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# Bismuth titanates candidates for high permittivity LTCC

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## Abstract

$Bi_2O_3$–$TiO_2$ composites are known to possess attractive microwave dielectric properties. However, producing LTCC analogues with equally promising dielectric properties is problematic. Here, we show that judicious choice of both $TiO_2$ starting powders and dopants can produce composites with excellent properties. Three $TiO_2$ powders were evaluated: 1 μm-anatase, 1 μm-rutile and a nanosized (30 nm) mixture of 75–25 anatase-rutile. The best dielectric properties were obtained by using uncalcined nanosized anatase/rutile with $Bi_2O_3$ powder. By doping this $Bi_2O_3$–$TiO_2$ powder mixture with 0.112 wt.% CuO dielectric properties of $Q \times f = 9000$ GHz, $\varepsilon_r = 80$ and $\tau_f = 0$ ppm/K (at 300 K) were obtained at a sintering temperature of 915 °C.

## 1. Introduction

The microwave characterisation of the binary system $Bi_2O_3$–$TiO_2$ has been published previously.[1,2] By using a molar ratio of 11.34:1 $TiO_2$–$Bi_2O_3$, a ceramic consisting of two separate grains of $TiO_2$ and $Bi_2Ti_4O_{11}$ is formed. These two types of grain have both high permittivity and opposite signs of temperature coefficient of resonant frequency. $TiO_2$ has $\varepsilon_r = 100$ and $\tau_f = +430$ ppm/K and $Bi_2Ti_4O_{11}$ has $\varepsilon_r = 51$ and $\tau_f = -530$ ppm/K. The overall dielectric property of this 11.34:1 $TiO_2$–$Bi_2O_3$ is $Q \times f = 9{,}500$ GHz, $\varepsilon_r = 80$ and $\tau_f = 0$ ppm/K (at 300 K).[1] Previous studies used sintering temperatures well in excess of 1100 °C. The main target at this paper is to reduce the sintering temperature to LTCC level which is below 960 °C (silvers melting point).

## 2. Experimental procedures

The starting materials used were anatase (Aldrich, 99.8% purity), rutile (PIKEM, 99.9% purity) and nanosized (Degussa P25, >99.5% purity), which is predominantly anatase. Other materials were $Bi_2O_3$ (Aldrich 99.9%), CuO (BDH 98%), $V_2O_3$ (Aldrich 99.6%), $LiCO_3$ (Aldrich 99%), MnO (Aldrich 99%) and ZnO (Adrich 99.9%). The powders were mixed and prepared by a standard ceramics mixed-oxide routes.

The shrinkage and sintering behaviour was measured by a horizontal-loading dilatometer (Netzsch Instruments DIL 402C). The final powders were uniaxially pressed at 50 MPa to form pellets, 8 mm in diameter and 3 mm in thickness followed by sintering in air at temperatures between 870 and 1200 °C. Density was calculated by measuring mass and volume.

The structure and phase purity of the composites were examined by X-ray diffraction analysis (Philips XPert MRD) with diffractometer PW33. Polished and thermally etched samples were qualitatively and quantitatively analysed by Scanning Electron Microscopy (SEM; Hitachi 4300) equipped with an Energy Dispersive X-ray Spectrometer (EDXA; Oxford Instruments INCA system)

The resonant frequency (*f*), relative permittivity ($\varepsilon_r$) and quality factor ($Q$) were measured by a resonant cavity method using the $TE_{01\delta}$ mode using a network analyser (Hewlett-Packard 8720D) described elsewere.[1] The cavity was placed on a coldhead inside a closed–cycle cooling system for $\tau_f$ measurements.

## 3. Results and discussion

Previous research found that the uncalcined, titania-rich $Bi_2O_3$–$TiO_2$ mixtures resulted in similar dielectric properties as the pre-calcined counterpart.[1] $Bi_2O_3$, which is often used as a flux due to its low melting point, forms a secondary phase when reacting with $TiO_2$ at around 750–800 °C. This secondary phase, $Bi_2Ti_4O_{11}$, is the only other phase present in this type of binary composite. The potential of using P25 as a $TiO_2$ source was studied by dilatometry analysis, see Fig. 1. The first two types of $TiO_2$ were with the same particle size, rutile (1 μm) and anatase (1 μm) and then an anatase-rich sub micrometre particle Degussa P25 (30 nm).

