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Barium perovskites as humidity sensing materials

M. Viviani [a,*], M.T. Buscaglia [a], V. Buscaglia [a], M. Leoni [a], P. Nanni [b]

[a] *Institute for Physical Chemistry of Materials, National Research Council, via De Marini 6, 16149 Genoa, Italy*
[b] *Department of Process and Chemical Engineering, University of Genoa, P.le Kennedy Pad. D, 16129 Genoa, Italy*

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Abstract

The response to humidity of porous ceramics with composition $BaMO_3$, with M = Ti, Zr, Hf or Sn, was studied. Samples were obtained by cold isostatic pressing and sintering of fine powders prepared by wet chemical synthesis. Sensitivity and response time have been obtained by electrical impedance measurements realised in different conditions of relative humidity (R.H.) at 25°C. An increase of both capacitance and conductivity with humidity was observed in all samples with open porosity. Sensitivity increased with R.H. and decreased with frequency, indicating a major contribution from the surface of crystals exposed to water vapour, particularly in $BaTiO_3$ where 4000% change in permittivity was registered over the range 20–80% R.H. Time response was in the typical range of capacitive humidity sensors, with fast (10–100 s) equilibration time for intermediate values of R.H. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The measurement of humidity has received great attention during the last two decades due to the recognised importance of water partial pressure in many industrial processes and in the market of air-conditioning systems for the automatic regulation of living environments.[1]

A number of humidity sensors is nowadays available based on the measurement of electrical impedance (resistance or capacitance) of sensing materials exposed to the atmosphere. In general, commercial sensors are intended to operate in relatively narrow ranges of humidity and/or temperature, as all materials investigated for this pourpose show good characteristics under certain conditions but also limitations outside. For example, sensors based on polymeric organic films possess high sensitivity in the whole range of relative humidity (0–100% R.H.), but cannot be operated at high temperature and require temperature compensation. On the contrary, ceramic-based sensors can be used over a wider temperature range, especially at high temperature, but are seriously affected by adsorption of impurities at the surface that must be removed by periodic thermal cycling.[1]

Ceramic materials used for detection of humidity are represented by metal oxides, for which different mechanisms of conduction in a humid environment have been reported, each corresponding to a class of sensors, i.e. ionic, electronic, solid electrolites and heterocontacts.[1,2]

Whatever the origin of impedance variation, the interaction with water can be described by means of three basic phenomena, represented by the formation of a chemically adsorbed layer of OH^- ions bonded to metal ions at the oxide surface, the successive growth of a multilayer of physisorbed H_2O molecules and the further condensation of liquid water into pores with size in the mesopore range (1–250 nm).[3]

Contributions to surface conductance can be expected from both protons (H^+) hopping between adjacent H_2O adsorbed molecules (Grotthus chain reaction) and electrolysis of the condensed liquid. In addition, an electronic type conductance in the bulk is likely to arise from electrons released from surface states after the chemical adsorption of water molecules.[4] The possibility of reorientation under an external field of molecules in the physically adsorbed layer has to be also considered as an explanation to the variation of capacitance with humidity.

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[*] Corresponding author. Tel.: +39-010-6475-703; fax: +39-010-6475-700.

E-mail address: viviani@icfam.ge.cnr.it (M. Viviani).

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Perovskite-type oxides, well known and used as dielectrics, ferroelectrics, semiconductors and high-temperature ionic conductors, have been also considered for their response to humidity, one of the main advantages of such compounds being the possibility to obtain sensing materials that can be operated both at low temperature ($<100°$C) as ionic sensors and at higher temperatures ($\cong 400°$C) as semiconductors. A few paper report the modifications to electrical behaviour induced by humidity in $BaTiO_3$,[5,6] $Ba_{0.5}Sr_{0.5}TiO_3$,[7,8] $CaTiO_3$[9] and $SrSnO_3$,[10] generally in the form of porous bulk ceramics and added with alkali or La atoms at concentrations of 1–5 mol%. Recently the a.c. and d.c. electrical response to humidity was investigated on $BaTiO_3$ porous ceramics obtained from fine powders prepared by a low-temperature chemical synthesis.[11] In this work the observations have been extended to different Ba perovskites obtained by the same chemical route and, for comparison sake, to some materials prepared by conventional solid state reaction. Experimental results are presented and discussed according to the surface protonic conduction model.

