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$MgAl_2O_4$ spinel powders from oxide one pot synthesis (OOPS) process for ceramic humidity sensors

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Abstract

$MgAl_2O_4$ spinel powders can be prepared via the oxide one pot synthesis (OOPS) process. Porous ceramic oxide bodies can be produced with these powders and used as humidity-sensing materials. Pellets were characterized by SEM and their electrical properties were measured using impedance spectroscopy in the frequency range from 10^{-2} to 10^{5} Hz at different relative humidity (RH) levels in the range 4–90%. The spinel pellets made of powder from the OOPS process exhibited good humidity sensitivity with a linear response of the logarithm of resistance with RH in the whole RH range tested. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Spinel; Humidity sensor; $MgAl_2O_4$; Electrical properties; Powders-chemical preparation

1. Introduction

In recent years, many synthetic routes have been developed to a wide variety of inexpensive preceramic polymers directly from the corresponding metal oxides or hydroxides. One of them, called the "oxide one pot synthesis (OOPS)" process, is very simple and straightforward.[1] It provides many advantages, as compared to other chemical techniques, while retaining purity, homogeneity and permitting low processing temperatures. Additionally, this process may provide new chemicals, polymers and ceramics, in one or two steps directly from mineral sources. Precursors containing any combination of aluminum, silica, with or without group I or II metals, are readily produced in ethylene glycol as solvent.[1] Therefore, this method allows the preparation at low temperatures of heterometallic oxides, like $MgAl_2O_4$ spinel.[2] The preparation of a spinel double alkoxide precursor via the OOPS process is based on the following reaction:[3]

$$2Al(OH)_3 + MgO + 3TEA + x'EG \xrightarrow{200^\circ C/-H_2O} \text{Spinel Precursor}$$

The spinel precursor was produced by reacting mixtures of $Al(OH)_3$ and MgO [or $Mg(OH)_2$] with triethanolamine (TEA) using ethylene glycol (EG) as solvent,[2] and characterized by positive fast atom bombardment mass spectrometry (FAB+−MS). From the mass spectral fragmentation pattern, the major peak was found to be the parent peak at m/z = 518. After pyrolyzing the precursor, spinel formation was confirmed by XRD data comparing with the standard JCPDS file; No. 21-1152.[2,3]

The spinel, $MgAl_2O_4$, is a pure ceramic material that might have many applications.[4] The spinel is characterized by high refractoriness and exceptional dielectric properties, and can be used as a refractory material in the ceramics industry because of its low density (3.58 g/cm^3) and its stability in harsh environment.[5] It can be also used as a fusion reactor power core insulating material due to its radiation stability.[6] In addition, spinel has been proposed as a humidity sensing material with interesting results in terms of sensitivity, stability and response time.[7–9]

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Humidity sensing has become ever more important, principally in controlled systems for industrial processes and human comfort.[10] Among the various ceramics proposed in recent years for humidity sensor,[11] spinel has been used as the active element for humidity sensing devices.[8,9,12–14] Indeed ceramics possess a unique structure consisting of grains, grain boundaries, surfaces and pores that make them suitable for use as chemical sensors when they have a controlled microstructure.[15]

Impedance changes at different levels of environmental humidity in porous spinel-type oxides occur because of two factors, adsorption and capillary condensation of water.[9] The conduction mechanism of porous spinel in humid environments, which is similar to that of many other ceramic oxides,[7,10] is of ionic type, with a transport of protons by a Grotthuss chain reaction.[16] When the dry ceramic oxide is exposed to humid atmosphere, a layer of water-vapor molecules on its surface is first chemisorbed with the formation of surface hydroxyl ions. In this stage, charge transport occurs firstly by a hopping mechanism between hydroxyl groups of protons coming from the hydroxyl dissociation. Subsequent layers of water molecules are physically adsorbed on the hydroxyl layers. The easy dissociation of physisorbed water, due to the high electrostatic field in the chemisorbed layer, produces protons which are responsible for the electrical conduction by hopping between water molecules.[7]

The humidity-sensitivity of ceramics is mainly dependent on their microstructure. The presence of open porosity permits greater conductivity due to the enhancement of the specific surface area available for water adsorption. In addition, the quantity of adsorbed and condensed water depends on the available pore sizes and their distribution.[14]

The aim of this report was to develop a humidity sensing element made of $MgAl_2O_4$ spinel, produced by the OOPS process and investigate its humidity-sensitive electrical properties by a.c. impedance spectroscopy. The effect of sintering on pellet microstructures as a function of conductivity was studied, as well.

