The influence of nickel ions substitutes in barium stannates used as humidity capacitive sensors

C. DOROFTEI[a*], P. D. POPA[b], F. IACOMI[a]
[a]*"Al. I. Cuza" University, Faculty of Physics, 11 Carol I Blvd, 7000506 Iasi, Romania*
[b]*Institute of Technical Physics, Bd. D. Mangeron 47, 700050 Iasi, Romania*

Barium stannate based perovskites with a submicron granular structure and humidity sensing capacitive were studied. These compounds can be used for sensors in humidity control in the domain of 11% RH - 98% RH. The study was concentrated on $BaSnO_3$ ceramic material and the effect of nickel ions on the microstructure and on the electrical capacity sensitivity to humidity was investigated. 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. All the studied samples ($Ba_{1-x}Ni_xSnO_3$, where x = 0; 0.1; 0.2; 0.5) show a significant sensitivity to humidity within 11% RH and 98% RH. The sample with the substitution x = 0.5 is characterized by a very fine structure (~250 nm) and a high effective porosity (47%). For this material, the capacity logarithmically increases by over 20 times at 100 Hz. As compared to the other samples, this sample presents a shorter response time, high sensitivity and linearity of the logarithmic sensitivity characteristic.

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1. Introduction

Humidity sensors are in great demand for quality control of production processes and products in a wide range of industries, such as the production of electronic devices, precision instruments, textiles and foodstuffs [1], and also in many domestic applications, such as the smart control of living environment in a building.

Capacitive humidity sensors have been widely used in humidity measurement and control, ever since the development of the first stable sensor of this type by Nelson and Amdur in 1965 [2].

The capacitance change upon exposure to moisture is mainly caused by the replacement of air with water molecules absorbed in the pore space. The capacitance response of porous structures is often attributed to the replacement of air with water molecules adsorbed in the pores [3,4].

A wide variety of materials have been studied and used as sensing elements in a humidity measurement device [5].

In the recent years, barium stannates received much attention due to their applications in humidity sensors [6-8]. For a perovskite (ceramic) sensor, the microstructure and electric properties of the sensor element are the two key parameters on which its performance depends.

Generally, $BaSnO_3$ powders were prepared by solid-state reaction of $BaCO_3$ and SnO_3 at high temperature above 1300°C. These powders contain impurities and are coarse grained [9]. The different wet chemical syntheses, such as hydrothermal method [10], sol-gel method [9] and polymerized complex method [11,12] were recently reported for the preparation of the fine $BaSnO_3$ powders.

The present work presents 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 humidity capacitive sensors at different frequencies. The method used to obtain these materials is the precursor method of self-combustion followed by heat treatments [13,14]. 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. Sensor fabrication and measurement setup

Nickel-doped barium stannates having the general formula $Ba_{1-x}Ni_xSnO_3$, where x=0-0.5 ($BaSnO_3$ (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) were prepared by self-combustion method followed by heat treatments. Fig. 1 shows the flow diagram of the sample preparation process.

We used metal nitrates or chlorides as starting materials (starting from barium and nickel nitrates and stannous chloride as raw materials). Polyvinyl alcohol was added to make a colloidal solution. The combustion reaction converts the dried gel in a loose powder with nanogranular structure. The obtained powders were mixed in a ball mill and biaxial pressed in a disc shape in a stainless steel die under a pressure of about $3 \cdot 10^7$ N/m^2. The pressed pellets (17 mm diameter, ~1.8 mm thickness) were sintered in air, at 1000°C for 40 minutes and slowly cooled in the furnace.

