ZrO_2 Influence on Microstructure and Microwave Characteristics of $Ba_2Ti_9O_{20}$ Dieletric Resonators for Telecommunication Applications

Yuliya Koldayeva[1]; *Maria do Carmo de Andrade Nono Nono*[1], *and Pedro José de Castro* [2]

Instituto Nacional de Pesquisas Espaciais – INPE
[1] Laboratório Associado de Sensores e Materiais
[2] Laboratório Associado de Plasma
Av. dos Astronautas, 1758 – 12227-010 São José dos Campos, SP, Brazil
E-mail: yuliya@las.inpe.br

Several kinds of special ceramics for applications as dielectric resonators (DRs) in microwave telecommunications have been developed. These DRs should have high value of dielectric constant, high quality factor due to dielectric losses and small coefficient of resonant frequency variation with temperature. Barium nanotitanate ceramic ($Ba_2Ti_9O_{20}$) has fulfilled these requirements. The ZrO_2 addition has yielded such devices with better microwave dielectric properties. In the present work the effect of ZrO_2 addition on the microstructure and crystalline phases of $Ba_2Ti_9O_{20}$ ceramics is investigated. Optimization of the ceramic processing was performed by the synthesizing and the sintering in a single step. The results showed that the performed ceramics present better densification degree at lower sintering temperature and grain-structure homogeneity in comparison to the data from the international literature. The microwave dielectric parameters pointed out suitable values of dielectric constant, quality factor and temperature coefficient for telecommunications applications.

Keywords: dielectric resonator, ceramic processing, microstrucure, microwave characteristics

1. INTRODUCTION

In the last two decades of 20's century, the communications by radio wave have revealed a fast increasingly application both due to the miniaturization of the microwave circuits and the use of dielectric resonators (hereafter DRs)[1,2]. A ceramic can work as a DR only if it has a reasonably high dielectric constant (ε_r >20) and low dielectric loss (i.e., high quality factor, Q > 10^3). $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ (hereafter BT4 and B2T9, respectively) are the Ti-rich compound in the $BaO\text{-}TiO_2$ system reported by several authors[3,4]. Both BT4 and B2T9 have high ε_r and Q, and low resonance frequency variation with temperature τ_f (τ_f tending to zero value)[1-10]. However, B2T9 ceramics have slightly higher ε_r and lower τ_f due to these microwave properties, so it has found place in RD industries for using in wireless, cellular communications and other microwave devices (filters, oscillators). Both industries and researchers have been carrying out detailed studies because of their attractive dielectric properties and complex structure-property relationship[1-10] .

B2T9 ceramics is the highest Ti-rich compound in the $BaO\text{-}TiO_2$ system, which contains 81.8 mol % of TiO_2 and 18.2 mol % of BaO. For the preparation of pure phase B2T9 from $BaCO_3$ and TiO_2 by solid state reaction, the stoichiometry and fabrication parameters must be precisely controlled, since there are various thermodynamically stable compounds in the vinicity of this composition as BT4 and titanium dioxide. The presence of small percentage of TiO_2 in B2T9 ceramics as a secondary phase increases the ε_r and τ_f, due to the high values of these parameters for titanium oxide (90 and 400 ppm.K^{-1}, respectively). By the other hand, small fraction of BT4 phase not seriously affects the dielectric properties of B2T9 ceramics. Besides that, a curvature of B2T9 equilibrium phase boundary in $BaO\text{-}TiO_2$ system at high temperature creates an additional difficulty to obtain monophase $Ba_2Ti_9O_{20}$ at room temperature. Several researches reported the need of the calcinations step at 1100-1200^oC for the complete transformation of the mixed powder into pure

B2T9. However, this calcinated powder mixture had hard agglomerates and required a long time milling step and, even so, the sintered ceramic presented inadequate porosity[3-9]. Castro and Nono[10,11] reported on optimization in the structural density of this ceramic by the adoption of synthesizing of B2T9 crystalline phase and sintering of the ceramic in a single step. They also minimized the TiO_2 segregation at ceramic surface by the immersion of the sample in a B2T9 powder during the synthesizing/sintering step.

