbO<sub>4</sub> powder was mixed with 1 wt.% V<sub>2</sub>O<sub>5</sub>–CuO mixtures (V1C0–V<sub>2</sub>O<sub>5</sub> only, V3C1–V<sub>2</sub>O<sub>5</sub>:CuO = 3:1 mass ratio, V1C1–V<sub>2</sub>O<sub>5</sub>: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.

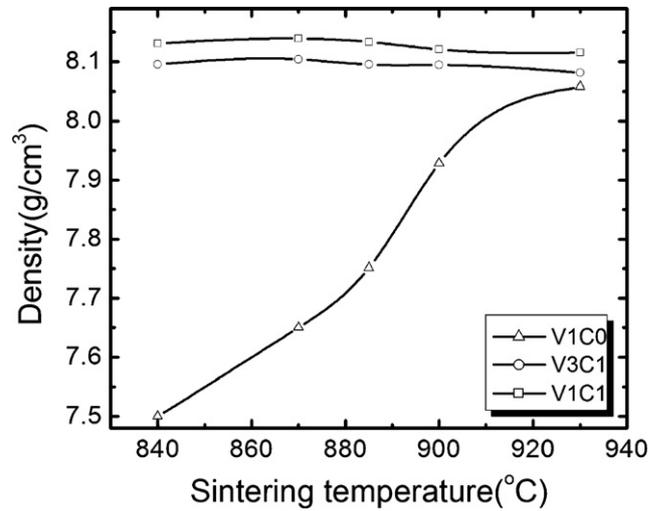
\* Corresponding author. Fax: +86 029 82668794.

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



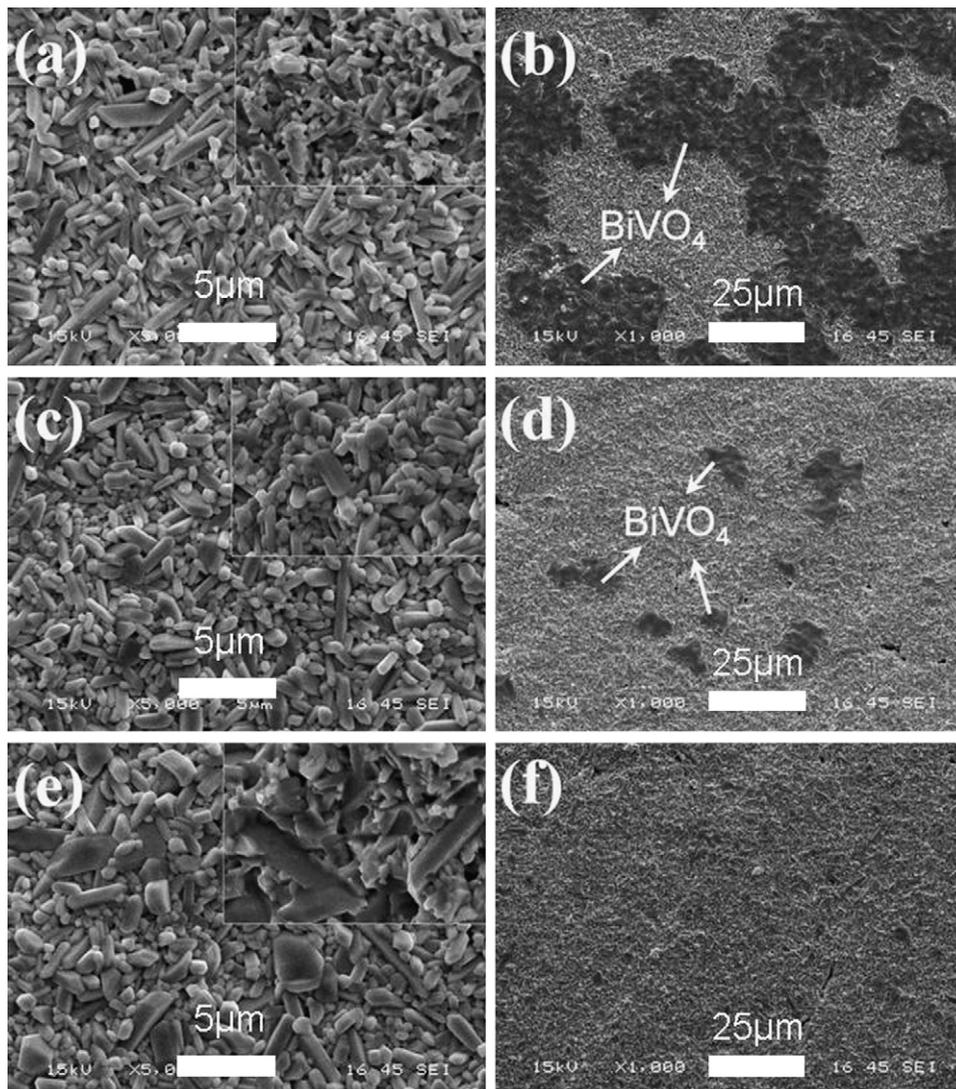
**Fig. 1.** XRD patterns of BiSbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>-CuO addition sintered at 900 °C for 2 h.