2. Experimental

2.1. Materials

Aluminum hydroxide hydrate [$Al(OH)_3.xH_2O$] and magnesium oxide (MgO) powders were purchased from Aldrich Chemical and Carlo Erba, respectively. They were used as received. Ethylene glycol (EG, $HOCH_2$-CH_2OH) was purchased from Carlo Erba (Barcelona) and distilled before using. Triethanolamine [TEA, $N(CH_2CH_2OH)_3$, 99.5% purity] was purchased from Merck Chemical Co. (Germany), stored in a dried bottle and used as received. All reactions are moisture sensitive; therefore, all operations were carried out with careful exclusion of moisture and air. Reaction were run under a nitrogen atmosphere.

3. Procedure

3.1. Preparation and characterization of magnesium aluminate spinel by the OOPS process

$MgAl_2O_4$, spinel-type oxide powders were prepared by the following procedure; aluminum hydroxide hydrate, [$Al(OH)_3.xH_2O$ (62.7% as Al_2O_3, 16.26 g, 100 mmol)], magnesium oxide [MgO (95% as MgO, 4.24 g, 100 mmol)], 3 mol equivalent of triethanolamine (40.0 ml, 300 mmol) and 150 ml of ethylene glycol as solvent, were put into a two-neck, round bottomed flask. The mixture was then heated to 200°C to distill off EG and by-product water produced during the reaction. The reaction was distilled continuously for approximately 7 h, and the precursor solution was then distilled further under vacuum (approximately 0.01 torr) to remove EG for 6 h. The products obtained were characterized by FAB+–MS (707 VG Autospec-ultima mass spectrometer, Manchester, England) employing a direct probe inlet and using the Cs gun to ionize the sample. The peaks were calibrated using CsI as the reference. Samples were mixed with glycerol, used as a matrix. The mass range was set from $m/z = 40$ to 3000. Additionally, the precursor products obtained were characterized by ^1H- and ^{13}C-NMR (Bruker AM 400 NMR spectrometer at the Department of Chemical Science and Technology, University of Rome "Tor Vergata", Italy). The NMR spectrometer operating in the quadrature mode was used to obtain ^1H- and ^{13}C-NMR spectra. Typical ^1H-NMR spectra consisted of 64–128 transients of 8192 data points over a 8 KHz bandwidth using a 5.8 μs at 90° pulse. Typical ^{13}C-NMR spectra consisted of 12,000 transients on a 35 kHz bandwidth using a 10 μs at 90° pulse. Deuterated chloroform ($CDCl_3$) was used as a standard solvent.

The precursor was pyrolyzed in an alumina boat in a horizontal tube furnace at 1100°C for 2 h, and ground with an alumina mortar and pestle. The samples were characterized by XRD (Philips PW 1830/00 No. DY 1241) at the range of 5–80°2θ and a scan speed of 1.5°2θ/min in 0.02°2θ increment. SEM (Leica-Cambridge mod. Steroscan 360, Cambridge, UK) was carried out to identify the microstructure of the powder samples. The powders were glued on aluminum stubs using a liquid carbon paste and coated with Au/Pd to avoid particle charging. Finally, the four point BET method using N_2 as adsorbate (Micromeritics Instrument Corporation, FlowSorb II model 2300) was used to determine the specific surface area of the samples. The gaseous mixture of nitrogen and helium using a gas mixer was allowed to flow through the system at a constant rate of 30 cc/min. Each powder sample was dried at 200°C and degassed for 1 h.

3.2. Studies of magnesium aluminate pellets as humidity sensors

The spinel powder, obtained after sintering the precursor at 1100°C for 2 h in air, was prepared into pellet form, 12 mm in diameter and 1 mm thick, by uniaxially pressing at 20 MPa. Pellets were sintered under air atmosphere at 1100°C for 2 h and at 1300°C for 8 h. The microstructure of the pellets was investigated by a mercury porosimeter (Carlo Erba Instruments mod. 2000). The volume of mercury penetrating the pores of the sample was measured as a function of the pressure exerted. SEM was also used to confirm the microstructure of the pellets.

