

Thermal processing and properties of BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ dielectric resonators

WEN-YI LIN, ROSARIO A. GERHARDT, ROBERT F. SPEYER
*School of Materials Science and Engineering, Georgia Institute of Technology,
 Atlanta, Georgia 30332-0245*
 E-mail: robert.speyer@mse.gateck.edu

JEN YAN HSU
Materials Research Laboratory, ITRI, Chutung, Taiwan

Sn-doped and undoped barium titanates pressed powder pellets were sintered at 1360 and 1390 °C for 5 h. Though batched to form $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, a two-phase microstructure of BaTi_4O_9 and TiO_2 formed from the undoped system. The dielectric constant at 6 GHz was 40 without SnO_2 additions. Doping with 1.64 mol % SnO_2 stabilized $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and formed a single-phase microstructure but resulted in higher porosity. Dilatometry studies implied that SnO_2 additions facilitated a greater fraction of reaction to occur in the solid state, causing a lower quantity of pore-filling fluid to form above 1317 °C. As a result of the higher porosity, the dielectric constants and quality factors were also reduced. © 1999 Kluwer Academic Publishers

1. Introduction

Commercial wireless communication has seen an exponential growth in the 1990s. This technology advancement has been made possible in part with recent advances in miniaturization of microwave circuits by using low-loss and temperature-stable dielectric resonators (DR). Functioning as important components in communication circuits, DRs can create, filter, and select frequencies in oscillators, amplifiers and tuners.

Two candidates for telecommunication DRs are BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ since they both have high dielectric constants and quality factors (39 and ~10,000, respectively [1, 2]). However, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ has a reported temperature coefficient (4 ppm/°C) which is closer to zero than BaTi_4O_9 (14 ppm/°C). This makes $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ a more favorable choice. However, the difficulty in fabricating $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ has daunted its development for years [2]. There is disagreement regarding the mechanism by which SnO_2 stabilizes $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ [3–6].

While BaTi_4O_9 adopts an orthorhombic *Pnmm* crystal structure [7], $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ resembles a hexagonal close-packed cell [8] of Ba^{2+} and O^{2-} with Ti^{4+} in octahedral sites. This pseudohexagonal arrangement has a nine layer stacking sequence with a primitive triclinic cell. There are two coordinations of barium ions within the layers: half are 12-coordinated with oxygen and the rest are 11-coordinated with vacant Ba^{2+} sites adjacent to them. This crystal structure plays an important role in the dielectric properties, which in turn obey the dielectric dispersion equation, as described by Tamura *et al.* [9]. The loss factors of these microwave dielectrics are determined by damping constants which are related to the anharmonic terms in the potential energy of the crystal.

As an initial part of our research on microwave resonators, the current work focuses on the effects of SnO_2 and thermal processing on phase formation and corresponding microwave properties of a chemical system batched to form $\text{Ba}_2\text{Ti}_9\text{O}_{20}$.

2. Experimental

Raw materials were BaCO_3 (99.9%, AESAR, Ward Hill, MA), TiO_2 (anatase, 99.9%, Aldrich Chemical Company, Milwaukee, WI), and SnO_2 (99.9%, Aldrich Chemical Company, Milwaukee, WI). Two batches of powders in mol%: 18.2 BaCO_3 -81.8 TiO_2 and 18.2 BaCO_3 -80.2 TiO_2 -1.6 SnO_2 , were prepared. The powders were mixed with distilled water and dispersing agent in plastic bottles with ZrO_2 balls for 8 hours. The slurries were then dried for 12 h at 45 °C and then calcined by heating at 20 °C/min to 600 °C, then 40 °C/min to 975 °C, and holding at that temperature for 6 h. The powders were wet mixed using zirconia media again with Darvan for 24 h. 5.8 g of powders were uniaxially pressed into pellets and sintered at 1360 and 1390 °C for 5 h on a ZrO_2 plate.

