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Study of the influence of nickel ions substitutes in barium stannates used as humidity resistive sensors

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ABSTRACT

In the present work, we report the results of the influence of the Ni ions which partly substitute the Ba ions in the barium stannate ($Ba_{1-x}Ni_xSnO_3$, where $x = 0$; 0.1; 0.2; 0.5), on the structural and electronic properties, as well as on the sensitivity to humidity. With the view to obtain a porous and finer structure, thus providing a high specific surface, these materials were obtained through the precursor method of self-combustion (co-precipitation in a colloidal environment and self-combustion), followed by heat treatments. The phase composition and morphology were studied by XRD and SEM. The pure sample, as well as that with the substitution $x = 0.1$, are single phased after 40 min sintering at 1000 °C. For substitutions with $x > 0.1$ secondary phases appear, which favorably influence the humidity sensitivity. All the samples show a significant sensitivity to humidity within 22% RH and 75% RH for the substitution with $x = 0$ and 0.1, and 22% RH – 98% RH for the substitution with $x = 0.5$. For this interval, the material resistivity logarithmically decreases by over four orders. The sample with the substitution $x = 0.5$ is characterized by a very fine structure (~250 nm) and a high effective porosity (47%). This sample presents a shorter absorption response time than the other samples. Its high sensitivity, its sensitivity range, linearity of the sensitivity characteristic and the quick response time recommend the material with the composition $Ba_{0.5}Ni_{0.5}SnO_3$ for the realization of a very good resistive humidity sensor.

1. Introduction

Sensors are key elements in the rapidly evolving fields of measurements, instrumentations, and automated systems. Measurement of humidity is critically important in chemical/biochemical fields, food processing, civil engineering, air-conditioning, electronic processing, etc. [1,2].

The sensing mechanism of resistive sensors consists in the change of the electrical resistivity resulting from chemical reaction between water molecules and the material surface. The surface morphology has an essential role on the sensitivity of solid-state sensors [1,3,4]. The desirable characteristics of humidity sensors are high sensitivity, wide humidity range, sensitivity uniformity, quick response time, chemical and thermal stability, reversibility, long life and low cost [5]. For a perovskite (ceramic) sensor, the microstructure and specific resistance of the sensor element are two key parameters on which its performance depends. Concerning the applications of the vapor water sensors, materials with high porosities and high surfaces properties are preferred [6].

In the recent years more and more attention has been shifted to the study of the application of barium stannate as a humidity and gas sensor material [7–9]. It has been found that the electrical properties of barium stannate, such as conductivity, capacitance or impedance, are dependent on temperature, humidity, partial oxygen pressure, the nature and concentration of the measured gases [10–12].

In this work we meant to realize new materials with perovskite type structure (ABO_3) as sensitive to humidity as possible. In the case of barium stannate, the preference of the substitute ions to the A and B sites in the perovskite structure can modify the material sensitivity to humidity changes [12,13].

We chose the barium stannate for the following reasons:

- The barium stannate prepared through the precursor self-combustion method has a marked porosity;
- It has a fine granulation, as compared to that obtained through other classical preparation methods, which ensures a high specific surface;
- The Ba^{2+} ion ensure a high resistivity in dry condition.

Barium stannate is a cubic perovskite oxide compound that behaves as n-type semiconductor with a wide band gap of 3.4 eV and is stable at high temperature (up to 1000 °C) [14]. Various

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methods of synthesis of the barium stannate have been reported [15–19]. The humidity sensitive electrical properties of barium stannate have not been studied in detail [12,14].

The present work reports the results of the influence of Ni^{2+} ions which partially substitute the Ba^{2+} ion in the barium stannate ($Ba_{1-x}Ni_xSnO_3$, where $x = 0$; 0.1; 0.2 and 0.5), on the structural and electric properties, as well as the sensitivity to humidity. The Ni^{2+} ion was chosen as a substitute due to its ion radius very different from that of the Ba^{2+} ion which it replaces in the lattice to a small extent, up to $x = 0.1$ [20], while for bigger substitutions, the generation of secondary phases is expected, which improves the grain size, porosity and humidity sensitivity. The method used to obtain these materials is the precursor method of self-combustion followed by heat treatments [21,22]. This method has some advantages: the heat generated in the exothermal reaction accelerates the process, and the resulting perovskite powder is fine-grained and with porous structure.

2. Experimental

The following compositions of barium stannate with nickel substitutions were prepared: $BaSnO_3$ (BNS-0), $Ba_{0.9}Ni_{0.1}SnO_3$ (BNS-1), $Ba_{0.8}Ni_{0.2}SnO_3$ (BNS-2) and $Ba_{0.5}Ni_{0.5}SnO_3$ (BNS-3). The compositions were prepared by self-combustion method starting from barium and nickel nitrates and stannous chloride as raw materials. The preparation method includes:

- solution of nitrates $Ba(NO_3)_2$ and $Ni(NO_3)_2$ in de-ionized water;
- solution of stannous chloride ($SnCl_2{\cdot}2H_2O$) in de-ionized water;
- solution of polyvinyl alcohol $(C_2H_4O)_n$ (colloidal solution);
- stirring of solutions at 80 °C;
- NH_4OH addition to adjust pH to about 8;
- drying at 120 °C;
- self-combustion;
- pre-calcination of combusted powder at 600 °C.

