











UNIVERSITATEA ALEXANDRU IOAN CUZA IASI

ALEXANDRU IOAN CUZA UNIVERSITY OF IAȘI CHEMISTRY FACULTY

SYNTHESIS AND CHARATERIZATION OF Zn BASED OXIDES WITH SPINEL-TYPE STRUCTURE

PhD DISSERTATION

Scientific coordinator, Prof.Dr.Mircea Nicolae PALAMARU

> PhD student, Chem.Tamara CORMAN married SLĂTINEANU

> > 2012

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CLAIMS AND OBJECTIVES

Nanocrystalline ferrites with spinel structure represents a class of oxide compounds that are in the attention of researchers because of their magnetic and electrical extremely versatile properties, with applications to efficient information storage systems, magnetic cores, magnetic circuits, electromagnets, ferro-fluid, microwave absorbers, radar absorbent materials, catalysts, medical imaging contrast agents etc.

Rich information provided by crystallochemistry about oxide compounds with spinel structure leads to excellent opportunities for understanding and optimizing the electrical and magnetic properties of nanoparticles through chemical processing.

Previous studies in the literature have shown that magnetic and electrical properties of these types of oxide nanoparticles are profoundly influenced by the chemical composition and structural characteristics: crystallinity, purity, crystallite size, lattice defects, as a consequence of the synthesis method.

Thus, a growing importance is given to synthesis methods targeting cheap working conditions, economic energy, relatively low toxicity which ensures nanocrystalline monophase powders.

In particular, Zn nanoferrites draw particular attention to research new generations of materials used in electronics, telecommunications, catalysis, medicine, agriculture, environmental protection and that is why our attention has been directed mainly towards them.

It is known that, by substitution of divalent cation (Zn) and trivalent cation (Fe), can be improved the properties of unsubstituted $ZnFe_2O_4$ nanoferrite. Therefore, we turned to the synthesis, characterization and study of $Zn_{1-x}M_xFe_2O_4$ nanoferrite type properties, where M was chosen: a divalent nonmagnetic cation from alkaline earth metals group (Mg) and two divalent cations with magnetic properties of transition metal group (Ni and Co).

In the case of $Zn_{1-x}M_xFe_2O_4$ series we have chosen alumina as support for optimizing catalytic activity for decomposition of hydrogen peroxide reaction test.

For the composition with optimal magnetic properties, i.e., $Zn_{0,2}Ni_{0,8}Fe_2O_4$ we have chosen the substitution of iron cations with Dy^{3+} (in the literature, Dysprosium is considered to be difficult to place in the spinel structure due to a high ionic radius) to improve magnetic, dielectric properties and catalytic activity.

Given these considerations we aimed the following objectives:

• Synthesis by sol-gel modified of pure nanocrystalline particles of zinc based oxides with spinel structure.

• Study of the influence of zinc ion various divalent cations on the properties of nanocrystalline zinc ferrite.

• Study of the influence iron substitution with small quantity of Dysprosium on nanocrystalline Zn-Ni ferrite properties.

• Study of the structure-property relationships by proposing a cation distribution for the spinel-type lattice of as-obtained ferrites.

• Improvement of physicochemical properties of zinc ferrite by choosing optimal synthesis protocol and by changing the chemical composition.

• Microstructural and morphological study of the as-obtained compounds.

• Materials synthesis with industrial applications in various fields such as electronics, electromagnetic record playback devices, sensors, transformer cores, contrast agents in medical imaging etc.

• Investigation of catalytic activity of some spinel-type ferrites based on zinc obtained by sol-gel autocombustion method.

II. FINDINGS

II.1. Zn ferrite: synthesis by sol-gel autocombustion method and characterization

1. Introduction

Previous studies [Costa, 2010; Hu, 2011; Hwang, 2004] have made multiple arguments on the importance of choosing the type of combustion agent to provide certain dimensions of ferrite nanoparticles, pure spinel phase formation during sintering temperature synthesis as well as optimal microstructural characteristics and physicochemical properties.

This chapter shows the study of fuel agents influence in terms of thermal effects induced during the formation and stabilization of the spinel structure, structural characteristics, textural and morphological zinc ferrite nanocrystalline powders and magnetic and dielectric properties.

