MICROSTRUCTURE AND HUMIDITY AIR SENSITIVITY CHARACTERIZATION OF ZrO_2 AND TiO_2 FOR APPLICATIONS AS HUMIDITY SENSOR

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Abstract: *Ceramics, as ZrO_2 and TiO_2, and its solid solutions, are widely studied for humidity sensors. In this work were investigated the microstructure of ZrO_2, TiO_2 porous ceramic with individual anatase and rutile phase contents, and ZrO_2-TiO_2 solid solutions, and their sensitivity to air humidity. The ceramic from ZrO_2-TiO_2 (1:1.5 mol %) powder mixture and pure ZrO_2 and TiO_2 were compacted and sintered. The microstructure and crystalline phases characterization were been carried out using SEM and X-ray diffraction, respectively. The ZrO_2, TiO_2, ZrO_2-TiO_2 ceramic characterizations as air humidity sensor element was accomplished through capacitance measurements using a RLC bridge in a climatic chamber at 25^o C. The results showed that all materials had good reponse to change in the air humidity, being anatase the most sensitive material.*

Keywords: *Humidity sensors, titania, zirconia, microstructure*

1. Introduction

The research about materials is growing to provide more efficient products among several areas of science and technology, including environmental science. This segment is becoming important e its technical support as equipments, knowledge, etc, is being better to follow all researches about it. The instruments used to measure the environmental parameters need constants improvements to increase precision, quality, and range of applications and to optimize the price of the final product.

The air humidity is presented in almost all ambient in global earth. Its importance can be seeing in meteorology stations, industrial process, white goods, agriculture, etc. Due these different applications, different instruments are made, varying size, shapes, costs, materials e others (Adrian, 2007).

Recent researches are showing utilization of ceramic materials for application as air humidity sensors cause by the mechanical, thermo and chemical stability of these materials (Niranjan et al., 2001). The conventional sinterizing processes of ceramics, through the pressure and heater of the powder, promove the presence of pores in microstructure. These pores have the fundamental hole for a good work of the humidity sensor, because the working mechanism of this instrument is due the adsorption of water molecules on the superficial area in the ceramic (Traversa et al., 1996). In this way, electrical properties, as impedance and capacitance, are changed because the presence of adsortpted and condensed water, and could be measure showing the influence of this properties with humidity (Cosentino et al., 2003).

The materials chosen for the application as sensors need to present a large superficial area and have electrical properties well-defined. There are a lot of works which use zirconium oxide and titanium oxide as the main sensor material (Cosentino et al., 2007). Titania has three crystalline phases: anatase, rutile and brokite, and the last is rarely used as humidity sensor. Anatase and rutile have similar behavior with change in its electrical properties due the air humidity, but there are researches, where anatase is favorite because its better adsorption capacity than rutile (Chen and Lu, 2005), (Biju and Jain, 2008). Zirconia is much utilized in gas sensor applications, including humidity. The main works with zirconia as sensors are involving solid solutions with other oxides, specially titania (Wang et al., 2008), (Zou and Lin, 2004).

This work has the function to compare the humidity sensors performance made with zirconia and titania, mainly, the effects of rutile and anatase, to identify the better configuration to the sensor. There are five different configurations: pure zirconia, pure titania anatase, pure titania rutile, zirconia and titania anatase (1:1,5 mol), and zirconia and titania rutile (1:1,5 mol); and this five types of material will be analyzed in this paper as sensors.

The powders were pressed and sinterized at different temperatures in accordance with the temperature of each material and its crystalline phase. In the sequence, the materials were submitted to scanning electron microscope, x-ray diffraction and the analysis in a climate chamber to verify the changes in the electrical properties with the air humidity and the final performance of each material as air humidity sensor.

2. Experimental details

The sensor materials were prepared with these commercials powders: nano-zirconic and the titanium oxide rutile and anatase were Kronos. For the pure ceramics, the commercial powders were pressed without a previous prepare. The ceramics with titania and zirconia, both rutile and anatase, were mixed in a ball mill with a alcoholic solution and, after, the solutions were dried in a rotary evaporation equipment. When the mixtures were dried, they were sieved to obtain better powder distribution to avoid an irregular microstructure, to get a better pressed final ceramic.

All powders were weighed to obtain a thickness of 3 mm and pressed at 80 MPa. The temperatures of sinterization for each material were: 1100^o C for pure zirconia, 1000^o C for pure titania rutile and zirconia-titania rutile and, 800^o C for pure titania anatase and zirconia-titania anatase.

