

Barium Nanotitanate Microwave Ceramics Obtained by a Chemical Method

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Abstract—Dielectric resonators with high dielectric constant, low dielectric losses and high frequency stability have been widely used in microwave circuits for telecommunications as filters, oscillators, antennas. Among the compounds of the BaO-TiO₂ system, Ba₂Ti₉O₂₀ has met these requirements. However, such materials are difficult to obtain by conventional mechanical powder mixture due to the preferential formation of secondary phases and high sintering temperatures around 1300°C. In this investigation a new approach for obtaining B₂O₃-added Ba₂Ti₉O₂₀ is considered through a chemical method involving a co-precipitation process aiming to reduce the sintering temperature and to promote a high microstructural homogeneity of the compound. Therefore, cylindrical ceramics were sintered at 1000-1150°C presenting values of electric permittivity from 34.8 to 41.4, quality factor due to dielectric losses from 2945 to 3525, temperature coefficient from 6.2 to 10.2 ppm/°C and an overall tunable frequency range of 5.00-7.00 GHz, which yields promising properties for use as dielectric resonators.

Keywords— *dielectric resonators; barium nanotitanate; microwave properties; microwave ceramics.*

I. INTRODUCTION

Concerning the continuous development of wireless communications technology, there has been a growing demand for high-performance dielectric ceramics. To be an efficient material as dielectric resonator (RD), this element should have a high enough electric permittivity to allow miniaturization of components, low dielectric loss and high frequency stability. Among the compounds in the BaO-TiO₂ system, barium nanotitanate – Ba₂Ti₉O₂₀ (BTO) meets these requirements and has received great attention [1-3]. Nonetheless, hollandite-like structure Ba₂Ti₉O₂₀ materials are difficult to obtain due to the preferential formation of secondary phases, such as BaTi₄O₉ and BaTi₃O₁₁, during the calcinations of BaO-TiO₂ mixture. Besides that, pure Ba₂Ti₉O₂₀ phase is hard to obtain by the conventional solid-state reaction, even at high temperature treatments, around 1300-1400°C, along with its low densification. The addition of B₂O₃ in order to promote the liquid phase sintering has lowered the sintering temperature due to the improvement of diffusion paths. Generally, B₂O₃ is added to previously crystallized BTO powders. However, during the sintering treatment, reactions between the glass and ceramics may induce compositional changes and/or development of second phases due to local heterogeneities,

which may deteriorate the microwave dielectric properties [1-4]. To minimize these drawbacks several preparation methods have been used [4-10]. In this study a new approach for obtaining B₂O₃-added BTO nanopowder is considered by using a hybrid chemical and co-precipitation method. The microwave dielectric properties of the Ba₂Ti₉O₂₀ ceramics are reported.

II. EXPERIMENTAL PROCEDURE

To prepare the BTO powder, HNO₃ was added to an aqueous TiO₂ suspension under a 150 W ultrasound probe for 30 min; H₃BO₃ was added to this suspension and sonicated for 30 min, and BaCO₃ was also added as a Ba source. After drying at 110°C, the powder was milled in an agate mortar and calcined at 620°C for 2 h to decompose the Ba(NO₃)₂. Subsequently, the powder was calcined at 900°C for 2 h and milled in a high energy mill at 120 rpm for 1 h. The obtained powders were compressed by uniaxial and isostatic pressing into cylindrical form and sintered at temperatures ranging from 1000 to 1150°C. The crystal structure of the calcined powders was examined by X-ray diffractometry (XRD) (Philips, PW1830). The samples density was volumetrically calculated.

