Humidity Sensitive Characteristics of ZnO_2-TiO_2-Ta_2O_5 Ceramic

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Abstract. The humidity sensing behavior of a ceramic oxide based on the ZnO_2-TiO_2-Ta_2O_5 system was analyzed. Samples were uniaxially pressed and sintered at temperature range from 1000 to 1200°C. Electrical impedance and capacitance measurements were realized in different values of relative humidity (from 11 to 100%). The microstructures of the sintered samples were characterized by X-ray diffractions and SEM observations. Mercury porosimetry analyses were carried out to determine the open porosity and the surface area was measured by using the BET nitrogen method. The obtained results were correlated and discussed.

Introduction

The development of humidity sensors has received much attention during the last years due to the necessity of controlling and monitoring environments in many different fields, like industrial processes and domestic comfort [1-3].
Since each application field requests distinct operating conditions and generally sensor elements work in narrow ranges of humidity and temperature, the selection of a material should be based in order to assure the satisfactory operation of the humidity sensor, that includes good sensitivity, linearity over the range of application, fast response, low hysteresis, and stability in the exhibition to impurities present in the environment [3-6].
As a consequence, a wide variety of materials have been researched with the objective to study their sensitivity, usually variations of electrical parameters in relation to the humidity in the atmosphere. These materials are based on polymers, electrolytes, and especially ceramics [1,3].
At present, ceramic materials possess a certain prominence due to their properties, which exhibit advantages regarding their mechanical resistance, and physical and chemical stability. The humidity-sensitivity properties of a ceramic are mostly influenced through the porous microstructure and the surface reactivity with moisture. Porous ceramic materials based on metals oxides have been largely used as humidity sensors [2]. The principle of humidity measurement with ceramic sensors is the change in electrical capacitance and conductance owing to water vapor chemisorption and physisorption, and/or capillary condensation in the pores of the ceramic sensor. In contact with the humidity, water molecules dissociate at the surface of the sensor materials because of the high electrostatic field on the hydronium (H_3O^+) and hydroxide (OH^-) ions. Charge transport happens when the hydronium ion releases a proton to a neighboring water molecule. The water molecule accepts the proton and releases another one. The electrical conduction in the physisorbed water layer is known as the Grotthuss chain reaction. Porous sintered ceramic, at high humidity, permit water condensation within the pore structure, and electrolytic conduction occurs in addition to protonic transport [3,7-9].
The aim of this work is to present the humidity-sensing performance of ZnO_2-TiO_2-Ta_2O_5 ceramic material. The results of the electrical measurements, impedance and capacitance, are shown as a

function of relative humidity in the range from 11 to 100%. The experiments were realized at room temperature.

Experimental

The ceramic material studied in this work was prepared by mixing a proportional molar ratio of starting powders (ZnO_2, TiO_2, and Ta_2O_5) in a ball mills using ethyl alcohol as a medium. After mixture, the product was dried and the resultant powder was then uniaxially compacted into pellets of 10 mm diameter and 2-3 mm thickness under a constant load of 60 MPa. The pellets were sintered in air at temperatures of 1000, 1100 and 1200^{o}C for 3 hours.
All samples were characterized by X-ray diffraction data on a Philips model PW 1830/80 diffractometer using Cu-Kα radiation. The microstructure of the sintered bodies was observed by scanning electron microscope (Jeol-JMS 5310). Mercury porosimetry (Quantachrome model Autoscan 33) analyses were made in the sintered bodies to determine the pore size distribution and the BET low temperature nitrogen adsorption method was used to calculate the specific surface area.
The humidity sensitive properties of the ZnO_2-TiO_2-Ta_2O_5 ceramic (capacitance and impedance) were investigated under a controlled-humidity environment using a RLC meter (Fluke model PM 6304) at frequency of 1 kHz. Different salt solutions were used to obtain different relative humidity atmospheres in a closed chamber. All experiments took place at room temperature. The sintered pellets were covered on the both sides (50 nm thickness) with palladium to form electrodes for electrical measurements.

Results and Discussion

The XRD patterns of the sintered bodies (Fig. 1) show a diminution in the number of the peaks with the increase of the sintering temperature. Analyses indicate the reaction of the three compositions, with the possible formation of the phase $ZnTa_2O_6$ in all of the studied temperatures.

