

Development of zirconia-titania porous ceramics for humidity sensors

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Received 23 April 2003; received in revised form 15 July 2003; accepted 28 July 2003

Abstract

Porous ZrTiO₄ ceramic specimens were prepared by pressing and sintering at different temperatures (1150–1500 °C range) powders synthesized by the polymeric precursor technique. X-ray diffraction analysis shows that all specimens are orthorhombic single-phase ZrTiO₄. Average pore diameter had approximately 73% reduction for increasing the sintering temperature from 1150 to 1500 °C. Scanning electron micrographs of polished and thermally etched surfaces show also intergranular porosity reduction at the expenses of the increase of average grain size. Impedance spectroscopy measurements in specimens under controlled humidity conditions gave evidences of the ability of the porous ZrTiO₄ specimens to be used as humidity sensors.

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Keywords: Zirconia-titania; Porous ceramics; Humidity sensors; Impedance spectroscopy

1. Introduction

Porous ceramics find nowadays a large variety of applications in several devices like filters, acoustic absorbers, catalytic components, selective membranes, humidity sensors, among others [1].

There are two main kinds of porous ceramics: reticulate ceramics and foam ceramics. The former consists of interconnected voids surrounded by a web of ceramic; the latter has closed voids within a continuous ceramic matrix [2].

Various chemical routes, besides the conventional solid state reaction route, have been developed for obtaining porous ceramics without the use of additives to avoid unwanted impurities in the final ceramic piece. An attractive alternative route, due to its simplicity and low cost, is the polymeric precursor technique based on the Pechini's patent [3], that results in sinteractive homogeneous powders. Solid state sintering usually results in polycrystalline bodies with pores in the 100–1000 nm range [1]. Graphite has also been used successfully for increasing pore volume in ceramics [1]. In conventional ceramic sintering, by heating pressed powders, a porous network is usually formed in the spaces between the particles necks, porous stability being achieved by controlling the size of the particles [4]. An easy way

of controlling pore sizes during solid state sintering is to control particle sizes of the mixing powders as well as the sintering temperature and time [5]. A previous dilatometric analysis enables one to choose the suitable sintering temperature and time.

In this paper, we are interested in developing porous ceramics to be used in room temperature humidity sensors. Humidity sensors may use properties of polymeric and ceramic materials [6]. The latter has the following advantages over the former: higher chemical and thermal stability and faster response times [7]. The electrical impedance and capacitance of some porous ceramics are found to depend on the humidity. Ionic conductors are used for low temperature detection of humidity while for high temperatures electronic conductors are used [8]. The main mechanisms for humidity detection are either the physical adsorption of water molecules at the surfaces or water condensation in mesopores of the porous ceramics, leading to a decrease in the electrical impedance [9].

Humidity sensors operating at room temperatures take advantage of the H⁺ (protonic) conduction at the surface of the sensing material. At low humidity, water molecules are chemisorbed at preferential sites at these surfaces. Upon continuous exposure to humidity, additional water molecules are physically adsorbed and dissociate due to the high electrostatic fields in the chemisorbed layer. The dissociation reaction $2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ liberates protons released by H₃O⁺ to a neighboring water molecule starting a chain reaction (known as Grotthus chain reaction) for the provision

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of protons, which are the charge carriers responsible for the enhancement of the electrical conductivity of the sensor material [6,10,11].

In this paper, the preparation of $ZrTiO_4$ porous ceramic pellets using reactive powders prepared by the polymeric precursor technique is described [3]. Zirconium titanate has already been reported as a material widely used in electrical and optical devices such as capacitors, piezoelectric sensors, ultrasonic motors, microwave ceramic dielectric resonators [12–16], and good catalytic and electrolytic material [17]. The pellets were characterized by mercury porosimetry and by electrochemical impedance spectroscopy. The dependence of the electrical response of these pellets on the relative humidity was studied. The results show that they can be proposed as materials for humidity sensing devices.