2. Samples preparation

Powders with composition $BaMO_3$ (M = Ti, Hf, Sn) were prepared through the reaction between $Ba(OH)_2$ (98%, main impurity Sr) and the chloride or oxychloride of the relevant tetravalent cation (99.9%), in aqueous solution and with the addition of NaOH at 80°C under atmospheric pressure.[12,13] Chlorine was totally removed before drying by washing at room temperature with distilled water, while some amount (~800 ppm) of sodium was detected in the powders by plasma spectrometry (ICP).

For comparison sake, samples of $BaTiO_3$ and $BaZrO_3$ were prepared by solid-state reaction at high temperature using $BaCO_3$ and TiO_2 or ZrO_2. In this case the concentrations of both Na and Cl impurities were below 100 ppm. A doped composition was also obtained, by adding 0.3 mol% of $La(NO_3)_3$ to a chemically prepared $BaTiO_3$ powder (see Table 1) by wet ball milling in plastic jar with zirconia balls.

Cylindrical greens were formed by cold isostatic pressing at 150 MPa and sintered in air at different temperatures in order to obtain porous ceramics and, in the case of $BaTiO_3$, to obtain different pore size distributions. Sintered bodies were analysed by X-ray diffraction (XRD, Philips, PW1710), scanning electron microscopy (SEM, Philips 515) and N_2-adsorption porosimetry (Micromeritics, ASAP2010). The electrical response to humidity was investigated by a.c. electrical impedance measurements on disk-shaped samples (diameter = 10 mm, thickness = 1 mm), electroded with Ag–Pd–Al paste. Before measurement, electroded samples were annealed in air at 600°C for 1 h in order to reduce contact resistance. All characterisations were carried out into a cell at room temperature containing the sample, connected to a frequency response analyser (Solartron, SI1260) and a commercial humidity/temperature sensor (Rotronic, Hygroclip-S, polymeric capacitive type, response time $\leqslant 10$ s). The relative humidity inside the chamber was regulated by mixing two streams of dry and wet nitrogen gas. The capacitance and the conductance of the sample were recorded at fixed frequency as a function of time for step variations of R.H., while the whole impedance spectrum (10^{-2}–10^7 Hz) was measured at fixed R.H. and after long equilibration time (>30 min). Sensitivity was calculated from data as $\Delta C/C_m$, i.e. capacitance variation relative to the minimum measured in dry conditions.

Table 1
Composition and microstructural parameters of samples investigated

Sample	Composition (nominal)	Sintering temperature (°C)/time (h)	Grain size (μm)	D_{rel} (%)
BT1	$BaTiO_3$	1250/8	2	91
BT2[a]	$BaTiO_3$	1250/8	10	91
BTL	$BaTiO_3$ + 0.3 at.% La	950/2	0.2	68
BZ[a]	$BaZrO_3$	1380/0.5	0.6	88
BH	$BaHfO_3$	1500/2	0.6	91
BS	$BaSnO_3$	1700/2	9	59

[a] Refers to powders prepared by the solid-state route.

3. Results and discussion

XRD on sintered samples in all cases revealed the presence of the perovskite-like phase only, with tetragonal symmetry in $BaTiO_3$ and cubic in other oxides at room temperature. The average grain size, evaluated from SEM images of sintered samples after polishing and thermal etching is reported in Table 1.

The relative variation of capacitance with humidity is shown in Fig. 1 for different specimens. All samples present a good sensitivity when R.H. is above 50–60%, but huge differences appear at lower humidity levels. In particular, for BH the relative variation in capacitance is higher than 10% already at the lowest R.H. measured, whereas for others it is limited to a few per cent up to 50% R.H. The capacitance measurements reported in Fig. 1 substantially follow an exponential dependence with humidity described by the formula

$$\ln\frac{\Delta C(\mathrm{R.H.})}{\Delta C_{\max}} = \ln\left(\frac{C - C_{\mathrm{m}}}{C_{\mathrm{M}} - C_{\mathrm{m}}}\right) = -A(\mathrm{R.H.}_{\mathrm{M}} - \mathrm{R.H.}) \tag{1}$$

where C_M and C_m represent the maximum and the minimum capacitance respectively, $\mathrm{R.H.}_M$ the humidity