Simultaneous differential thermal and thermogravimetric analyses (STA 409C, Netzsch) were used to detect the reactions which occurred during heating of the raw materials. Sintering of calcined (pre-reacted) powders was monitored using a dilatometer (Orton Automatic Recording Dilatometer). The phases formed after heat-treatments interrupted at various temperatures were analyzed using X-ray diffraction (PW1800, Philips) with a step size of 0.015° and a sampling time of 1 or 3 sec. Diffraction patterns were taken from the surfaces of sintered bodies without crushing to a powdered

TABLE I Phases formed after various heat treatments

Temp (°C) Time (min)	Systems	Major phases	Minor phases	Traces
780, 120	BaO-TiO ₂	TiO ₂ (α), BaCO ₃	BaTiO ₃	—
780, 120	BaO-TiO ₂ -SnO ₂	TiO ₂ (α), BaCO ₃	SnO ₂ , BaTiO ₃	—
920, 5	BaO-TiO ₂	TiO ₂ (α), BaCO ₃ , BaTiO ₃	BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀
920, 5	BaO-TiO ₂ -SnO ₂	TiO ₂ (α), BaCO ₃ , BaTiO ₃	BaTi ₄ O ₉ , SnO ₂	Ba ₄ Ti ₁₃ O ₃₀
975, 5	BaO-TiO ₂	TiO ₂ (α), BaTiO ₃ , BaCO ₃	BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀
975, 5	BaO-TiO ₂ -SnO ₂	TiO ₂ (α), BaTiO ₃ , BaCO ₃	BaTi ₄ O ₉	SnO ₂ , Ba ₄ Ti ₁₃ O ₃₀
975, 360	BaO-TiO ₂	BaTiO ₃ , TiO ₂ (α)	BaTi ₄ O ₉	—
975, 360	BaO-TiO ₂ -SnO ₂	BaTiO ₃ , TiO ₂ (α)	BaTi ₄ O ₉ , Ba ₂ Ti ₉ O ₂₀	SnO ₂
1010, 5	BaO-TiO ₂	BaTiO ₃ , TiO ₂ (α), BaCO ₃	BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀
1010, 5	BaO-TiO ₂ -SnO ₂	BaTiO ₃ , TiO ₂ (α), BaCO ₃	BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀ , SnO ₂
1076, 5	BaO-TiO ₂	BaTiO ₃	TiO ₂ (β), BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀
1076, 5	BaO-TiO ₂ -SnO ₂	BaTiO ₃	TiO ₂ (β), BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀
1280, 5	BaO-TiO ₂	BaTiO ₃	TiO ₂ (β), BaTi ₄ O ₉	Ba ₄ Ti ₁₃ O ₃₀
1280, 5	BaO-TiO ₂ -SnO ₂	BaTiO ₃	TiO ₂ (β), BaTi ₄ O ₉ , Ba ₂ Ti ₉ O ₂₀	Ba ₄ Ti ₁₃ O ₃₀
1360, 300 (cross section)	BaO-TiO ₂	BaTi ₄ O ₉	TiO ₂ (β)	—
1360, 300 (cross section)	BaO-TiO ₂ -SnO ₂	Ba ₂ Ti ₉ O ₂₀	—	—
1390, 300 (cross section)	BaO-TiO ₂	BaTi ₄ O ₉	TiO ₂ (β)	—
1390, 300 (cross section)	BaO-TiO ₂ -SnO ₂	Ba ₂ Ti ₉ O ₂₀	—	—

form. For microwave measurements, the sintered bodies were cut with a diamond wafering blade and then polished into dimensions of 1.25 cm in diameter and 5.0 mm in length. Microwave properties were measured using the Kobayashi method [10] using a network analyzer (Wilton 360).