On both sides of the pellet samples, a 10 mm diameter gold electrode was applied by vacuum evaporation. Each pellet was dried at 400°C for 1 h before being tested by using a.c. impedance spectroscopy (Solartron 1255 Frequency Response Analyzer; FRA) coupled with a home-made impedance adaptor to read values up to 10^{11} Ω. Impedance spectra of pellet samples were recorded in the frequency range from 10^{-2} to 10^5 Hz. The resistance values were calculated on the complex impedance plane plots, from the intercepts of the semi-arc, extrapolated if necessary, with the real axis. The pellets were tested at 40°C at different levels of relative humidity (RH) in the range 4–90%, obtained by mixing controlled flows of water-saturated and dry air. Monitoring of RH was performed using a Multisens Inc. hygrometric probe, which gave accuracy to within ±2%.

4. Results and discussion

4.1. Preparation and characterization of magnesium aluminate spinel by the OOPS process

The spinel precursor was obtained as a yellow, hard and rigid precipitate after completion of the reaction and solvent removal by vacuum distillation. The solid product was easily dissolved in methanol, dichloromethane, chloroform, acetone, ethanol, butanol, isobutanol, and isopropanol. The parent peak of the precursor found in the mass fragmentation spectra was at *m/z* 518, as shown in Fig. 1. According to previous results,[2,3] the structure of the spinel precursor was proposed to be a trimetallic species, consisting of one TEA group per metal center. It was assumed that the Mg^{2+} was actually enfolded by the third TEA, in terms of charge separation. This structure reasonably minimizes the charge separation and appears to the most stable for the dipositive cation. Thus, the electrostatic interaction are diminished.

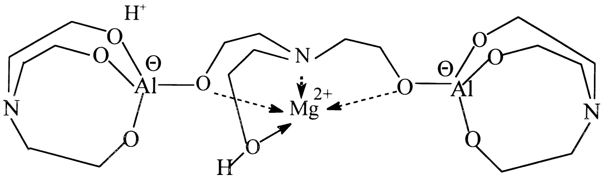

Fig. 1. Spinel precursor (*m/z* = 518, 100% intensity).

^{1}H-NMR results of the precursor are presented in Table 1 which shows the peak positions for methylene groups adjacent to oxygen and nitrogen atoms, occurring at chemical shifts of 3.73 ppm (triplet) and 2.72 ppm (triplet), respectively. The integration ratio of CH_2-O: CH_2-N was 1:1.

^{13}C-NMR of the spinel precursor (see Table 2) showed the peak positions corresponding to the carbon positions in the spinel precursor and in some free TEA. It is not possible to distinguish between free TEA and bridging groups. Furthermore, it is difficult to remove TEA from the reaction because of its high boiling point. The free TEA was thus retained in the precursor. However, TEA can be burned out during the pyrolysis of the precursor.

The spinel obtained after pyrolysis of the precursor at 1100°C for 2 h was a white powder. Since the precursor is highly viscous, this viscosity limited the escape of the decomposition products, namely, CO, CO_2, H_2O, and volatile hydrocarbon products, produced during the precursor decomposition. Thus, a gas-filled and foam-like structure formed which is retained as a porous structure during pyrolysis.

Table 1
^{1} H-NMR peak positions and assignments for the spinel precursor

Chemical shift (ppm)	Assignments
2.67 (t)	$N(\mathbf{CH_2}CH_2OH)_3$, free TEA
3.65 (t)	$N(CH_2\mathbf{CH_2}OH)_3$, free TEA
4.5 (br)	OH either from free of Mg^{2+} coordinated TEA or free TEA
2.72 (t)	$\mathbf{CH_2}$ adjacent to N
3.73 (t)	$\mathbf{CH_2}$ adjacent to O

Table 2
^{13} C-NMR peak positions and assignments for the spinel precursor

Chemical shift (ppm)	Assignments
52.7	$N(\mathbf{CH_2}CH_2OH)_3$, free TEA
52.8	$N(\mathbf{CH_2}CH_2O)Al$ (also free TEA)
56.7	Bridging, $N(\mathbf{CH_2}CH_2O)$
56.3	$N(CH_2\mathbf{CH_2}O)Al$
59.5	Bridging, $N(CH_2\mathbf{CH_2}O)$
63.6	$N(CH_2CH_2OH)_33$, free TEA