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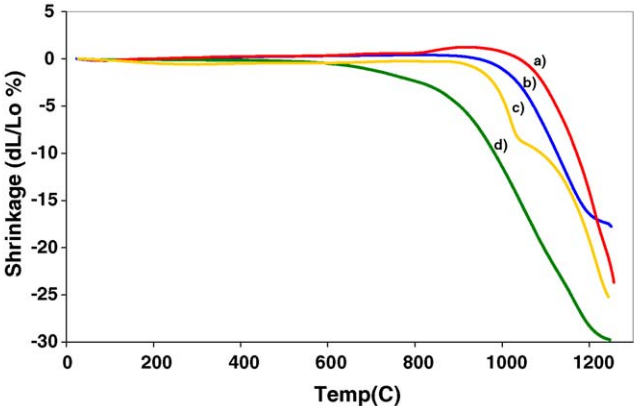

Fig. 1. Dilatometer analysis showing the shrinkage of different batches: (a) $Bi_2O_3$–$TiO_2$ (rutile 1 μm); (b) $Bi_2O_3$–$TiO_2$ (anatase/rutile/calcined/70 nm); (c) $Bi_2O_3$–$TiO_2$ (anatase 1 μm); and (d) $Bi_2O_3$–$TiO_2$ (anatase/rutile/uncalcined/30 nm).

The rutile composite started sintering at 1000 °C and stopped at 1225 °C. The anatase composite started at 900 °C and stopped at 1125 °C, while the P25 composite started at 800 °C and stopped at 1080 °C. The shrinkage of the composite using anatase shows a region between 1020 and 1060 °C where the shrinkage rate decreased. This abnormal decrease was also detected by Kim et al.[3] this discontinuity of shrinkage is due to the reduction of the specific volume when anatase transforms to rutile. This results in a temporary increase in porosity. The TGA/DTA analysis showed a weak exothermic peak at around 780 °C for $TiO_2$–Degussa P25-30 nm corresponding to the anatase-rutile transformation which is lower than that for the anatase 1 μm in which the onset of this transformation is at 1090 °C, see Fig. 2. The nanosized P25 reduced the sintering temperature significantly, and in addition, the anatase-rutile transformation takes place just before the onset of sintering inhibiting porosity development as a consequence of the phase change. The $Bi_2O_3$–$TiO_2$ (P25) mixture which was calcined at 900 °C prior to milling and homogenisation exhibited a sintering onset at 1000 °C and ceased at 1150 °C.

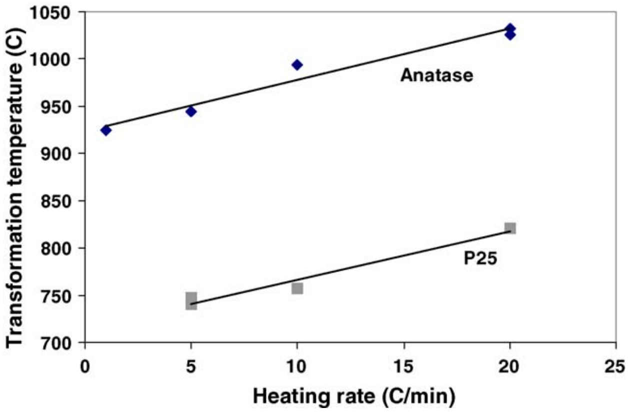

Fig. 2. Anatase-rutile transformation temperature change with different heating rates for (a) $Bi_2O_3$–$TiO_2$/anatase and (b) $Bi_2O_3$–$TiO_2$/Degussa P25.

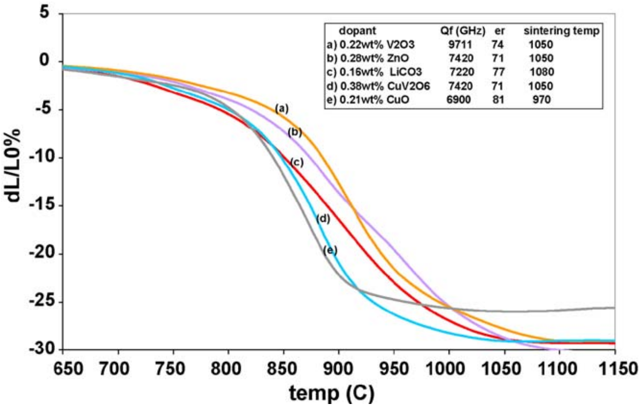

Fig. 3. Dilatometer analysis showing the reduced sintering temperature when dopants were added.