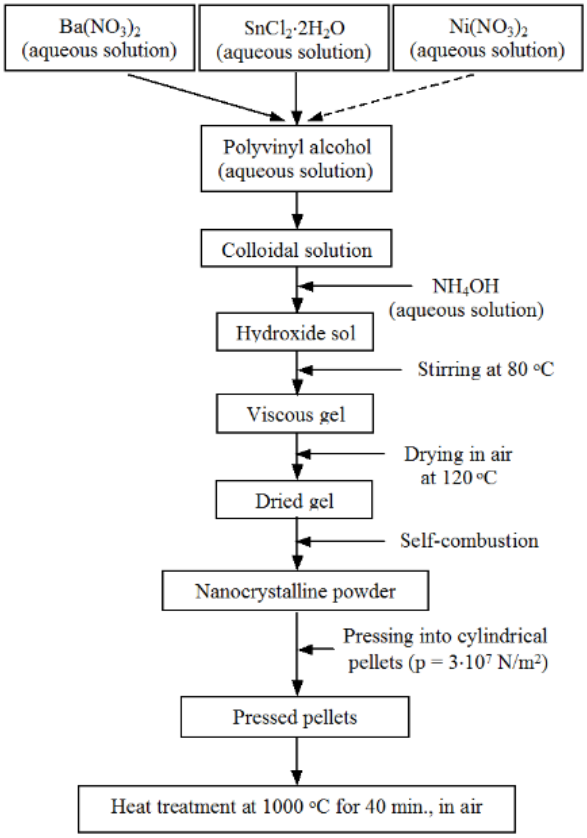

Fig. 1. Flow diagram for the fabrication process of $Ba_{1-x}Ni_xSnO_3$ (x=0-0.5) fine powders by self-combustion method.

In order to measure the electric capacitive sensitive to humidity, two porous disks shaped silver electrodes were applied on the plane parallel sides.

The electrical capacitance of the sample with silver electrodes was measured at 100 Hz, 1 kHz, 10 kHz and 100 kHz with a LRC METER PROTEC 9216A. The measurement voltage is 1V. For the humidity sensing measurements the sensor element was placed in a thermostatic enclosure at 25°C and exposed to different values of relative humidity (RH). Relative humidity ranging from 0% to 98% was obtained using saturated salt solutions as the humidity generating source [15,16].

The response time to humidity variation for all the samples was obtained by monitoring the capacitance variations when the relative humidity varied from 43% to 98% and back.

All the samples were studied as resistive humidity sensors in our work published previously [16]. The details concerning the sample structure and morphology were largely presented in the above mentioned work.

The BNS-0 and BNS-1 samples were single-phase. The BNS-2 and BNS-3 samples show several secondary phases [16]. The XRD data of the samples were indexed on the basis of a cubic unit cell space group Pm3m similar to the undoped $BaSnO_3$ reported in literature [17,18].

The porosity p of all the samples is high, between 62.6% and 67.6%, due to the preparation method. The effective porosity p_{ef} is diminished at the sample without nickel substitutions (10.1%) and much higher in the case of the nickel substitutions (46.7% - 50.2%). Generally, all the samples are characterized by a fine granulation. The average grain sizes ranges between 0.25 μm (BNS-3) and 1.1 μm (BNS-0). Large pores, above 1 μm in diameter, distributed along the grain agglomerations were observed. These pores are necessary for sensor rapid response, because the water adsorption rate is controlled by the diffusion rate of water vapors.

3. Results and discussion

3.1 Electric capacity response to humidity

Figs. 2 and 3 shows the sensors capacitance response to RH at 100 Hz and 100 kHz respectively. The sensors capacitance (C) increases significantly with increasing RH at all measuring frequencies, especially at high RH; at the same time, sensor capacitance decreases cu increasing measuring frequency. Yet the log C vs. RH curves are not linear in the full RH range from 0% to 98%. The best linearity is present in the sample BNS-3 within the range 11% - 98% RH.

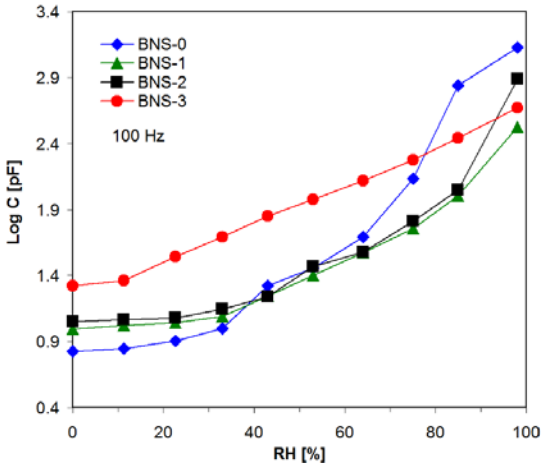

Fig. 2. The log C vs. RH characteristics for the studied samples at the frequency of 100 Hz.

