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Ni ferrite highly organized as humidity sensors

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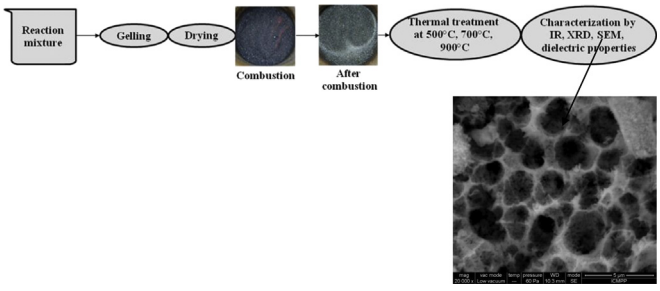
HIGHLIGHTS

- Ni ferrite with highly organized structure was obtained.
- Polyacrylamide-based hydrogel was used as a template agent.
- Ni ferrite was synthesized by sol–gel autocombustion method.
- The electrical investigations were carried out in different humidity conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis and characterization of nickel ferrite using polyacrylamide-based hydrogels as template agents for obtaining $NiFe_2O_4$ by the sol–gel autocombustion method was studied, the investigation representing a novelty in the field.

The polyacrylamide-based hydrogel used as a template agent, was synthesized by an original simultaneous polymerization-crosslinking method, using a monofunctional crosslinking agent. The ferrite was synthesized by the sol–gel autocombustion method, using citric acid as a chelating/fuel agent. The as-obtained hydrogel was characterized by IR, SEM and thermogravimetric techniques, as well as swelling behavior. As-synthesized ferrites were characterized by IR, SEM, XRD techniques, as well as by electrical and magnetic properties. The electrical investigations were carried out in different humidity conditions in order to highlight the influence of humidity on electrical properties, in this respect the prepared $NiFe_2O_4$ with highly organized structure was tested for applications as humidity sensors.

1. Introduction

In the last years, humidity sensors have attracted attention to researchers since humidity is an important environmental parameter in preservation, storage and transport operations. Besides, humidity is important in agricultural, food and medical areas since the product quality is affected by this parameter [1,2].

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Many porous polymeric materials and polymetallic oxides have been investigated as humidity sensors due to their applicability in diverse fields such as health care, industry process, environmental monitoring etc. [3,4].

J. Hong and co. [5] used polyacrylamide-based hydrogels for obtaining coated Fe_3O_4 nanoparticles. In recent years, hydrogels have been used as possible templates for obtaining nanometer-size oxidic compounds displaying highly organized structure [6]. Hydrogels are porous polymeric materials with a three-dimensional structure and high hypersorption capacity. These properties make hydrogels able to use as template agent for obtaining nanometer-size oxidic compounds. R. Ma and co. [7] applied the polyacrylamide gel method for the synthesis of $NiFe_2O_4$ substituted with Zn, while H. Zhao and co. [8] applied the same method for the synthesis of $NiFe_2O_4$ by the microwave technique. The three-dimensional polymer matrix, such as, for example, that of the polyacrylamide-based hydrogels, can be considered as a nanoreactor for the synthesis of oxide compounds [9]. These template compounds may be used as humidity sensors, catalysts, or targeted delivers of the active (antibiotic, antifungal, antitumoral) principles [10,11].

The present paper discusses the synthesis, structural characterization, electrical and magnetic properties of $NiFe_2O_4$ with spinel structure, obtained using polyacrylamide hydrogels as template agents. In this work, the polyacrylamide-based hydrogel was first time used as a matrix for the growth of $NiFe_2O_4$ crystallites. The as-obtained Ni ferrite with highly organized structure was tested for application as humidity sensor.

2. Materials and method

2.1. Synthesis

All chemicals employed in the syntheses are of analytical grade (Aldrich reagents) and were used without further purification.

2.1.1. Synthesis of the hydrogels used as template agents

Hydrogels were synthesized by an original simultaneous polymerization-crosslinking method using a monofunctional crosslinking agent. Synthesis was performed using acrylamide (C_3H_5ON) (Am) as a monomer, ammonium persulfate ($(NH_4)_2S_2O_8$) (I) as an initiator and a 37% formaldehyde solution (CH_2O) (FA) as a crosslinking agent [12]. The crosslinking agent itself, N,N′-methylene-bisacrylamide, is formed during the synthesis of the macromolecular compound.

