Thermistors manufactured from nioubium oxide in the ZrO2-Bi2o3

Termistores manufacturados de óxido de nioúbio no ZrO2-Bi2o3

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ABSTRACT
Thermistors are thermal resistors that allow high changes in the dielectric constant due to the sensible temperature change. The thermistors can be P.T.C.R and N.T.C.R. They are devices applied within the oil exploration industry, automobiles and electronics. The ceramic powders were obtained from stoichiometric quantities by ball milling with subsequent compaction, sintering and heat treatment from 825 ° C for 24 hours and cooled to room temperature. The samples were characterized by X-ray diffraction, scanning electron microscopy, calculation of the apparent density, dielectric constant and qualitative thermistor factors, called temperature coefficient and characteristic ratio. The samples from the mixture between the niobium zirconia-bismuth oxides obtained significant results for commercial and industrial application in the respective temperature ranges, between 30ºC-80ºC and 460ºC-600ºC.

Keywords: Thermistors, Zirconia, bismuth oxide, niobium oxide, P.T.C.R, N.T.C.R

RESUMO
Os termistores são resistências térmicas que permitem mudanças elevadas na constante dieléctrica devido à alteração sensata da temperatura. Os termistores podem ser P.T.C.R e N.T.C.R. São dispositivos aplicados dentro da indústria de exploração petrolífera, automóveis e electrónica. Os pós cerâmicos foram obtidos a partir de quantidades estequiométricas por moagem de esferas com subsequente compactação, sinterização e tratamento térmico a partir de 825ºC durante 24 horas e arrefecidos à temperatura ambiente. As amostras foram caracterizadas por difracção de raios X, microscopia electrónica de varrimento, cálculo da densidade aparente, constante dieléctrica e factores termistores qualitativos, chamados coeficiente de temperatura e relação característica. As amostras da mistura entre os óxidos de nióbio zircónio-bismuto obtiveram resultados

significativos para aplicação comercial e industrial nas respectivas gamas de temperatura, entre 30ºC-80ºC e 460ºC-600ºC.

Palavras-Chave: Termistores, Zircónia, óxido de bismuto, óxido de nióbio, P.T.C.R, N.T.C.R

1 INTRODUCTION

Thermistors are semiconductor devices that allow large variations in electrical resistance at small temperature ranges [1]. In this case, the thermal resistance of the thermocouples increases with increasing temperature and the N.T.C.R (negative temperature coefficients) decrease the electrical resistance with increasing temperature [2]. Therefore, the objective is to synthesize ceramic composites with characteristics of thermistors for commercial and industrial use through the behavioral analysis of the dielectric constant, the electrical resistivity and the calculation of the qualitative factors of thermistors α and β, respectively referred to as temperature coefficient and characteristic ratio.

2 THEORETICAL FOUNDATION

The zirconia being a type N semiconductor widely used as oxygen sensors, thermal barrier, fuel cells and with excellent thermal and electrical properties, it becomes a technological attraction to be searched as thermistor. This is because the mixing between zirconia and bismuth oxide allows the stabilization of the ferroelectric phase β_{III} –Bi_2O_3 where the effects N.T.C.R and P.T.C.R. can be observed [3]. The addition of silicon oxide in bismuth oxide enables the formation of bismuth silicate that crystallizes in the non-centrosymmetric space group and promotes instantaneous polarization, which is interesting for the generation of the N.T.C.R. effect. In the case of the addition of niobium oxide the mixture of bismuth and zirconium oxides allows to obtain cubic phases through the system $Bi_2Nb_{1-x}Zr_xO_{7+x/2}$ which increases the stability of the crystalline structure and reduces the effect of material degradation caused by the mobility of both cationic vacancies and oxygen vacancies [4].