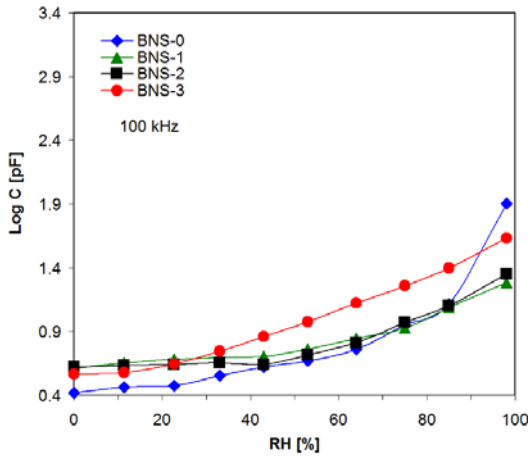

Fig. 3. The log C vs. RH characteristics for the studied samples at the frequency of 100 kHz.

Fig. 4 presents for comparison the log *C* vs. RH characteristics for the BNS-0 and BNS-3 samples at the four measuring frequencies. One can notice that the BNS-3 sample has linear characteristics at all the frequencies, and the highest slope is obtained at 100 Hz, where the sample capacity varies from 20 pF at 11% RH to 470 pF at 98% RH.

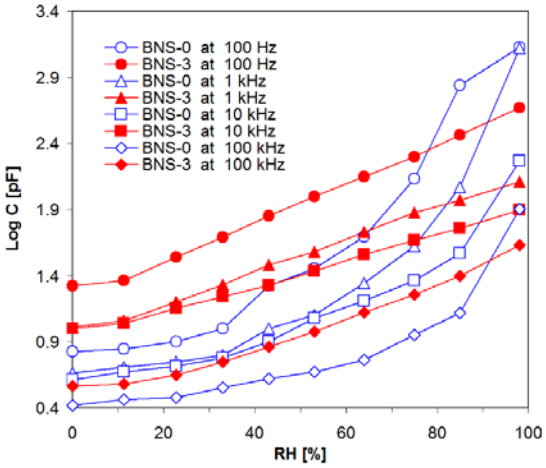

Fig. 4. The log C vs. RH characteristics for the BNS-0 and BNS-3 samples at different frequencies.

3.2 Response time

The humidity time response characteristics at 25°C for the sample BNS-0 and for the sample BNS-3 within the interval 43% - 98% RH at the frequencies of 100 Hz and 100 kHz are shown in Fig. 5. For the BNS-0 sample, the response time is of 6 min at absorption (43-98% RH) and 7 min at desorption (98% - 43% RH) at both frequencies. For the BS-3 sample, the response time is of 3 min at absorption (43% - 98% RH) and 4 min at desorption (98% - 43% RH).

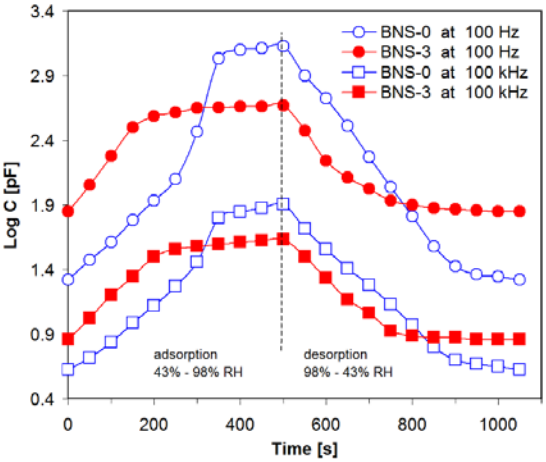

Fig. 5. Humidity-time response characteristics for BNS-0 and BNS-3 samples.