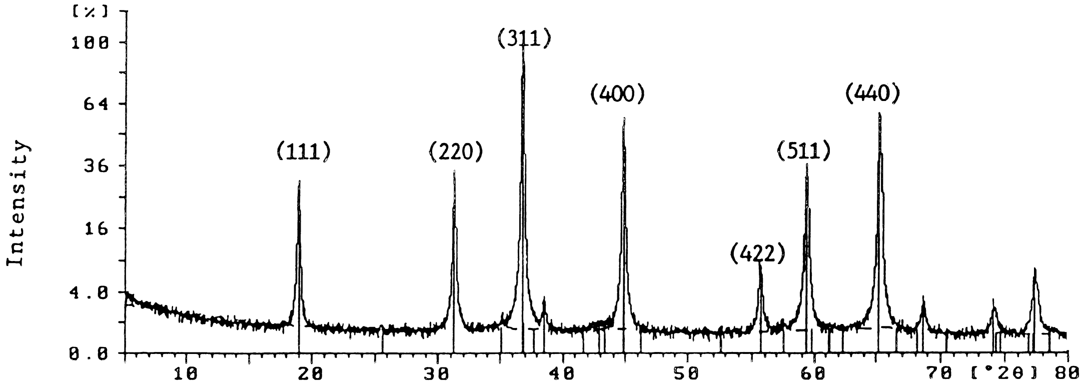

Fig. 2. XRD pattern of the spinel powder obtained after pyrolysis of the precursor at 1100°C for 2 h in air.

Fig. 2 shows the X-ray diffraction analysis conducted on spinel samples heated to 1100°C for 2 h under air. All the peak positions were identified by comparing with JCPDS file No. 21-1152 ($MgAl_2O_4$, cubic structure). The major peaks for spinel were the 311 hkl reflection (d=0.244 nm, I=100%) and 400 hkl reflection (d=0.202 nm, I=56%). The method of Pasquier et al. (1991)[2,3] was used to follow the phase evolution as a function of pyrolysis temperature by comparing the relative intensity ratio of the 400 and 311 peaks. The ratio value of 0.6 was found for a commercial high purity spinel,[2,3], whereas the relative intensity ratio of the 400 and 311 peaks of the product obtained after pyrolysis, was 0.56, as the material transforms to pure spinel. Additionally, the XRD pattern exhibited sharp scattering peaks of typical crystalline materials.[2,3] The average crystallite sizes of spinel powder determined using the Debye-Scherrer equation from a line broadening technique, which measures the full width at half-intensity of the largest intensity reflection of XRD pattern, was 390 nm.

The specific surface area of the 1100°C spinel powder was measured by BET analysis to be 11.2 m^2/g. The equivalent spherical diameter predicted from the BET surface area was 150 nm.

The SEM micrograph of the spinel powder prepared at 1100°C is shown in Fig. 3. The powder was irregularly shaped with blocky particles possibly due to heavy agglomeration occurring during the precursor pyrolysis. The sizes ranged from submicron to greater than 50 μm. Each agglomerate was, however, made of smaller particles, of about 400 nm.

4.2. *Studies of magnesium aluminate pellets as humidity sensors*

Initial studies on the use of spinel as a humidity sensing element focused on the pellet form. The microstructures of the pellets sintered in air at 1100°C for 2 h and at 1300°C for 8 h were studied using SEM and mercury porosimetry measurements. SEM micrographs are shown in Figs 4 and 5 for both pellets.

The mercury porosimetry is suitable for characterization of the pore size distribution in the compact. This measurement was used to confirm the SEM results, as well. Fig. 6 shows the pore size distribution of the

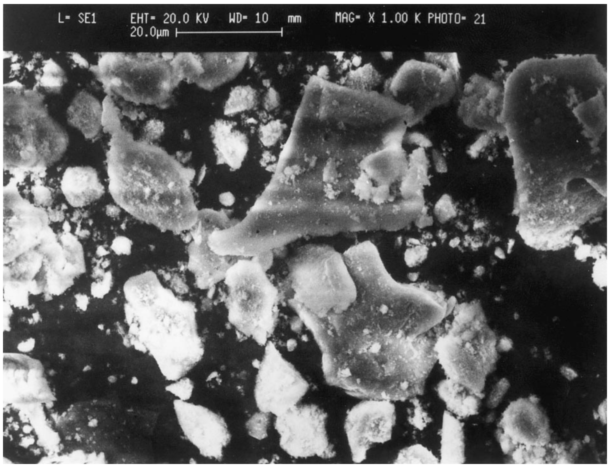

Fig. 3. SEM of spinel powder obtained after pyrolysis of the precursor at 1100°C for 2 h in air.