On the other hand, it was reported that a small amount of solid solution additives, such as SnO_2, SrO, MnO, Nb_2O_5 or ZrO_2, is essential for the formation and stability of pure B2T9 crystalline phase[12,13]. Lin et al[14,15] used ZrO_2 for stabilization of the phase B2T9. The mechanism of the stabilization for this phase was not completely clear. Thus, it was assumed that the mechanism of interaction between the B2T9 phase and the zirconium cation is based on the partial substitution of Ti^{4+} by Zr^{4+}. The result from that is a formation of a solid solution, which occurs only at low zirconium concentration (up to 3.85 mol% ZrO_2), due to its solubility limited by relatively large Zr^{4+} in relation to Ti^{4+}. In this way it is not possible to achieve that substitution without distorting the B2T9 crystalline net. Therefore, the B2T9 phase might be produced using a small amount of zirconium as doping agent yielding better microwave characteristics in relation to the undoped ceramics.

2. EXPERIMENTAL PROCEDURE

The raw materials used in this study were $BaCO_3$, TiO_2 and ZrO_2, all with purity grade above 99 %. They were mixed according to the chemical compound stoichiometry: 18.2 mol% of BaO and 81.8 mol% of TiO_2 for preparation of undoped B2T9 ceramics. The doped ceramics were prepared with equimolar substitutions of TiO_2 for ZrO_2 (1.0, 2.0, 2.46, 3.0 and 4.0 mol%). The powder mixture was compacted using a uniaxial (40 MPa) and an isostatic (300 MPa) pressure to produce cylindrical test bodies with pre-established relationship H/D (where H is height and D the diameter of the test body), in order to obtain sintered ceramics with suitable dimensions for a desired resonant frequency range (6-7 GHz). The synthesis and sintering procedures were accomplished with a single step. In this way all samples were sintered for 3 hours at 1300 °C in air atmosphere. B2T9 powder involving the samples was used to minimize the TiO_2 segregation on the their surfaces. The furnace was heated at 10°C/min. X-ray diffraction (Philips X-rays diffratometer, Model PW3710) was used for ceramic crystallographic phases analyses. The scanning electron microscopy (SEM, JEOL, Model JSM-5310) was used for surface and fracture microstructures characterization of the ceramics.

The values of the dielectric parameters were measured at microwave frequencies: resonant frequency (f),dielectric constant (ε_r), unloaded quality factor (Q_o) and temperature coefficient (τ_f). The microwave measurements were performed according to the test setup shown in Figure 1 using a test box made from golden copper for housing the dielectric resonator The DR was excited by means of an electric probe with optimum coupling. Another electric probe is used as a receiving device to detect the sign radiated by the resonator.

In particular, for determining the dielectric constant the device was placed between two parallel conducting plates. This configuration when the metal plates make contact with the DR allows that it can operate at the electromagnetic mode TE_{011}, that has the largest energy portion. Among all the frequency modes, this is the only one the frequency of which decreases as the metal plate moves away from the resonator. Knowing the experimental value of the resonant frequency we can determine the dielectric constant through a field equation relating resonant frequency, dielectric constant and resonator dimensions. The calculation was made running the software "Mathematica" in a microcomputer.

As for the quality factor, providing the test box dimensions are at least three times the resonator size and inserting the DR between low-loss teflon spacers, then the metallic losses can be negleted.

The resonant frequency variation with temperature is carried out placing the test box into a burn-in chamber, where the temperature was cycled. The chamber works in flow rate of air forced convection and, besides that, dry nitrogen gas is used in order to keep the atmosphere inside the chamber as dry as possible. The temperature measurements are achieved by a thermocouple placed inside the test box. The resonant frequency was measured as a function of temperature from –20 °C to +50 °C with 5°C steps. In these tests, no temperature compensation technique was used.

3. RESULTS E DISCUSSÃO

3.1. Characterization of the Synthesized/Sintered Ceramics

The X-rays difratograms show that all the ceramics doped with 1.0, 2.0, 2.46, 3.0 and 4.0 mol% ZrO_2 present the B2T9 as the major phase (Figure 2). For the undoped sample and doped ones with 1 and 4 mol % ZrO_2, difratograms show the presence both of B2T9 and BT4 phases. Only the sample containing 4 mol % ZrO_2 has small quantities of TiO_2. These results point out that amount of 1 mol% ZrO_2 seems not to be enough to stabilize the barium nanotitanate phase in this experiment condition. According to Lin et al[14] e Wang et al.[12], ZrO_2 concentrations above 3,85 mol% exceed the limit of solubility of this doping in the B2T9, causing imbalance in the stoichiometry of the system, thus explaining the presence of the TiO_2 in ceramics with 4 mol% ZrO_2.

