



Synthesis and functional properties of the $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ferrites

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ABSTRACT

Nanocrystalline $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x=0; 0.17; 0.34; 0.5$) ferrite powders were successfully synthesized using the sol–gel combustion method, by using nitrates as cations source and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) as combustion/chelating agent. The reaction advancement was observed by means of IR absorption spectroscopy, by monitoring two characteristic bands for the spinel compounds at about 600 cm^{-1} and 400 cm^{-1} , respectively. The as-synthesized powders were characterized by IR spectroscopy, X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The magnetic study shows that the saturation magnetization decreases with increasing the Mn addition, as result of the particle size reduction. The dielectric properties were measured as a function of frequency in the range of 10 Hz to 1 MHz. The real part of permittivity has values of ~ 88 at 1 kHz and ~ 7 at 1 Hz for $x=0$. An increasing dielectric permittivity with increasing the amount of Mn is observed. For all the investigated compositions, both the real and imaginary parts of permittivity decrease with frequency.

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1. Introduction

Due to their magnetic and dielectric properties, the nanocrystalline spinels ferrites with the general formula MFe_2O_4 ($\text{M}=\text{Mn}, \text{Ni}$) are important materials with multiple applications, such as: magnetic recording media and magnetic fluids for storage and/or retrieval of information, catalysts, magnetically guided drug delivery, magnetic resonance imaging (MRI) enhancement, microwave absorbers, sensors and pigments [1].

Large-scale applications of ferrites with small particles have promoted the development of various chemical methods for the preparation of the nanosized spinel ferrites [2–9] as alternatives to the solid state reaction methods, which result in large agglomerated particles, with limited degree of homogeneity, and low sinterability [10]. The studies have shown that the synthesis protocol determines the structural characteristics of materials, which in turn, influence their magnetic and electrical properties.

Lately, a high importance is given by synthesis methods with low toxicity, or by economical methods in terms of energy consumption, enable to produce fine, nano-sized, single-crystalline and single phase powders. Spinel ferrites are generally synthesized using the standard ceramic technique [10] which implies high tem-

peratures and leads to particles with small specific surface. In order to obtain ferrites with larger specific surface and higher degree of homogeneity, alternative methods like: co-precipitation [2,11], polymeric gel [3], hydrothermal [4], micro-emulsion [5], heterogeneous precipitation [6,12], sono-chemistry [7], combustion [8], sol–gel [9] methods, etc. were used.

In particular, the synthesis by combustion reaction technique has been shown to have great potential in the preparation of ferrites [13] and involves an exothermic and self-sustaining chemical reaction between the desired metal salts and a suitable organic fuel. The sol–gel self-combustion technique is a method that combines the chemical sol–gel process with the combustion process. Citric acid is often used as chelating agent and the obtained nitrate–citrate gel exhibits self-propagation combustion if ignited in air. This process was successfully used in producing a large variety of ferrites with homogeneous nanosized particles. It has also the advantages of autocombustion, use of inexpensive precursors, simple equipment and low temperatures for synthesis [14–16].

The MnFe_2O_4 has a spinel crystal structure (space group $\text{Fd}3\text{m}$), in which O^{2-} cations form a compact cubic structure, with Mn^{2+} and Fe^{3+} cations placed in two types of interstitial or crystallographic positions. These positions display a tetrahedral (denoted as A) and octahedral coordination (denoted as B) with respect with oxygen, and in this way their local symmetry is different. In the normal spinel structure, the bivalent ions (Mn^{2+} in MnFe_2O_4), occupy only the tetrahedral positions, while the trivalent ions (Fe^{3+} in MnFe_2O_4) populate the octahedral positions. In the inverse spinel