3 METHODOLOGY

3.1 MATERIALS AND METHODS

The experimental procedure used the mixture of commercial starting powders widely used for their low cost and simplicity of execution. Two different compositions

will be applied: The first will be the mixture of starting powders containing ZrO_2 , Bi_2O_3 and Nb_2O_5 and the second will contain ZrO_2, Bi_2O_3 and Nb_2O_5 The purity of the ceramic powders is 99.9% obtained from the Aldrich industries and the stoichiometry is based on the liquid lines indicated in the phase diagram ZrO_2 –Nb_2O_5. The general equations for stoichiometry are given in Table 1.

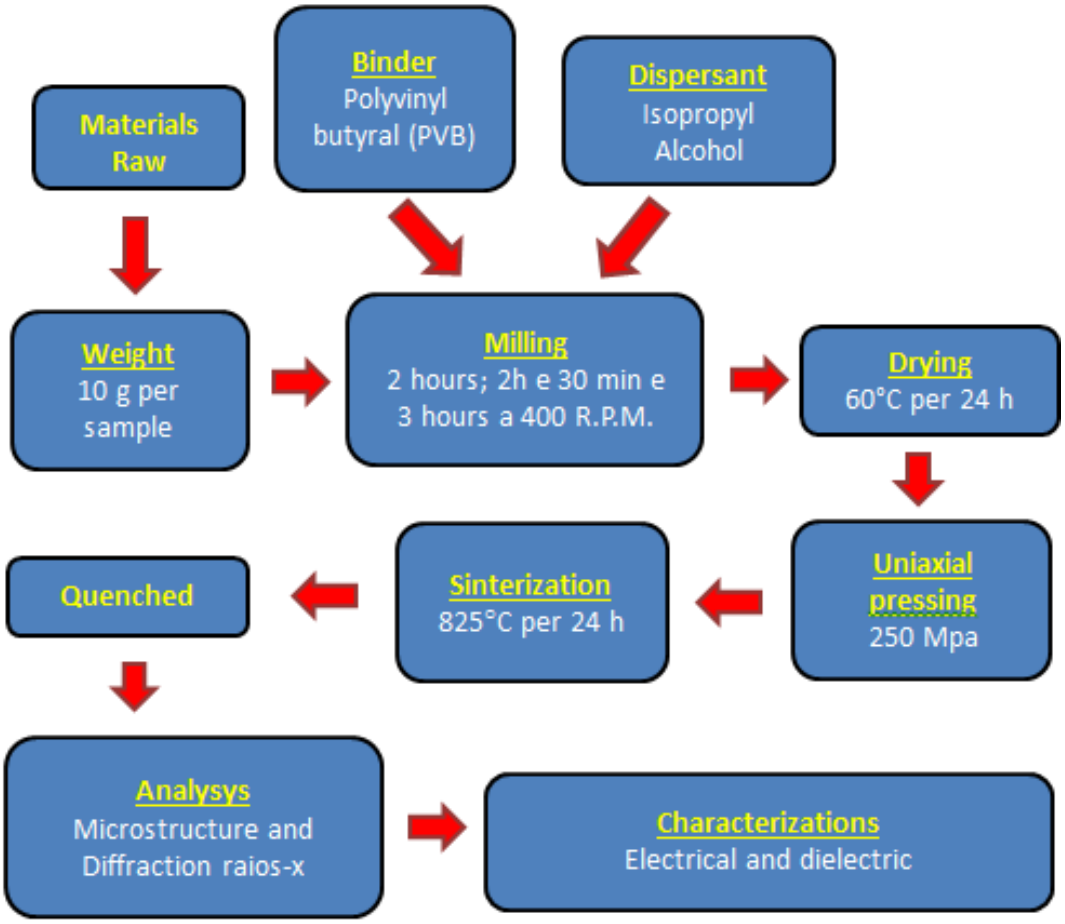
The compositions was obtained with 10 grams of duly mixed post-admixtures weighed in analytical balance according to tab. 1 and 2, ground in a zirconia ball mill with a diameter of 3 mm in the ratio of 5: 1 by weight and in the rotation of 400 R.P.M. The grinding time for the compositions was from two hours, two and a half hours and three hours. Polyvinyl butyral (P.V.B) was used as a binder in the proportion of 1.5% by weight for each composition in order to provide mechanical strength for the subsequent compacting of the ceramic powders. The dispersant used was the isopropyl alcohol used in the proportion of 3 ml for each 1 g of the composition according to gram equivalent between the atomic mass of the oxides and the atomic mass of the dispersant.