2. Materials and methods

 $ZnFe_2O_4$ ferrite single phase (denoted ZF) powder was obtained by sol-gel autocombustion method, using as precursors nitrates $Zn^{2+},\ Fe^{3+}$ and different fuel agents: citric acid, egg white, tartaric acid, glycine, glucose and urea.

General reaction of zinc ferrite synthesis can be represented as follows:

$$Zn(NO_3)_2 + 2Fe(NO_3)_3 + fuel \rightarrow ZnFe_2O_4 + volatile$$

Table II.1.1 and Fig.I.7.2 presents a summary of protocol data. The obtained samples were denoted ZFAC, ZFAO, ZFAT, ZFGLy, ZFGLu, ZFU according to fuel agents.

Sample	Combustion	Molar ratio	Time of gel	Temperature	Heating
	agent	ferrite: fuel	formation at	of sand bath	duration post-
		agent	353 K	at the	combustion
				combustion	until 623 K
				moment	
ZFAC	Citric Acid	1:3	2h	523 K	3h
ZFAO	Egg White	**	2 h 30 min	523 K	3h
ZFAT	Tartaric Acid	1:3	2h	573 K	2h
ZFGLy	Glycine	1:1.5	10h	423 K	5h
ZFGLu	Glucose	1:3	2h	623 K	1h
ZFU	Uree	1:6	5h	473 K	4h

Table II.1.1.Protocol synthesis details.

*Tables and figures notations were preserved as in PhD thesis manuscript. **Weight ratio, ferrite:egg white = 1:22.2.

Samples taken at different stages of synthesis were characterized by the following techniques: IR spectroscopy, TG / DTA, XRD, SEM. The original program used to obtain the inversion degree, considering previous studies in the literature [Bathu, 2007, Shannon, 1976; Sickafus, 1999], was developed in Java software using NetBeans IDE integrated development environment. Magnetic properties at room temperature of ferrites annealed at 973 K and 1173 K were studied based on M = f (H) curves type. With an impedance analyzer dielectric properties were investigated for annealed ZF compounds at 1173 K.

3. Results and discussions

3.1. Characterization by IR absorption spectroscopy and TG / DTA

It is known that IR spectra of normal spinel-type ferrite has four active modes in crystalline state according to O_h^7 symmetry group selection rules [Waldron, 1955]. These are denoted by v_1 , v_2 , v_3 , v_4 . According to the literature, v_1 and v_2 vibrational modes are usually located in the range 568 \div 536 cm⁻¹ and 425 \div 369 cm⁻¹, respectively and they are assigned to stretching vibrations of the M-O bonds corresponding to tetrahedral and octahedral coordinations [Waldron, 1955; Lavat, 2006].

Table II.1.2 summarizes values of wave numbers ZF samples identified by the 3 stages of heat treatment. There is a slight change in the value of the wave number depending on the nature of combustion agent and heat treatment to which they were subjected ZF powders. These differences can be attributed to the relationship between vibration modes simultaneously and crystallite size in nanostructured materials [Thomas, 2009] and redistribution of metal cations between the two coordination spheres which affect the default length or the strength of their [Pradeep, 2011].

From TG / DTA data, reduced mass loss for gels obtained using glycine, glucose and urea confirms observations during synthesis namely, a large amount of gas was released sudden and violent during heating on the water and sand bath respectively, before samples collection for analysis. This may be due to the existence of amino group within glycine and urea structure, which in the presence of nitrogen oxides are formed at relatively low temperatures, leading to a rapid and exothermic decomposition reaction gas as proposed by Hwang et al. [Hwang , 2004], on the other hand to the strong reducing glucose character.

3.2. Caraterization by XRD and SEM

XRD patterns recorded for ZF samples annealed at 973 K (Fig.II.1.4a) and at 1173 K (Fig.II.1.4b) confirms the formation of spinel phase. We notice the influence of combustion agent in obtaining the spinel phase.

Influence of combustion agent on the ferrite morphology and grain size using sol-gel autocombustion can be seen from SEM micrographs for the samples annealed at 1173 K (Fig.II.1.5).

