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SYNTHESIS OF POLYMETALLIC OXIDES WITH HIGH ORGANIZED STRUCTURE

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Abstract: The synthesis and characterization of high organized and nanostructured polymetallic oxides were studied. The samples were synthesized by sol-gel autocombustion method, using glycine as chelating/fuel agent and polyacrylamide-based hydrogel as template agent. This polymer has a porous microstructure with well-individualized and regularly-dispersed pores. The as-obtained samples were characterized by IR spectroscopy, XRD, SEM. The magnetic properties were studied. As-synthesized polymetallic oxides have the morphological structure given by the three-dimensional lattice structure of hydrogel used as template agent.

Keywords: Polymetallic oxides; Spinel structure; Template; Polyacrylamide hydrogel; X-ray diffraction.

Introduction

Polymetallic oxides of spinel type are the compounds with the general formula AB_2O_4, where A is a divalent metal (i.e. Ni^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}) and B is a trivalent metal (i.e. Fe^{3+}, Mn^{3+}). In the spinel-type

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structure, the metal cations can occupy tetrahedral (A) and/or octahedral sites [B] inside a compact pseudo-cubic lattice packing.[1,2] These compounds are characterized by chemical and thermal stability that makes possible the use of polymetallic oxides in various applications, such as catalysts, gas sensors, data storage devices and/or recovery of information, microwave devices, pigments, anodes for Li-ion batteries, in biomedical applications such as contrast agents in diagnosis and magnetic-guided devices for targeted and pulsed release of active principles, etc.[3,4]

Nickel ferrite is the most important polymetallic oxides used as soft magnet due to its magnetic properties, low conductivity, reduced current losses and high chemical stability. These polymetallic oxides can be obtained by various synthesis methods such as sol-gel classical and modified method, co-precipitation, hydrothermal, host template.[5,6] The sol-gel method has several advantages, allowing stoichiometric control, nanometer-size particles synthesis, high specific surface area and selectivity. Also, this method provides a high degree of particles homogeneity and results reproducibility.

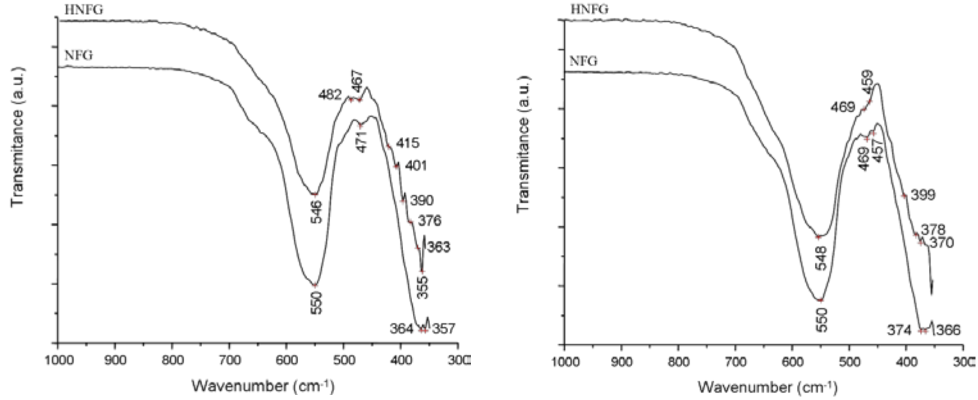
In the present paper, the comparative results obtained for $NiFe_2O_4$ samples are being presented. These samples were synthesized by sol-gel autocombustion method, using glycine as chelating/fuel agent and polyacrylamide-based hydrogel as template agent. Glycine as a chelating/fuel was chosen because it was found that glycine leads to polymetallic oxides with high purity at relatively low temperature of thermal treatment.[7] On the other hand, glycine provides high temperature necessary for the reactions that occur during the synthesis process and energy needed to create the nucleation sites.

In specialized literature it is noted that polyacrylamide-based hydrogels can be used for obtaining coated Fe_3O_4 nanoparticles.[8] Also, hydrogels can be used as possible template agents for obtaining nanometer-size polymetallic oxides displaying a highly organized structure.[9]

Results and discussion

IR spectra. Because the characteristic absorption bands for organic phases were not identified, IR spectra for as-obtained samples thermally treated at 500 and 900°C were showed in a 1000 – 300 cm^{-1} wavenumber range (Figure 1).