After the sinterization, the materials were prepared for the electrical properties analysis setting a silver layer on the ceramic and electrodes to conduct and measure the electric sign desired.

The SEM and DRX analysis were made for the powders and the final ceramic; the results were used to compare the behaviors of the sensors at the climate chamber with their microstructure.

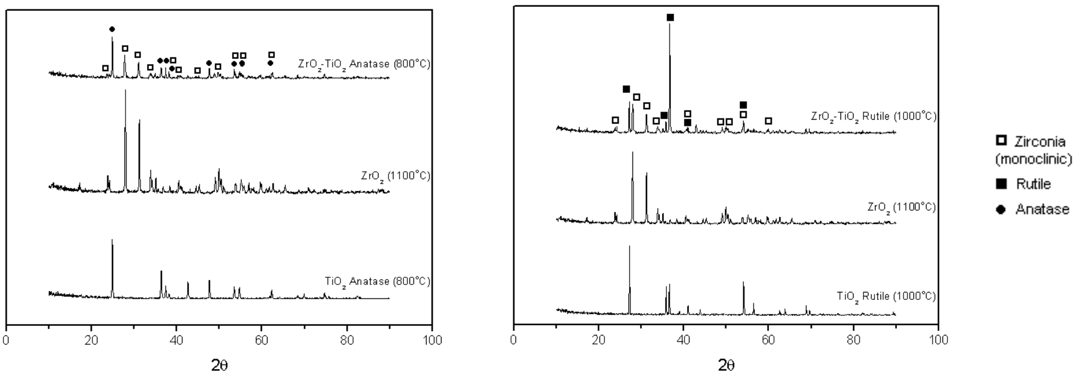
The analysis at the climate chamber for each sensor was made with a relative humidity varying since 35% till 95%, at 25^o C, that is specified an environmental temperature.

3. Results and discussions

The fig. 1 shows the x-ray diffraction pure ceramic and the final solid solution sinterized.

Figure 1.a shows the diffraction of TiO_2 and monoclinic ZrO_2 and compares it with a ZrO_2-TiO_2 solid solution with anatase phase present. All peaks are with their respectively phase indicated on the figure, except the peak around 44^o that doesn't belong to anatase phase in the pure TiO_2 anatase curve. A possible explanation is the start of change to rutile phase that in some literature begins at 800^o C [10]. And this peak isn't observed at the solid solutions in the same figure 1.a. So, these materials are representing the behavior of anatase phase pure and in solid solution with zirconia as an element sensor of humidity.

Figure 1.b compares the TiO_2 rutile phase with zirconia and the solid solution of these materials. The peaks in mixed material are coherent with the diffraction of pure ZrO_2 and TiO_2. These materials are analyzing the sensitivity to air humidity of TiO_2 rutile phase.



a b

Figure 1. X-ray diffractions of ceramics of TiO_2 anatase and rutile, and ZrO_2

Figure 2 shows a SEM micrograph of a typical fracture section of each material: the pure ceramics and the solid solutions ceramics. Figure 2.a and 2.d are TiO_2 and ZrO_2-TiO_2 with anatase phase sinterizes at 800^o C, respectively. The images 2.b and 2.e are TiO and ZrO_2-TiO_2 with rutile phase sinterized at 1000^o C, and figure 2.c is pure monoclinic zirconia sinterized at 1100^o C.

The rutile phase in picture 2.b shows greater grains and pores than the anatase phase showed in 2.a. probably this happened because of the higher sinterized temperature of the first one. Besides zirconia in 2.c was sinterized in the highest temperature, its micrograph shows the smallest grains and pores size. It could be because of the size of the powder that is nanometric. In the pictures 2.d and 2.e the influence of zirconia in the microstructure could be seen clearly, because of the diminished of the size of the grains and the pores, mainly in the case of pure titania rutile.