By varying the heating rate, it was clear that the anatase-rutile transformation temperature decreased with lower heating rate, see Fig. 2. As a result the heating rate used was 2 °C/min to ensure that only rutile was present at the onset of sintering.

Fig. 3 shows the effect of the dopants on the shrinkage behaviour of the $Bi_2O_3$–$TiO_2$ mix. The onset of the sintering is shifted to a lower temperature and reaches the maximum sintering between 900 and 970 °C for all dopants.

Kim et al.[4] discovered that CuO (<0.5 wt.%) reduced the anatase-rutile phase transformation temperature resulting in pure rutile phase at 875 °C. It is evident that there are three major aspects contributing to reduction of the sintering temperature of the $Bi_2O_3$–$TiO_2$ mix here. First is the use of sub-micron particles reducing the sintering temperature, second is the utilization of the exothermic anatase-rutile phase transformation prior the onset of sintering, and third is the further reduction of anatase-rutile transformation temperature plus an introduced liquid phase when CuO dopant is added.

The activation energy, $E_a$, of the three types of $TiO_2$ sources and with CuO dopant was analysed by varying the heating rate (Table 1). The shrinkage ($dL/L_0$) of the samples was measured against temperature, $T$, by the dilatometer for each heating rate. The experimental determination of $E_a$ was calculated using the Arrhenius expression given by

$$\ln k = \frac{-E}{R}\left[\frac{1}{T}\right] + \ln Z$$

where the activation energy, $E_a$, will be the slope of the plot multiplied with the gas constant $R$ (=8.3145 J $K^{-1}$ $mol^{-1}$).

Table 1
Activation energy and standard deviation for different $TiO_2$ sources and with different amount of CuO dopant (1 standard deviation in parenthesis)

| Material | Activation energy (kJ $mol^{-1}$) |
|---|---|
| $Bi_2O_3$–$TiO_2$ (PiKem) uncalc. | 741 ± 100 |
| $Bi_2O_3$–$TiO_2$ (anatase) uncalc. before trans. | 342 ± 15 |
| $Bi_2O_3$–$TiO_2$ (anatase) uncalc. after trans. | 845 ± 150 |
| $Bi_2O_3$–$TiO_2$ (P25) uncalc. | 208 ± 14 |
| $Bi_2O_3$–$TiO_2$ (P25) calcined | 337 ± 43 |
| $Bi_2O_3$–$TiO_2$ (P25) + 0.7 wt.% CuO uncalc. | 580 ± 90 |
| $Bi_2O_3$–$TiO_2$ (P25) + 0.2 wt.% CuO uncalc. | 168 ± 14 |
| $Bi_2O_3$–$TiO_2$ (P25) + 0.1 wt.% CuO uncalc. | 200 ± 30 |

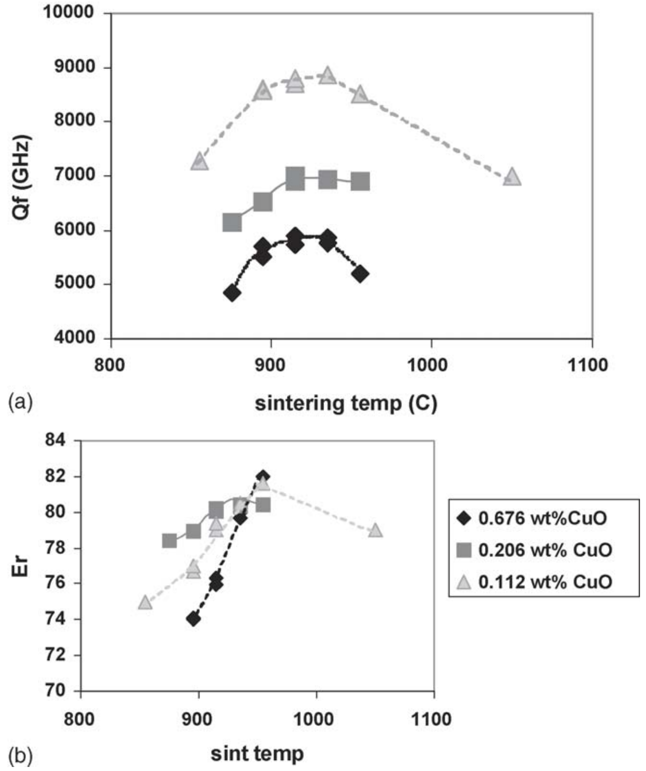

Fig. 4. Variation of (a) $Q \times f$ and (b) $\varepsilon_r$ over sintering temperature for the three different levels of CuO dopants.