Parameter	Wavenumver value after heating at 773 K (cm ⁻¹)		Wavenumver value after heating at 973 K (cm ⁻¹)			Wavenumver value after heating at 1173 K (cm ⁻¹)			
Sample	ν_1^*	ν_1	V ₂	ν_1^*	v ₁	V ₂	v_1^*	ν_1	V ₂
ZFAC	670	558	394	670	554	400	675	554	416
ZFAO	618	558	413	618	559	427	619	559	429
ZFAT	676	562	415	674	557	415	670	560	420
ZFGLy	669	552	398	675	560	418	-	560	392
ZFGLu	680	552	454	674	560	419	680	560	419
ZFU	700	559	413	680	557	420	700	557	424

Tabelul II.1.2. IR spectra data for ZF samples heat treated at 773 K, 973 K and 1173 K.

All samples of zinc ferrite powder have nano-sized grains. In the case of ZFU sample (Fig.II.1.5f) is obvious the coexistence of rectangular grains with the ones of spherical shape. High macroporosity stands for ZFGLy sample (Fig.II.1.5d) due to crosslinking microstructure which leads to the idea of a potential catalyst that could be investigated in future studies.

3.3. Magnetic properties study

Magnetization curves with the data recorded at room temperature, for ZF samples annealed at 973 K and 1173 K, are shown in Fig.II.1.6.

From the magnetization curves shape one can observe the influence of the fuel agent and heat treatment, respectively on the magnetic behavior of ZF samples. Thus, we can classify the samples into two categories of soft magnetic materials: paramagnetic (ZFAC, ZFAO, ZFAT) and low ferrimagnetic (ZFGlu, ZFU, ZFGly).



Fig.II.1.4. XRD patterns for ZF samples: (a) sintered at 973 K, (b) sintered at 1173 K.



Fig.II.1.5. Imaginile MEB pentru probele ZF tratate termic la 1173 K: (a)ZFAC, (b) ZFAO, (c) ZFAT, (d) ZFGLy, (e) ZFGLu, (f) ZFU.



Fig.II.1.6. Magentization curves for ZF samples: (a) heated at 973 K, (b) heated at 1173 K.

3.4. Dielectric properties study

Were investigated dielectric properties of the ZF samples annealed at 1173 K namely, dielectric permittivity variation depending on the frequency in the range 100 Hz \div 1 MHz at room temperature. Factors that may influence the dielectric constant at low frequencies and constant temperature are multiple: grain size, density, porosity, large number of Fe³⁺/Fe²⁺ ion pairs in adiacent B interstices between which conduction mechanism take place. It can be said, linking data from XRD with the investigated dielectric properties, that ZF samples with high dielectric constant are ZFGLy, ZFAC, ZFAT, ZFU for which there is a combined effect of structural characteristics: particle size, high X-ray density, high concentration of ions Fe²⁺ (i.e. ZFGLy sample) and Fe³⁺ within B interstices.

II.2.Synthesis, characterization and properties study of nanocrystalline Zn, Mg, Co and Ni ferrites

1. Introduction

This study aims to elucidate some comparative aspects about synthesis by sol-gel autocombustion and characterization of AFe_2O_4 type ferrites, where A = Zn, Mg, Co, Ni. From the reported data of a previous study (see II.1 section) tartaric acid was chosen as optimum combustion agent to obtain single spinel phase particles with nanoscale dimensions.

3. Results and discussions

3.1. Caraterization by IR spectroscopy

Wavenumber values have similar magnitude, but slightly different, due to the influence of as-synthesized ferrite composition. Thus, as the X-O bond is shorter and stronger, the wavenumber value is higher. Can be noticed that the strongest X-O bond, specific to A sublattice, corresponds to NF sample ($v_1 = 541 \text{ cm}^{-1}$), and the lowest belongs to ZF sample ($v_1 = 526 \text{ cm}^{-1}$). This is explained by the covalent degree of X-O bond and the different ionic radii of the cations depending on the coordination sphere.

3.2. Characterization by XRD

XRD patterns of the single-phase ferrite samples, showed in Fig.II.2.2, were indexed according to the standard data for each sample. Diffraction peak (311), typical for cubic spinel structure appears clearly in all 4 XRD patterns.



Fig.II.2.2. XRD patterns of spinel monophase ferrite samples.

3.3. Magnetic properties study

Hysteresis curves recorded at room temperature were represented in Fig.II.2.3. Typical paramagentic behavior is observed for ZF sample while a ferrimagnetic behavior is noticed for MF, CF and NF samples. Table II.2.3 shows a summary of magnetic properties (Ms and Hc) values which are in agreement with some previous studies from literature [Varma, 2008; Huo, 2009]. In the case of MF sample, nanosize particles is reflected in a poor ferrimagnetic behavior at room temperature, which is consistent with other studies from the literature [Liu, 2007].



