

# SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE ZIRCONIA BY PECHINI METHOD USING AS STABILIZING ADDITIVE A CONCENTRATE RARE EARTH ELEMENT FOR USE IN OXYGEN SENSORS

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**Abstract.** In this paper we propose the obtaining of ceramic powder form  $ZrO_2:12 \text{ mol\% } Re_2O_3$  by the polymeric precursors method (Pechini), where  $Re_2O_3$  is a rare earth elements concentrate that has 76.88% of yttrium oxide ( $Y_2O_3$ ), 12.1% of Dysprosium oxide ( $Dy_2O_3$ ), 4.04% of Erbium oxide ( $Er_2O_3$ ) and 1.94% of Holmium oxide ( $Ho_2O_3$ ) mainly. In this way the cubical phase transformation is favored making possible the use of ceramic material in electrical applications, such as oxygen sensors. The main objective was to obtain reactive powder (particle size of nanometer) and dense sintered ceramics pieces. In order to obtain the ceramic material by the Pechini method, citric acid and ethylene glycol were mixed up in a (1/4): 1 relation, the mixture was warmed up at a temperature of 70°C to favor the dissolution of citric acid in ethylene glycol. The solution was let to cool down and the  $Re_2O_3$  and zirconium precursors were added. All the process was carried out with complete agitation. The powder obtained after this procedure is treated in furnace at 400, 500, 600 and 700 °C during two hours, obtaining the mentioned ceramic material. The powder were characterized by diffraction of x-rays and infrared spectroscopy to guarantee the obtaining of its cubical phase. The results indicate the formation of the cubic zirconium oxide. After the ceramic material was obtained, the synthesized ceramics were compacted and studied to obtain a solid electrolyte with an appropriate ionic conductivity. The electrical properties were studied by means of impedance spectroscopy.

**Keywords:** characterization, cubical phase of the zirconium, Pechini method, rare earth elements, synthesis process, zirconium

## 1. INTRODUCTION

Zirconium oxide ( $ZrO_2$ ) is an oxide which has increased their consumption in recent years, mainly in applications with electronics, chemical, biological, and mechanics properties. Their main properties are: high melting point (2680°C), corrosion resistance, low thermal conductivity, high mechanical strength, high toughness, thermal shock resistance, high refractive index and good ionic conductivity (Paiva et al, 2006).

The pure zirconium oxide ( $ZrO_2$ ) shows polymorphism on crystalline structure, from room temperature to melting point. These changes of phase always occur with a change of heat. The monoclinic crystalline phase (M- $ZrO_2$ ) prevails at atmospheric pressure and room temperature. At 1150 °C tetragonal zirconia occurs (T- $ZrO_2$ ) and at 2370 °C there is a transition to cubic zirconia with fluorite structure (F- $ZrO_2$ ), (Zhuiykov, 2008). These transformations are reversible during cooling. However, cation incorporation with small valence numbers such as alkaline earth or stable rare earth cations to form substitutional solid solution, causes formation of tetragonal and cubic zirconia phases, stable at lower temperatures. Particularly, when yttrium oxide is added to pure zirconia,  $Zr^{4+}$  ions are partly replaced by  $Y^{3+}$  ions to create oxygen vacancies inside their structure. The generated oxygen vacancies allows  $O^{2-}$  ionic conduction, making the stabilized zirconia suitable for use as oxygen sensor, (Mineiro, 2008). Using the Kroger-Vink notation (Kröger, Vink, 1956), this reaction can be described according to equation 1:



where the yttrium atoms were assumed to occupy at  $Zr^{4+}$  ( $2Y'_{Zr}$ ) and oxygen vacancy ( $V_o$ ) is created to satisfy charge neutrality.