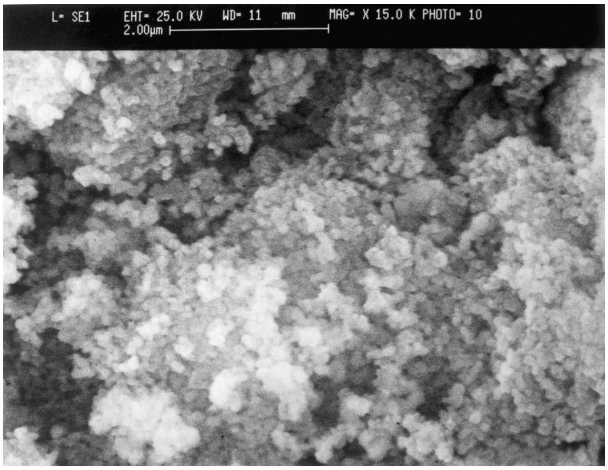

Fig. 4. SEM micrograph of the pellet sintered at 1100°C for 2 h in air.

Fig. 5. SEM micrograph of the pellet sintered at 1300°C for 8 h in air.

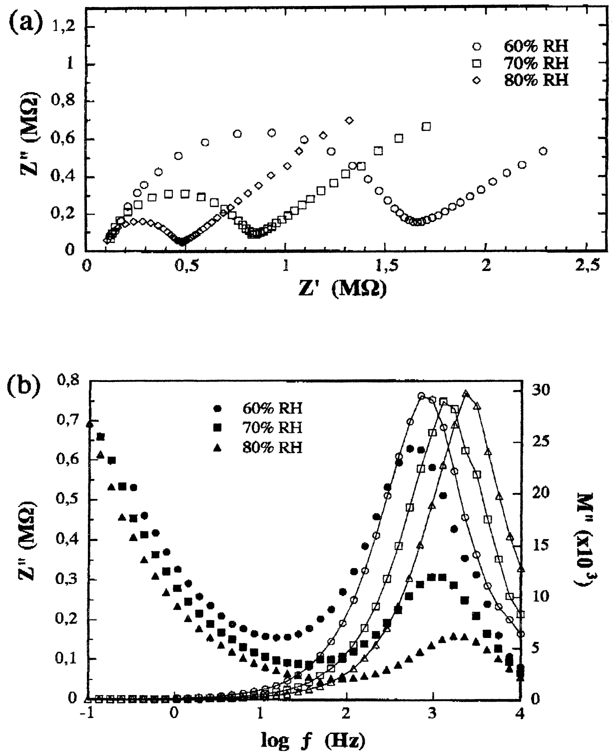

Fig. 7. Impedance data at 40°C as a function of RH for the $MgAl_2O_4$ pellet sintered at 1300°C for 8 h, presented (a) in the complex impedance plane plot, and (b) in the *Z*" (black symbols) and *M*" (white symbols) spectroscopic plots.

$MgAl_2O_4$ pellets sintered at 1300°C for 8 h [Fig. 6(a)] and at 1100°C for 2 h [Fig. 6(b)]. The results indicated that the variation in the sintering temperature and time affected not only the total open porosity but also the pore size distribution. The fired pellet at 1100°C exhibited a bimodal pore size distribution. The pellet sintered at 1300°C for 8 h had a 29.1% total porosity, with 21.1% of the pores smaller than 100 nm, while the remaining pores were concentrated in the range 100–1000 nm. Pellets sintered at 1100°C for 2 h had a total porosity of 40%, with 60.5% of the pores being <100 nm and 39.5% of pores in the 100–1000 nm range.

