THE ANALYSIS OF Nb_2O_5-DOPED ZrO_2-TiO_2 CERAMIC AS SOIL WATER CONTENT SENSOR ELEMENT IN CONTROLLED ENVIRONMENTS

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Abstract: *In this work, the behavior of ZrO_2-TiO_2 porous ceramics doped with controlled percentages of Nb_2O_5 for application as sensor elements of soil water content is presented. The goal of this research was to correlate the capacitance and impedance variation of the sensing elements, when immersed in soils previously selected, with the ceramic microstructure. The results obtained evidenced that the ZrO_2-TiO_2 porous ceramics presented potential to be applied as sensor elements for soil moisture.*

Keywords*: porous ceramics, sensor elements and soil moisture.*

1. Introduction

Despite ceramic materials are known since thousands of years ago, their study in depth, however, is quite recent. Advanced ceramics, for its turn, present applications in several areas, from structural materials to electric ceramics and semiconductors. In this sense, the rapid evolution of the present market of automation and environmental parameters control has motivated the members of the Engineering and Science Group of Micro and Nanostructure Ceramics and Solid Surfaces (SUCERA) of the Space Researches National Institute (INPE) to search for new materials and improve measurements and signal processing techniques (Kuranaga; Nono; Silva and Mineiro, 2004).

The researchers of SUCERA have been working since 1997, on the development of ceramic materials, specifically metallic oxides, for application as relative humidity sensor elements and, since 2001, on the monitoring of soil water contents (Kuranaga; Nono; Silva and Mineiro, 2004 and Oliveira; Nono; Kuranaga and Mineiro, 2004). In this way, the development of ceramic sensing elements for soil water contents, proposed in this work, was based on studies on relative humidity sensing elements performed by the SUCERA Group, owing , mainly, to the similarity of the adsorption/ desorption mechanisms in both sensing elements. The water molecules adsorption features on the ceramic surfaces are the great responsible for changing in the electrical properties, allowing for the uses of these materials as humidity sensor elements, at whatever operation principle (Fagan and Amarakoon, 1993 and Yang and Wu, 1991). The understanding of the water adsorption mechanism on the surface of these solids makes possible the improvement of modifications on their microstructure and the suitable choice of their chemical compositions. Among the materials analyzed for humidity monitoring, the choice lay on ceramics, mainly due to their unique microstructure, consisting of grains, grain boundaries, surfaces and pores that favor the water movement in their interior, since they have a controlled porous microstructure and a suitable chemical composition (Shimizu; Arai and Seiyama, 1985 and Gusmano, et al., 1991). In this work, in so far as, a ZrO_2-TiO_2 solid solution was used, doped with controlled percentages of Nb_2O_5, to promote the increasing of active sites on sensing surfaces, and, consequently, to generate higher reliability on the ceramic sensors responses in water molecules quantification for several kinds of soils (Bueno, et al., 1996).

It deals about a subject of great originality in world-wide terms, mainly concerning to the influence of the shape and of the size distribution of pores in the capacity of chemical and physical interaction of water molecules with the sensor material surface.

1.1 Water molecules adsorption mechanisms on ceramic faces

The humidity ceramic sensing elements, when exposed to humid environments, allow the water molecules to pass freely through their microstructure for capillary action and wetting of the pore surfaces, starting a water adsorption process in the metallic oxides, and, consequently, monitoring the humidity when related to electrical measurements. The oxygen atoms in the water are electrostatically attracted by the ceramic surfaces metallic atoms, due to the oxygen dipole moment (δ-) and the non balanced forces on the solid surfaces, which bring about these surfaces to behave as Lewis acid (δ+). The metallic atoms on the solid surfaces attract the partial negative charge of the oxygen atoms of the water while repel the partial positive charge of the hydrogen atoms in the water molecule. On account of this, it is supposed that the water molecules agglomerate themselves around the metallic toms, with the oxygen atoms steering inward and the hydrogen atoms steering outward this new surface (Kulwicki, 1991). Next, the water molecules are chemically adsorbed in available sites of the metallic oxide surface, preferentially on crystal grain boundaries, through covalent bonds between the oxygen of the water and the metal of the ceramic surface. In this case, the water molecules behave themselves as a base of Lewis, since they donate a pair of electrons to surfaces of metallic oxides, that, for their turn, behave themselves as a Lewis acid(as previously mentioned) receiving that pair of electrons (Atkins and Jones, 2006). In the moment that a covalent bond occurs between the metal and the oxygen, the O-H bond of the water molecule is broken, in order to recovery one electron, since in M-O bond formation, the oxygen gives one electron, thus acquiring a positive charge. Through this dissociative mechanism, two hydroxyl ions (OH⁻) are formed for each water molecule. In each water molecule, the hydroxyl group (-OH) is adsorbed on the metal present in the surface layer of the grains, which have a high local charge density in a strong electrostatic field and the proton is added to the oxygen atom of the surface of the nearby metallic oxides, to form a second group -OH. The chemically adsorbed layer, once formed, in not affected any more by the humidity exposure.