A doping level of 6–12 mol% of yttria stabilizes zirconia in the cubic phase (YSZ), a more favorable phase for ionic conduction at high temperatures, (Ramamoorthy, 1999). The yttria stabilized zirconia is a good oxide ion conductor and, to different partial pressures of oxygen ( $PO_{\text{Teste}}$  and  $PO_{\text{Ref}}$ ), the electromotive force is given by a form of the familiar Nernst equation, equation 2, (Leitão, 2002), (Steil et al, 2002):

$$E = \frac{RT}{4F} \ln \left( \frac{p O_{Teste}}{p O_{Ref}} \right) \quad (2)$$

where E is measured in volts (V), F is the Faraday Constant ( $9.65 \times 10^4$  C/mol), T is the absolute temperature (K), R is the gas constant ( $8.134$  J/mol\*K),  $PO_{Teste}$  and  $PO_{Ref}$  are the partial pressures of oxygen on two sides.

The objective of the present work is obtaining ceramic powder with the form  $ZrO_2:12$  mol% CTR by the polymeric precursors method (Pechini), aiming high ionic conductivity for future use as oxygen sensors.

## 2. EXPERIMENTAL

The precursors used in this work were zirconium (IV) butoxide (TBZ) and a rare earth elements concentrate that has 76.88% of yttrium oxide ( $Y_2O_3$ ), 12.1% of Dysprosium oxide ( $Dy_2O_3$ ), 4.04% of Erbium oxide ( $Er_2O_3$ ) and 1.94% of Holmium oxide ( $Ho_2O_3$ ) mainly. Three separate solutions were prepared to obtain zirconia stabilized powders using polymeric precursor method: Citric acid (CA) solid was dissolved in ethylene glycol (EG) to obtain the first solution (1); TBZ liquid was dissolved in a solution 1.6 molar nitric acid solution to obtain the second solution (2); finally the rare earth concentrate was dissolved in a solution 0.1 molar nitric acid solution to obtain the third solution (3). All three procedures were maintained under agitation.

After obtaining all the solutions, the second and the third solution were added immediately to the first one. This solution was heated to a temperature of  $120^\circ C$ , favoring the formation the polymerization reaction to form a gel, which subsequently, was transformed into a viscous resin. After this step, we performed the drying of the material, corresponding to the resin pyrolysis. Pyrolysis was done at  $250^\circ C$  for 18 hours in a muffle type furnace. All process is illustrated in Figure 1. The deagglomeration from the obtained material, was done in an agate mortar. Finally, the powder was thermally treated ( $400, 500, 600, 700$  and  $1100^\circ C$ ), to obtain the ceramic material. The resulting material was characterized by DRX and FTIR