After being ground, crystalline structures of ceramics were investigated using an X-ray diffractometry with CuK $\alpha$  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 (JEOL JSM-6460, Japan). The precipitated phases in



**Fig. 2.** Apparent density of BiSbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>-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 TE<sub>018</sub> 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  $\tau_f$ /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<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>–CuO additions sintered at 900 °C for 2 h are shown in Fig. 1. The main phases of all samples were monoclinic BiSbO<sub>4</sub> phase. For V1C0 sample, two weak peaks were observed and indexed as BiVO<sub>4</sub> phase. The peaks of BiVO<sub>4</sub> phase became weaker as CuO amount increased and V<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>7</sub> (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<sub>4</sub> ceramics.



BiVO<sub>4</sub> could be formed by solid-state reaction method at a low temperature as reported by Valant and Suvorov [28]. In this work BiVO<sub>4</sub> phase seemed to be formed firstly when V<sub>2</sub>O<sub>5</sub> addition was enough. Then main phase BiSbO<sub>4</sub> were secondarily formed. Since the radius of V<sup>5+</sup> (0.54 Å) and Cu<sup>2+</sup> (0.73 Å) are smaller than that of Sb<sup>5+</sup> (0.6 Å) and Bi<sup>3+</sup> (0.76 Å) respectively and considering the electrovalence balance, V<sup>5+</sup> and Cu<sup>2+</sup> might partially substitute for the A site and B site in BiSbO<sub>4</sub> structure respectively and form solid solution of (Bi,Cu)(Sb,V)O<sub>4</sub>. This assumption might explain where the Cu<sup>2+</sup> 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<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>–CuO addition as a function of sintering temperature are shown in Fig. 2. For V1C0 samples, density increased sharply from 7.5 g cm<sup>-3</sup> to 8.06 g cm<sup>-3</sup> 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<sup>-3</sup> in the sintering temperature range from 840 °C to 930 °C. This indicates that mixtures of CuO and V<sub>2</sub>O<sub>5</sub> were more effective to lower the sintering temperature of BiSbO<sub>4</sub> ceramics than pure V<sub>2</sub>O<sub>5</sub> addition. The BiVO<sub>4</sub> additive was ever used lower the firing temperatures of ZnNb<sub>2</sub>O<sub>6</sub> and MgTiO<sub>3</sub> ceramics, etc. [30,31] because of its low densification temperature [28]. In this work, it seemed that addition of CuO or substitution of Cu<sup>2+</sup> was more effective on BiSbO<sub>4</sub> ceramic than BiVO<sub>4</sub> addition. The density of BiSbO<sub>4</sub> is about 8.459 g cm<sup>-3</sup> 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<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>–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× magnification, it is clear that big grains of BiVO<sub>4</sub> could be observed as shown in Fig. 3(b) and (d) according to EDS analysis. It is seen from Fig. 3 that BiVO<sub>4</sub> amount decreased obviously as V<sub>2</sub>O<sub>5</sub> amount decreased and CuO amount increased, which supports the XRD analysis above. In V1C1 ceramic, there are almost