When the layer of chemisorbed hydroxyls is formed, the subsequent water molecules layers are chemisorbed by it, as well, through hydrogen bonds. The physisorbed water easily dissociates itself to form a hydroniun (H_3O^+) on account of the high electrostatic fields in the chemisorbed layer. The first physisorbed water molecules layer is characterized by the double hydrogen bond of a simple water molecule. The physisorbed monolayer easily changes to multilayer as the water amount adsorbed by the sensing element porous microstructure increases. The water molecules in the succeeding layers are just lonely bonded and present a liquid behavior. On account of this, the water molecules lonely bonded are able to form dipoles and re-orientate themselves freely, under an electrical field externally applied, resulting in the increase of the dielectric constant (Kulwicki, 1991).

2. Experimental Procedure

The ceramic specimens used as sensing elements were prepared from the mechanical mixture of commercial powder in the ratio of 1:1 of ZrO_2 and TiO_2 (in weight) and doped with 1, 5, 10, 15 and 20 % of Nb_2O_5. After the mixture preparation, the material was uniaxially compressed, to a pressure of 100 MPa in steel matrix, in the form of tablets, the dimensions of which being 2 mm of thickness and 10 mm of diameter. The tablets had been sintered in the temperature of 1100 ºC for approximately 2 hours in oven type chamber. A silver layer was deposited in the two sides of the ceramic tablet, serving as electrode to create the capacitive effect of the sensor. The characterizations of the ceramics were carried out using measurements of scanning electron microscopy (microscope - SEM, LEO 400) and X-ray diffraction (conventional diffractometer PHILIPS - 1840). The porous ceramic characterization as soil moisture sensor element was accomplished through capacitance and impedance measures using a RLC bridge (FLUKE-PM6304). The ceramic sensor was immersed in the selected soil, previously characterized as non-plastic soil, in which were added, in 9 steps of 24 hours each, fractions of the deionized water in

quantity of 3.45 g, that corresponds to 11.13 % of the total soil drying mass, until to reach the soil saturation point (liquidity limit). At every 24 hours the capacitance and the impedance values were measured. These measurements were carried out at 40 ^{o}C and 90 % relative humidity, in order to simulate actual climatic conditions underwent by the soil at countryside.

3. Results and Discussion

In this work, ZrO_2-TiO_2 ceramic tablets, doped with 1, 5, 10, 15 and 20 % of Nb_2O_5, sintered at 1100 ^{o}C, were characterized through x-ray diffraction and scanning electron microscopy techniques. As electrical characterization of these ceramic elements, capacitance measurements in function of growing water content in a sandy clay type soil, under climatic conditions of temperature and relative humidity, were performed.

The x-ray patterns in Fig. 1, show the presence of typical peaks of monoclinic phase ZrO_2, tetragonal phase TiO_2 and monoclinic phase Nb_2O_5. The characteristic peaks of Nb_2O_5 were getting more and more defined as its added percentages increased. At 20 % of Nb_2O_5, peaks presented higher intensity in comparison to peaks of sample with 1 % of Nb_2O_5. However, concerning to ZrO_2 and TiO_2 characteristic peaks, their intensity remained practically constant, in all samples.
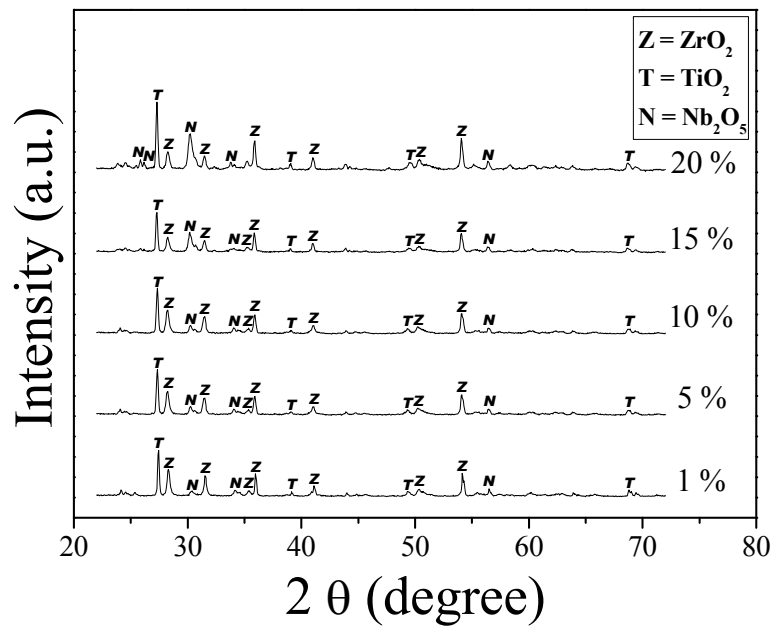
Figure 1. X-ray patterns of ZrO_2–TiO_2 ceramics tablets, doped with 1, 5, 10, 15 and 20 % of Nb_2O_5, sintered at 1100 ^{o}C.