2. Experimental

$(ZrO_2)_{0.05}(TiO_2)_{0.05}$ ceramic powders were prepared by the citrate technique [3] using zirconium oxychloride, which was obtained by adding hydrochloric acid to zirconium oxide produced at this Institute, titanium chloride, 99.5% citric acid, and ethylene glycol. The powder preparation consists essentially on the following: zirconium oxychloride and titanium chloride are mixed on the desired stoichiometry and kept at 60 °C; afterwards citric acid is added. Ethylene glycol is then added and the temperature of the solution is raised to 110 °C for the formation of the resin. The calcination of the resin is performed in two steps: first at 250 °C during 1 h, resulting in a brownish glassy powder; second at 730 °C during 1 h, with a 2°/min rate, resulting a fine white ceramic powder.

Simultaneous thermogravimetry and differential thermal analyses were carried out in the glassy powder in the room temperature–1000 °C range, at a 10°/min rate under flowing synthetic air using a model 409/C/E Netzsch Simultaneous Thermal Analyzer.

X-ray diffraction (Cu $K\alpha$ radiation) analysis was performed in the final white powder in the 25–65° 2θ range with a Bruker-AXS D8 Advance X-ray diffractometer.

The powders were uniaxially pressed (147 MPa) to 7 mm diameter disks for dilatometric analysis in air at 10°/min up to 1500 °C/2 h (Netzsch DIL 402/E/7 dilatometer) and sintering. The specimens were sintered at 1150, 1300, and 1500 °C with 10°/min heating and cooling rates without any dwelling time. As soon as the samples reached the programmed temperature, cooling started at the same rate used for heating. The idea was to produce specimens with different degrees of porosity and approximately the same average grain size.

The porosity morphology of the specimens was studied by the mercury porosimetry technique (Micromeritics Autopore III), which consists basically in exposing the specimen to an environment of high pressure of mercury up to 414 MPa for the determination of pore distribution in the 360–0.003 μm (30 Å) range.

Scanning electron microscopy (LEO 440I Scanning Electron Microscope) experiments were performed for determination of average grain size and observation of porosity in ceramic specimens sintered at different temperatures. Specimens for SEM analysis were vacuum impregnated with a polymeric resin, polished with SiC powder followed by 15, 6, 3, and 1 μm diamond pastes. Thermal etching was performed at temperatures 100 °C below the temperature the specimen was sintered. For SEM observation, the specimens had gold deposited by sputtering under argon (SCD 040, Balzers).

The electrical characterization was carried out at room temperature by impedance spectroscopy measurements with a Hewlett-Packard 4192A Impedance Analyzer connected to a series 900 model 362 HP controller. A special software was used to collect, store, and analyze the (Z'' , Z') data [18]. The analysis of a (Z'' , Z') diagram consists in the deconvolution, in the frequency domain, of the impedance responses due to different contributions as a function of frequency, which are usually composed of overlapping semicircles. Silver electrodes were prepared by painting with colloidal silver and curing at 400 °C for 15 min for removal of the organic binder. A special sample chamber was designed and built in with a glass chamber, a Teflon® cover lid and stainless steel electrodes and terminal leads. The humidity of the specimens inside the sample chamber was controlled by setting saturated solutions of KCl and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ salts. At room temperature (~20 °C), the sample chamber with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and KCl saturated solution has 32 and 85% relative humidity, respectively [19,20]. Impedance spectroscopy measurements were carried out with the sample chamber without the covering lid (~60% relative humidity), and with the chamber closed containing either KCl or $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

3. Results and discussion

Fig. 1 shows results of simultaneous thermogravimetric and differential thermal analyses performed in powders calcined at 250 °C. Mass loss, 76% of the resin initial mass, occurs up to 600 °C due to elimination of water and organic

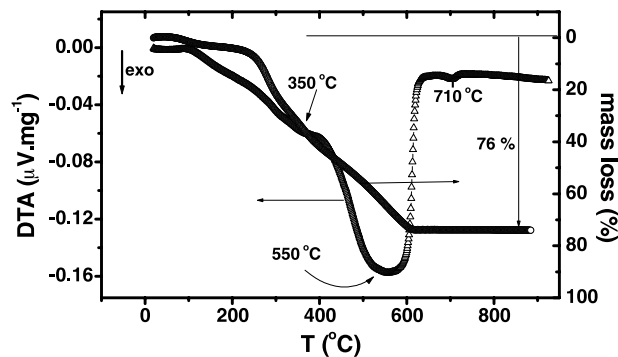


Fig. 1. Thermogravimetric and thermal differential curves of the polymeric resin obtained by the citrate technique and calcined at 250 °C/1 h.

substances. DTA peaks at 350 and 550 °C are related to removal of organic compounds. An exothermic reaction without mass loss occurs at approximately 710 °C due to the crystallization of the ZrTiO₄ phase. Most of the zirconium titanate powders prepared by chemical routes crystallize at approximately 700 °C [21].