The dielectric characteristics at microwave frequencies as electric permittivity (ϵ), quality factor (Q), and temperature coefficient of the B₂O₃-BTO ceramics were measured using a metal cavity method. The parallel-plate dielectric resonator can be used to measure the electric permittivity of a dielectric material: a cylindrical sample is placed between two metal disks (Fig. 1) in a gold electrodeposited copper cavity (Fig. 2.a). This cavity is 50 mm wide with adjustable height, so that no space above and below the sample remains. Coaxial magnetic probes are adjusted for optimum coupling to the measuring circuit. The resonant frequency of the TE₀₁₁ mode is measured for a DR knowing its radius a , and height H . This mode can be easily identified among others, making it the only one whose frequency decreases, since the metal disk moves away from the DR. The accuracy of the electric permittivity depends on the precision of the measurements taken for the resonator's size and frequency. The characteristic equation proposed by Hakki and Coleman [11] relating resonant frequency, electric permittivity and resonator dimensions for TE₀₁₁ mode is:

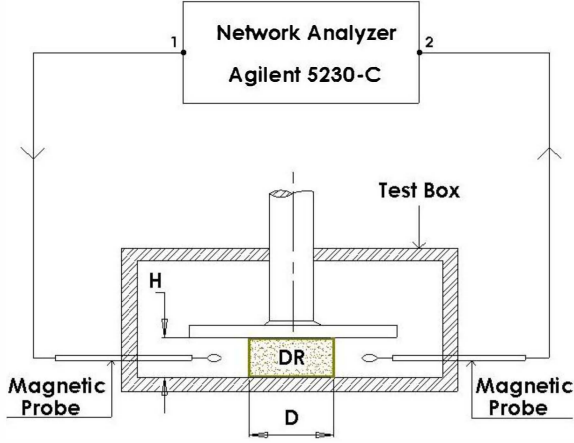


Fig. 1. Experimental arrangement for measuring the resonant frequency and the corresponding dielectric constant of the dielectric resonators.

$$k_{rd}a \frac{J_0(k_{rd}a)}{J'_0(k_{rd}a)} + k_{ro}a \frac{K_0(k_{ro}a)}{K'_0(k_{ro}a)} = 0 \quad (1)$$

where $k_{rd}^2 = \left(\frac{2\pi f}{c}\right)^2 \varepsilon - k_z^2$; $k_{ro}^2 = k_z^2 - \left(\frac{2\pi f}{c}\right)^2$

$$k_z = \frac{\delta\pi}{H}, \quad \delta = 1 \text{ (for TE}_{011} \text{ mode)},$$

and J_0 and K_0 are the Bessel functions and the modified Bessel functions of order zero, a is the resonator radius, and c is the speed of light.

The quality factor (Q) is determined by the half-power bandwidth method at -3 dB point [12]. To perform a reliable measurement for the quality factor of the DR, the metal cavity should be a good conductor as well as have its walls far enough from the resonator, thus metallic losses can be neglected. Therefore, the measured unloaded Q can be considered as the Q of the dielectric material. Moreover, in the current case the resonator is placed between polystyrene disks inside the test cavity to prevent metallic losses (Fig. 2.b).

Furthermore, for applications in microwave circuits, a frequency range was measured by mechanical tuning, coupling the DR to a microstrip line printed on an alumina substrate (Fig. 2.c). Moving a metal disk over the resonator perturbs the electromagnetic fields, thus modifying its resonant frequency. It is a typical structure for microwave integrated circuit (MIC) application, where the DR is mounted on a dielectric substrate, and the resonant frequency can be either an increasing or a decreasing function of the tuning disk position (d). The resonant frequency calculation for the TE₀₁₈ mode as a function of the distance d comes from the equations based on boundary conditions in the interfaces DR- substrate and DR- air layer [13-14].