The analyses of the X rays difratograms from ceramics produced in this work showed that the ZrO2 addition has contributed for stabilizing the B2T9 crystalline phases. According to Wang et al[14,15], from stoichiometric mixtures of $BaCO_3$ and TiO_2 to obtain the B2T9, the first compound about to form is BT4 and, after that the B2T9. In this way, the following chemical reactions might occur in the solid state:

$$BaCO_3 (s) + 4TiO_2 (s) \rightarrow BaTi_4O_9 (s)$$

$$2BaTi_4O_9 (s) + TiO_2 (s) \rightarrow Ba_2Ti_9O_{20} (s)$$

Our results agreed with the those reported by other authors, who had investigated this kind of ceramic without any additives obtidos[3-8]. So, the beginning of reaction to produce BT4 occurs close to 1150°C and reacts with TiO_2 to produce B2T2, these reactions occur simultaneously. However, their efficiency depends on homogeneity and initial mixture stoichiometry of powders. Lin et al[14,15] and Wang et al[12] investigated also the influence of the zirconia amount in the stabilization of the B2T9 crystalline phase and came to conclusion that up to 3,85 mol % ZrO_2 (solubility limit of this oxide in barium nanotitanate) the referred additive behave like a stabilizer of this crystalline structure in the temperature range 1150-1300°C. Above this temperature, the B2T9 begins to decompose into BT4 and TiO_2.

The microstructures presented in Figure 3 are similar to the all other ceramics. They are a dense microstructure with both very few small and large pores. The average size of the grains increases with the ZrO_2 percentage.

The analyses from data showed a higher densification degree of produced ceramics in comparison to those produced by other authors [14,15]. The synthesizing and the sintering procedure at the same step developed by Nono and Castro[12], have minimized the quantity of the dense agglomerates, thus improving the state of powder compaction and, consequently, increasing the number of particle-particle contacts.

Results of this investigation pointed out that the way used for obtaining the powder mechanical mixtures (via particle suspension in ethylic alcohol) reveal that occurred a reduction of the synthesizing/sintering temperature.

3.2. Microwave Characterization of the Dielectric Resonators

In Table 1 are shown the experimental results ot the investigated ceramic resonators.

A variation of the closed pores in the ceramics was not detected. once ε_r and Q_o values are not associated to this kind of defects. Values relatively low of the dielectric constant and the quality factor might be related to the fact these measurements were carried out at higher frequencies than those reported by the literature (3 GHz). This fact is explained by the increase of dielectric losses with the frequency. A maximum value of Q_o was observed for 2 mol% ZrO_2 and for Lin et al[15] too.

In Table 2 are presented the experimental results of the applicable frequency range using the DRs on alumina substrate and coupled to microstrip line. as it is commonly used in microwave integrated circuits. The resonant frequency is dependent on the distance between the top of the resonator and the superior conductor plane; this distance is adjusted by a screw-disc tuner. Different DRs here developed present a tuning frequency range around 1100 - 1200 MHz.

Resonant frequency variations from 5.6 GHz covered the temperature range -20 to +50^{o}C in this study. while Lin et al[14] investigated the 25 to 120^{o}C range based on 3 GHz. In this way. the results obtained in this work are not comparable to the mencioned literature. Moreover. the B2T9 DR with 1 mol% ZrO_2 among doped ceramics obtained the lowest temperature coefficient.

4. CONCLUSION

The barium nanotitanate ceramics doped with zirconia presented a relatively high densification degree with few pores, as a consequence of the particle packing flaws. The results showed that ZrO_2 is a suitable stabilizing agent of the B2T9 crystalline phase up to the solubility limit (3.85 mol%). The values of the dielectric constant, the Q factor and the temperature coefficient for the doped ceramics are adequate for using as dielectric resonators in Earth and space telecommunications.

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FIGURE CAPTIONS

Figure 1. Experimental setup for measuring of the microwave parameters[10,11].

Figure 2. X-rays diffraction patterns for the ceramics synthesized and sintered at 1360°C.

Figure 3. SEM images of fracture surface microstructure for the investigated ceramics: (a) B2T9 pure, (b) 2 mol % ZrO_2, (c) 2.46 mol % ZrO_2, and (d) 3 mol % ZrO_2.