The thermal analyses allowed for choosing 730 °C as the calcination temperature for the powders; at that temperature, all organic materials have been already removed and the powder is in the crystallized form. Powders calcined at 730 °C/1 h have been analyzed by several techniques: the sedimentation technique for the determination of the distribution of average particle (or agglomerates of particles) size, the BET gas adsorption for the evaluation of the surface area, scanning electron microscopy for particle morphology and average size, and X-ray diffraction for phase content.

3.1. Powder analysis

Analysis by the sedimentation technique showed a monomodal distribution with an average particle size of about 3.5 μm.

The surface areas of ZrO₂:TiO₂ powders prepared by the citrate technique, determined by the BET method, is shown in Table 1. The corresponding equivalent spherical diameter D (μm) was determined using equation $D = 6/(\rho S)$; ρ (g/cm³) is the density and S (m²/g) is the surface area of the powder.

The large difference between mean particle diameters determined by the two techniques means that a good dispersion has not been accomplished for the sedimentation of the powders, D_{sed} representing actually an average size of particle agglomerates.

The results of the X-ray diffraction of the powders calcined at 600 and 730 °C are shown in Fig. 2a and b, respectively.

The results of Fig. 2b are in good agreement with the thermal analyses results: calcination at 730 °C/1 h leads to crystallization of the ZrTiO₄ orthorhombic phase. That temperature is actually well below the temperature required for obtaining zirconium titanate by solid-state synthesis (1200–1400 °C) [22]. Fig. 2a shows the X-ray diffraction patterns of the powder calcined at 600 °C, meaning that even after removal of the organic material, the powder remains in the amorphous state.

Large agglomerates in the micrometer range are seen with a 7500× magnification (Fig. 3a), in agreement with the agglomerate size determination by the sedimentation technique

Table 1

Values of average equivalent spherical diameter determined by the sedimentation technique (D_{sed}) and by gas adsorption analysis (D_{BET}), and of specific surface area (S) by the BET method

D_{sed} (μm)	D_{BET} (μm)	S (m ² /g)
3.5 μm	0.023	56.9

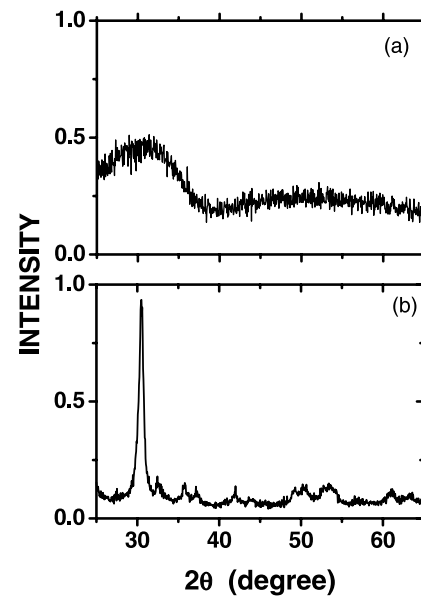


Fig. 2. X-ray diffraction patterns of the powders prepared by the citrate technique after calcination at 600 °C/1 h (a) and 730 °C/1 h (b).

described above. Micrographs with 100,000× magnification (Fig. 3b) show that these agglomerates are indeed composed of nanosized particles (smaller than 100 nm), in agreement with the average particle diameter determined by gas adsorption analyses (see above).

The powders after calcination were pressed to pellets by uniaxial pressing (220 MPa) for dilatometric analysis. The results are shown in Fig. 4.