Table 1 – Samples of zirconium, niobium and bismuth oxides

Samples	**Composition in % mol**				**Mass percentage of raw matter**		
	ZrO_2	Nb_2O_5	Bi_2O_3	→	$3ZrO_2$	$2Bi_2O_3$	$(x)Nb_2O_5$
ZrNbBi 1	**70,0**	**5,0**	**25**		**51,23**	**46,3**	**2,63**
ZrNbBi 2	**75,0**	**5,0**	**20**		**58,13**	**39,08**	**2,79**
ZrNbBi 3	**80,0**	**5,0**	**15**		**65,88**	**31,15**	**2,96**

The obtained powders were compacted unixially in a model manual hydraulic press (Marcon MPH-30) at a pressure of 250 MPa and with a force of 2000 kgF. After forming in cylindrical metal mold the specimens were obtained with 10 mm of diameter and 3,0 mm of thickness. The specimens were sintered at 825 ° C at a rate of 5 ° C / min in a Quimis type resistive muffle furnace.

Figure 1 - Ceramic processing sequence for samples



3.2 CALCULATION PROCEDURES

3.2.1 Dielectric Constant

The dielectric constant also known as relative permissiveness consists of a complex It is calculated from equation 1 at 4 below:

$$\varepsilon_r = \varepsilon' + i\,\varepsilon'' \quad (1)$$

$$\varepsilon' = \frac{C\,.\,x}{\varepsilon_0\,.\,A} \quad (2)$$

ε' represents real part, C represents capacitance, x thickness, ε_0 dielectric permissivity in vacuum 8,85 x 10-12 F.m-1 and cross section of samples.

$$\varepsilon'' = \varepsilon'.Tan\delta \quad (3)$$

$$Tan\delta = \frac{1}{2\pi fRC} \quad (4)$$

Tanδ represents loss angle tangent, f is Frequency Khz, R is Electrical Resistance, C is capacitance.

3.2.2 Qualitative Measurements of Thermistors

The equation of Hart Steinhart it is possible to calculate the α temperature coefficient and the characteristic resistance ratio β, equation 5 and 6. The equation 7 determine the discontinuity between bands:

$$\alpha = -\frac{\beta}{T^2} \quad (5)$$

$$\beta = \left(\frac{T_O \,.\, T}{T - T_O}\right) \ln\left(\frac{R_O}{R}\right) \quad (6)$$