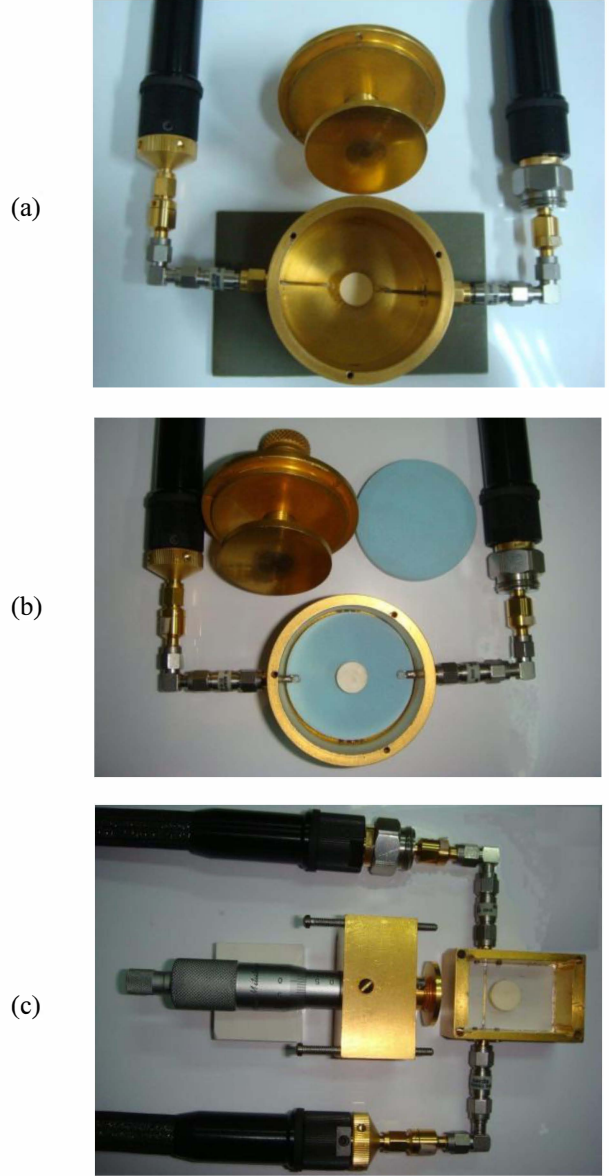


Fig. 2. Metal cavity with dielectric resonator for following measurements: (a) electric permittivity and temperature coefficient of resonant frequency, (b) quality factor, (c) tuning frequency range.

The resonant frequency variation with temperature is commonly represented by the temperature coefficient (τ_f). The temperature coefficient of resonant frequency was also performed in the configuration of the resonator between parallel plates, but in this case, with the test cavity placed in a Weiss WKL100 programmable climatic chamber. The resonant frequencies were measured as function of temperature from -20°C to +50°C in steps of 10°C. The abbreviation “ppm” (parts per million) is often used to denote the term 10^{-6} . The coefficient temperature is then calculated using the following equation:

$$\tau_f = \frac{1}{f_i} \frac{\Delta f}{\Delta t} \quad [\text{ppm}/^\circ\text{C}] \quad (2)$$

where Δf (GHz) is the difference between the final and the initial frequencies, Δt is the difference between the final and the initial temperatures and f_i (GHz) is the resonant frequency in the beginning of the process for every temperature interval.

III. EXPERIMENTAL RESULTS

Fig. 1 shows the XRD patterns of the starting powder, and after having been calcined at different temperatures. The XRD patterns showed that the starting powder presented only the TiO_2 (anatase) and $\text{Ba}(\text{NO}_3)_2$ phases (Fig. 3a). It is known that $\text{Ba}(\text{NO}_3)_2$ melts at around 590°C [15]. In Fig. 3b, it can be seen that after calcining the powder at 620°C for 2 h, $\text{Ba}(\text{NO}_3)_2$ was completely decomposed and the main phase of the powder was TiO_2 , along with a little BaTiO_3 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, suggesting that even at such low temperature the diffusion of Ba was greatly enhanced due to the liquid phase formed by the melting of $\text{Ba}(\text{NO}_3)_2$ at around 590°C . After calcining the powder at 900°C for 1 h, TiO_2 was still observed as the main phase, however, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was also detected together with $\text{BaTi}_5\text{O}_{11}$ and BaTi_4O_9 , which indicates that $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was formed at this temperature. When the temperature rose to 1000°C and 1100°C , the amount of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase increased, but other secondary phases, such as Ba_2TiO_4 and $\text{BaTi}_4\text{O}_{10}$ were also observed. However, the low intensity feature of the XRD patterns hinders an accurate identification due to the overlapping peaks. It is worth noting that at higher temperatures, no borate phases were detected, suggesting that the liquid phase was still present, due to an eutectic formed at 840°C (as reported in [1,10]), improving the Ba-Ti diffusion.