Fig. 4 shows results on the time dependence of the linear retraction and the linear retraction rates of zirconium titanate specimens heated at constant rate. The temperature of 1230 °C corresponds to an order–disorder transition in the orthorhombic structure, with a volume reduction due to a decrease in the b value, known to occur in the 1100–1200 °C range [23]; at 1500 °C, on the other hand, a maximum of the linear retraction occurs. These results suggest that three sintering temperatures, namely, 1150, 1300, and 1500 °C, could be chosen for preparing porous ceramics with different porosity content.

3.2. Analysis of the sintered porous ceramics

Fig. 5 shows scanning electron micrographs of polished surfaces of ZrTiO₄ ceramics sintered at different temperatures.

The increase in the sintering temperature produced more dense ceramics, with enhanced grain growth and large pores. Ceramics sintered at 1150 °C have grain sizes of approximately 100 nm, the average grain size reaching approximately 5 μm for ceramics sintered at 1500 °C.

The sintered ceramics had their pore volume and distribution analyzed by mercury porosimetry. Fig. 6 is a plot of the incremental intrusion as a function of pore diameter of

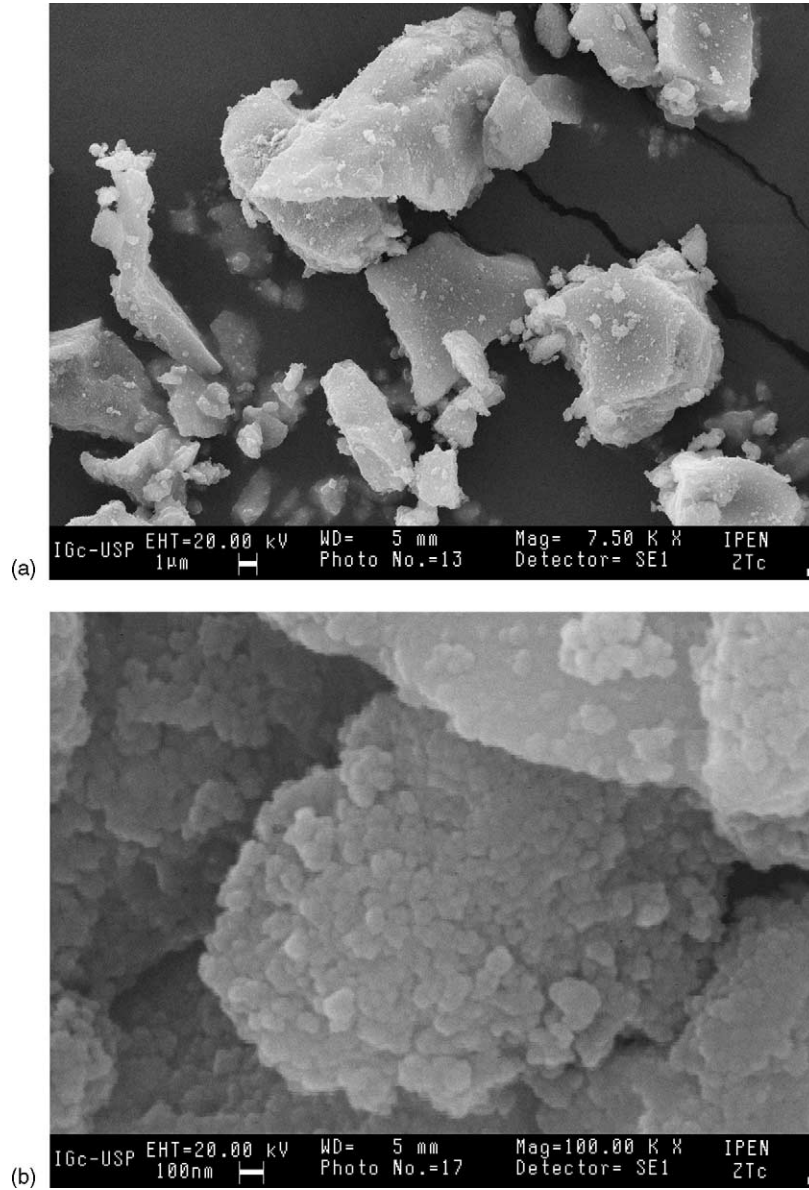


Fig. 3. Scanning electron micrographs with 7500× (a) and 100,000× (b) magnifications of the zirconia-titania powder calcined at 730 °C/1h.