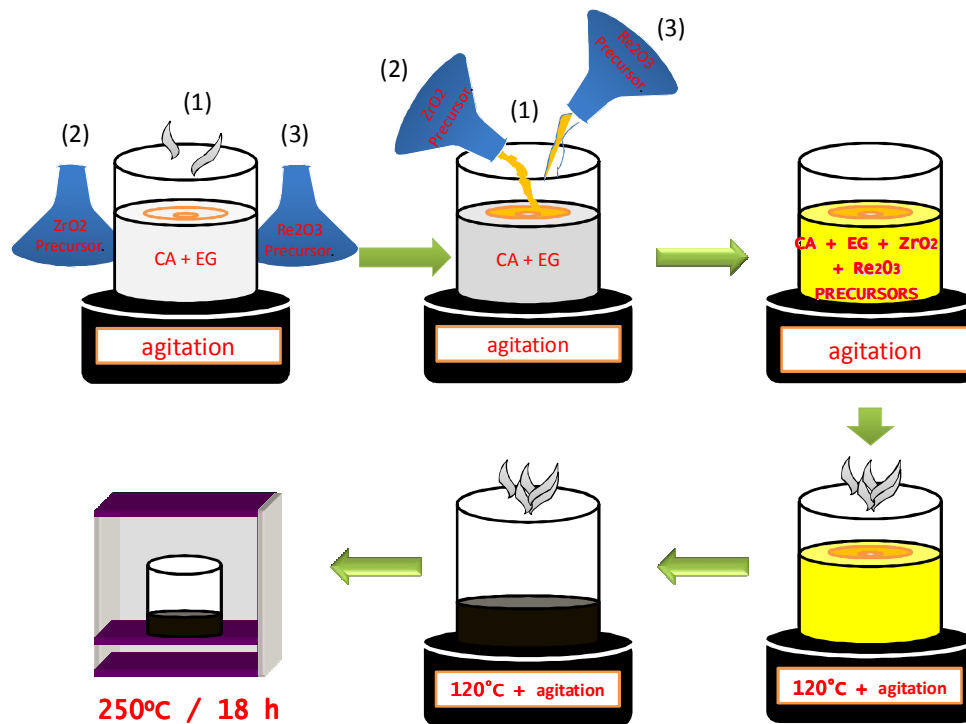


Figure 1. Experimental procedure aiming to obtain powder of  $Re_2O_3$  stabilized zirconia using the Pechini method.

Using the cold uniaxial pressing, experimental pellets of 13 mm diameter were manufactured in a cylindrical matrix. The pressure applied was approximately 180 MPa, using a press SCHULZ PHS. Sintering was carried out in an

electric muffle furnace for a period of 120 min at 1400 °C, with heating rate of 3 °C/min. Archimedes' principle was used to determine the bulk density with immersion of the pellet in distilled water.

Finally, electrical measurements were carried out using Solartron Analytical equipment model 1260, in the Vitreous Materials Laboratory-LAMAV. For this, samples were sanded with 400 and 1200 sandpaper. The electrolyte pellets were provided with a platinum paste electrode (Demetron 308-A) in the parallel faces of the samples, and this samples were cured at 900 °C for 20 minutes. The impedance spectra was measured in three samples simultaneously. The used frequency range from 13 MHz up to 5 Hz and range from temperatures 240 up to 423 °C. The voltage applied to the sample was 1000 mV.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the Infra-red spectra absorption in the region of 4000-400  $\text{cm}^{-1}$  for the pre-calcined ReSZ powders at 250 °C for 18 hours. Qualitative analysis of the present functional groups determined a band located at 3748  $\text{cm}^{-1}$  associated with isolated O-H group adsorbed by metal (RE) inferring the presence of  $\text{Re}_2\text{O}_3$  segregated on the surface of  $\text{ZrO}_2$  (Stuart, 1996). The absorption band 3440  $\text{cm}^{-1}$  is caused by the O-H stretching mode of a water molecule. The band of  $\text{CO}_2$  is revealed at 2360  $\text{cm}^{-1}$  (Souza et al, 2007), water hydration at about 1627  $\text{cm}^{-1}$  (spasibencko *et al*, 1979) and the vibrations of Zr-O-C groups are observed at 1097  $\text{cm}^{-1}$ . Finally, the bands located at low wave number region, 1000-400  $\text{cm}^{-1}$ , are of interest because there are metal-oxygen vibrations, very important in the analysis of oxides. The region presents three well defined bands that can be assigned to Zr-O groups and the possible coexistence of the tetragonal phase (586, 470  $\text{cm}^{-1}$ ) with the monoclinic phase (670  $\text{cm}^{-1}$ ) (Pecharroman et al, 1996).