After the IR spectra analysis, the presence of absorption bands characteristic to the M – O bonds for all studied samples can be seen. Thus, for samples thermally treated at 500°C, the broad absorption bands from 550 cm^{-1} (NFG) and 546 cm^{-1} (HNFG) can be assigned to the lattice vibrations corresponding to the Fe^{3+} – O^{2-} links from tetrahedral sites (A). Absorption bands identified in 400 – 350 cm^{-1} wavenumber range can be assigned to the lattice vibrations corresponding to the Fe^{3+} – O^{2-} links from octahedral sites [B]. These differences between wavenumbers corresponding to the absorption bands from tetrahedral and octahedral sites are due to the different distance between Fe^{3+} and O^{2-} ions from specified sites.[7]



a b

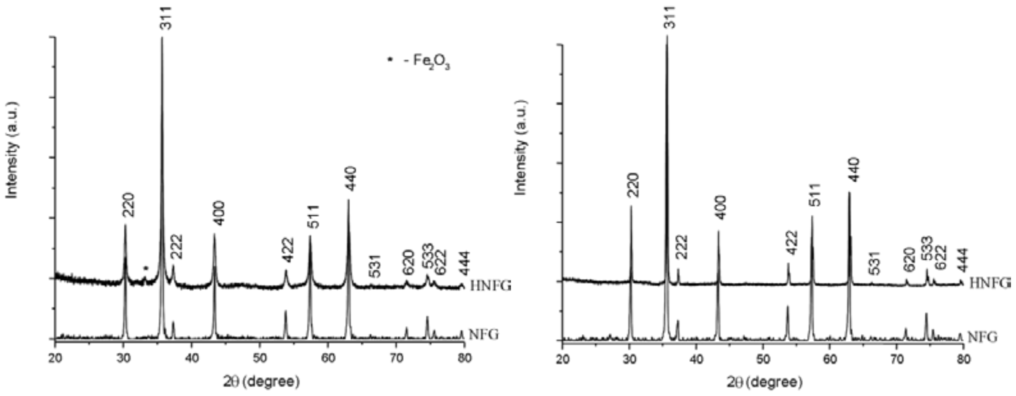
Figure 1. IR spectra for samples thermally treated at 500 (a) and 900°C (b).

The low amplitude absorption bands from 480 – 460 cm^{-1} wavenumber range can be assigned to asymmetrical lattice vibrations corresponding Ni^{2+} – O^{2-} bonds.

The same absorption bands, slightly displaced to left or right, can be observed, as well, for samples thermally treated at 900°C. These displacements can be attributed to the ordering of metal cations in spinel lattice that occurs with increasing thermal treatment temperature. On the other hand, the displacement of absorption bands for HNFG sample can be attributed to template agent that obliges metal cations to distribute in spinel lattice in accordance to the template agent structure. This structure of template agent constitutes the matrix for crystal growth of polymetallic oxides.[9]

X-ray diffraction. The diffractograms registered for samples thermally treated at 500 and 900°C are shown in Figure 2.

From diffractograms analysis can be seen that for NFG sample pure phase at thermal treatment temperature of 500°C is being obtained. The as-obtained pure phase at relatively low temperature is due to the extremely violent combustion that leads to a high release among gases with favouring of crystallites growth and spinel phase formation. For HNFG sample thermally treated at 500°C, besides to the characteristic diffraction peaks of the spinel structure, also appears a diffraction maxim assigned to the secondary phase identified as α-Fe_2O_3 also appears.



a b

Figure 2. X-ray diffraction patterns for samples thermally treated at 500 (a) and 900°C (b).

For samples thermally treated at 900°C it can be seen that polymetallic oxides with high purity were obtained.

All diffraction peaks were identified and indexed in according with the referred database of the International Centre for Diffraction Data (ICDD)[10] and are characteristic to the spinel cubic structure, belonging to the Fd3m space group with 8 $NiFe_2O_4$ units per cell unit.[1] The characteristic diffraction peak of spinel cubic structure belonging to (311) Miller plane was identified at $2\theta \approx 35.5^o$.

From XRD results, crystallographic data were obtained. Thus, crystallite size, D_c, was calculated using Scherrer's relationship:[11]

$$D_c = \frac{0.94\lambda}{\beta_{1/2}\cos\theta}$$

where λ = 1.5405 Å; $\beta_{1/2}$ denotes a peak full width at half-maximum intensity (radians); the lattice parameter, a, was determined using the following relationship:[12]

$$a = d_{hkl}\sqrt{\left(h^2 + k^2 + l^2\right)}$$

where d_{hkl} is the distance between the adjacent Miller planes (h k l), calculated with Bragg relation:

$$d_{hkl} = n\lambda/2\sin\theta$$

with n = 1 for the cubic system.

To determine crystallite sizes, the 3 most intense diffraction lines (311, 511 and 440) were used.