Fig. 4 shows a sample set of DR manufactured and tested.

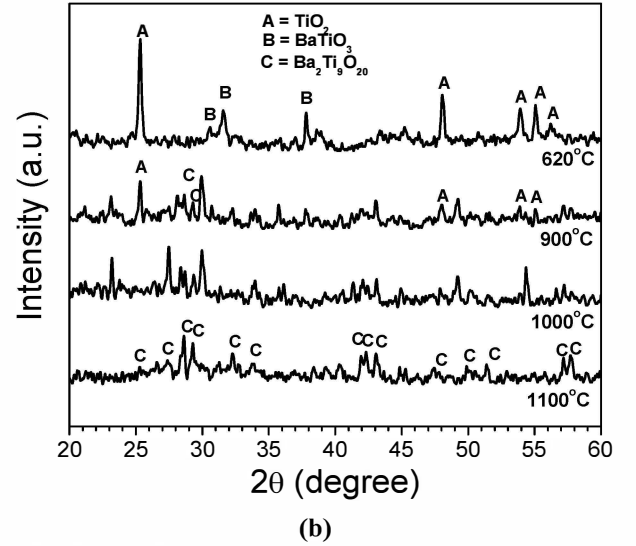
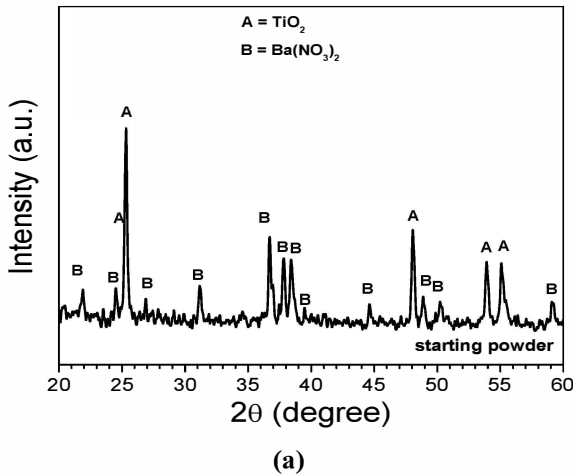


Fig. 3. X-ray diffraction results for: (a) the starting powder; (b) after calcining at different temperatures.

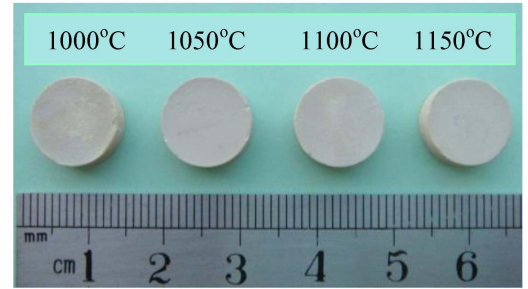


Fig. 4. Set of sintered samples under investigation.

The microwave measurements show the influence of the sintering temperature on the dielectric properties of BTO ceramics. From Table I, it is observed that the electric permittivity (ϵ) ranges from 35 to 41, the Q factor from 2950 to 3400, the temperature coefficient (τ_f) from 6.2 to 10.2 ppm/ $^\circ\text{C}$, and the overall tunable frequency range of 5.12-6.95 GHz. Some results are in agreement with those obtained by Tang [7], although their samples were sintered at quite higher temperatures ($>1200^\circ\text{C}$).

Uniaxial and isostatically pressed pellets were sintered at temperatures ranging from 1000 to 1150°C . The density of the produced samples was measured by the Archimedes method, and the best densification (91.9% at 1050°C) was reached at 1050°C , as it can be seen in Fig. 5, verifying that the dielectric constant increased as the relative density increased.