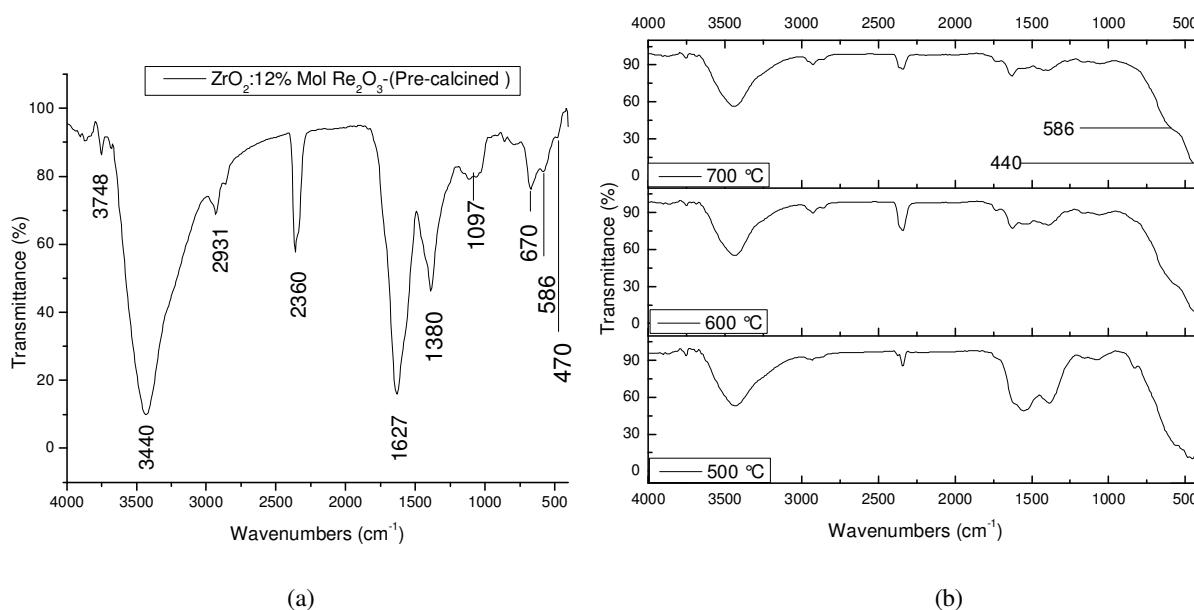


Figure 2. Infra-red spectra absorption in the region of 4000-400  $\text{cm}^{-1}$  (a) for the pre-calcined ReSZ powders at 250 °C for 18 hours and (b) heat-treated samples at temperatures 500, 600 and 700 °C for two hours

In the heat-treated samples at temperatures 700 °C for two hours it is evident a considerable reduction in the intensity of the bands associated with OH groups, HOH and functional groups containing carbon. The low wave number region shows a band around 440  $\text{cm}^{-1}$  associated with the Zr-O linkages of cubic zirconia. In this spectral region another absorption band also appears, 586  $\text{cm}^{-1}$ , and is assigned to the vibrations of Zr-O of the tetragonal zirconia. The qualitative analysis of the FTIR spectra shows that for this heat-treated sample (700 °C/2h), it is still evident the coexistence of tetragonal and cubic phases of zirconia.

X-ray diffraction studies were performed for the following samples: pre-calcined and heat-treated at temperatures 400, 500, 600, 700 and 1100 °C (figure 3), where we can appreciate how is the evolution of crystalline phases with increasing temperature. Clearly the pre-calcined sample shows a typical amorphous structure, and the same sample with a heating treatment to 400 °C resulted in a very broad peak around 30°, where the most intense peak of the tetragonal and cubic zirconia is identified. At 500 °C the powder has a low crystallinity that is verified by the broadening in the x-ray diffraction lines.