In Fig. 2, it is observed the presence of pores in the microstructure of the ZrO_2-TiO_2 ceramic tablets, doped with controlled percentages of Nb_2O_5. The porous microstructure formed in the process is necessary, according to the consulted technical literature, to allow the water to pass freely and the condensation of its molecules in the capillarity of the pores between the grains surfaces.
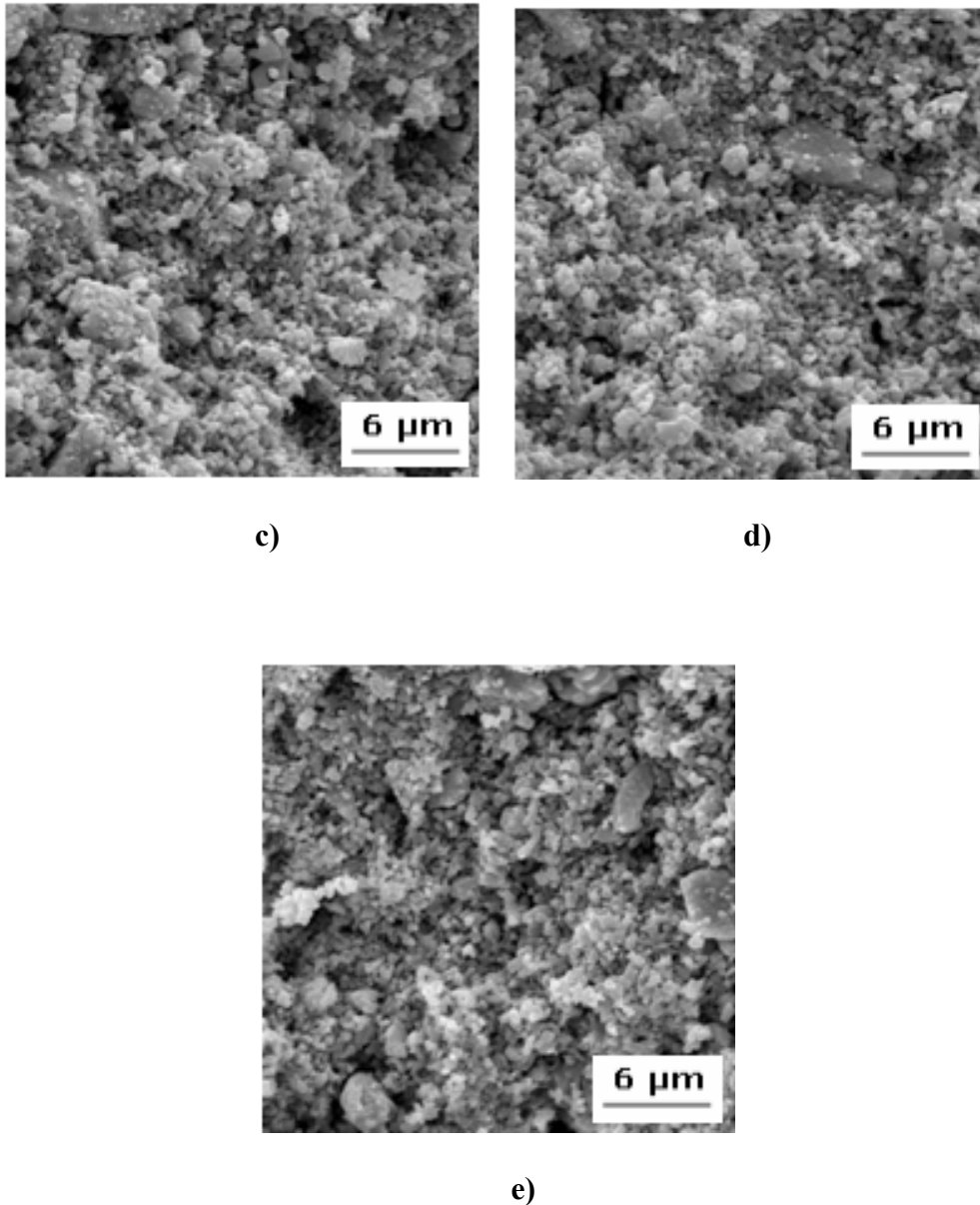