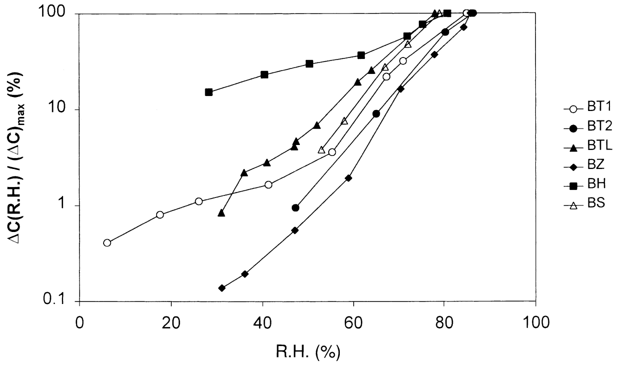

Fig. 1. Capacitance sensitivity vs. relative humidity. Data were collected at 1 kHz for the BT series and at 20 kHz for other samples.

value for which $C = C_M$ and A is a quantity related to the spreading of sensitivity. The expression (1) is not valid when $C = C_m$ and when the capacitance is not affected by humidity variation but it is useful to plot together and compare the behaviour of materials with very different sensitivities: the lower A, the wider is the humidy range over which the capacitance variation is distributed, meaning a better response of the material. Results of linear fitting on data of Fig. 1 are reported in Table 2 together with the relative capacitance variation over the range 20–80% R.H. It can be seen that samples with lower sensitivity have also a narrower spreading of sensitivity, even though for $BaHfO_3$ wide spreading and quite low sensitivity have been found and BTL shows the highest capacitance variation on a relatively narrow range.

The frequency dependence of capacitance at various humidity levels is reported in Fig. 2 for the sample BT1. A dispersion of sensitivity is clearly observed at low frequencies (below 100 Hz in this sample). This feature is common to all samples, to both fine and coarse-grained $BaTiO_3$ and also to paraelectric Stannate, Zirconate and Hafniate, indicating that the capacitive response to humidity is mainly due to surface processes like physisorption and condensation, and is not strictly connected to the electrical properties of crystals (e.g. ferroelectricity). Further confirmation comes out from conductance data, that present the same behaviour.

Table 2
Relative mesopore specific volume ($V_{mesopores}/V_{pores}$), sensivity spreading index (A), relative capacitance sensitivity ($\Delta C/C_m$), and time constants of the response relative to a humidity step variation ($\cong$ 15%)

Sample	$V_{mesopores}/V_{pores}$ (%)	A $(\%)^{-1}$	$\Delta C/C_m$ (%)	τ_1 (s)	τ_2 (s)
BT1	12.9	0.077	154	12	650
BT2	11.5	0.117	11	15	250
BTL	24.7	0.098	3560	220	1000
BZ	7.1	0.127	65	8	45
BH	32.4	0.038	84	25	190
BS	12.0	0.121	5	7	170

The time response to humidity has been investigated by recording the impedance after the application of a step-like variation of R.H. The assumption of instantaneous equilibration of the humidity is supported by the use of fluxing gas as carrier of water vapour, ensuring a total replacement of the testing environment in less than 1 s. The variation of capacitance as a function of time ($C(t)$-$C(0)$) was compared with two exponential functions with different time constants (τ_1, τ_2) expressed by

