Influence of TiO₂ Crystalline Structure on Dielectric Resonator Properties from ZnO-Nb₂O₅-TiO₂ Ceramic System for Use in Telecommunications

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Abstract. This paper presents an investigation of the correlation between dielectric properties and microstructure and TiO₂ crystalline-phase characteristics (rutile and anatase) in ZnO-TiO₂-Nb₂O₅ system ceramics. Such ceramics were produced from powder mixtures of zinc oxide, niobium oxide and titanium oxide. Powder mixtures were compressed by pressing (100 MPa uniaxial and 300 MPa isostatic) and sintered at 1100, 1200 and 1250 °C. The sintered ceramics were characterized on the crystalline phases, density and microstructure and microwave frequencies. As for the microwave dielectric properties, dielectric constant, quality factor and thermal coefficient in the temperature range from -20 to 50 °C were measured. The results showed that the type of titanium oxide structure (rutile or anatase) causes influence on the type and quantity of crystalline phases in relative density of sintered ceramics and, consequently in their dielectric properties measurements.

Introduction

The dielectric resonator (DR) is a ceramic component used in electronic circuits that operate at the microwave frequency range; in this case the DR plays the role of resonant element and enables the construction of high selectivity filters and high stability oscillators [1,2].

The growing telecommunications development boosts the demand for new technologies that allow the improvement of the equipment performance. The ceramics found application as dielectric resonators in communication systems operating at microwave frequencies. To obtain a dielectric resonator there is a need for a specific set of properties: high value of dielectric constant (ϵ_r) and quality factor (Q), high frequency stability with temperature, that is best characterized by the so-called coefficient of resonant frequency variation with temperature or thermal coefficient (τ_f). The dielectric constant is a measure of the amount of energy stored in the material in the form of electric field. The loss factor is a measure of the energy dissipated in the form of heat within the material. In practice the loss factor determination is performed from the measurement of the quality factor that corresponds to the inverse of the loss factor.

The dielectric properties of a resonator are related to their macroscopic characteristics (shape and size) and microscopic (chemical composition, crystal structure, microstructure, polarizability and conductivity).

This work presents a study of the influence of the precursors of the TiO₂ crystalline phases as anatase and rutile in dielectric properties of the ZnO-TiO₂-Nb₂O₅ ceramic system. The relationship between the TiO₂ crystalline structures and chemical compound formation and their microstructural characteristics are also examined.

The investigation of dielectric ceramics for use as RDs seeks to identify the influences of chemical composition and microstructure characteristics in dielectric properties. Recent and old studies indicate the family of niobium-based ceramics as a material interesting for applications in microwaves [4-9]. These ceramics are sintered at temperatures between 1000 and 1400 °C. The dielectric constant values vary between 17 and 45 and the coefficient of resonance frequency variation with temperature (τ_f) between -75 and 22 ppm/°C.

Experimental Procedure

Such ceramics were produced from powder mixtures: zinc oxide, niobium oxide and titanium oxide. Mixtures of powders were compressed by pressing (uniaxial with 100 MPa and isostatic with 300 MPa) and sintered at temperatures of 1100, 1200 and 1250°C. The sintered ceramics were characterized as for the density (Archimedes' method), crystalline phases (X-ray diffraction) and microstructure (scanning electron microscopy).

Microwave dielectric properties are measured by the test arrangement using an Agilent N5230C vector network analyzer and a metal box (Figure 1). To perform any measurement, the sample must be shielded to eliminate radiation losses. The relative dielectric constant (ϵ_r) of the material is required to evaluate the dimensions (thickness H and diameter D) of the resonator for a given frequency or frequency range. This parameter is typically measured placing the dielectric resonator between two metal plates [10] as shown in Fig. 1, coupling to two antennas of the type magnetic probe to detect the signal radiated by the resonator. A field equation [1] relates the resonant frequency, the dielectric constant and the resonator's dimensions: measuring the resonant frequency value, the dielectric constant can be easily calculated.