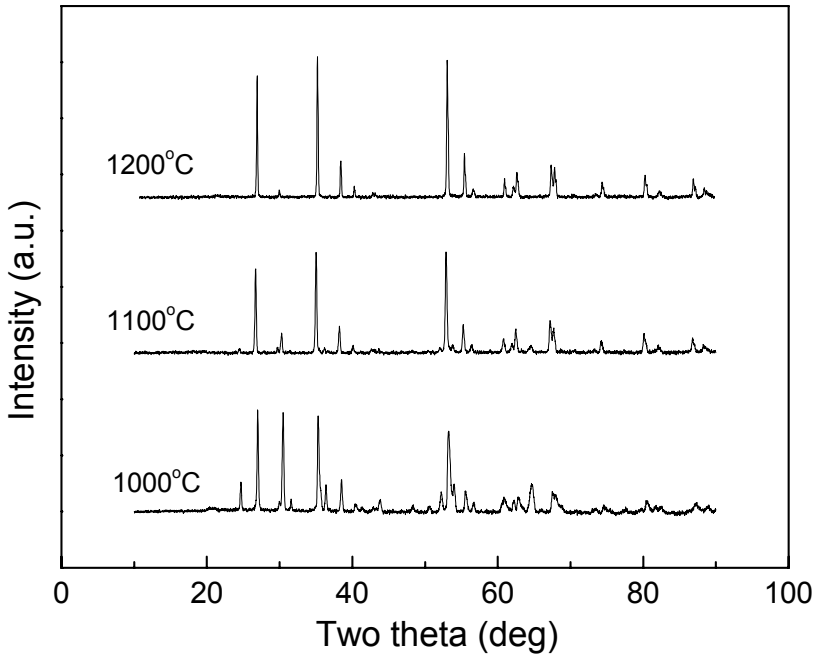

Figure 1 X-ray diffraction patterns of ZnO_2-TiO_2-Ta_2O_5 sintered ceramics.

Shown in figure 2 is the BET surface area according to the sintering temperature. The BET surface area calculated for the sample sintered at 1000°C is 0.78m^2/g. This value falls to 0.42m^2/g and 0.06m^2/g for the samples sintered at 1100 and 1200°C, respectively. The decrease of the specific surface area of the ceramics with an increase of the sintering temperature occurred because of the pore size reduction and the closure of the superficial pores. That is confirmed by the pore size distribution (Fig. 3). The ceramic sintered at 1200°C did not present pore volume of introduced mercury, while the sample sintered at 1100°C presented a distribution of macropores measuring between 0.5-1μm. The highest pore volume measured belongs to ceramic sintered at 1000°C, with a distribution of mesopores (0.01-0.03μm) and macropores (0.4-0.9μm).

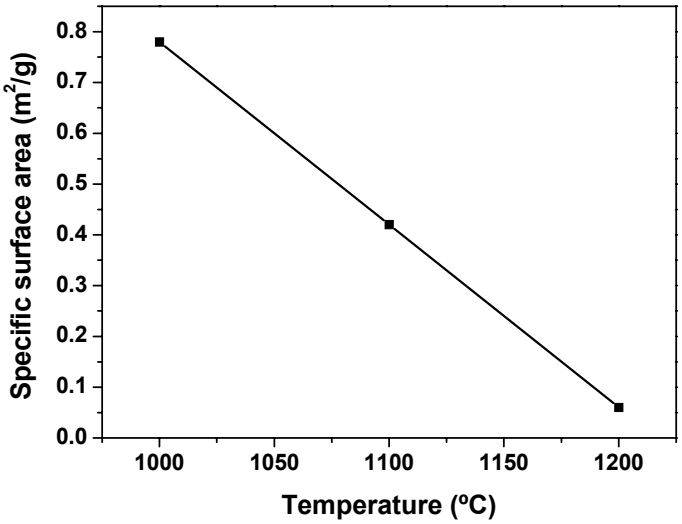

Figure 2 Specific surface area for the ZnO_2-TiO_2-Ta_2O_5 sintered ceramics measured by BET nitrogen adsorption.