The highest value for the electric permittivity did not result in the highest one for the Q factor among the investigated DRs. The main $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase probably prevailed in the ceramic which obtained the highest Q factor ($Q = 3525$) due to having the best microwave property concerning dielectric losses.

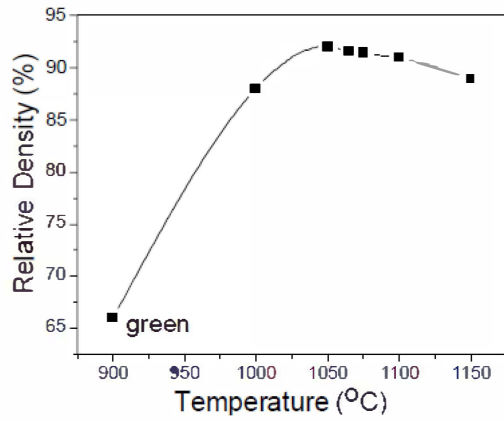


Fig. 5. Relative density of BTO samples as a function of the sintering temperature.

TABLE I. Microwave properties of the ceramics sintered for 3 h at different sintering temperatures.

Temp. (°C)	D±0.1 (mm)	H±0.1 (mm)	$\epsilon \pm 0.3$	Q ± 100 @ ~5GHz	MIC Freq. (GHz)	τ_f (ppm/°C)
1000	11.54	4.25	34.8	3045	5.76-6.95	6.2
1050	11.46	4.55	41.4	3410	5.12-6.04	10.2
1100	11.29	4.51	36.8	3120	5.33-6.53	7.8
1150	11.26	4.57	37.0	3525	5.45-6.43	8.0

Fig. 6 shows the evolution of the resonant frequency variation with temperature during the thermal process in the range -20°C to +50°C for the DRs under tests. The final average value for the temperature coefficient is taken from the values measured for every 10°C temperature.

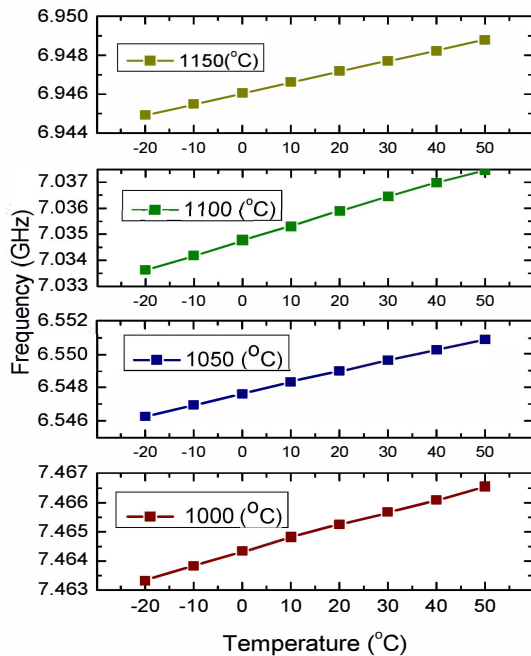


Fig. 6. Measurements of resonant frequency variations with temperature in the range -20°C to +50°C for the investigated DRs.

Different results among microwave dielectric properties are caused by intrinsic and extrinsic factors. The intrinsic factors occur by inherent structure of materials, while the extrinsic ones are induced in the manufacturing process such as pores, secondary phases, grain size and, oxygen vacancy.

CONCLUSIONS

A B_2O_3 -doped $Ba_2Ti_9O_{20}$ powder has been prepared by a hybrid chemical and co-precipitation method. The $Ba_2Ti_9O_{20}$ phase was detected at 900°C, confirming the role of B_2O_3 in lowering the crystallization and densification temperature of BTO ceramics, mainly when it is added during the synthesis. The current results suggest that this method allows preparing BTO ceramics with high yielding and with good microwave properties, which makes it cost effective for dielectric resonator applications.

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