3. Results

Thermal analyses of the starting powders are shown in Fig. 1. STA schedules were halted at 780, 920, 1020, 1175, and 1280 °C (after 5 min hold) and the quenched specimens were analyzed using XRD (Table I). Thermal effects in these specimens were not of high intensity, hence baseline noise is clearly apparent. Endotherms onset at 810 and 970 °C appear for both compositions containing BaCO₃. They correspond to the γ-β, and β-α polymorphic phase transformations in BaCO₃ [11]. The TG trace for BaCO₃ alone shows that weight loss has no correlation to the polymorphic trans-

formation endotherms; a broad decomposition to BaO, starting at ~1000 °C is apparent. In contrast, the onset of weight loss for the BaCO₃-TiO₂ mixture is recorded at temperatures as low as 600 °C. This weight loss correlates well with the onset of observed BaTiO₃ from XRD of a sample heat treated to 780 °C. The endotherm onset at 1020 °C corresponds to a surge in weight loss and a sharp increase in BaTiO₃ based on relative XRD peak heights. XRD shows that no BaO (or Ba(OH)₂) formed at any of the analyzed quench temperatures.

The thermal effects of tin oxide additions to the batch are shown in Fig. 2. These additions had little effect on the temperatures of reactions, or the corresponding phases formed as indicated by XRD of specimens heat-treated up to 1280 °C. SnO₂ additions facilitated complete conversion from BaTiO₃ to Ba₂Ti₉O₂₀ after an extended soak at 1360 °C. Without SnO₂ additions, BaTi₄O₉ and residual TiO₂ were detected. The same phases were observed for those samples heat-treated to 1390 °C.

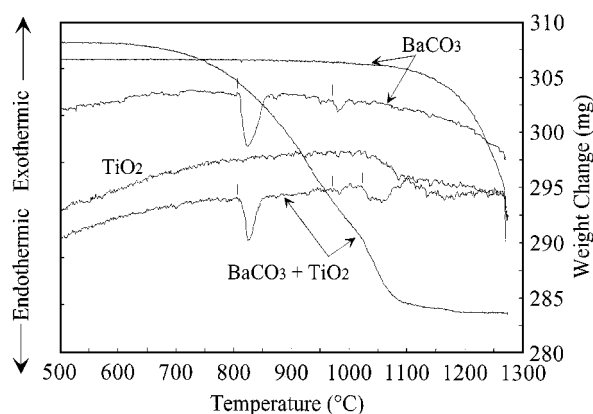


Figure 1 DTA and TG traces of raw batch materials BaCO₃, TiO₂, and the two combined in molar ratio of 18.2BaCO₃-81.8TiO₂, heated in air at 10 °C/min.

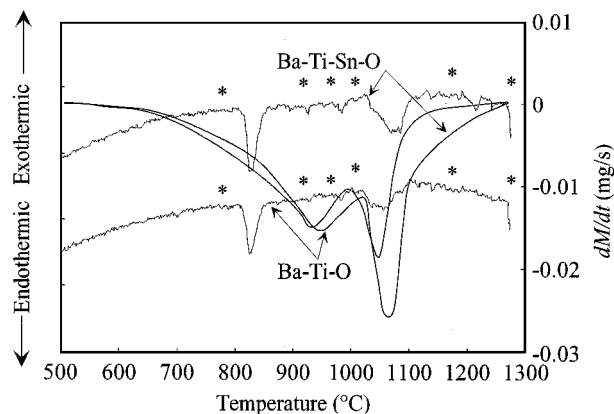


Figure 2 DTA and DTG (visually smoothed time derivative of TG signal) traces of the BaO-TiO₂ and BaO-SnO₂-TiO₂ systems. Asterisks represent maximum temperatures prior to quench for XRD analysis.