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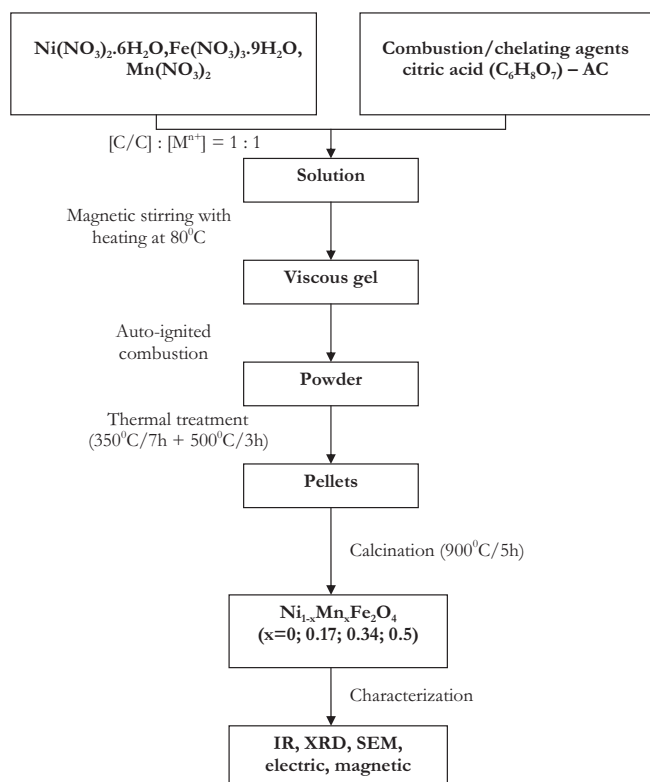


Fig. 1. The synthesis protocol flowchart for the preparation of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ with various compositions: $x = 0; 0.17; 0.34; 0.5$.

structure, the bivalent ions occupy half of the B positions, and the trivalent ions are placed in the rest of the B positions and in all A positions. In the MnFe_2O_4 ferrites obtained at high temperatures ($>900^\circ\text{C}$), 20% of the Mn^{2+} ions are migrating from A to B positions resulting in a ferrite with mixed spinel structure [17]. Using neutron diffraction, Ghazanfar et al. [18] measured the distribution of manganese ions among the tetrahedral and octahedral sites in $\text{Mn}_{1-x}\text{Fe}_{2-x}\text{O}_4$, and they found that 30% of the octahedral sites are occupied by Mn^{3+} with the distribution $\text{Mn}_{0.9}^{2+}\text{Fe}_{0.1}^{3+}[\text{Mn}_{0.6}^{3+}\text{Fe}_{1.6}^{3+}\text{Fe}_{0.1}^{2+}]\text{O}_4^{2-}$. This class forms the soft ferrites group, which is characterized by high magnetic permeability and low hysteresis losses [19].

Nickel ferrites NiFe_2O_4 belong to the category of the most important ferrites with inverse spinel structure with ferrimagnetic properties. For these ferrites the Fe^{3+} ions are placed on the tetrahedral sites and the Ni^{2+} ions are placed in octahedral sites [20].

The aim of this work was to study the structure, magnetic and dielectric properties of the nickel ferrites substituted by manganese: $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ with compositions $x = 0; 0.17; 0.34; 0.5$ obtained by using the self-combustion method.

2. Sample preparation and experimental details

The $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0; 0.17; 0.34; 0.5$) ferrite powders were prepared using the combustion reaction by using as cations source nitrates: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2$ obtained in situ from metallic Mn and HNO_3 (20%), and citric acid $\text{C}_6\text{H}_8\text{O}_7$ as combustion agent. The citric acid is a low cost adequate ecological fuel and its decomposition generates high temperatures during the burning process, leading to the obtaining of the complete ferrite phase in external conditions.

The homogeneous solutions of nitrates were jellified in the presence of the combustion/chelating agents and the obtained gel was then thermally treated according to the synthesis protocol described in Fig. 1.

In order to monitor the spinel structure formation, FTIR spectroscopy was employed (with a Jasco 660 plus FTIR spectrophotometer using the KBr pellet).