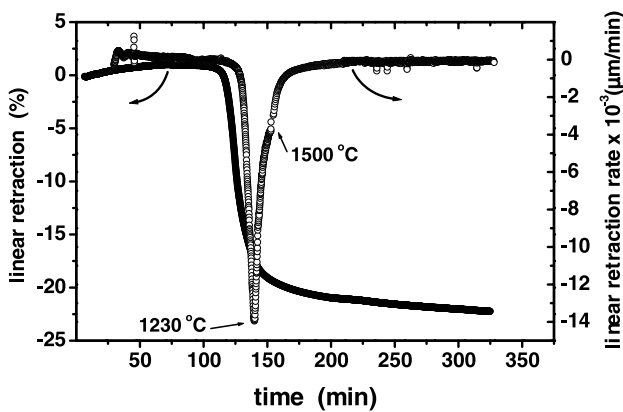


Fig. 4. Linear retraction (%) and linear retraction rate ($\mu\text{m}/\text{min}$) as a function of time (min) of ZrTiO_4 pressed powders.

ZrTiO_4 ceramics sintered at 1150, 1300, and 1500 °C, showing the pore distribution in these ceramics. The increase in sintering temperature leads to elimination of small pores and reduction of the volume of the large pores, resulting in an increase of the average pore size and reduction of the total volume of pores. These results agree with the observations on the SEM micrographs.

Table 2 shows values of the relative apparent densities of zirconium titanate ceramics sintered at different temperatures determined by the Archimedes method and by mercury porosimetry.

All relative densities determined by mercury porosimetry are smaller than the ones determined by the Archimedes method. This occurs because the high pressure for the intrusion of mercury (60,000 psi) allows for the detection of small pores not detectable by the hydrostatic Archimedes method.

Table 2

Values of apparent densities of ZrTiO₄ ceramics, sintered at 1150, 1300, and 1500 °C, determined by the Archimedes method and by mercury porosimetry

Sintering temperature (°C)	Apparent density—Archimedes (%TD)	Apparent density—Hg porosimetry (%TD)
1150	41.8	37.7
1300	65.7	58.8
1500	84.8	76.9

Fig. 7 shows impedance spectroscopy results on ceramic specimens under different humidity conditions. Two specimens were used for these measurements: one with 19% porosity and other with 62% porosity.

Only one semicircle is shown in the impedance diagrams of the 19% (Fig. 7a and the inset for the measurement under 85% relative humidity) and 62% (Fig. 7b and the inset for the measurement under 85% relative humidity) porosity ZrTiO₄ specimens. The total electrical resistivity is taken at the intercept of the semicircle with the real axis at the low frequency limit. The higher is the humidity inside the sample chamber, the lower is the total resistivity of both specimens. The electrical resistivity of both 19 and 62% porosity specimens has a two orders of magnitude decrease for increasing the relative humidity from 32 to 85%. The zirconia-titanate ceramic sintered at 1500 °C (19% porosity) has higher electrical resistivity than the ceramic sintered at 1150 °C (62% porosity) for measurements at all studied humidity