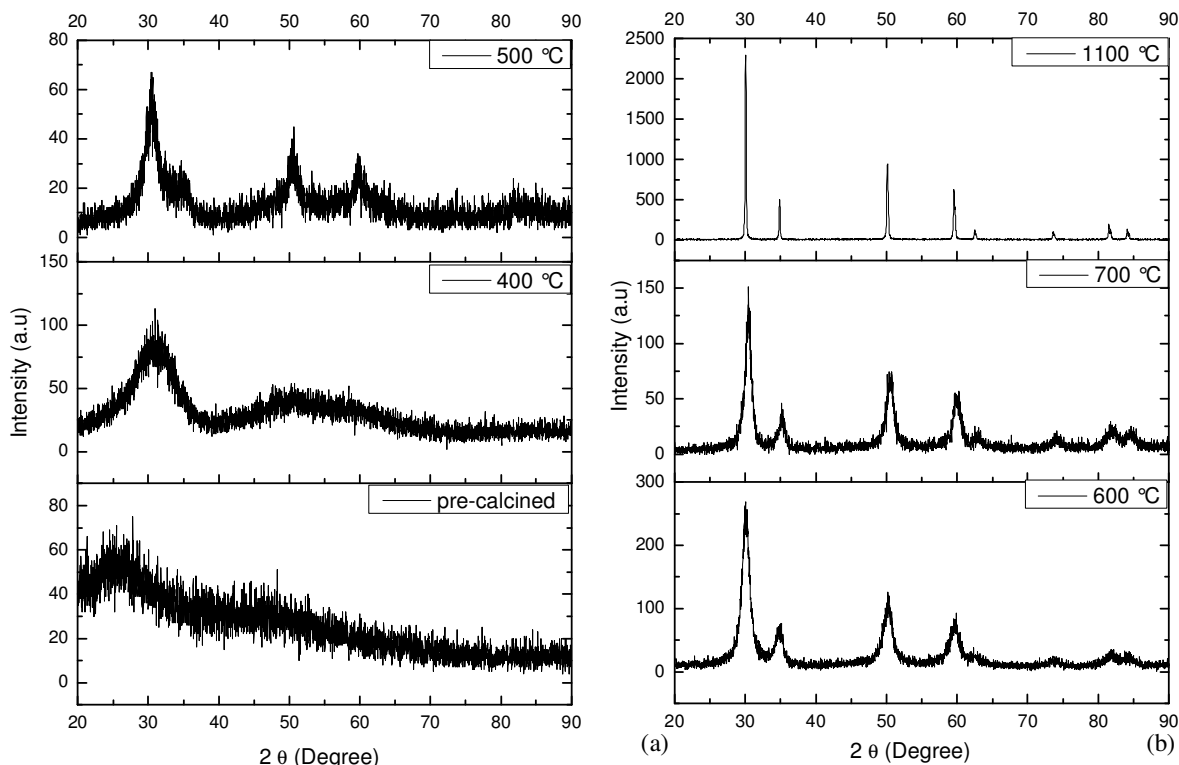


Figure 3. XRD spectrum of the ReSZ for the pre-calcined ReSZ powders at 250 °C for 18 hours and heat-treated samples at temperatures 400, 500, 600 and 700 °C for two hours

At temperatures of 600 and 700 °C the samples indicate an increase in their structural order making possible their comparison with existing databases. For the present study we used the database of crystallographic Search-Match, finding that for these temperatures of heat treatment two crystalline phases coexist: tetragonal and cubic of yttria-stabilized zirconia with PDF corresponding to 48-224 and 30-1468, respectively. It is not clear the presence of these two phases because of the vicinity of the lattice parameters of polymorphs (Castro et al, 2006). Thus, it was necessary to refine the crystal structure by Rietveld method, figure 4. In this Figure it can be seen more clearly the phases present in the sample heat-treated at 700 °C. The software used in this work was GSAS (General Structure Analysis System).

The residue  $\chi^2 = 1.257$  shows a good approximation between the observed and calculated diffraction pattern. For this reason the result of the refining gives a good approximation of the percentage of phases, separating and quantifying them: cubic phase majority with 88.2% wt and the tetragonal phase minority with 11.8% wt. Finally, the heat-treated samples at temperatures 1100 °C for two hours shows the crystalline phase of interest, the cubical phase (PDF 30-1468 with a residue of  $\chi^2=1.285$ ), that for our application in oxygen sensors has a higher value of ionic conductivity, (Jiawen et al, 2004).

In the previous study, we conclude that the increase in temperature favors the stabilization and crystallization of the cubic phase probably due to the formation of oxygen vacancy. For this reason we chose a comparatively high temperature of 700° C as suitable for heat treating the pre-calcined powder because it has good crystallinity, a considerable reduction of functional groups associated with carbon, and it presents the major cubic crystalline phase.