a)   b)

c)

d)

e)
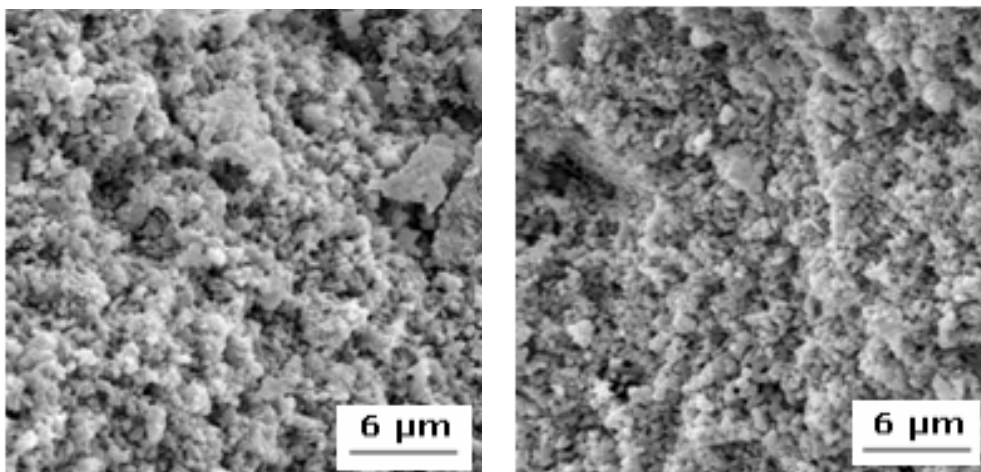
Figure 2. SE micrographs. Fracture surfaces of ZrO_2- TiO_2 sensors elements doped with: a) 1, b) 5, c) 10, d) 15 and e) 20 % of Nb_2O_5, sintered at 1100 ^{o}C.

The capacitance measurements, in function of increasing water content, obtained with ceramic sensor in a sample of sandy clay type soil, up to its saturation, indicate a near approach to linear behavior, in agreement with the consulted literature (Fig. 3). In this sense, one can observe, for instance, that the sensor element doped with 5 % of Nb_2O_5 presented a correlation coefficient equal to 0.95306 (Fig. 3b), near to 1, and, on the other hand, the sensor element doped with 10% of, presented a coefficient equal to 0.65775 (Fig. 3c). In so far as, the sensor element doped with 5 % of Nb_2O_5 presented the highest sensitivity to water, followed by the other sensor elements, namely,