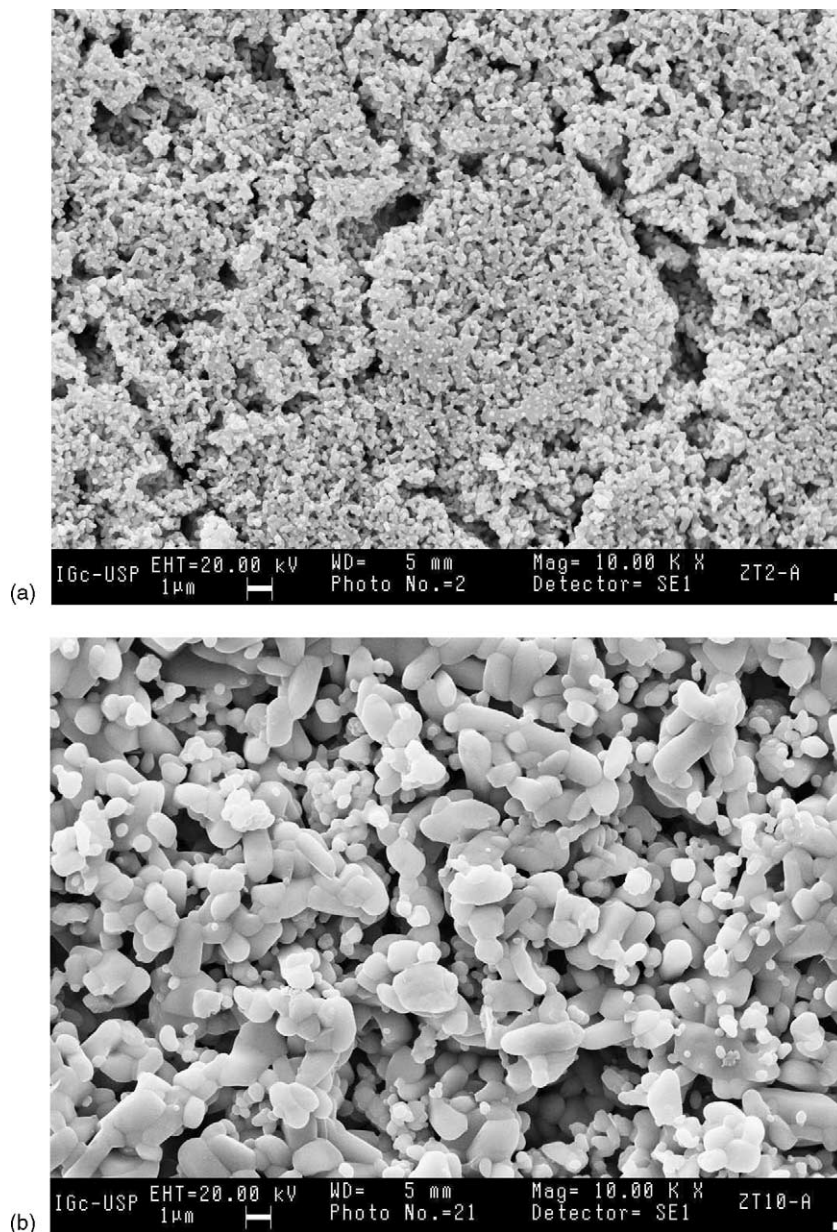


Fig. 5. Scanning electron micrographs of polished surfaces of ZrTiO₄ ceramics sintered at 1150 °C (a), 1300 °C (b), and 1500 °C (c).

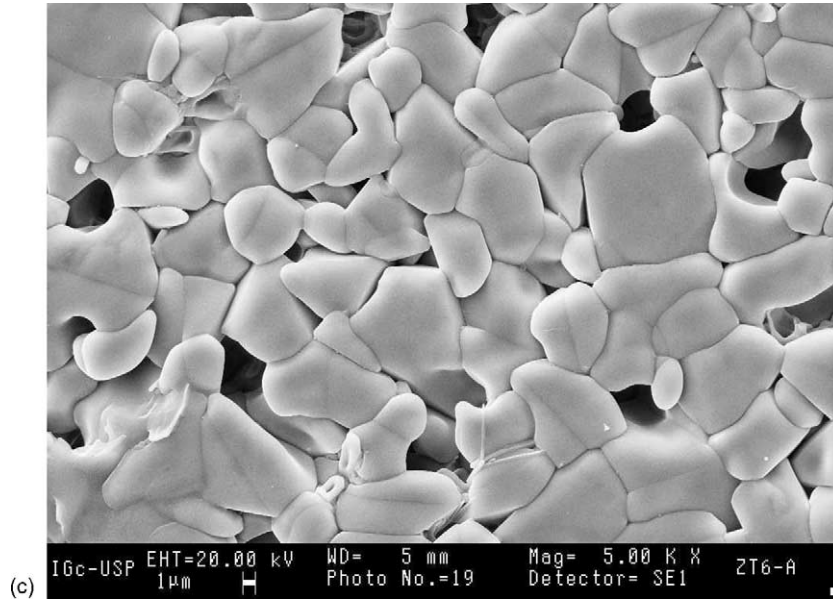


Fig. 5. Scanning electron micrographs of polished surfaces of ZrTiO₄ ceramics sintered at 1150 °C (a), 1300 °C (b), and 1500 °C (c).