Both samples present a good reversibility within the investigated humidity range. Due to the composition, the high effective porosity (46.7%) and large specific surface area (10.1 m^2/g), the sample with high nickel substitutions (BNS-3) is twice as quick as the sample without nickel substitution (BNS-0).

These results suggest that the adsorption or desorption rate of water vapor is controlled by the diffusion rate of vapor through the micro pores, which in turn depends on the size and distribution of large pores. The same humidity time response characteristics were obtained for the BNS-0 and BNS-3 samples in the work [16] that studies the resistivity response to humidity at the measuring frequency of 10 Hz. One can state that, both for the resistance and the electric capacity of the studied samples, the humidity time response characteristics only depend on composition and microstructure and do not depend on the measuring frequency.

4. Conclusions

• The barium stannates doped with nickel, prepared by self-combustion method can be successfully used as capacitive humidity sensors.

• Their capacitance increasing environmental humidity and decreases with the measuring frequency.

• The response time is short due to the sample fine grain structure, high specific surface and porosity.

• The best properties as humidity sensor can be found in the $Ba_{0.5}Ni_{0.5}SnO_3$ perovskite prepared through the self-combustion method and treated in air for 40 minutes at 1000°C, used at the measuring frequency of 100 Hz, namely: a good linearity of the log C vs. RH characteristic within the interval 11-98% RH, a high sensitivity (the capacity increases by over 20 times) and a minimum response time (3 min).

Acknowledgements

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References

[1] S. Upadhyay, P. Kavitha, Mater. Lett. **61**, 1912 (2007).
[2] C. C. M. Luijten, M. E. H. van Dongen, L. E. Stormborm, Sens. Actuators B **49**, 279 (1998).
[3] Y. Wang, S. Park, J. T. W. Yeow, A. Langner, F. Muller, Sens. Actuators B 1**49**, 136 (2010).
[4] J. Das, S. M. Hossain, S. Chahraborty, Sens. Actuators A **94**, 44 (2001).
[5] M. J. Yang, G. Casalbore-Miceli, N. Camaioni, C. M. Mari, H. Sun, Y. Li, M. Ling, J. Appl. Electrochem. **30**, 753 (2000).
[6] J. Cerda, J. Arbiol, R. Diaz, D. Dezanneau, J. R. Morie, Mater. Lett. **56**, 131 (2002).

[7] Y. Shimizu, Y. Fukuyama, T. Nrikio, H. Arai, T. Seiyama, Chem Lett. **3**, 377 (1985).
[8] B. Ostrick, M. Fleischer, U. Lampe, H. Meixner, Sens. Actuators B **44**, 601 (1997).
[9] M. Licheron, G. Jouan, E. Husson, J. Eur. Ceram. Soc. **17**, 1453 (1997).
[10] T. R. N. Kutty, R. Vivekanandan, Mater. Res. Bull. **22**, 1457 (1987).
[11] C. P. Udawatte, M. Kakihana, M. Yoshimura, Solid State Ionics **108**, 23 (1998).
[12] S. Y. Jung, K. Seungwan, J. Ind. Eng. Chem. **7**, 183 (2001).
[13] C. Doroftei, P. D. Popa, N. Rezlescu, J. Optoelectron. Adv. Mater. **12**(4), 881 (2010).
[14] N. Rezlescu, P. D. Popa, E. Rezlescu, C. Doroftei, Rom. J. Phys. **53**(3-4), 545 (2008).
[15] N. Rezlescu, E. Rezlescu, C. Doroftei, P. D. Popa, J. Phys.: Conf. Ser., **15**, 296 (2005).
[16] C. Doroftei, P. D. Popa, F. Iacomi, Sens. Actuators A **173**, 24 (2012).
[17] J. Smith, A. J. E. Welch, Acta Crystallogr. **13**, 653 (1960).
[18] H. D. Megrav, Proc. Phys. Soc. London **58**, 133 (1946).

*Corresponding author: docorneliu@yahoo.com