$$n = \frac{1}{\rho q \mu} = Se^{\frac{E_d}{2kT}} \quad (7)$$

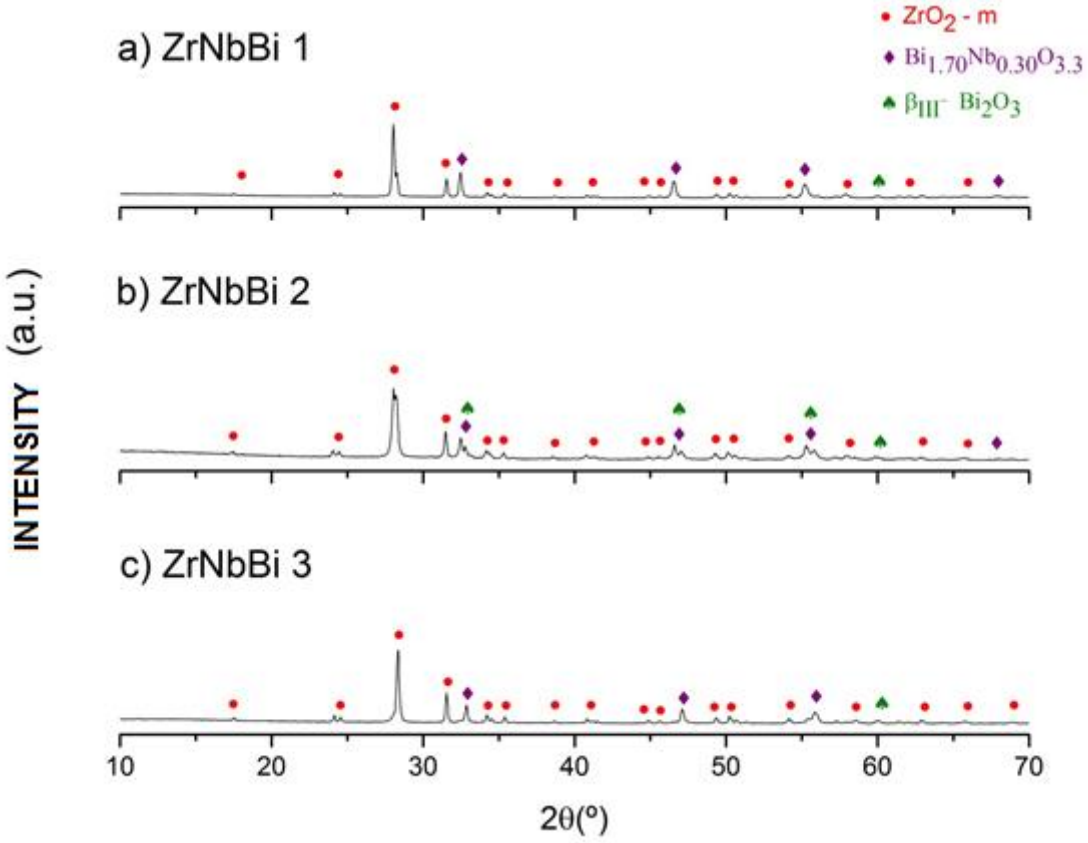
η represents of the charge mobility, ρ is electrical resistivities in Ω.cm, q is electric charge of the electron, μ is ion mobility, S is correction, Ed is discontinuity energy, k boltzman constant and T temperature in kelvin.

4 RESULTS AND DISCUSSION

4.1 DIFFRACTION OF X-RAYS

The diffractograms of the compositions ZrO_2-Nb_2O_5 –Bi_2O_3,figure 2, the identified phases were the monoclinic zirconia by the file (ICSD-68782), the cubic phase $Bi_{1.70}$ $Nb_{0,30}O_{3.3}$ in file (ICSD-160392) and the phase tetragonal oxide of bismuth oxide – $Bi_{1.85}Zr_{0,16}O_{3.075}$ [3,4] in file (ICSD-93499).

Figure 2 - Diffractogram of the system phases ZrO2-Nb2O5-Bi2O3



In Table 2, the higher concentration of bismuth oxide allows the increase of the stabilization of the cubic phase of bismuth. In addition, the tetragonal phase is also stabilized as a minority phase.

The reduction of the monoclinic zirconia in the composition ZrNbBi-1 table 2. On the other hand, the compositions ZrNbBi-2 and ZrNbBi-3, demonstrated an increase in the molar fraction of monoclinic ZrO2 with respect to stoichiometry. A larger molar fraction of the tetragonal phase of bismuth in the composition ZrNbBi 2 is also noted, which is in agreement with that reported in the (100-x) ZrO_2 .(x) Bi_2O_3 system [5].

Table 2 – Molar fraction of the phases found for the system ZrO2-Nb2O5-Bi2O3

Samples	Molar Fraction of Phases found			Mass percentage Of Raw Materials		
	ZrO_2	**$Bi_{1.70}Nb_{0.30}O_{3.3}$**	**$Bi_{1.85}Zr_{0.16}O_{3.075}$**	**$3ZrO_2$**	**$2Bi_2O_3$**	**$(x)Nb_2O_5$**
ZrNbBi 1	**48,6**	**47,8**	**3,5**	**51,23**	**46,3**	**2,63**
ZrNbBi 2	**60,4**	**30,9**	**8,7**	**58,13**	**39,08**	**2,79**
ZrNbBi 3	**68,8**	**29,9**	**2,2**	**65,88**	**31,15**	**2,96**

4.2 SCANNING ELECTRON MICROSCOPY

The samples ZrNbBi 1, it is possible to observe the reduction of the porosity as a function of the gradual decrease of the bismuth oxide content, figure 3, 4 e 5.