From XRD data, density ρ_x of the samples was also calculated, using the relationship:

$$\rho_x = \frac{ZM}{Na^3}$$

where Z is number of molecules per cell unit (for polymetalic oxides with cubic spinel structure, Z = 8); M – molecular weight of the sample (g/mole); N – Avogadro's number ($6.023 \cdot 10^{23}$ atom/mole); a – lattice parameter (cm).[13]

The specific surface area of the samples, S, was calculated using relationship:

$$S = \frac{6000}{D_c \cdot \rho_x} \cdot 100$$

where D_c – crystallite size (nm) and ρ_x – density calculated from XRD data (g/cm^3). The XRD results are presented in Table 1.

Table1. Crystallographic data for as-obtained polymetallic oxides.

Sample / Parameter	NFG		HNFG	
	500°C	900°C	500°C	900°C
D_c (nm)	51	47	39	66
a (Å)	8.34	8.36	8.34	8.34
V (Å^3)	580.093	584.696	580.093	580.093
ρ_{DRX} (g/cm^3)	5.366	6.823	8.288	4.897
S (m^2/g)	2.484	1.871	1.856	1.856

The data from Table 1 show that the obtained lattice parameter value (8.34 Å) is in accordance to the data reported in the literature.[14] Also, it can be seen that the crystallite sizes are influenced both the thermal treatment applied and using the template agent. Increase of thermal treatment temperature leads to crystallite agglomeration that determines an increase of the sizes thereof. On the other hand, the structure of three-dimensional lattice for the template agent leads to an organizing of polymetallic oxides crystallites that can determine a crystallites agglomeration inside the meshes of the three-dimensional lattice.

The interionic distances were calculated from XRD data, with the following relations:[1,14]

Cation–anion distances at A-site, d_{AL}	$d_{AL} = a\sqrt{3}(u - 0{,}25)$
Cation–anion distances at B-site, d_{BL}	$d_{BL} = a\left(3u^2 - \frac{11}{4}u + \frac{43}{64}\right)^{1/2}$
Distance of closest anion–anion approach, tetrahedral edge, d_{AE}	$d_{AE} = a\sqrt{2}(2u - 0{,}5)$
Shared octahedral edges, d_{BE}	$d_{BE} = a\sqrt{2}(1 - 2u)$
Unshared octahedral edges, d_{BEU}	$d_{BEU} = a\left(4u^2 - 3u + \frac{11}{16}\right)^{1/2}$
Radius of the ions at tetrahedral site, r_{tetr}	$r_{tetr} = a\sqrt{3}(u - 0{,}25) - R_O$
Radius of the ions at octahedral site, r_{oct}	$r_{oct} = a\left(\frac{5}{8} - u\right) - R_O$

where a – lattice parameter obtained from XRD (Å); u – oxygen parameter (0.375 Å); R_o – radius of oxygen ion (1.32 Å).

The as-obtained results are presented in Table 2.

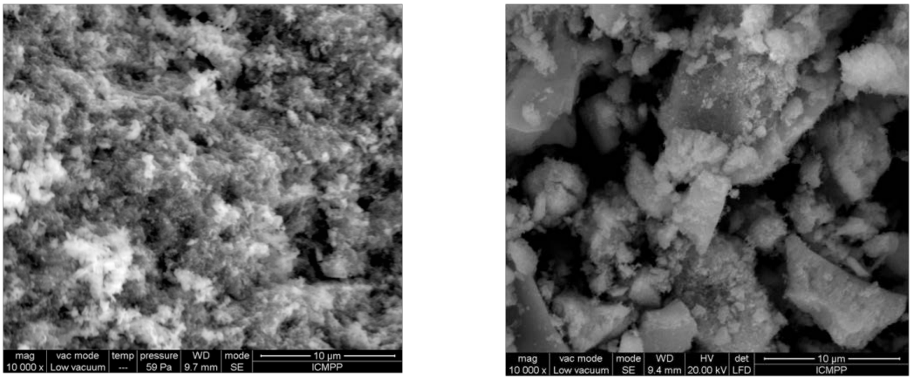
Table 2. Interionic distances for as-obtained polymetallic oxides.

Sample / Parameter	NFG		HNFG	
	500°C	900°C	500°C	900°C
a (Å)	8.34	8.36	8.34	8.34
d_{AL}	1.805	1.810	1.805	1.805
d_{BL}	2.085	2.090	2.085	2.085
d_{AE}	2.948	2.956	2.948	2.948
d_{BE}	2.948	2.956	2.948	2.948
d_{BEU}	2.948	2.956	2.948	2.948
r_{tetr}	0.485	0.490	0.485	0.485
r_{oct}	0.765	0.770	0.765	0.765

Data from Table 2 shows a correlation between the lattice parameter and the ionic radius, and the mode of metal cation distribution in the spinel crystal lattice, respectively. The difference between tetrahedral and octahedral ionic radius can be attributed to octahedral sites that significantly influence the cation distribution in crystal lattice.