The quality factor due to the dielectric losses (Q) is determined by half-power bandwidth method at -3 dB point [11], situation in which the resonator is placed between polystyrene plates inside the test box to reduce metallic losses. Moreover, for applications in microwave circuits, a frequency range was measured by mechanical tune, coupling the DR to a microstrip line printed on an alumina substrate. Moving a metal disk over the resonator, that perturbs the electromagnetic fields and modifies its resonant frequency.

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

The resonant frequency variation is commonly represented by the temperature coefficient (τ_f). The resonant frequency variation was also performed in the configuration of the resonator between parallel plates, but in this case, with the test box placed in a Weiss WKL100 programmable climatic chamber. The resonant frequencies were measured as function of temperature from -20 °C to +50 °C in 10 °C steps. 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:

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

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

Results and Discussions

Characteristics of ceramics with TiO₂ crystalline phases - rutile and anatase

The crystalline phases of ZnO-Nb₂O₅-TiO₂ ceramic system obtained with addition of precursor powders of TiO₂ rutile and anatase crystalline phases are shown in Table 1. Most ceramics presented the formation of three crystalline compounds, with perovskite structures of type columbite: Zn_{0.15}Nb_{0.3}Ti_{0.55}O₂, Zn_{0.17}Nb_{0.33}Ti_{0.5}O₂ and ZnNb₂TiO₈. However, the ceramics with addition of TiO₂ anatase crystalline phase and sintered at 1200 and 1250 °C did not indicate the presence of crystalline chemical compound ZnNb₂TiO₈.

Table 1. Crystalline-phase relative quantities from XRD of sintered ceramics where A = anatase and R = rutile.

SAMPLE	T _{SINTERING} [°C]	Relative Quantity of Crystalline phases
A1	1100	43 % Zn _{0.15} Nb _{0.3} Ti _{0.55} O ₂ 43 % Zn _{0.17} Nb _{0.33} Ti _{0.5} O ₂ 13 % ZnNb ₂ TiO ₈
A2	1200	52 % Zn _{0.15} Nb _{0.3} Ti _{0.55} O ₂ 48 % Zn _{0.17} Nb _{0.33} Ti _{0.5} O ₂
A3	1250	52 % Zn _{0.15} Nb _{0.3} Ti _{0.55} O ₂ 48 % Zn _{0.17} Nb _{0.33} Ti _{0.5} O ₂
R1	1100	36 % Zn _{0.15} Nb _{0.3} Ti _{0.55} O ₂ 36 % Zn _{0.17} Nb _{0.33} Ti _{0.5} O ₂ 28 % ZnNb ₂ TiO ₈
R2	1200	42 % Zn _{0.15} Nb _{0.3} Ti _{0.55} O ₂ 42 % Zn _{0.17} Nb _{0.33} Ti _{0.5} O ₂ 16 % ZnNb ₂ TiO ₈
R3	1250	49 % Zn _{0.15} Nb _{0.3} Ti _{0.55} O ₂ 45 % Zn _{0.17} Nb _{0.33} Ti _{0.5} O ₂ 6 % ZnNb ₂ TiO ₈

In Figures 2 and 3 are shown the microstructures obtained by SEM of the ceramics sintered at 1100, 1200 and 1250 °C. The microstructures of ceramic fracture surfaces show the increase of grain sizes in function of temperature increase, fact that is consistent with the literature.

The data shown in Table 2 indicate that the relative density values varied little with increasing sintering temperature. Ceramics sintered with addition of TiO₂ anatase crystalline phase showed relative porosity values lower than 4.50 %. On the other hand, the ceramics with addition of TiO₂ rutile crystalline phase showed very high values of relative porosity between 21 and 26 %. These results can be confirmed by SEM images of the fracture surfaces of ceramics shown in Figures 2 and 3. In these micrographes it is observed that the growth of grain is not directly related to the decrease in the volume of pores.