Figure 3 - Micrograph of composition ZrNbBi 1

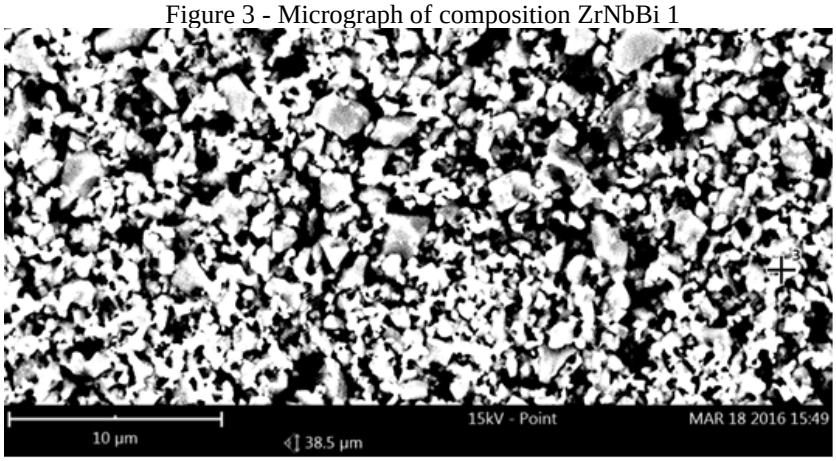


Figure 4 - Micrograph of composition ZrNbBi 2

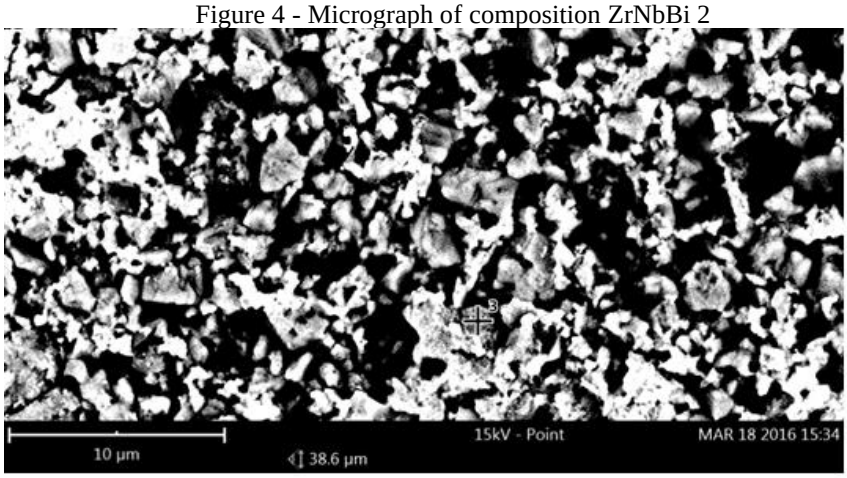
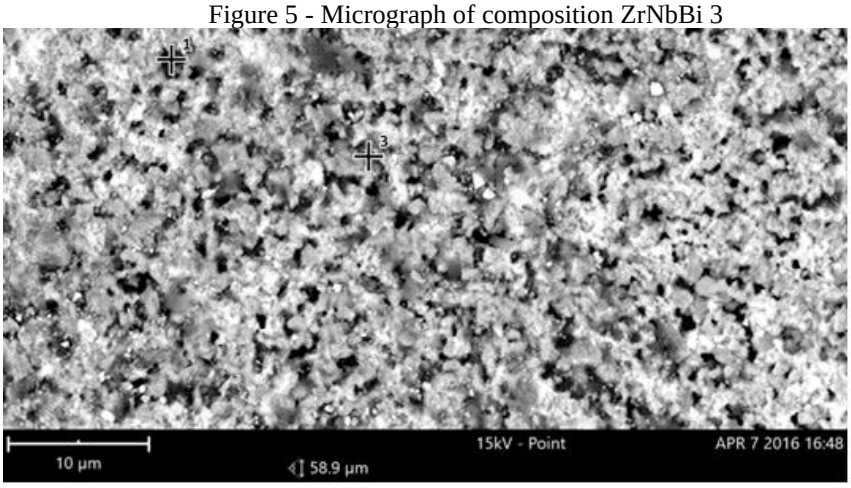