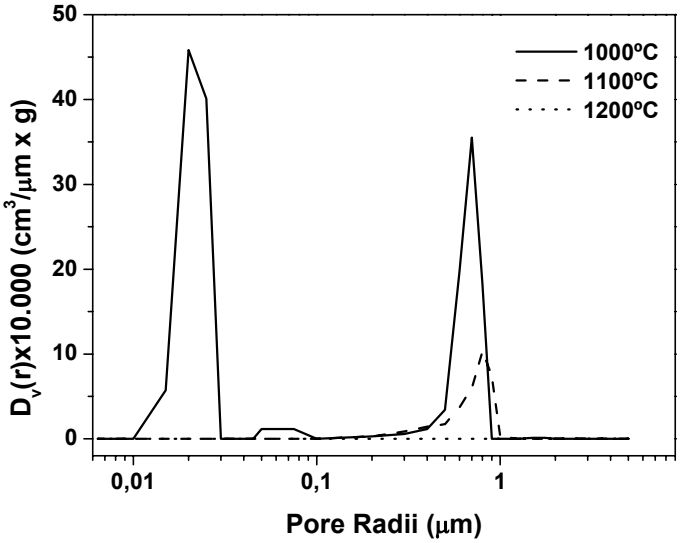

Figure 3 Pore size distribution curves of the sintered ceramics calculated from the mercury porosimetry data.

SEM photomicrographs obtained by secondary electrons are shown in Figure 4. At 1000°C occurred the grain growth and the formation of necks through the mechanisms of mass transport, joining the particles in contact (Fig. 4a). The presence of dense agglomerates can also be observed in the microstructure. At 1100°C took place the increase of grain size and the coalescence of the grains (Fig. 4b). The pore distribution is uniform over the entire sample, with pore sizes larger than 0.5 μm. The microstructure of the sample sintered at 1200°C became very dense, but presenting residual pores with sizes up to 2 μm between the grain boundaries and also inside the pore, indicating the final stage of sintering (Fig 4c).

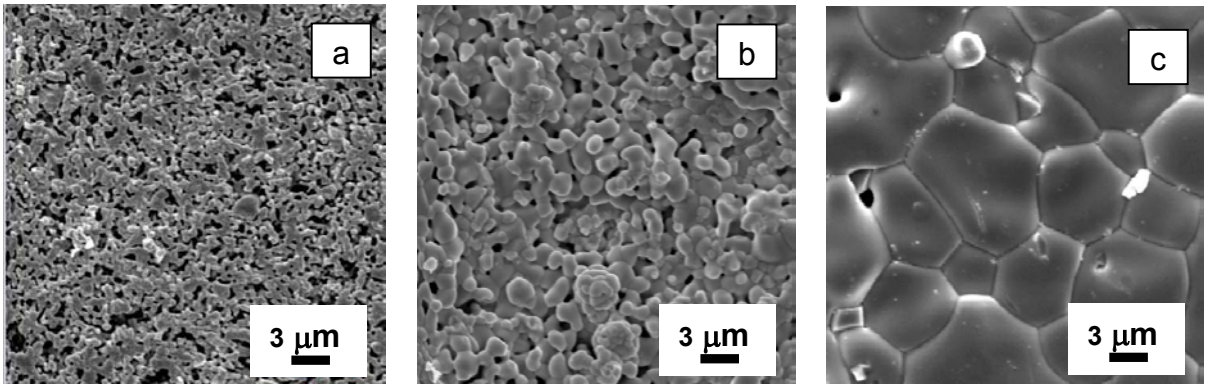

Figure 4 SEM micrographs of ZnO_2-TiO_2-Ta_2O_5 ceramics sintered at 1000°C (a), 1100°C (b) and 1200°C (c).

In Figure 5 are presented the dielectric measures (capacitance and impedance) of the ZnO_2-TiO_2-Ta_2O_5 ceramics. The ceramic sintered at 1000°C provided better results for impedance and capacitance variations for different relative humidity values. As can be seen on the capacitance graphic (Fig. 5a), the ceramic body is sensible to humidity, however, the pore size distribution as well as the specific superficial area are not still ideal, because the capacitance curve has no linearity in the relative humidity focused. In relative humidities below 40%, where the mechanism of humidity detection is featured through the physical and chemical absorption of water molecules on the pore surface, the inclination of the curve is little accentuated. This behavior indicates that the specific superficial area is relatively small in order that the conduction mechanisms are activated with larger efficiency. In relative humidities above 40% the inclination of the curve is more accentuated. In this region, the mechanism of humidity detection is characterized by the water condensation for capillarity in the pore volume. Impedance measurements, shown in Figure 5b, presented the same behavior describes to capacitance measures. The data obtained for the sample sintered at 1100°C certainly possesses some experimental errors, because both capacitance and impedance measures invert its behavior starting from 43% of relative humidity, being in disagreement with the expected results. Due to the main sensitivity mechanism of the ceramic for humidity variations to concentrate on open porosity, the microstructure observed of the sample sintered at 1200°C (Fig. 4c) explains the bad impedance and capacitance results that were obtained (absence of pores).