To determine the changes which occur during the heating process the TG-EGA-FTIR apparatus consisted of a Diamond TG/DTA (Perkin Elmer) thermo-balance, a Spectrum 100 (Perkin Elmer) FTIR spectrophotometer, a TG-FTIR (Perkin Elmer)

gas transfer accessory (1.6 m stainless steel 1.5 mm tube heated at 220°C) and a heated gas cell of 100 mm length with KBr windows (heated at 150°C). The Spectrum TimeBase (Perkin Elmer) software records every 15 s a single spectrum within the $700\text{--}4000\text{ cm}^{-1}$, at a resolution of 4 cm^{-1} . The analysis was run with 10 mg sample placed into a platinum crucible, under dynamic dry air atmosphere (100 mL min^{-1}) at a heating rate of 10 K min^{-1} , within the $30\text{--}900^\circ\text{C}$ temperature range.

X-ray diffraction measurements were used to investigate the phase purity of the spinel phase of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0; 0.17; 0.34; 0.5$) by using a Seifert diffractometer (type XRD 3003 PTS) with a CuK_α radiation ($\lambda = 1.5405\text{ \AA}$). A VEGA TESCAN scanning electron microscope coupled with EDX was used to analyze the morphology and agglomeration tendency of the synthesized powders, as well as the microstructure of the resulted ceramics and to check the local stoichiometry of the samples. The permeability vs. frequency measurements in the frequency domain (1 MHz–3 GHz) at room temperature were realized by using an E4991A RF Impedance/Material Analyzer on toroidal ceramic samples with sizes of $\sim 1.4\text{ mm} \times 4\text{ mm} \times 12\text{ mm}$ (thickness, inner diameter and outer diameter). In order to determine the $M(H)$ hysteresis loops in the range 0–1.4T (14,000 Oe), a Micro-Mag™ magnetometer VSM (Vibrating Sample Magnetometer) model 3900 system from Princeton Measurements Co. was used. The dielectric properties vs. frequency in the 10 Hz–1 MHz frequency domain at room temperature were determined by performing complex impedance measurements with an Impedance/Gain-Phase analyser SOLARTRON 1260A. Ceramic samples were cut into plane-parallel geometry and placed inside a dielectric holder containing a guard ring, needed to reduce non-homogenous field edge. The real and imaginary part of the impedance at different frequencies were determined and then the permittivity vs. frequency dependence.

3. Results and discussion

3.1. Thermal analysis

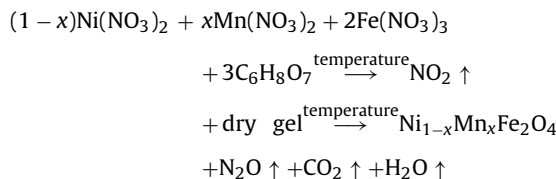
In order to determine the appropriate heat treatment adequate for obtaining the spinel ferrites, a thermal analysis was firstly performed.

In the first stage of the gel formation, it was observed an emission of a brown gas, NO_2 . After the jellifying phase, the obtained product was dried and thermally analyzed.

The thermal decomposition of the $x = 0$ ferrite (Fig. 2a) reveals that the process for obtaining the spinel ferrites is ending at about 400°C heating after this temperature has no effect for the weight of the sample.

The components of released gaseous mixtures have been monitored and identified mostly on basis of their FTIR reference gas spectrum available on world wide web in the public spectrum library of NIST. In the FTIR spectra recorded at 189°C (Fig. 2b), the presence of H_2O , CO_2 [21] and N_2O [22] is observed. The evolution of the absorption at characteristic wavenumber for these gases with the temperature is presented in Fig. 2c.

In agreement with the obtained results, for the ferrite formation, are proposed the following reaction sequences:



Three steps are present in the TG-EGA-FTIR analysis (Fig. 2a): the sample drying (below 150°C), a decomposition of the nitrates and burning of the organic materials. Exothermic effect recorded on heat flow curve at the peak around 290°C is about $\Delta H \sim -5000\text{ J/g}$.

As shown in Fig. 2(a, d–f) the thermal decomposition on synthesis of ferrites powders series is also divided into three steps. The first is a weight loss upon drying the sample (below 150°C), and the moisture is released at this stage (10–12% low); this thermal effect is endothermic. The second stage is ranging between 150 and 262°C (weight loss is about 21–25%). In this stage, on the DTG curves, the shape of the curve is depending on the composition: for

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