The reactions for $BaSnO_3$ can be schematized as follows:

$$Ba(NO_3)_2 + 2NH_4OH \rightarrow Ba(OH)_2 + 2NH_4NO_3 \quad (1)$$

$$SnCl_2 + 2NH_4OH \rightarrow Sn(OH)_2 + 2NH_4Cl\uparrow \quad (2)$$

$$C_2H_3OH + 5NH_4NO_3 \rightarrow 2CO_2\uparrow + 12H_2O\uparrow + 8N_2\uparrow + Q \quad (3)$$

$$Ba(OH)_2 + Sn(OH)_2 \rightarrow BaO + SnO + 2H_2O\uparrow \quad (4)$$

$$BaO + SnO + O \rightarrow BaSnO_3 \quad (5)$$

The resulting powders were mixed in a ball mill and biaxial pressed in a disc shape in a stainless steel die under a pressure of about 3×10^7 N/m^2. The pressed pellets (17 mm diameter, ~1.8 mm thickness) were sintered in air, at 1000 °C for 40 min and slowly cooled in the furnace. The weight and dimensions of the pellets were measured at room temperature, to determine bulk density d and effective porosity p_{ef} (for open pores) using the Archimedes's principle [5,12].

The phase composition was identified by X-ray diffraction (XRD) using a diffractometer type DRON-3 and the CoK_α radiation ($\lambda = 1.7889$ Å). The values of the lattice parameter for all samples were obtained by the least square fitting of the XRD data using the "Crystalographica" software. The X-ray density, $d_x = M/Na^3$ [23] (where M is the molecular weight, N is Avogadro's number and a is the lattice constant) was used to evaluate the porosity $p = 1 - d/d_x$. The morphology was examined using a scanning electron microscope VEGA-TESCAN. The average grain size D_m was determined from SEM micrographs. The specific surface area was calculated from equation $A_{sp} = s/v{\cdot}d = 6/D_m{\cdot}d$ [6,24], where s and v are the particle surface and volume respectively, D_m is the average grain size, d is the bulk density and 6 is the shape factor. It is assumed that all the particles have the same size and shape.

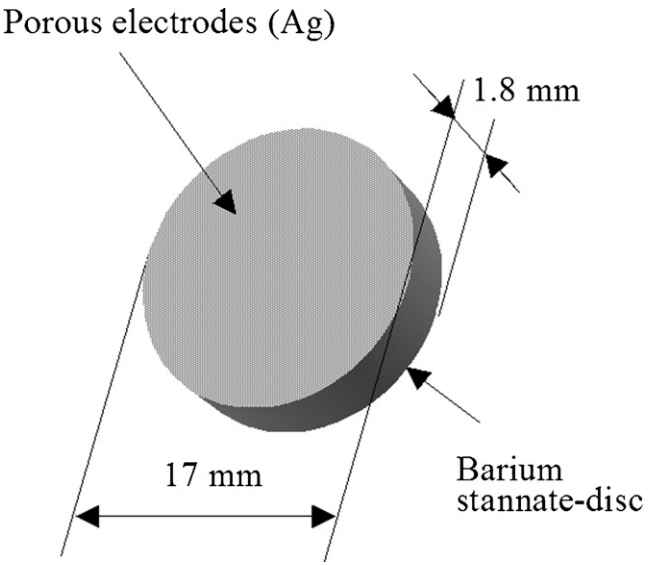

Fig. 1. Sample with silver porous electrodes on the plan parallel sides (sensor element for humidity).

To measure the electric resistance sensitive to humidity, two porous silver electrodes were applied on the plane parallel sides in shape of disks, like in Fig. 1, and the disc cylindrical surface was lacquered, to avoid current loss during measurements. The SEM micrography of the electrodes is presented in Fig. 2, where one can see numerous pores with diameters of about 10 μm.

The electrical resistance of the sample with silver electrodes was measured at 10 Hz with a d.c. ohmmeter by means of switching electronic device executed with this purpose. The measurement of the wet sample electric resistance excludes the direct current utilization due to the electrochemical phenomena that appear at the sample contact with the electrode (polarization), and the utilization of the a.c. bridges over 100 Hz is not indicated, due to the high resistance of the samples at small humidity values. For the humidity sensing measurements the sensor element was placed in a thermo-

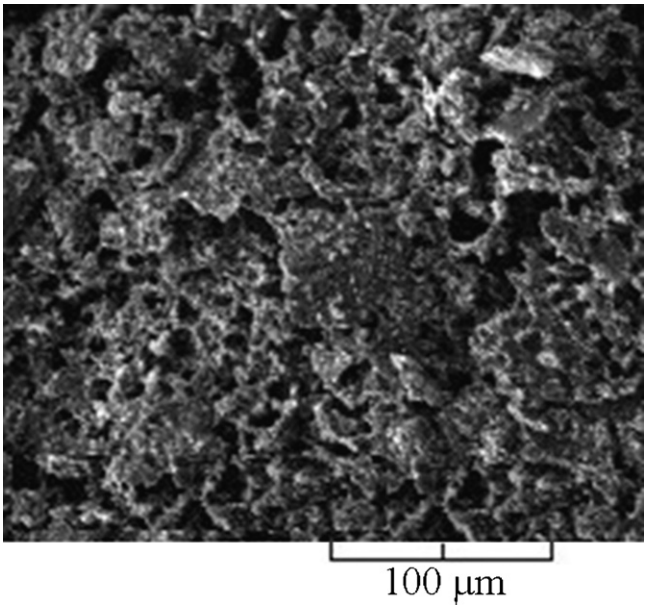

Fig. 2. SEM micrography of silver electrodes.