$$C(t) - C(0) = k_1(1 - e^{-t/\tau_1}) + k_2(1 - e^{-t/\tau_2}) \qquad (2)$$

The results of non-linear fitting of experimental data with the Eq. (2) are reported in Table 2. It is important to remark that the time constants are substantially the same during adsorpion and desorption and are not influenced by the actual values of humidity. Only at very high R.H. levels ($>$90%) a slowing down of the response is observed. Eq. (2) can be explained by the existence of two distinct processes with different activation energies and kinetic constants (Fig. 3). Alternatively, the existence of one single process of interaction among water molecules and solids that develops under various conditions (two as a first approximation), can be assumed. From spectroscopic experiments on defective single crystals surfaces[14] it is known that chemisorption in perovskites is likely to be completed at a water pressure of the order of 0.1 Pa, and for this reason can be discarded at higher humidity levels. On the contrary, physical adsorption and capillary condensation take place in the whole range and the time required to reach equilibrium can be related to the time necessary for the H_2O pressure to establish into the various parts of the solid. As a consequence, microstructure and particularly size distribution of pores must be considered to explain the electrical properties presented here. As can be seen comparing data in Table 2, the first response time is determined by the amount of mesopores, being shorter in samples with little porosity in that range. From size distributions of pores (Table 3) it is also possible to

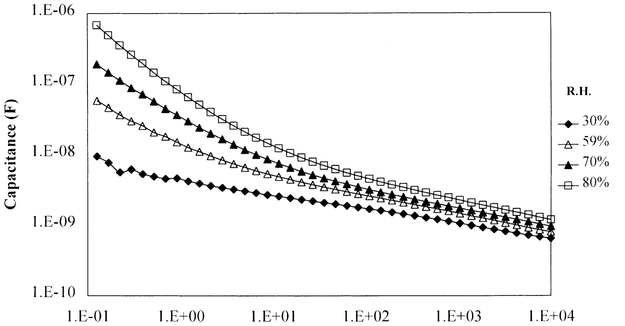

Fig. 2. Frequency dependence of capacitance for different R.H. in the sample BT1.

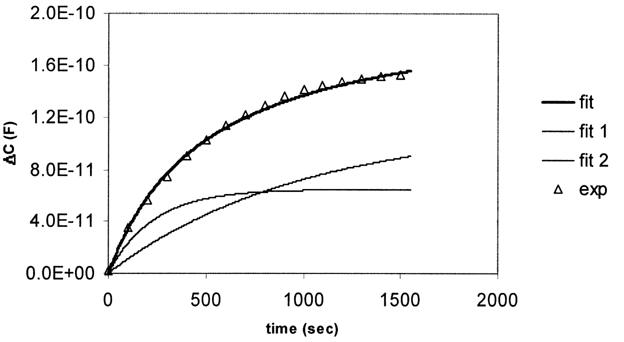

Fig. 3. Time dependence of capacitance for a step variation of relative humidity (10%) in the sample BTL. Experimental data are fitted with Eq. (2) and single components are also reported ($\tau_1 = 220$ s, $\tau_2 = 1000$ s).

Table 3
Volume (V) pore size distribution in the mesopore range (1–250 nm). Intervals of pores width (r) are expressed in nm

Sample	$V(r<6)$ (%)	$V(6<r<20)$ (%)	$V(20<r<60)$ (%)	$V(60<r<250)$ (%)	V_{mesopore} cm^3 g^{-1}
BT1	26	6	7	62	2.12E-03
BT2	32	3	8	57	1.89E-03
BTL	9	46	13	32	1.92E-02
BZ	11	5	9	75	6.14E-03
BH	9	5	7	79	3.91E-03
BS	0	0	0	100	1.17E-02

conclude that a uniform distribution is beneficial in giving a good spreading of sensitivity. These considerations particularly apply to BH and BTL samples which have the biggest relative mesopore volume, long time constant (τ_1) and lowest A. The second time constant is less clearly related to the microstructural properties, even though it can be noted that the lowest τ_2 values are related to reduced amount of mesoporosity (BZ) or to large average pore size (BS). Accordingly, the slowest response time is found in the sample with the highest amount of porosity of width below 20 nm.

4. Conclusions

The capacitive response to humidity of different perovskites has been investigated. Samples with general composition $BaMO_3$ (M = Ti,Zr,Hf,Sn) were prepared with very different microstructural features, i.e. density, grain size and pore size distribution. The highest sensitivity and good sensitivity spreading index was found in highly porous $BaTiO_3$ with the addition of 0.3 at.% of La. The major factors affecting the sensitivity and response time were porosity and pore size distribution in the mesopore range, as supported by the index of spreading of sensitivity found in $BaHfO_3$. Due to the high values of permittivity and sensitivity obtainable, $BaTiO_3$ can be considered for the realisation of ceramic capacitive humidity sensors.

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