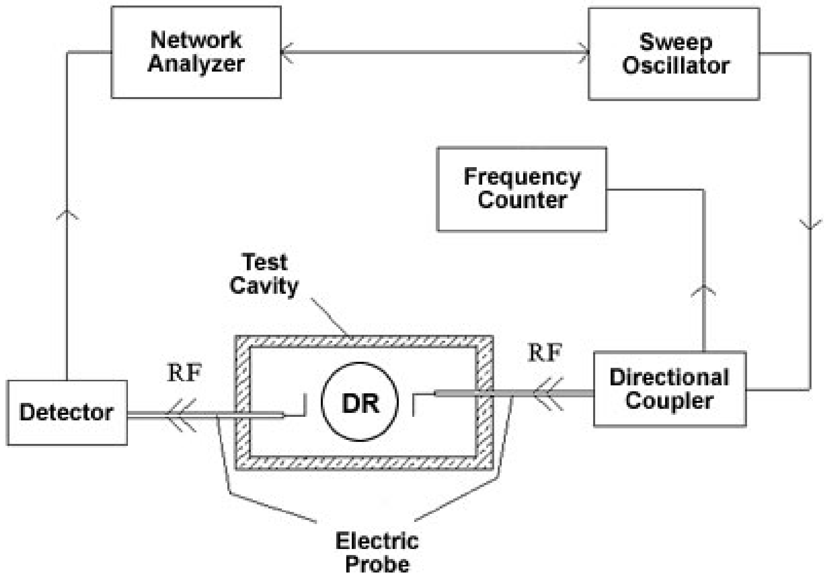
Table 1. Measured values of the microwave parameters for the ceramic resonators.

ZrO_2 [% mol]	f $\pm 1,5\times 10^{-3}$ [GHz]	$\rightarrow \in_r$	Q_o (*)	τ_f (**) [ppm/°C]
0	7.86543	28.5	3800	6.2
1.00	7.85144	28.5	3846	6.8
2.00	7.86612	28.9	4305	12.1
2.46	7.87046	29.1	3365	10.0
3.00	7.87292	29.2	3430	-
4.00	7.87820	29.6	3571	-

(*) unloaded Q factor measured around 5.60 GHz
(**) temperature coefficient measured around 5.60 GHz in the temperature range from -20°C to +50°C

Table 2. Experimental results of the applicable frequency range by mechanical tuning using the investigated DRs on alumina substrate and coupled to a microstrip line.

ZrO_2 (mol %)	**Frequency range (GHz)**
0	5.8 – 7.0
1.00	5.8 – 7.0
2.00	5.7 – 6.8
2.50	5.7 – 6.8
3.00	5.7 – 6.8
4.00	5.7 – 6.8



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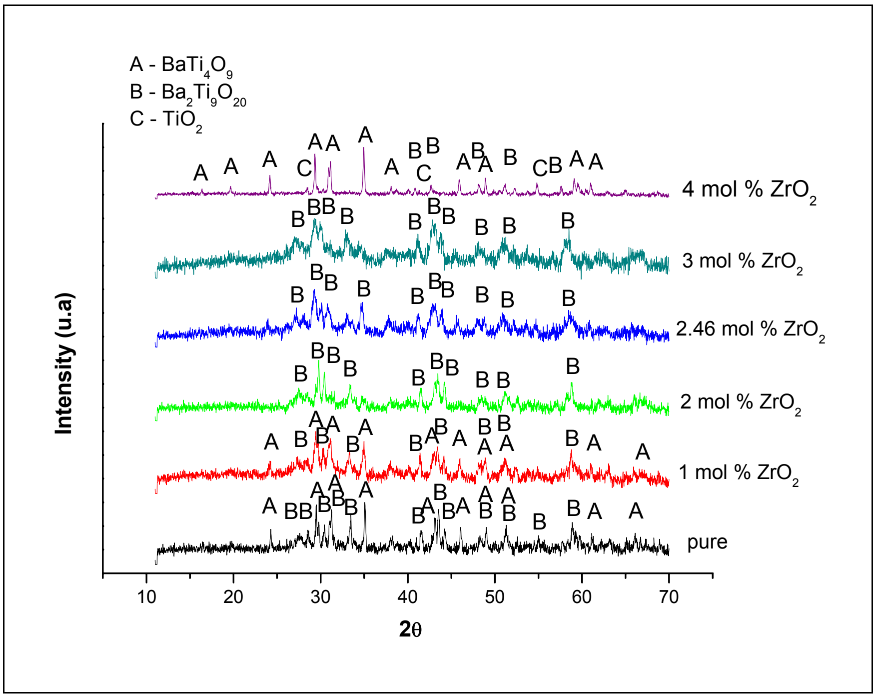