In the batch using anatase, the porosity developed from the transformation further slows down sintering as the activation energy increases by more than a factor of 2 after the transformation. By using sub-micron P25 the activation energy decreases further, as expected with a decrease in particle size. It is noted that the higher volume of CuO increases the activation energy significantly. When examining the shrinkage behaviour of the batch using a higher level of CuO, it is seen that the sintering starts before the anatase-rutile transformation in addition to a second section of reduced shrinkage rate occurring at 800 °C.

The three levels of CuO dopants were studied further and it was found that there was little difference between them. Most noticeable is the decrease of $Q \times f$ with an increased amount of CuO dopant but the permittivity remains almost constant, see Table 2 and Fig. 4. All had density over 95% so there could be several reasons for the variation of dielectric loss. One of them is that there is a small amount of Cu that can form solid solution with $TiO_2$ and $Bi_2Ti_4O_{11}$. This single-phase region for $TiO_2$ corresponds to $Ti_{0.996}Cu_{0.004}O_{1.992}$ [4] and is unknown for $Bi_2Ti_4O_{11}$. In increased CuO levels, there will be more CuO phase (which increase the dielectric loss) plus the possibility of secondary phases when CuO reacts with $Bi_2O_3$.

XRD analysis, Fig. 5 indicates that the majority phases are $TiO_2$ and $Bi_2Ti_4O_{11}$ even when dopants are added. This is because the doping levels are very low and the possible secondary phases would therefore be in minimal quantity. A pre-calcined sample shows higher intensity of the $TiO_2$ peaks.

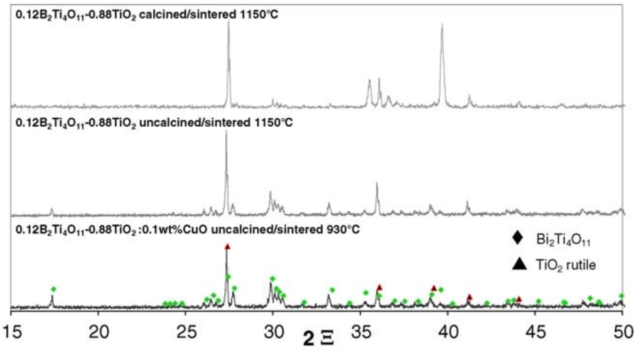

Fig. 5. XRD of (a) 0.1 wt.%CuO doped uncalcined/sintered at 930 °C 11.3:1 $TiO_2$–$Bi_2O_3$ (0.88$TiO_2$–0.12$Bi_2Ti_4O_{11}$) (b) undoped uncalcined/sintered at 1150 °C 0.88$TiO_2$–0.12$Bi_2Ti_4O_{11}$ and (c) calcined and sintered at 1150 °C 0.88$TiO_2$–0.12$Bi_2Ti_4O_{11}$.

SEM/EDAX showed that with the highest level of CuO, 0.7 wt.%, there was a visibly increased level of porosity. This is in agreement with the result from the dilatometer analysis. It was also only at this slightly higher level of dopant there was a noticeable Cu-rich interface between the grains. The grain size distribution was similar in 0.11 wt.% CuO doped (sintered at 915 °C) as undoped bismuth titanate (sintered at 1150 °C) with an average grain size of 3 μm but there was a small increased level of porosity as well as different grain appearance, see Fig. 6.