2.1.2. Synthesis of the ferrites

Ferrite is synthesized by the sol–gel autocombustion method using citric acid ($C_8H_{12}O_7$) (CA) as a chelating/fuel agent. This method ensures stoichiometric control of the final product and allows obtaining of nanometer-size particles. Nickel nitrate hexahydrate, $Ni(NO_3)_2{\cdot}6H_2O$, and ferric nitrate nonahydrate, $Fe(NO_3)_3{\cdot}9H_2O$ were used as cation sources. The atomic ratio of metal cations Ni^{2+}: Fe^{3+} = 1:2 and molar ratio ferrite:chelating/fuel agent was 1:3 [13].

Two samples were synthesized. The former one, coded P_1, was obtained by mixing a solution containing $Ni(NO_3)_2$, $Fe(NO_3)_3$ and CA at the stoichiometric ratio indicated above, with a solution containing acrylamide (Am), formaldehyde (FA) and ammonium persulfate (I). The employed quantities correspond to a ferrite:hydrogel = 1:2 (w/w) ratio. The as-obtained mixture was transformed into a brown-colored gel, by heating in a water bath at 75 °C, under vigorous stirring. The as-obtained gel was subjected to drying in a sand bath. After combustion, the sample was thermally treated at 500 °C, 700 °C, 900 °C (Fig. 1(A)).

The latter sample, coded P_2, was obtained by immersing 0.5 g dried hydrogel with an optimal swelling degree into a solution containing $Ni(NO_3)_2$, $Fe(NO_3)_3$ and CA at the stoichiometric ratio indicated above. The solution was adjusted to pH = 7 with ammonia. The ferrite:hydrogel ratio was 1:2 (w/w). The hydrogel swollen in the solution of metal cations – CA was heated in a water bath at 75 °C. The hydrogel containing a brown gel of metal cations inside the meshes of the three-dimensional network was further subjected to drying in a sand bath. After autocombustion, the sample was thermally treated at 500 °C, 700 °C, 900 °C (Fig. 1(B)).

Post-combustion treatments were necessary for both samples, P_1 and P_2, for removal of the secondary phases and obtaining of highly organized high purity ferrite of spinel type.

2.2. Characterization methods

2.2.1. Characterization methods of the hydrogels used as template agents

IR spectroscopy was used for monitoring of crosslinking bond formation. IR spectra were registered in the mid infrared range (4000–1000 cm^{-1}) using a DIGILAB FTS 2000 and the potassium bromide pellets technique.

Morphological characterization of hydrogels was performed using scanning electron (SEM) and transmission electron microscopy (TEM) techniques. Scanning electron micrographs were registered with a Quanta 200 microscope equipped with an EDAX elemental analysis system. Transmission electron micrographs were registered using a TESLA BS 531 A microscope. Samples preparation was performed by a complex method described in detail elsewhere [14].

Thermal behavior of polyacrylamide hydrogels was analyzed using a Mettler Toledo derivatograph. Thermogravimetric curves were obtained under the following conditions: samples weight around 3 mg, temperature range: 25–600 °C, heating rate: 10 °C/min. Differential scanning calorimetry (DSC) curves were obtained using samples weight around 3 mg, in the temperature range 0 °C–200 °C, on applying a 3 stage heating: the first stage – heating from 0 °C to 200 °C at a heating rate of 10 °C/min, the second stage – cooling from 200 °C to 0 °C with a rate of −10 °C/min and the third stage – heating from 0 °C to 200 °C with a rate of 10 °C/min.

The swelling behavior of hydrogels was studied on an original installation based on the same principles as the Dogatkin device. Measurements were performed at ambient temperature.

The swelling degree, α, was calculated using relationship:

$$\alpha = (W_w/W_p)\cdot 100$$

where: W_w – mass of absorbed water; W_p – mass of dried polymer.

The swelling rate constant, k, was evaluated from the semi-logarithmic representations of the swelling degree *versus* time, using MathCad 7 Professional program.

$$\ln\frac{\alpha_{max}-\alpha_t}{\alpha_{max}} = kt$$

2.2.2. Characterization methods of the ferrites

IR spectroscopy was applied for tracking the disappearance of the organic and nitrogen phases, and also for monitoring spinel structure formation. IR spectra were registered at ambient temperature in the mid infrared range (4000–300 cm^{-1}), using a Bruker TENSORTM 27-type spectrophotometer with Fourier transform (FTIR) and an attenuated total reflection (ATR) cell, at a resolution of 2 cm^{-1}.

The spinel-type structure and single phase formation of the as-