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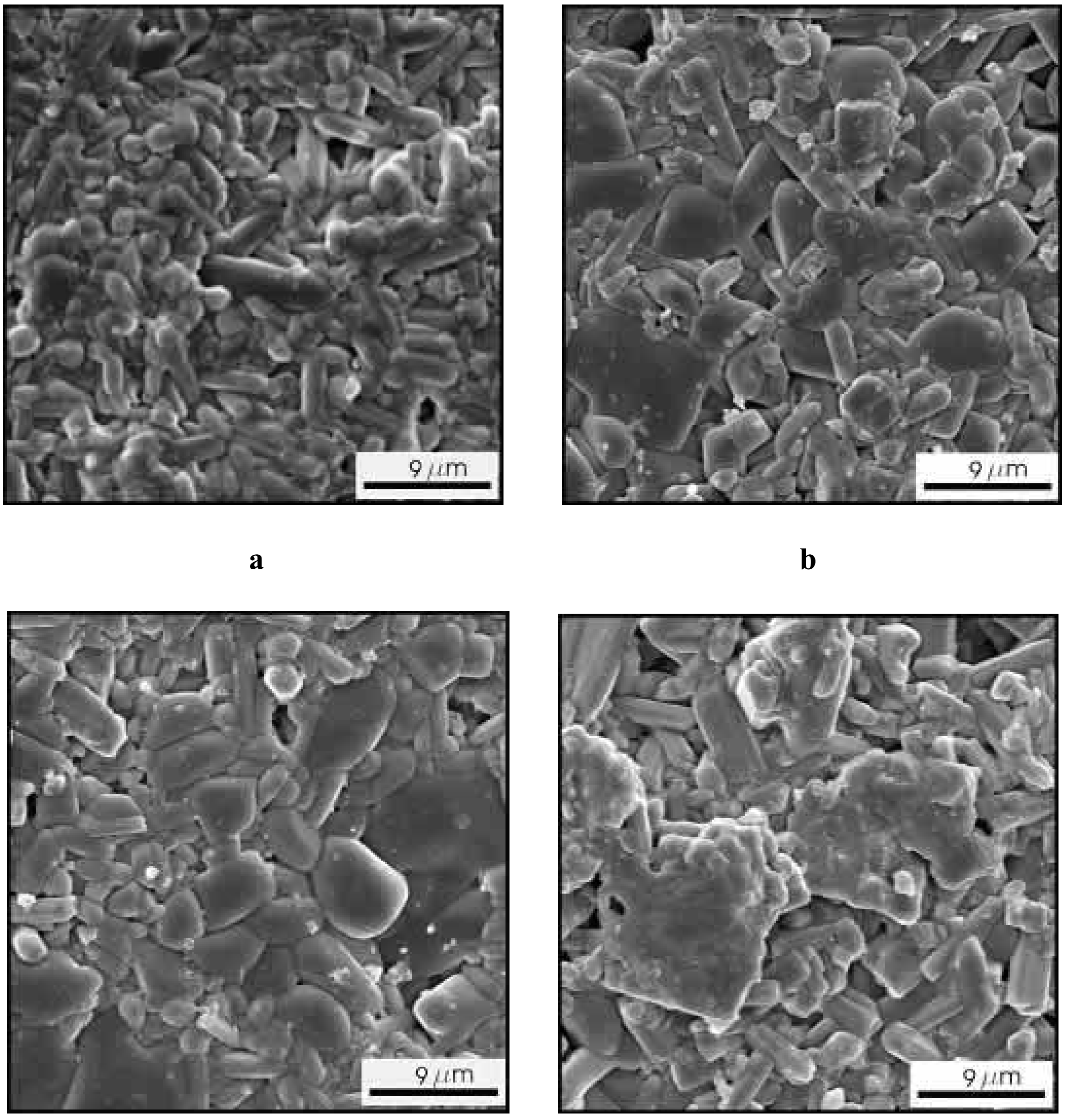

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