TABLE II Properties of sintered microwave ceramics

System	ρ (g/cm ³)	Q (6 GHz)	ϵ_r (6 GHz)	ϵ_r (10 MHz)	ϵ_r (4 kHz)
BaO-TiO ₂ (1360 °C)	4.4	3202	39.8	36.7	38.8
BaO-TiO ₂ (1390 °C)	4.4	3243	40.2	38.4	40.9
BaO-TiO ₂ -SnO ₂ (1360 °C)	4.3	—	23.3	32.2	34.5
BaO-TiO ₂ -SnO ₂ (1390 °C)	4.3	2176	28.9	31.7	35.6

For the pellets without SnO₂ additions, the bottom surface in contact with zirconia plates during heat treatment developed different phases than those observed in the cross section. The bottom surfaces were mainly composed of Ba₂Ti₉O₂₀ as well as traces of BaTi₄O₉ and TiO₂ while the top surface (exposed to air) had no detectable Ba₂Ti₉O₂₀.

Fig. 3 shows dilatometry traces of the two compositions. The onset of sintering in both systems was at 1000 °C; however, the initial rate of sintering was suppressed in the BaO-TiO₂-SnO₂ system. A second surge in sintering occurred with a maximum rate at 1350 °C

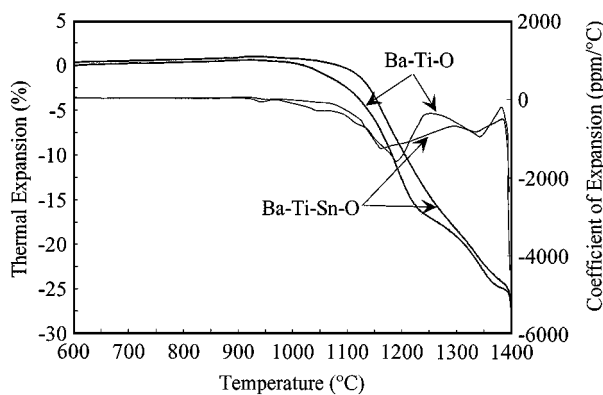


Figure 3 Dilatometry traces (expansion and temperature derivative of expansion) of calcined/pre-reacted (975 °C, 6 h) pressed powder pellets heated at 3 °C/min.

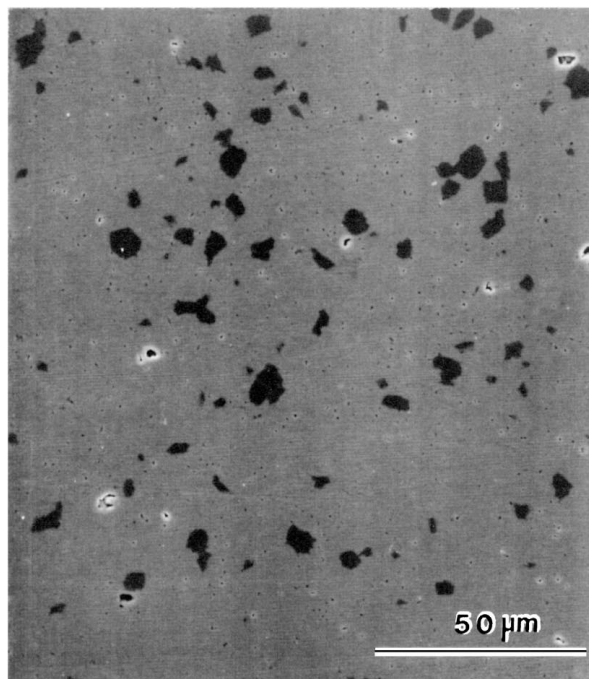
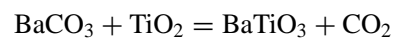
for the BaO-TiO₂ system. This surge was present but attenuated in the BaO-TiO₂-SnO₂ system.

Microstructures of the BaO-TiO₂ and BaO-TiO₂-SnO₂ specimens, heat treated at 1360 °C for 5 h are shown in Fig. 4a and b, respectively. No difference was visible in the microstructures of the BaO-TiO₂-SnO₂ specimens heat treated at 1390 °C (not shown). A subtle difference in the BaO-TiO₂ specimen after heat treatment at 1390 °C was removal of minute pores (~0.5 μm). Tin oxide additions resulted in microstructures with increased porosity in the sintered material. Black grains in Fig. 4a were shown via energy dispersive spectroscopy to be TiO₂.