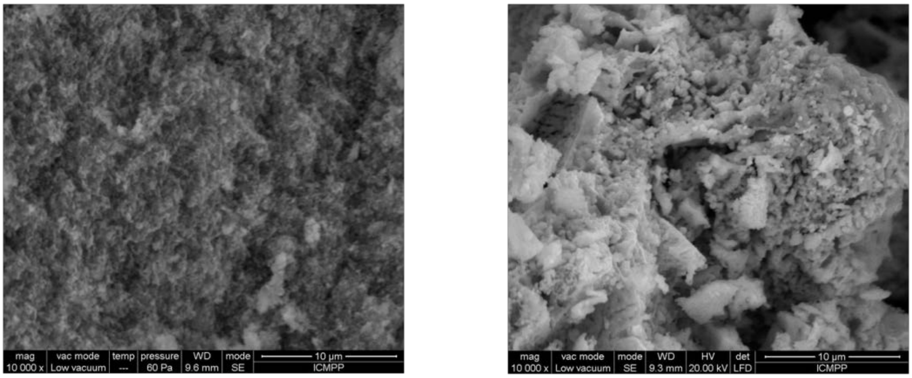
The as-obtained XRD data make possible establishing the cation distribution on tetrahedral and octahedral sites. For the as-obtained polymetalic oxides, it was found that have an inverse spinel-type structure and the following general formula was proposed for the cation distribution: $\left(Fe^{3+}\right)^{[4]}\left[Ni^{2+}Fe^{3+}\right]^{[6]}O_4$. This formula indicates that the Fe^{3+} ions have migrated from the octahedral [B] to the tetrahedral (A) sites. Consequentially, Fe^{3+} can occupy both tetrahedral and octahedral sites in spinel lattice structure while Ni^{2+} ions especially preferred the octahedral sites.[16]

Electronic microscopy. SEM micrographs for the as-obtained samples thermally treated at 500 and 900°C are showed in Figures 3 and 4.



NFG HNFG

Figure 3. SEM micrographs for samples thermally treated at 500°C.



NFG HNFG

Figure 4. SEM micrographs for samples thermally treated at 900°C.

For the NFG sample, the SEM micrographs show a spongy porous microstructure with agglomerate pores. For HNFG sample, the SEM micrographs highlight an organized structure determined by the template agent used. Thus, the HNFG crystallites growth on porous structure of hydrogel occupies both the meshes of the three-dimensional structure and the walls that form the three-dimensional lattice of hydrogel.

Magnetic properties. The magnetization registered as function of external magnetic field applied was recorded at room temperature (25°C), for a maximum applied field of 6 kOe for samples thermally treated at 900°C. The as-obtained results are showed in Figure 5.

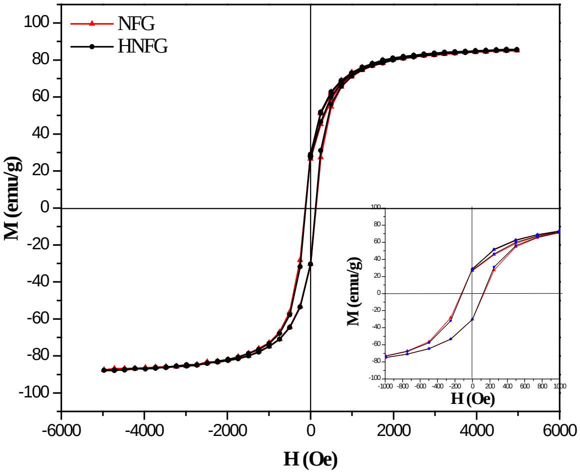


Figure 5. Room temperature hysteresis behavior for samples thermally treated at 900°C.

It can be seen that both analysed samples show a narrow hysteresis cycle, indicating a characteristic behavior of soft magnetic materials. Also, it can be seen that hysteresis curves' shape is characteristic to a ferromagnetic behaviour for both samples, which is in accordance to the data reported in the literature.[14] Hysteresis curves' shape is influenced by the synthesis procedures, cation distribution, crystallite sizes and chemical composition.

The data from the graphs (Figure 5) shows an increase in magnetization with an increase of the applied field. The saturation and remanent magnetization are identical for both samples analysed (Table 3).