Figure 5 - Micrograph of composition ZrNbBi 3



In the sample ZrNbBi 1 there is an increase of the crystal size when compared to the other compositions with lower bismuth content according to table 3.

This is due to the difference between the zirconia and bismuth oxide melting points. Although the bismuth oxide is a densifying agent, zirconia has the Frenkel type defect in its crystalline structure, which, together with niobium oxide, increases the amount of cation and anion vacancies created, leading to the reduction of the relative density according to table 3.

As the concentration of defects is reduced in the sample ZrNbBi 2, the size of the crystal is also reduced, increasing the relative density with respect to the composition with higher content of bismuth oxide ZrNbBi 1.

In the ZrNbBi 3 sample, the largest reduction in crystal size occurs because of the smaller defect encapsulation.

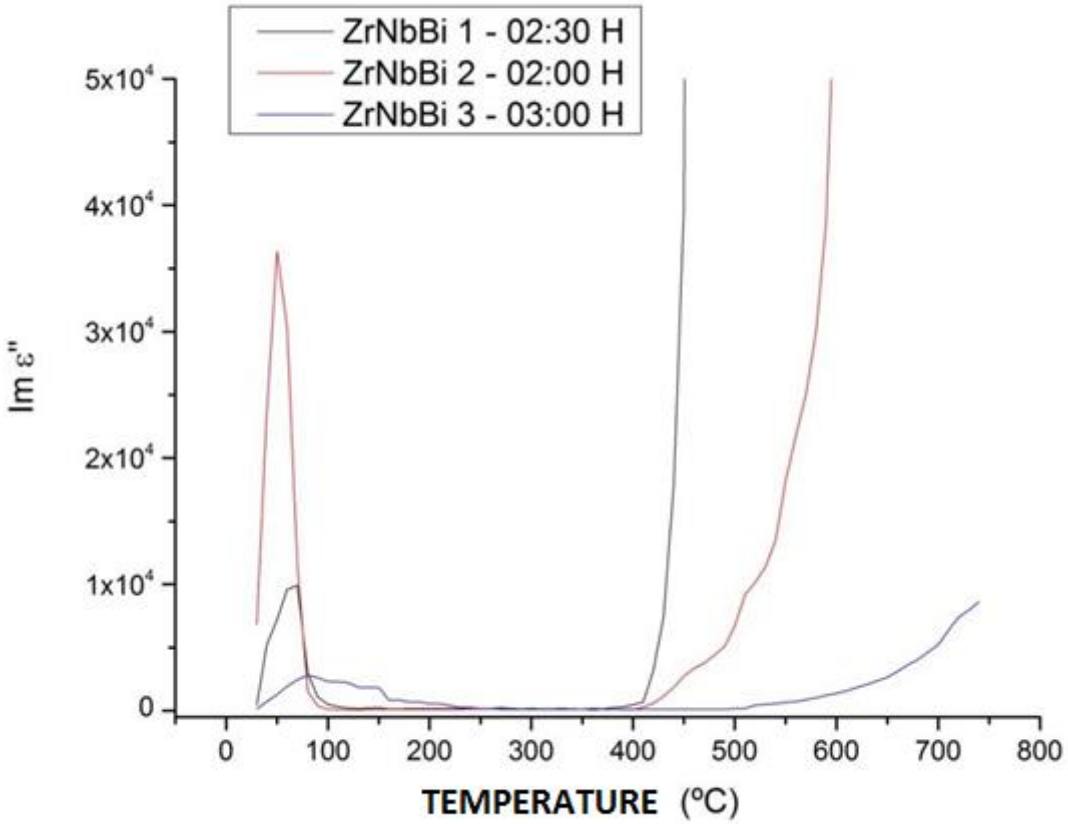
Table 3 – Values of particle size, porosity and relative density of ZrO_2-Nb_2O_5-Bi_2O_3 samples