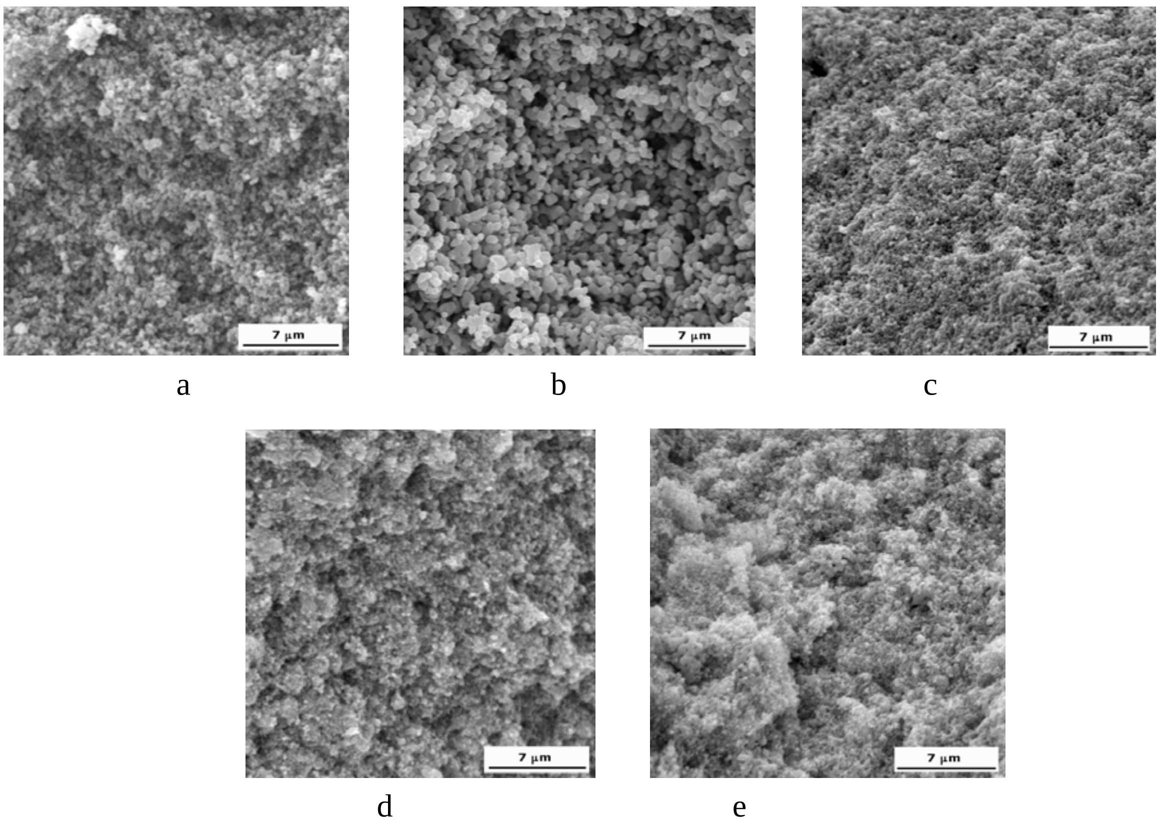


Figure 2. SEM micrograph 5000x: a) titania anatase, b) titania rutile, c) zirconia, d) zirconia:titania anatase, e) zirconia:titania rutile

The fig. 3 presents all curves of capacitance analysis of each material working as humidity sensor in the processes of increasing and decreasing the humidity values.

The figures are the capacitance curves per humidity relative of titania anatase (3.a), zirconia-titania anatase (3.b), zirconia (3.c), titania rutile (3.d) and zirconia-titania (3.e).