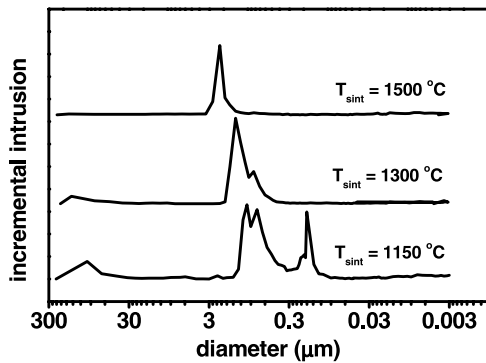


Fig. 6. Pore distribution in ZrTiO₄ ceramics sintered at different temperatures.

conditions. The specimen with higher pore volume is expected to adsorb more water molecules at its surface, enhancing then its electrical conductivity. Even though further detailed experiments are necessary to evaluate the speed, the

selectivity and the stability of ZrTiO₄ ceramic specimens to humidity, these results show that both specimens are candidates for humidity sensors due to their sensitivity.

4. Conclusions

A chemical route based on the citrate technique has been developed for the preparation of ZrTiO₄ polycrystalline ceramic powders with average particle size in the nanometric range. The crystallization temperature of the ZrTiO₄ powders, required for keeping its humidity sensing property, has been determined as 730 °C, well below the crystallization temperature of ZrTiO₄ prepared by the conventional solid-state synthesis route.

ZrTiO₄ sintered pellets with different pore densities, suitable for ceramic humidity sensing devices, have been obtained by suitable choice of the sintering conditions. The impedance spectroscopy results show that the higher is the

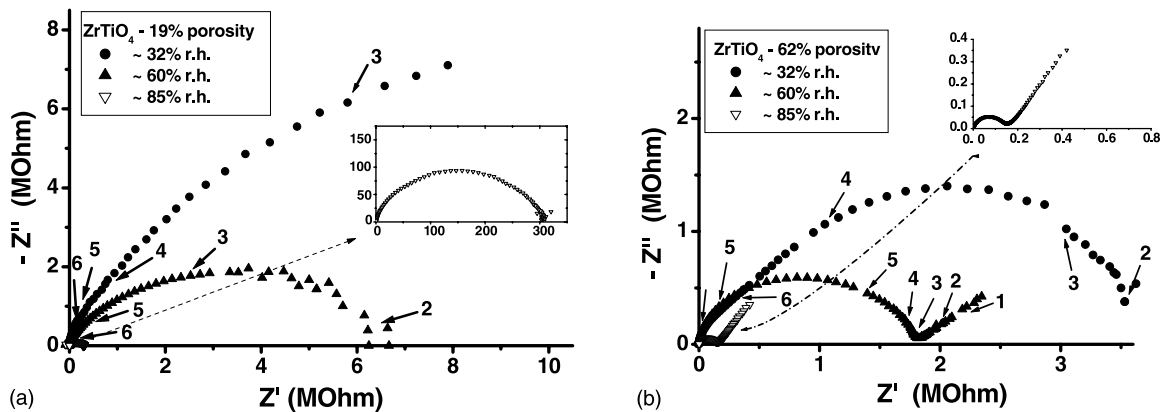


Fig. 7. Impedance spectroscopy diagrams of ZrTiO₄ ceramics with 19% (a) and 62% porosity (b) under different humidity conditions.

sintering temperature of the $ZrTiO_4$ compacts, the higher is the density, the lower is the pore density, and the lower is the total electrical resistivity.

The dependence of the electrical resistivity on the water molecules adsorbed on the ceramic surfaces shows that $ZrTiO_4$ ceramics sintered using powders prepared by the citrate technique have high room temperature sensitivity to humidity.

Acknowledgements

The authors acknowledge to CNEN, FAPESP (95/5172-4, 96/9604-9, 99/10798-0), and PRONEX for financial support and also to CNPq (306496/88-7 and 300934/94-7).

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