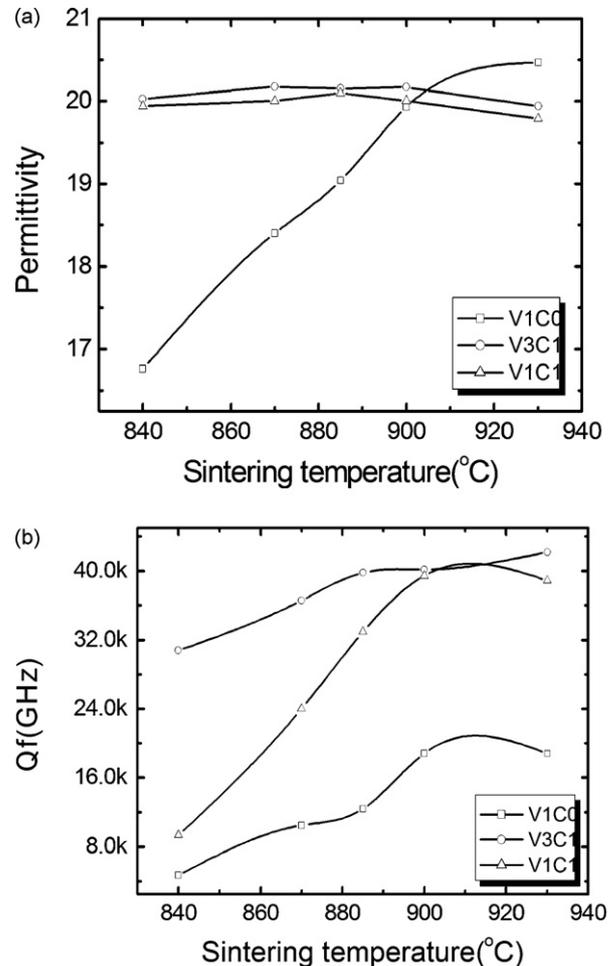


Fig. 4. Microwave dielectric constant (a) and Qf values (b) BiSbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>–CuO addition as a function of sintering temperature.

no BiVO<sub>4</sub> grains revealed as shown in Fig. 3(e) and (f). However, BiSb<sub>2</sub>O<sub>7</sub> grains could not be observed in V1C1 sample. This might be attributed to the small BiSb<sub>2</sub>O<sub>7</sub> amount and its similar chemical composition to BiSbO<sub>4</sub>.

Microwave dielectric properties of BiSbO<sub>4</sub> ceramics with V<sub>2</sub>O<sub>5</sub>–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<sub>4</sub> phase affected microwave dielectric properties seriously. Pure BiVO<sub>4</sub> ceramic possessed microwave dielectric properties of  $\epsilon_r = 68$ ,  $Qf = 8000$  GHz and  $TCF = -243$  ppm °C<sup>-1</sup> as reported by both Valant and Suvorov [28] and Wee et al. [30]. It is obvious that the existence of BiVO<sub>4</sub> phase increased permittivity of BiSbO<sub>4</sub> from 19 to about 20.5 but deteriorated its Qf values seriously. Generally speaking, excess BiVO<sub>4</sub> phase would have many detrimental effects on the microwave dielectric properties of BiSbO<sub>4</sub> ceramic.

Temperature coefficients of resonant frequency of three kinds BiSbO<sub>4</sub> ceramics are shown in Fig. 5. As V<sub>2</sub>O<sub>5</sub> amount increased, TCF values shifted from  $-71.5$  ppm °C<sup>-1</sup> for C1V1 sample to

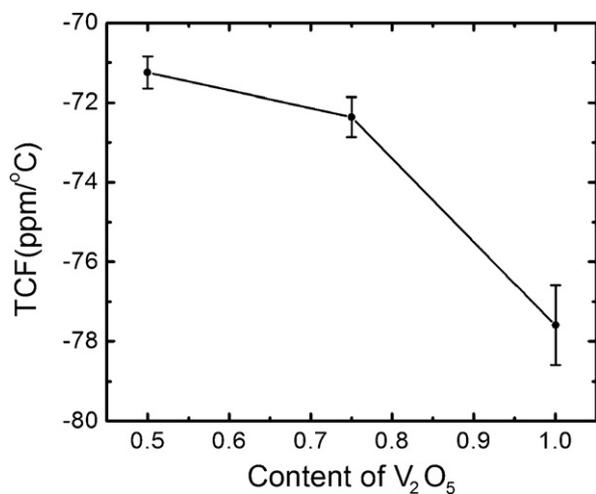


Fig. 5. TCF of BiSbO<sub>4</sub> ceramics as a function of content of V<sub>2</sub>O<sub>5</sub>.

−77.8 ppm °C<sup>−1</sup> for C1V0 sample. This is caused by the increase of BiVO<sub>4</sub> phase (TCF = −243 ppm °C<sup>−1</sup> [28]). As discussed above, although the sintering temperatures of BiSbO<sub>4</sub> ceramics were lowered to below 960 °C successfully by V<sub>2</sub>O<sub>5</sub>–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 TiO<sub>2</sub> is the often used method to modify the TCF of systems with negative values [33,34]. Therefore the BiSbO<sub>4</sub> ceramic could be used as a potential material for fabrication of ceramic composites with positive TCF ceramics.

#### 4. Conclusions

Additions of 1.0 wt.% V<sub>2</sub>O<sub>5</sub>–CuO mixtures can effectively lower the sintering temperature of BiSbO<sub>4</sub> ceramic from above 1050 °C to around 930 °C because of the formation of BiVO<sub>4</sub> phase and substitution of Cu<sup>2+</sup>. Microwave permittivity of BiSbO<sub>4</sub> ceramic with V<sub>2</sub>O<sub>5</sub>–CuO addition is about 20 and a little bigger than that of pure BiSbO<sub>4</sub> ceramic because of the existence of BiVO<sub>4</sub>. Good microwave

dielectric properties and low sintering temperatures were obtained in V3C1 and V1C1 samples and this will extend the application for BiSbO<sub>4</sub> ceramics.

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