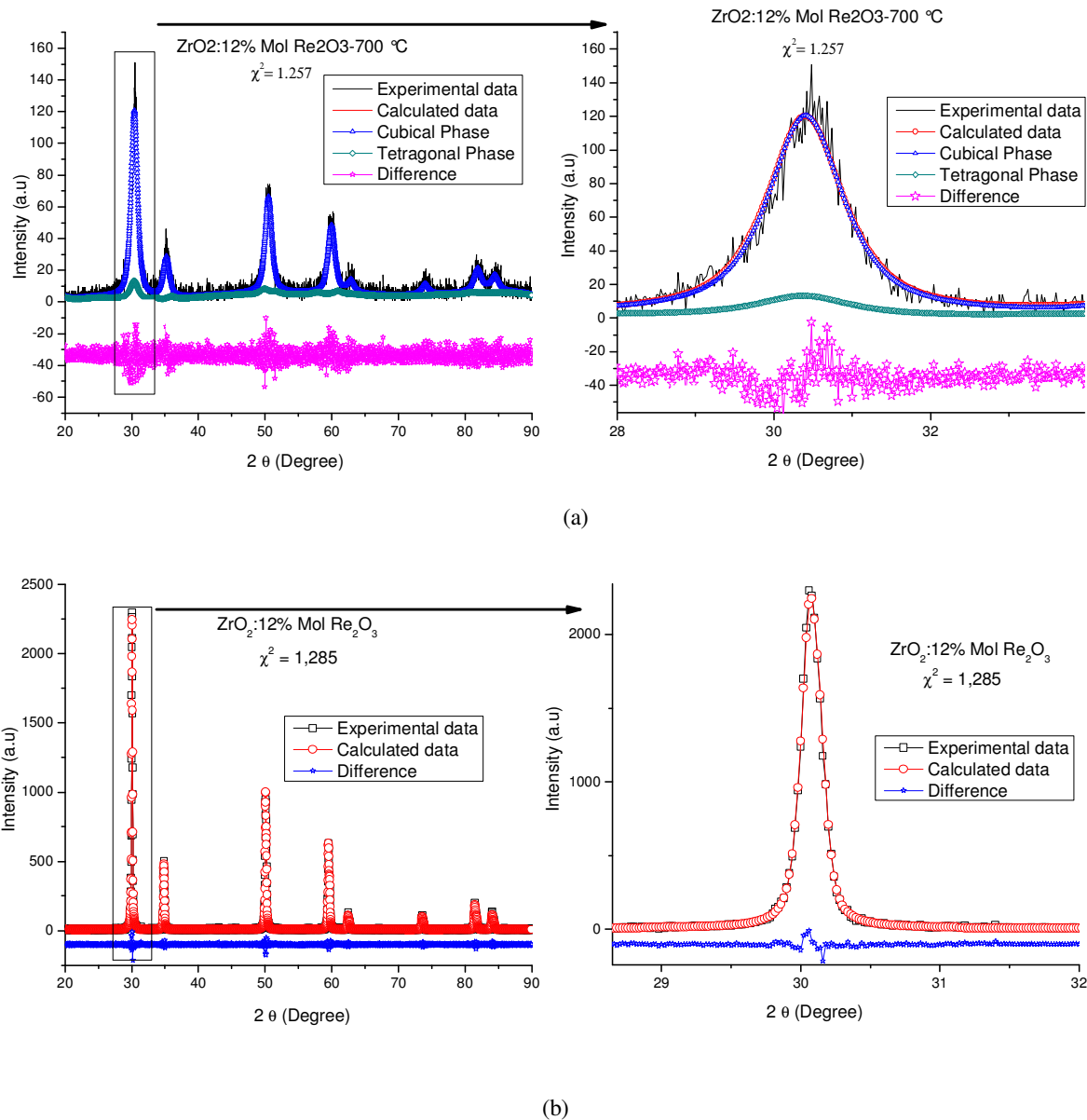


Figure 4. Rietveld refinement plot of a heat-treated samples at temperatures (a) 700 and (b) 1100 °C for two hours

After the molded samples were conformed and sintered, the density was measured by the Archimedes' method. The values obtained in three samples, 5.10, 5.09 e 5.10 g/cm<sup>3</sup>, are related to the theoretical density for cubic zirconia (5.96 g/cm<sup>3</sup> as reported by Pfoertsch and McCarthy in 1977) resulting in a low density with value of 85.6% if we compare this with the theoretical density. For the used pressure it was expected a higher density but these low values can be justified due to the presence of agglomerates hindering their sintering as found in previous studies (Muñoz *et al*, 2009).