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doped with 20 % of Nb_2O_5 (0.93988) (Fig. 3e), with 15 % of Nb_2O_5 (0.84341) (Fig. 3d), with 1 % of Nb_2O_5 (0.71611) (Fig. 3a) and at last, with 10 % of Nb_2O_5 (0.65775) (Fig. 3c). The climatic conditions of temperature (40 ^oC) and relative humidity (90 %), influenced the saturation of the sample of the sandy clay type soil, for, initially, 7 capacitance measurements were proposed up to the soil saturation, but, afterwards, it is noticed that 10 measurements were performed up to the soil saturation. Consequently, the ceramic sensor elements responded in a coherent way, even with the soil saturation delay owing to the simulated climatic conditions.
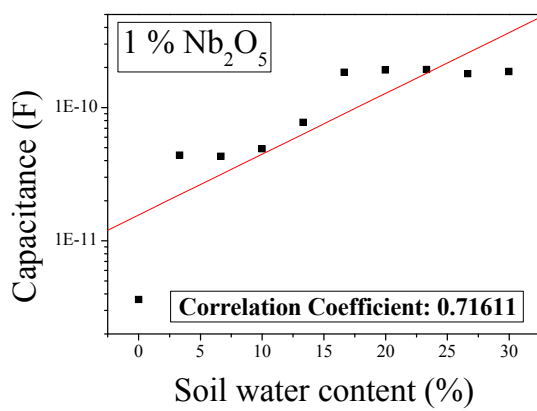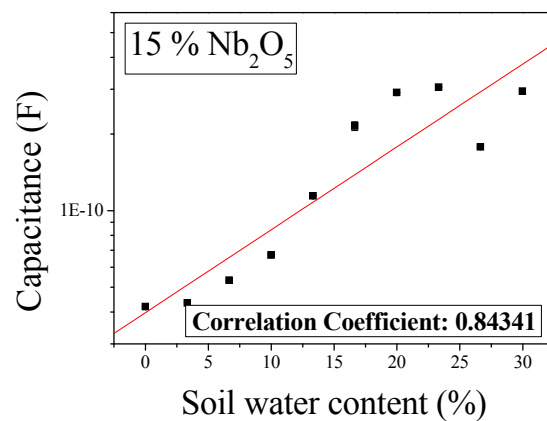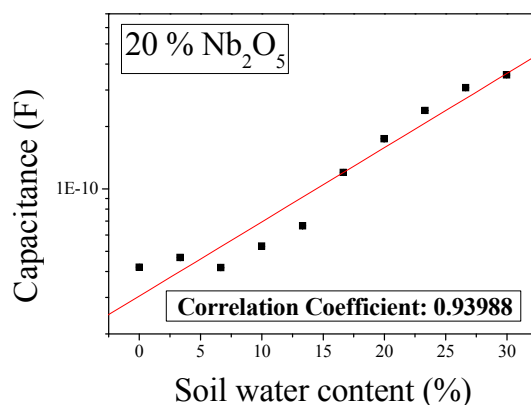
a)
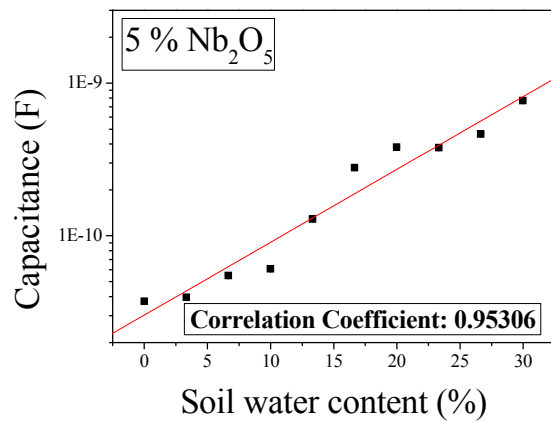
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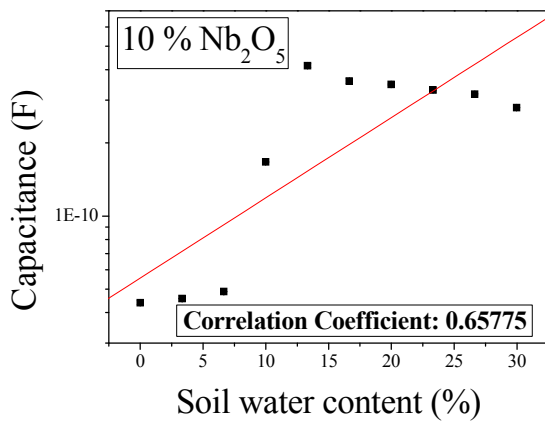
c)

d)

e)

Figure 3. Capacitance measurements of the ZrO_2- TiO_2 ceramic sensor elements doped with a) 1, b) 5, c) 10, d) 15 and e) 20 % of, sintered at 1100 ^{o}C, under climatic conditions of 40 ^{o}C and relative humidity 90 %.

4. Conclusion

According to the x-ray spectra, the ceramic sensing elements are composed by three distinct crystalline phases, namely, ZrO_2, TiO_2 and Nb_2O_5 forming a ZrO_2-TiO_2 solid solution, with controlled additions of Nb_2O_5. The ceramic processing used to fabricate the ceramic tablets made possible the formation of a porous microstructure more suitable to be applied as ceramic sensor, due to the agglomeration of particles and their subsequent coalescence. The ZrO_2- TiO_2 sensor element doped with 5 % of Nb_2O_5, presented the best response to water contents.

5. References

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