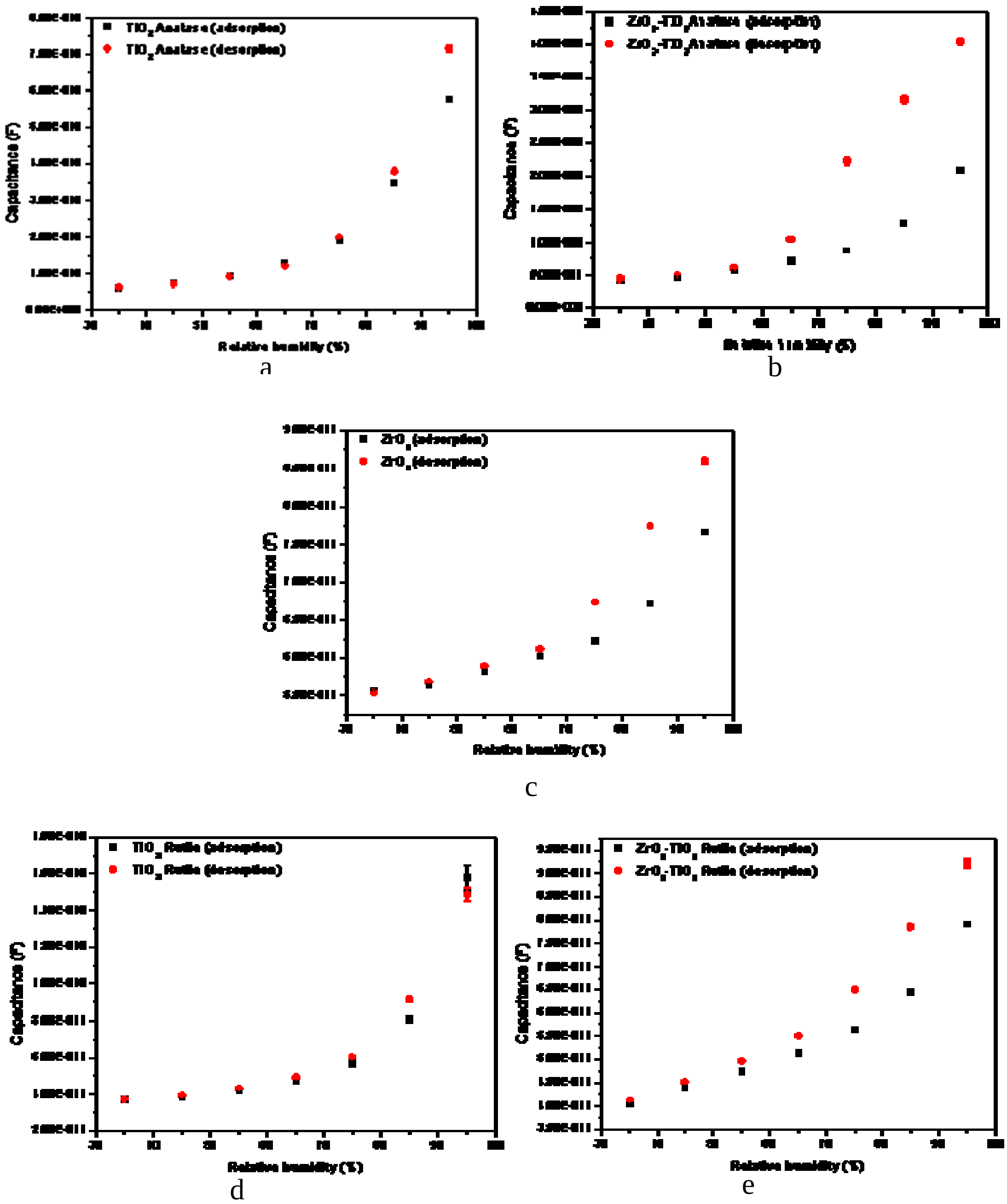


Figure 3. Capacitance curves at 25° C of a) TiO_2 Anatase, b) ZrO_2-TiO_2 Anatse, c) ZrO_2, d) TiO_2 Rutile and e) ZrO_2-TiO_2 Rutile

These curves show that all materials are sensible to the change in the air humidity. The sensitivity of the capacitive type humidity sensor can be expressed as Eq (1)

$$S = (C_u/C_l - 1) \text{ x } 100\% \qquad (1)$$

Subscripts *u* and *l* represent the values at the upper and lower limits of the operating range, respectively (Kim et al., 2009).

The table 1 shows the values of each material and their sensitivity with the average of adsorption and desorption process.

Table 1 – Values of humidity air sensitivity of all materials analysed

	TiO_2 Anatase	ZrO_2-TiO_2 Anatase	ZrO_2	TiO_2 Rutile	ZrO_2-TiO_2 Rutile
Lowest (F)	6.02E-11	4.34E-11	5.54E-11	4.09E-11	3.69E-11
Upper (F)	6.45E-10	3.06E-10	8.13E-11	8.56E-11	1.53E-10
Sensitivity (%)	972.1337	605.9556	46.6973	109.4554	315.72

The table 1 shows that titania anatase is the material with the highest sensitivity and pure zirconia is the the poorest sensitivity material. But, zirconia improvement the sensitivity property of titania rutile.

Inspite of the air humidity response, the process of adsorption had worst results in the ceramics with zirconia contents. These results could be happened due the nanometric scale of zirconia powder that influenced the same properties of the sensor during this process.

All materials present a similar linearity in low values of humidity untill around 70%, in high values the materials present a little bit of instability during the measurements what increased their errors.

4. Conclusion

This work shows that zirconia and titania, and their solid solutions are good materials to measure humidity sensor. The phase rutile and anatase are important in the comportment of the sensor and the anatase phase is the best sensitive material. Nano-zirconia didn't present a great improvement in the properties of the sensor, only with titania in rutile phase, but zirconia presents the most linear curve per relative humidity. And nanozirconia increased the time of desorption of water molecules in the sensor resulting a histerese curve.

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