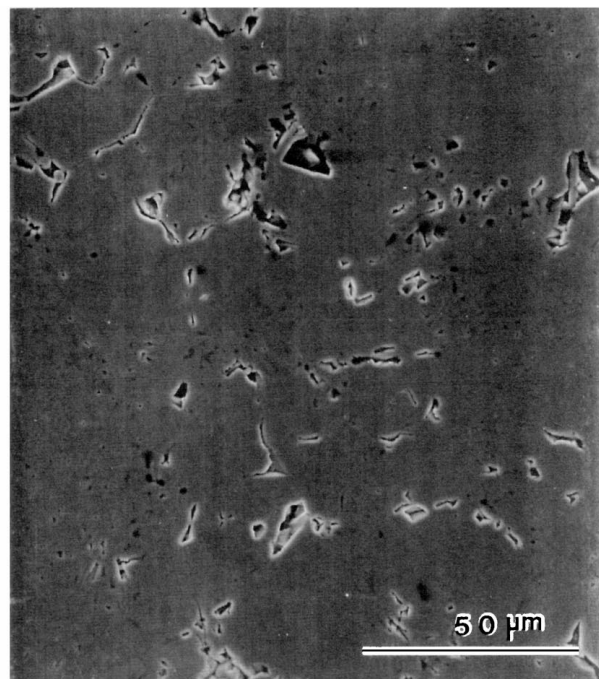
Table II shows the dielectric constants for the two compositions of specimens after the two heat treatment temperatures, over three frequency ranges. Resonance frequencies for BaO-TiO₂-1360 °C, BaO-TiO₂-1390 °C, BaO-TiO₂-SnO₂-1360 °C, and BaO-TiO₂-SnO₂-1390 °C, were 6.0, 5.7, 6.4, and 6.6 GHz, respectively.

4. Discussion

It is interpreted that BaTiO₃ diffusion barrier shells formed around TiO₂ particles. The shells formed by solid state reaction of BaCO₃ particles in contact with anatase particles via:



(a)



(b)

Figure 4 Microstructures of polished sections of sintered specimens heat treated at 1360 °C for 5 h. (a) BaO-TiO₂, (b) BaO-TiO₂-SnO₂. Dark regions with white edges are porosity, while black regions are TiO₂.

BaTiO₃ coatings on BaCO₃ are less likely since the release of the CO₂ product would tend to fragment the particle. Since no BaO was observed in XRD traces of powdered samples heat treated to various temperatures (marked in Fig. 1), the TG traces in Figs 1 and 2 are good indicators of the pace of BaTiO₃ formation. The surge in weight loss associated with the broad endotherm onset at 1020 °C implies particulating of the coated anatase particles, motivated by expansion mismatch between coating and host particle, in turn providing fresh TiO₂ surface for reaction with as yet unreacted BaCO₃.

Tin oxide additions did not alter the crystalline phases formed after heat treatments up to 1280 °C. The JCPDS data for BaSnO₃ shows a unique pattern which was at no time detected. This indicates that the tin must have entered into solid solution with titanium in the detected barium titanate phases (predominantly BaTiO₃ with minor amounts of BaTi₄O₉). Zr⁴⁺ must play a similar role. From the X-ray diffraction results, it is not established whether SnO₂ was soluble in BaTiO₃, BaTi₄O₉, or both. Tin oxide additions fostered formation of the as-batched Ba₂Ti₉O₂₀ stoichiometry; the deformation of the unit cell by this substitution clearly stabilized the Ba₂Ti₉O₂₀ structure. This implies that this phase is not an equilibrium phase in the BaO-TiO₂ phase diagram, and can only be realized in a doped compound. This is consistent with some investigations [3, 5], but conflicts with the findings of another [4]. Jonker and Kwestroo [3] stated that the phase could only be formed with substitution of small amounts of SnO₂ or ZrO₂ for TiO₂. This was later confirmed by O'Bryan *et al.* [5]. Besides, tin and zirconium oxides, Yu *et al.* [6] reported that Al₂O₃ and Bi₂O₃ stabilized Ba₂Ti₉O₂₀. However, all of their mixtures contained SnO₂ and therefore, such a conclusion is not warranted without further study using a system without SnO₂ additions.