Fig. 2. SEM micrograph of fracture surface for anatase ceramics sintered at 1100, 1200 and 1250°C.

Fig. 3. SEM micrograph of fracture surface for rutile ceramics sintered at 1100, 1200 and 1250 °C.

Table 2. Relative density and relative porosity values for ceramics with TiO₂ rutile and anatase crystalline phases.

Sample	T _{SINTERING} [°C]	Relative Density* [%]	Relative Porosity [%]
A1	1100	94.34	5.66
A2	1200	94.17	5.83
A3	1250	95.78	4.22
A1	1100	74.07	25.72
A2	1200	78.02	21.98
A3	1250	74.28	25.93

* Theoretical density considering the types and amounts of crystalline compounds shown in Table 1.

Microwave Dielectric Properties

Table 3 shows the results of the measurements of the microwave dielectric properties of sintered ceramics.

Table 3. Measured values of DR parameters.

Sample DR	Diameter [mm]	Height [mm]	f[GHz] → ϵ_r	Q @ f [GHz]	τ_f [ppm/°C]	Tuned Band [GHz]
A1	11.63	4.96	5.076 → 61.0	2562 @ 3.6	279.4	-
A2	11.64	4.67	4.796 → 64.4	3186 @ 3.4	304.6	3.81-4.35
A3	11.64	4.67	5.145 → 64.1	2844 @ 3.5	283.7	-
R1	12.62	5.24	6.904 → 28.9	1085 @ 4.8	186.2	-
R2	12.48	5.08	5.898 → 41.6	2383 @ 4.1	262.3	4.65-5.54
R3	11.64	4.66	6.101 → 45.7	2317 @ 4.2	259.5	-

Dielectric Constant Correction due to Porosity

Under conditions, the values of the dielectric constant should be mainly influenced by the chemical composition of the crystalline compounds and porosity.

The influence of porosity on sintered ceramics on the value of dielectric constant can be corrected using the equation [4]:

$$\varepsilon_r = \varepsilon_r' \left(1 - \frac{3P(\varepsilon_r' - 1)}{2\varepsilon_r' + 1} \right) \quad (2)$$

where ε_r is the relative dielectric constant, ε_r' is corrected one, and P is the fraction of porosity measured.

The values of the dielectric constant corrected correspond to the ceramic without pores. In this way, these values can be correlated to the types and amounts of crystalline compounds in each ceramic (Table 4).

The ceramics A1 and R2 present the three crystalline compounds (Table 1), but in different amounts. However, the values of dielectric properties measurements were quite different (Table 3).

Table 4. Dielectric constant correction considering porosity fraction.

Ceramic	ε_r	P	ε_r'
A1	61.00	0.0566	66.52
A2	64.43	0.0583	70.46
A3	64.14	0.0422	69.37
R1	28.91	0.2572	46.93
R2	41.63	0.2198	61.37
R3	45.72	0.2593	73.94

Conclusions

The microwave dielectric properties measurements were: relative permittivity ($61 < \varepsilon_{\text{anatase}} < 65$ and $28 < \varepsilon_{\text{rutile}} < 46$), quality factor ($2500 < Q_{\text{anatase}} < 3200$ and $1080 < Q_{\text{rutile}} < 2400$) and temperature coefficient ($280 < \tau_{f(\text{anatase})} < 305$ and $185 < \tau_{f(\text{rutile})} < 260$) in the temperature range from -20 to +50 °C. The results showed that the type of crystal structure of titanium oxide (rutile or anatase) influence on the type and quantity of inherent crystalline phase, values of relative density of sintered ceramics and, consequently, in dielectric properties measurements. These results allow concluding that ZnO-Nb₂O₅-TiO₂ ceramic system obtained from TiO₂ anatase crystalline structure present both dielectric constant and quality factor values suitable for manufacture of microwave dielectrics resonators. The values of the temperature coefficient indicated that these resonators can be used in conditions of small temperature variation or with temperature compensation system.

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