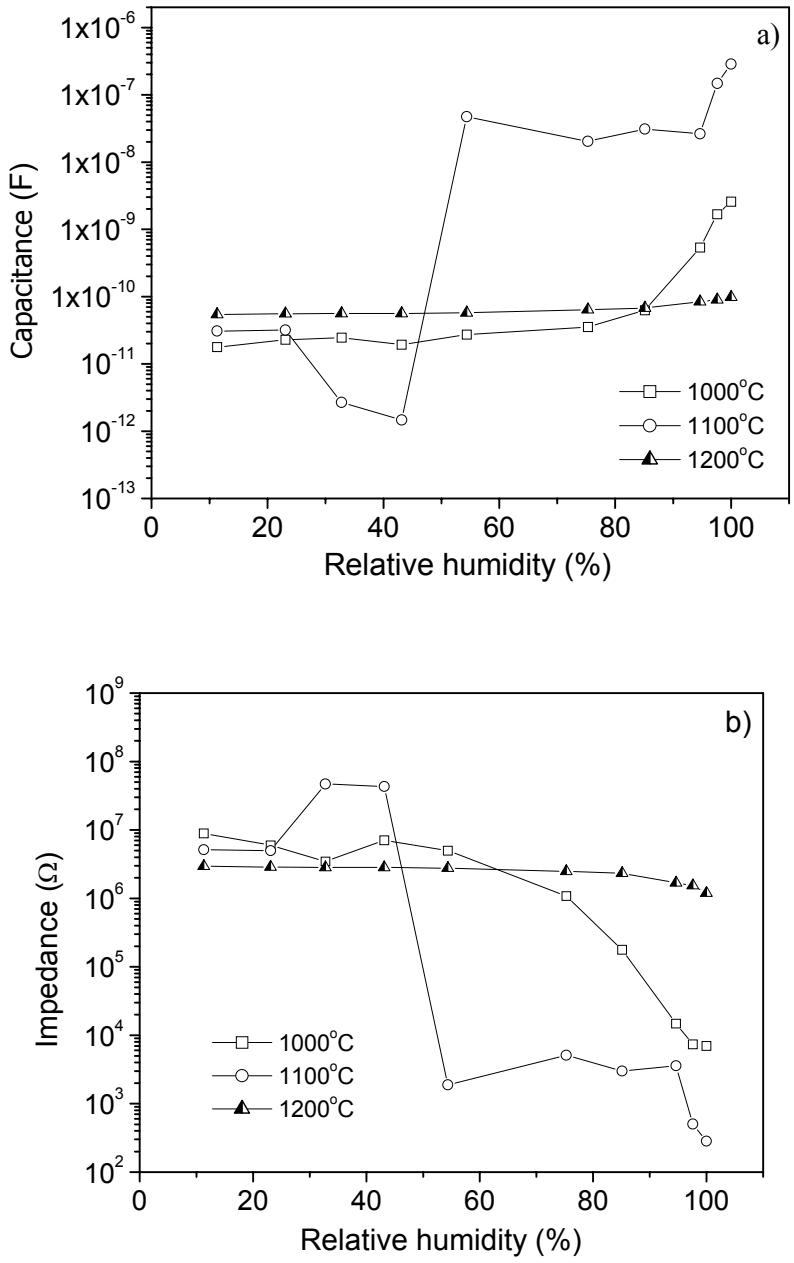

Figure 5 Dielectric properties according to change in relative humidity for ZnO_2-TiO_2-Ta_2O_5 ceramic: a) impedance and b) capacitance measures.

Conclusion

It was observed an increase in the densification of the ceramic, resulting in the closure of the pores, with the increase in the sintering temperature. Considering that the open porosity and pore size distribution have a great influence on the sensitivity of ceramic, the microstructures observed of the samples sintered at 1100 and 1200°C indicate that they are not appropriate for use as humidity sensor. The ceramic sintered at 1000°C resulted in more favorable microstructures for use as humidity sensor, due to its high porosity in the desired range to enhance sensitivity. Despite the sample sintered at 1100°C to present a uniform pore distribution, the pores should have minor sizes to maximize the sensibility to humidity. The ideal pore size distribution includes nanopores, mesopores and micropores. Attempts for the improvement in the sensitivity properties of this ZnO2-

TiO_2-Ta_2O_5 ceramic material for humidity measurements are necessary, including lower sintering temperatures and changes in the starting powders composition.

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