Sample	Size Crystal	Relative Density	Porosity Apparent
ZrNbBi 1	195,0 nm	75,00 %	25,00 %
ZrNbBi 2	120,5 nm	77,78 %	22,22 %
ZrNbBi 3	88,0 nm	80,95 %	19,05 %

4.3 ELECTRICAL AND DIELECTRIC CHARACTERIZATION

In Figure 6, The first occurs at low temperatures between 30ºC-70ºC. Among the samples, ZrNbBi 2 shows higher polarization at the temperature of 70ºC. However with the increase in temperature, from the temperature 70 ºC the dielectric constant begins to decrease until it extinguishes.

Figure 6 - Graph of Dielectric Permissivity x temperature for ZrNbBi samples with different milling time



In the Table 4, the sample ZrNbBi 1 shows a small reduction of the GAP of energy at 70 ° C in order of magnitude of 10^3 with the elevation of the GAP at the temperature of 120° C.

Table 4 – Dielectric properties of composition ZrNbBi 1 milled for 02h 30 min

Sample	Temperature (ºC)	Dielectric Constant	Discontinuity Bands (Ev)
ZrNbBi 1	70	9,93 x 10^3	- 0,0059
	120	2,13 x 10^2	0,661
	410	6,82 x 10^2	- 0,188
	750	4,18 x 10^8	- 0,707

In the case of samples ZrNbBi 2 and 3, they present reduction of discontinuities, respectively in the temperatures of 50ºC and 80ºC, table 5.

Table 5 – Dielectric properties of composition ZrNbBi 2 e 3 milled for 03 hours

Samples	Temperature ºC	Dielectric Constant	Discontinuity Bands (Ev)
ZrNbBi 2	50	4,40 x 10^4	-0,0476
	750	2,05 x 10^5	-0,0371
ZrNbBi 3	80	2,80 x 10^3	-0,0210
	750	8,63 x 10^3	-0,119

The Samples milled for two and a half hours and three hours showed different dielectric behavior than the one previously mentioned in Figure 7 and 8. Report anomalous behavior similar to that of the $2Bi_2O_3.3ZrO_2$ [6]

Figure 7- Graph of the dielectric permittivity x temperature of the composition ZrNbBi 2 milled for 02hours e 30 min