In contrast to these results, Ba₂Ti₉O₂₀ formation without solid solution additions was reported by Wu and Wang [4] who calcined their batch at 1100 °C for 3 h and then sintered at 1400 °C for 6 h. This resulted in a mixture of Ba₂Ti₉O₂₀ and BaTi₄O₉. Phase pure Ba₂Ti₉O₂₀ was reported [4] to be formed by reaction of raw materials mixed by a coprecipitation method.

There is no implication from STA results or from the pertinent binary phase diagram [13, 14] that a liquid phase had formed up to 1300 °C. Hence the baria-titania compounds detected after thermal processing up to this temperature formed by solid state reaction. Dilatometry traces of pre-reacted pellets showed a second surge in sintering rate starting at ~1300 °C. X-ray diffraction (Table I) showed that the compounds present in the pellets of pre-reacted powders were predominantly BaTiO₃ and TiO₂. Based on the BaO-TiO₂ phase diagram [13, 14], these two compounds should react to form intermediate compounds and a liquid phase at temperatures above 1317 °C. The aforementioned second surge in sintering rate is thus correlated to the onset of liquid phase formation. This fluid phase fills pores as well as facilitates reaction between grains of different phases. More rapid sintering is indicated in the BaO-TiO₂-SnO₂ system in the temperature range 1200–1300 °C (Fig. 3). This implies that substitution of Sn⁴⁺

for Ti⁴⁺ forms a product phase (Ba₂Ti₉O₂₀) which does not impede further solid state reaction between BaTiO₃ and TiO₂. As a result, there is a lower fraction of reactants remaining at the temperature where eutectic liquid forms between BaTiO₃ and TiO₂ (1317 °C). Thus, a lower quantity of liquid phase would be expected to form in the BaO-TiO₂-SnO₂ system as compared to the BaO-TiO₂ system. The microstructures in Fig. 4 show lower porosity in the sintered BaO-TiO₂ system as compared to the BaO-TiO₂-SnO₂ system. This is consistent with the densities displayed in Table II. The higher fraction of fluid phase in the BaO-TiO₂ system would explain the observed lower porosity.

The dielectric constants in Table II show a slight increase for the samples sintered at 1390 °C, as compared to 1360 °C. This corresponds to a slight increase in density since the presence of porosity is expected to diminish the dielectric constant. The dielectric constants measured in the gigahertz range correlate quite well with literature values for BaTi₄O₉ [9]. This, however, may be fortuitous in the sense that the remaining porosity in the samples in this study would lower the dielectric constant, but the segregated TiO₂ phase would increase the dielectric constant—providing compensating effects. The dielectric constants did not change appreciably as the frequency decreased to 10 MHz and 4 kHz. The quality factors were in the region of 3200, similar to those reported by O'Bryan [5].

The Ba₂Ti₉O₂₀ phase formed in the BaO-TiO₂-SnO₂ system showed a dielectric constant in the gigahertz range which was lower than those reported in the literature [2]. The comparatively high porosity associated with this phase is considered to be the cause of these differences. It is believed that more rapid heating of pre-reacted powders to temperatures in excess of 1317 °C will discourage solid-state reaction, allowing more liquid phase to form as an intermediate product in the formation of Ba₂Ti₉O₂₀. This would facilitate elimination of residual porosity.

5. Conclusion

Barium titanates, sintered without dopants at 1360 and 1390 °C for 5 h had a dielectric constant of ~40, comparable to the literature values at ~6 GHz. Doping with 1.64 mol % of SnO₂ stabilized Ba₂Ti₉O₂₀ but decreased the density of the sintered body. Consequently, the effective dielectric constants and quality factors were reduced.

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