The Figure 5 shows the impedance spectra for the samples, obtained at a temperature of 315 °C. In this figure, the numbers placed above the experimental points represent the logarithm of frequency. As expected, we observed three distinct semicircles corresponding to the responses of grain conduction (high frequency), grain boundary conduction (low frequency) and electrode processes. We can see that with an increase in temperature the resistances associated with each of the three processes decreased drastically.

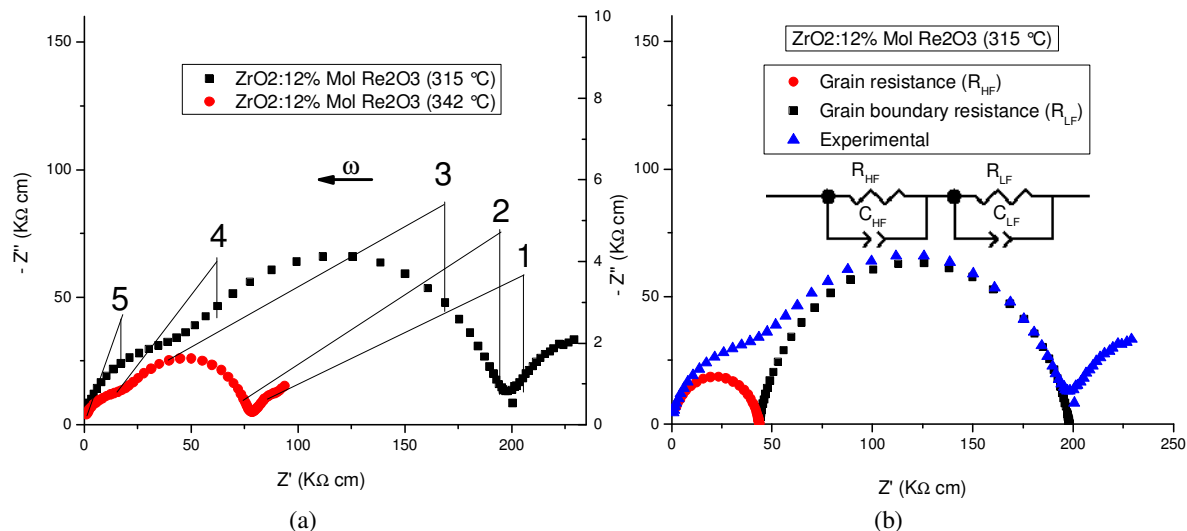


Figure 5. (a) Nyquist plots for the samples obtained at temperatures of 315 and 342 ° C (b) impedance spectra deconvolution

Another important information is the decentralization angle of the semicircles which make up the impedance spectrum. The decentralization angle of the semicircle of the grain obtained at 316 ° C was equal to 16° and the semicircle attributed to grain boundary was 11°. Multiple interpretations were proposed to explain the decentralization of the semicircles in the impedance diagrams of ionic conductors. One of the most accepted explanation is that which regards the decentralization of the semicircles as the result of chemical heterogeneities of the material (Kleitz, 1981). Another one says that we can attribute this phenomenon to the shape and distribution of electrodes in the material.

As it can be seen in Figure 5, the component of the grain boundaries is the most resistive. This may mean a high density of grain boundaries or the grain boundaries contain a considerable fraction of impurities able to block the charge carriers, facts that have to be clarified in further research. We observe also that at high frequencies we observe a partial overlap of the semicircles, therefore, the spectra was deconvoluted to minimize errors at the time of the construction of Arrhenius plots. As reported by Mucillo in 2009, the impedance spectroscopy diagram may be modeled by a resistor in parallel with a constant phase element ( $R_{HF} \parallel C_{HF}$ ), representing the grain response, in series with another resistor in parallel with a capacitor ( $R_{LF} \parallel C_{LF}$ ), representing the grain boundaries response, figure 5 (b).