Fig. 7 shows the impedance data for the $MgAl_2O_4$ pellet sintered at 1300°C for 8 h, measured at 60, 70 and 80% RH. Fig. 7(a) shows the complex impedance plane plots and Fig. 7(b) the spectroscopic plots of the imaginary part of the complex impedance, *Z*", and of the imaginary component of the complex electronic modulus, *M*".[17] For both pellets, the complex impedance plane plots recorded at low RH values (<20% RH) showed a single semicircle which was slightly inclined to the real axis and did not start from the origin. At larger RH values, the spectrum loci decomposed in a semicircle at higher frequencies and in a linear spur at low frequencies, which was a Warburg-like line. The larger the RH, the smaller the impedance of the pellets. The frequency at which the relaxation of the RC element occurred, increased with increasing RH. The value of the intercept at high frequencies with the real axis did not change with RH.

As it is well known,[18] a semicircle on the complex impedance plane plot is due to a resistive and a capacitive element in parallel. At the low RH, the equivalent

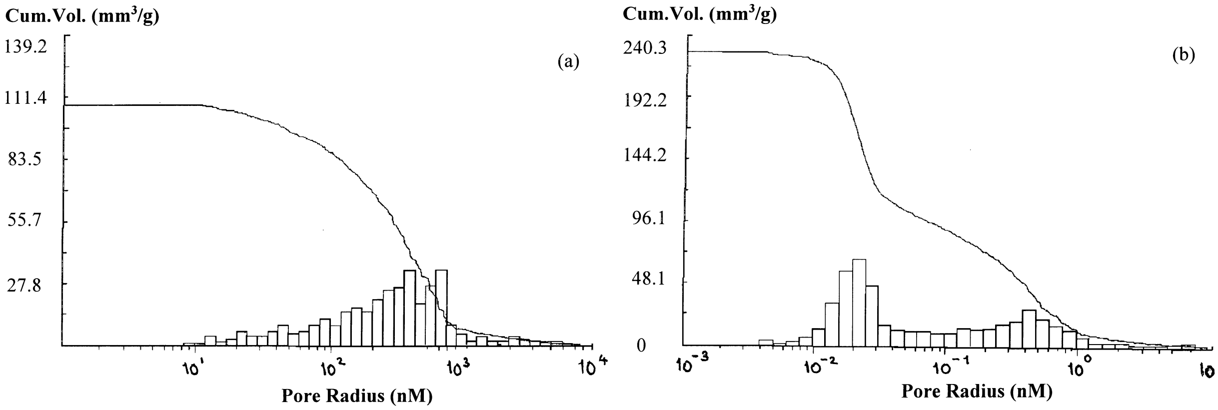

Fig. 6. Pore size distribution of the $MgAl_2O_4$ pellets: (a) sintered at 1300°C for 8 h and (b) sintered at 1100°C for 2 h in air.

electrical circuit can be described by a parallel RC element with a pure resistive element corresponding to the contribution of the grain surface due to the fact that the semicircle does not start from the origin.[19] The semicircle at high frequencies can be ascribed to the grain surface conductivity, which is RH-sensitive. The resistive part of the circuit can be attributed to bulk conduction, which is not sensitive to RH changes.

The impedance spectra of electroceramics can also show the presence of distinct features attributable to intergrain, or bulk and intergrain, or grain boundary regions, assigned on the magnitudes of capacitances.[17] The capacitances obtained for both pellets were in the range of 10^{-11} F at all the relative humidity levels, which is in agreement with the hypothesis made of grain surface conductivity.

The linear spur at low frequencies was due to polarization effect at the electrode–electrolyte interface. The electrodes used are made of Au, which is an electronic conductor. At low frequencies, there is a charge build-up at the blocking metal electrodes, because the charge carriers are protons. Given that pellets are porous, the porous structure permits the proton migration at the electrodes, through the oxide surface, and protons cause the electrode polarizations.[20] The excess charge at the electrodes causes a polarization effect that increases with increasing RH.

The spectroscopic plots confirmed these two results; two peaks can be observed in the *Z*" plots, at high and low frequencies, while in the *M*" plots only the peak at high frequencies was observed. This means that the capacitance in correspondence with the *Z*" peak at low frequencies is very large, and this is in agreement with the capacitance build-up due to the electrode polarization.

The resistivity values, calculated from *R* values considering the geometrical parameters for the pellets, decreased with increasing RH, as shown in Fig. 8. The protonic-type sensing is in good agreement with the RH-response of these pellets.