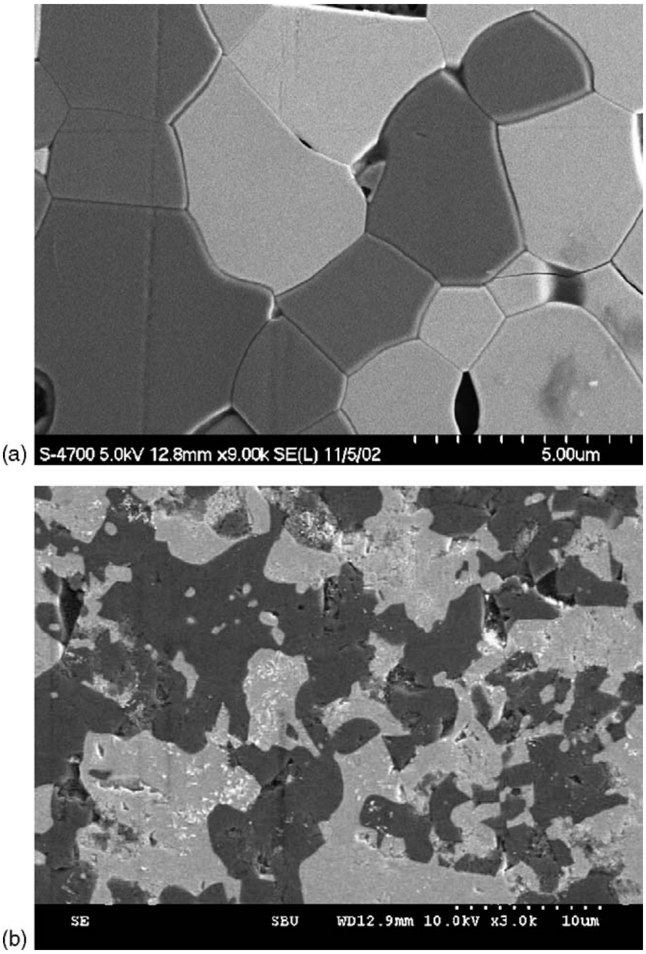

Fig. 6. SEM of (a) undoped and (b) doped 11.3:1 $TiO_2$–$Bi_2O_3$.

Table 2
Overview of dielectric properties, optimal sintering temperature and $TiO_2$ source of $Bi_2O_3$–$TiO_2$ batches

| $TiO_2$ source in $Bi_2O_3$–11.3 $TiO_2$ | Dopant | Amount (wt.%) | Sintering temperature (°C) | $Q \times f$ (GHz) | $\varepsilon$ |
|---|---|---|---|---|---|
| Anatase uncalc. | – | – | 1100 | 3000 | 47 |
| Rutile | – | – | 1175 | 4000 | 72 |
| P25 calcined | – | – | 1150 | 9500 | 83 |
| P25 uncalc. | – | – | 1150 | 9600 | 78 |
| P25 uncalc. | CuO | 0.112 | 915 | 8900 | 81 |
| P25 uncalc. | CuO | 0.206 | 915 | 7030 | 81 |
| P25 uncalc. | CuO | 0.676 | 930 | 5800 | 80 |
| P25 uncalc. | CuO/$V_2O_5$ | 0.220 | 930 | 6100 | 82 |
| P25 uncalc. | CuO/MnO | 0.237 | 930 | 8150 | 69 |

## 4. Conclusions

Low fired CuO doped bismuth titatanate showed promising dielectric properties of $Q \times f = 8000$ GHz, $\varepsilon_r = 80$ and $\tau_f = 0$ ppm/K (at 300 K) when 0.11 wt.% CuO was added and sintered at 915 °C/2 h. It was observed that the source and morphology of starting $TiO_2$ had a great influence on the porosity and sintering behaviour. A sub-micron anatase-rich $TiO_2$ (P25) which results in poor dielectric properties when sintered on its own, proved to be most promising in combination with $Bi_2O_3$. By omitting the calcination step, two desired phases, $Bi_2Ti_4O_{11}$ and $TiO_2$, were still obtained offering potential cost savings. The sintering time was reduced by introducing CuO. It was found that an increased amount of CuO was not necessary to improve the sintering as the higher level ($x = 0.68$ wt.% CuO) introduced more porosity as the anatase-rutile phase transformation occurred after the initial neck-formation between the grains. This phase-transition changes the specific volume of the $TiO_2$ and it is necessary that it take place before the onset of sintering.

Also the reaction between the $Bi_2O_3$ and $TiO_2$ has to take place just after the anatase-rutile transformation. This reaction occurs at ~780 °C.

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