The analysis of measurements in the temperature range studied (240 and 423 ° C) allowed to build the Arrhenius plots of conductivity of the grain, grain boundary and total conductivity, as seen in figure 6.

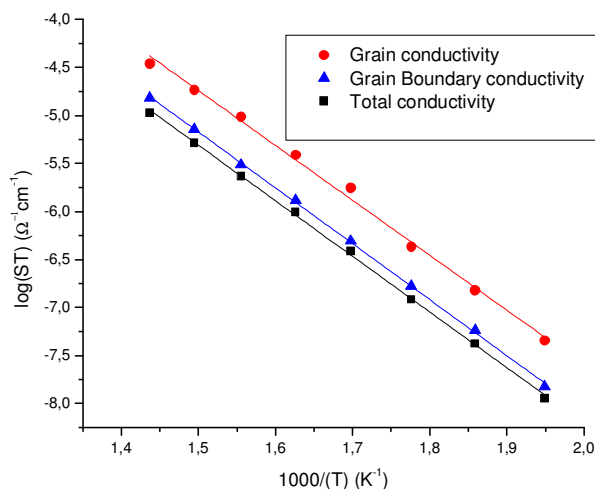


Figure 6. Arrhenius plot of overall electrical conductivity

The Arrhenius' graphic of Ionic conductivity vs. temperature plots is linear in the temperature range of measurement because it shows no changes in conduction mechanisms. We can use the slope of the Arrhenius' plot to find the activation energy  $E_a$  to the grain, grain boundary and total activation energy, according to the following equation:  $\rho = \rho_0 \text{Exp}(E_a/K.T)$ . These values are presented in Table 1. The Activation Energy, usually denoted by its symbol  $E_a$ , is defined as the minimum amount of energy required to initiate a particular process, therefore, if the activation energy is low, the greater the mobility of charge carriers. The values of activation energies obtained in this study are consistent with those normally observed for oxygen ion conductors in the literature (~ 1.2 eV) (Baptist, 2010).

Tabela 1. Valores de energia de ativação do grão, contorno de grão e total para eletrólitos sólidos sinterizados na temperatura 1400 °C/2h

Amostra	Energia de Ativação do grão (eV)	Energia de Ativação do contorno de grão (eV)	Energia de Ativação total (eV)
ZrO <sub>2</sub> :12 mol% CTR	1.13	1.15	1.15

#### 4. CONCLUSIONS

The best heat treatment for pre-calcined powder was 700 ° C for two hours, because the samples showed good crystallinity and a considerable reduction in the band associated with of the C-O vibration and vibration of the H-O-H band.

For the sample treated at 700° C, FTIR spectra, XRD data and Rietveld refinement showed coexistence of cubic zirconia with 88.2 wt% and tetragonal zirconia with 11.8% wt. For high temperatures (1100 ° C) analysis confirmed 100% of the cubic zirconia.

It is verified in the impedance diagrams that ionic conductivity values are dependent on test temperature, showing a decrease in resistivity while increasing this, confirming the fact that conductivity is a thermally activated process. The conductivity activation energy of the components of the grain, grain boundary and total are respectively, 1.13393, 1.15456 and 1.14874 eV, in agreement with literature values.

The main conclusion is that an experimental procedure was developed, via the polymeric precursor method (Pechini method), which allowed the production of ceramic solid electrolytes for potential applications in oxygen sensors. The system (ZrO<sub>2</sub>-Re<sub>2</sub>O<sub>3</sub>) showed stabilization of the cubic zirconia phase of the form Y<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>1.93</sub> (PDF 30-1468). Since the stabilizing additive used was a powder containing various rare earth oxides, the results presented are attractive to use this kind of powders and replace commonly used for such purposes, which are of high purity.

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