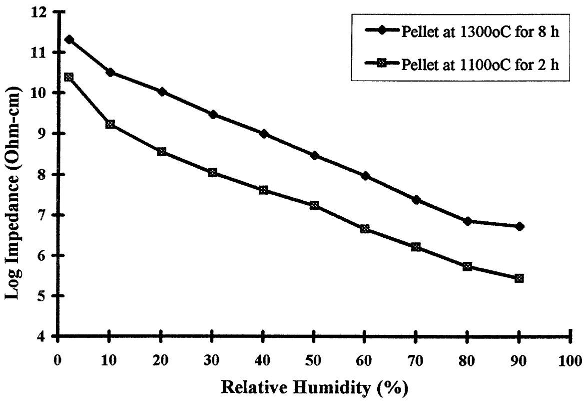

Fig. 8. Relationship between the log resistance of $MgAl_2O_4$ pellets sintered at 1100°C for 2 h and at 1300°C for 8 h in air, and at relative humidities in the range 4–90%.

The conduction mechanism for sintered $MgAl_2O_4$ pellets is ionic and conductivity increases with increasing chemisorption, physisorption, and/or capillary condensation of water within the pore structure.[11,13] The resistance decreased with increasing relative humidity, showing that the conduction occurred mainly at the grain surface by means of ionic carriers and was governed by total water molecules content. For both samples, the resistance change in the whole RH range tested was of about four orders of magnitude.

The humidity-sensitive electrical response of the pellets was related to their microstructure. The electrical behavior of the pellets is influenced by both total porosity and pore size distribution.[14,21] The lower resistance values are found to be related to larger total open porosity, and to the presence of a greater number of pores larger than 100 nm. As expected, pellets sintered at 1100°C for 2 h had the lowest impedance, based on the higher open porosity. The decrease in resistance at low relative humidity is also related to the larger presence of pores, and thus larger specific surface area. In fact, from the results obtained by SEM and porosity measurements, the resistance of the pellet sintered at 1100°C for 2 h was lower than that of the pellet sintered at 1300°C for 8 h due to the effect of the larger total porosity. The pellet sintered at 1300°C for 8 h had about 0.38% of porosity in the pore radii in the range 1–10 nm, while it was 3.47% for the pellet sintered at 1100°C for 2 h. Thus, the pellet sintered at 1300°C for 8 h had much higher impedance at high relative humidity level then the other pellet.

The recovery time is the time needed to change the resistivity value from one RH value to another and vice-versa. The recovery time for the spinel pellets was fast within a few seconds (2–3 s). For this experiment, the temperature was controlled at 40°C during the measurement. In addition, there is a small hysteresis ($\sim$1–2%) after lowering the humidity. When pellets were exposed to a humid environment for a long time, an increase in resistance was observed. This is called "the drift effect" which is caused by gradual formation of stable chemisorbed OH- ions on the oxide surface followed by prolonged exposure in a humid environment.[15] Due to the ionic type humidity sensing mechanism, proton hopping is adversely affected by the presence of surface hydroxyl ions instead of water molecules, thereby decreasing the surface conductivity. In addition, another problem affecting the sample response is the deterioration due to the adhesion of dust, dirt, oil, or other organic vapors.[22] The humidity sensitivity degraded remarkably even for short exposure times. However, heat cleaning at >400°C for 5 min recovered the spinel performance effectively. The results indicated that the pellets exhibited a good humidity sensitivity, good linearity and reproducibility in relative humidity range from 4–90%. The use of pellets sintered at lower temperature (1100°C) was more effective because it showed lower resistances over the entire RH range and the same sensitivity. This can be attributed to larger total porosity, and to the pore size distribution. The homogeneous distribution of pores in the whole range of sizes has been found to be a key factor to obtain a good RH response.[14]

5. Conclusions

The production of $MgAl_2O_4$ spinel powders from very inexpensive and relatively abundant starting materials was obtained via the one oxide pot synthesis (OOPS) process. The spinel prepared from this process could be used for fabricating humidity-sensing elements, which showed similar performance as compared to those obtained by other methods. The relationship between the log of resistance and the relative humidity (RH) gave good linearity. Good sensitivity and reproducibility of this powder were observed, as well. Furthermore, it was found that the microstructure of pellets, namely, the pore size distribution and total porosity, affects their conduction and humidity response. The use of these powders for the preparation of thick films by screen printing technology will also be possible, while thin films might be prepared directly from the viscous solutions of the precursor.

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