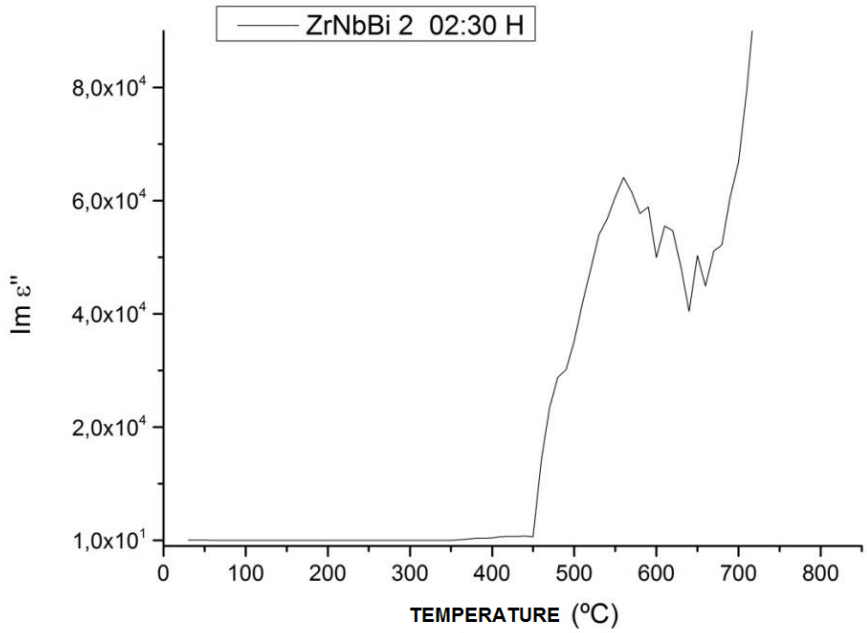
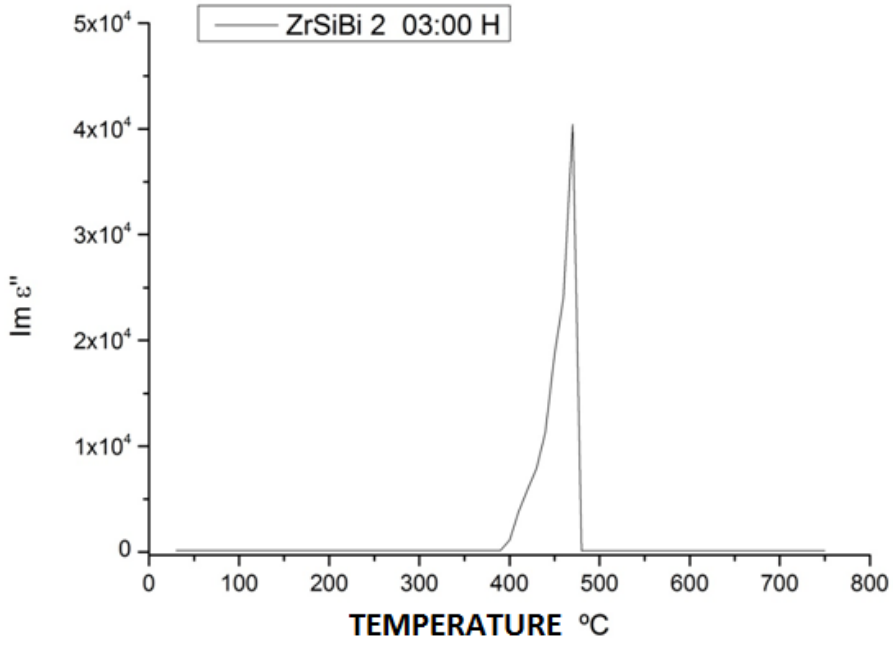


Figure 8- Graph of the dielectric permittivity x temperature of the composition ZrNbBi 2 milled for 03 hours.



4.4 QUALITATIVE ANALYSIS OF THERMISTORS

The parameters used to determine the quality of the thermistor are the temperature coefficient and the characteristic resistance ratio, respectively, called α and β factors The commercial values for β are between 2000-6000 K . Negative values for α, imply behavior N.T.C. table 8 shows the calculated values for the qualitative parameters for samples studied in this work.

SAMPLES	Temperature Range	α %/K	β K
ZrNbBi 1 – milled 2:30 H	30ºC -70ºC	- 7,0	7.856,03
ZrNbBi 2 - milled 2:00 H	30ºC-50ºC	-.7,0	7.719,89
ZrNbBi 2 - milled 2:30 H	460ºC-600ºC	-0,75	5.742,17
ZrNbBi -2- milled 3:00 H	510ºC-600ºC	-1,85	14.116,66
ZrNbBi 3 - milled 3:00 H	30ºC - 80ºC	-4,73	5.893,17
ZrSiBi 2 - milled 3:00 H	380ºC - 470ºC	-5,00	26.691,95
ZrSiBi 3 – milled 3:00 H	30ºC - 50ºC	-10,0	10.103,48

5 CONCLUSION

The composition ZrNbBi 2 milled for both 02 hours 30 min and for 03 hours which shows the double behavior N.T.C-P.T.C. The longer grinding time influenced the increase in load polarization by an order of magnitude higher.

The composition ZrNbBi 2 and 3 ground for two and a half hours and three hours respectively obtained 78% and 81% of the theoretical density, respectively, and they showed to be within the range of commercial and industrial application as a function of the qualitative factors α and β.

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