On the basis of magnetic behaviour of the as-obtained polymetallic oxides can be concluded that magnetism in as-obtained polymetallic oxides is due to the indirect exchange interactions between the tetrahedral and octahedral sublattice.

Table 3. Magnetic parameter measured at room temperature for as-obtained samples thermally treated at 900°C.

Parameter Sample	M_s	H_c	M_r	M_r/M_s
NFG	85	133	28	0.33
HNFG	85	120	28	0.33

Experimental

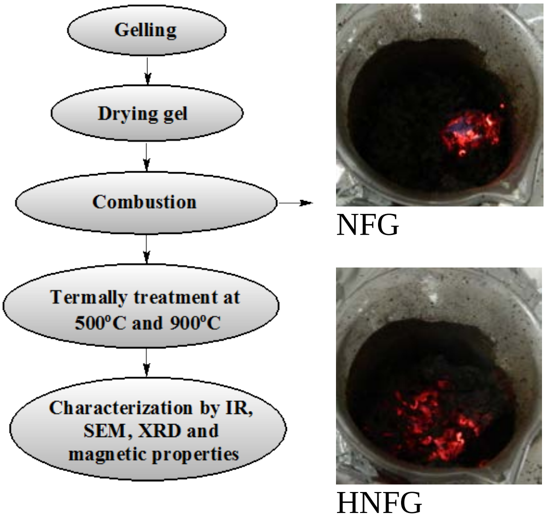
Polymetallic oxides of spinel type with formula $NiFe_2O_4$ were synthesized by sol-gel autocombustion procedure using glycine as chelating/fuel agent and polyacrylamide-based hydrogel as template agent. Ferric nitrate nonahydrate,$Fe(NO_3)_3·9\ H_2O$ and nickel nitrate hexahydrate, $Ni(NO_3)_2·6H_2O$ were used as cations sources. Atomic ratio of metal cations is Ni^{2+} : Fe^{3+}= 1:2 and molar ratio polymetallic oxide: glycine was 1:3. Two samples were synthesized. The former one, coded NFG, was obtained by mixing $Fe(NO_3)_3$, $Ni(NO_3)_2$, glycine and distilled water at the stoichiometric ratio indicated above. The as-obtained solution was transformed into a brown-colored gel, by heating in a water bath at 75°C.

The latter sample, coded HNFG, was obtained by mixing a solution containing $Fe(NO_3)_3$, $Ni(NO_3)_2$ and glycine at the stoichiometric ratio indicated above, with a solution containing acrylamide (Aam) (C_3H_5ON), formaldehyde (FA) (CH_2O) and ammonium persulfate (I) ($(NH_4)_2S_2O_8$). Details about the synthesis and characterization of polyacrylamide-based hydrogels were published elsewhere.[17,18] The used solution quantities correspond to polymetallic oxides: 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.

After drying and combustion, both samples were thermally treated at 500 and 900°C. The synthesis protocol is showed in Figure 6.

The synthesized samples were structural and morphological characterized by IR spectroscopy, XRD and SEM. 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 room 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}.

XRD technique was used to confirm spinel-type structure and single phase formation of the as-obtained samples. The XRD patterns were registered using a Shimadzu LabX 6000 diffractometer equipped with a graphite monochromator, with Cu K_α ($\lambda = 0.15405$ Å) radiation, for 2θ ranging between 20 and 80°, at a scanning rate of 0.02°/s.



NFG – polymetallic oxide with glycine as chelating/fuel agent, without template agent

HNFG – polymetallic oxide with glycine as chelating/fuel agent, with polyacrylamide hydrogel as template agent

Figure 6. Synthesis protocol used for obtaining of polymetallic oxides.

SEM was used for morphological characterization of as-obtained polymetallic oxides, and also to confirm high organized structure. Electron micrographs were registered with a Quanta 200 microscope and an integrated EDAX system.

For as-obtained polymetallic oxides, the magnetic permeability was investigated. The measurements were recorded at room temperature using a Vibrating Sample Magnetometer System (VSM 3900 Princeton).

Conclusions

Nanostructured polymetallic oxides of spinel type were obtained by sol-gel autocombustion method.

Using the polyacrylamide-based hydrogel as template agent leads to polymetallic oxides with a high organized structure and high purity.

The as-obtained polymetalic oxides have an inverse spinel-type structure with the following general formula for cation distribution: $\left(Fe^{3+}\right)^{[4]}\left[Ni^{2+}Fe^{3+}\right]^{[6]}O_4$.

SEM analyses highlight an organized structure determined by the polyacrylamide-based hydrogel used as template agent.

Magnetism for as-obtained polymetallic oxides is due to the indirect exchange interactions between the tetrahedral and octahedral sublattice.

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