Table II.2.3. Magnetic properties values measured at room temperature.

Sample	M _s (emu/g)	H _c (Oe)
ZF	-	-
MF	19	71
CF	75	535
NF	41	100

Fig.II.2.3. Curbele de histerezis la temperatura camerei pentru probele monofazice de ferită.

3.4. Dielectric properties study

At very high frequencies of the applied electric field ε' values become constant because the conducted field cannot follow the applied frequency. In the case of NF sample it is noticed the highest ε' value at low frequencies, which can be explained by the high X-rays density and narrow intergranular layer. On the other hand, for all 4 samples were recorded low dielectric losses (tg\delta) which means that these materials are suitable for high frequency applications, e.g. microwave applications.

Dielectric relaxation is remarkable only for samples ZF, CF and NF due to specific peaks visible in the curves of dielectric losses vs. frequency.

III. GENERAL CONCLUSIONS AND PERSPECTIVES

The start up of our scientific research was to optimize the synthesis of fine particles (powder) of Zn ferrite by sol-gel autocombustion method as a function of different behavior of chelating-combustion agents (fuels) during synthesis. Thus, we have chosen organic compounds from different classes: citric acid, tartaric acid, glycine, glucose, urea and egg white.

 $ZnFe_2O_4$ powder obtained with tartaric acid, citric acid and glycine required a relatively short reaction time at low sintering temperature. In these mentioned cases, structural analysis by IR and DRX indicated the existence of pure crystalline spinel phase at 973 K sintering temperature, the average crystallite size being about 50 nm.

Cation distribution within tetrahedral and octahedral sites has proven to be influenced by the fuel agent and heat treatments. Mixed spinel structure was theoretically estimated for all the samples with different inversion degree value.

Study correlating data from magnetic and dielectric properties of zinc ferrite obtained using tartaric acid and citric acid, respectively show optimal behavior compared to the other samples. Thus, zinc ferrite samples obtained using glycine, tartaric acid and citric acid can be recommended as radar absorbent materials, capacitors and microwave resonators due to high dielectric constant (≈ 20) and low dielectric loss (tg $\delta \le 0.5$) values at low frequencies (100Hz) at room temperature.

Tartaric acid was selected for the synthesis of ferrites that constituted the next stage of our scientific approach.

Comparative study of AFe_2O_4 ferrite samples with different divalent cations (A = Zn, Mg, Co and Ni) synthesized by sol-gel autocombustion method concluded that the nature of divalent cation significantly influences the structural characteristics, magnetic and dielectric behavior.

The smallest crystallites (29 nm) correspond to Ni ferrite which presents the highest value of dielectric constant (34) among the analyzed samples. On the other hand, Co and Ni ferrites have high levels of saturation magnetization (75 emu/g, 41 emu/g) which recommends them for high frequency or biomedical applications.

Further step in our research way was to synthesize and study the properties of ferrite series with chemical composition $Zn_{1-x}M_xFe_2O_4$ ($0 \le x \le 1$ with a step of 0.2), where M= Ni, Mg and Co. Therefore, ferrite series were successfully synthesized by sol-gel autocombustion method using tartaric acid as fuel.

IR spectra study of ferrite series terms stated Ni cation influence when replacing Zn cation within cubic spinel-type structure. The increase of metal-oxygen bond length from octahedral site and the decrease of metal-oxygen bond length from tetrahedral site determined the inversely change of corresponding wavenumber values.

UV-Vis spectra study confirmed the presence of specific absorption bands of Ni²⁺ and Fe³⁺ with octahedral coordination within cubic spinel-type lattice. We can speculate on the possible performance of these materials as photocatalysts in the visible range, worthy of future study.

X-ray patterns confirm the formation of cubic spinel structure for samples annealed at 973K. Therefore, it was revealed the obtaining of a single phase with high crystallinity.

Increasing Ni content for $Zn_{1-x}Ni_xFe_2O_4$ series it was observed, based on dynamic distribution of cations between tetrahedral and octahedral sites, the emergence of differences between assynthesized samples, concerning nanometer range crystallite size, interplanar distance, lattice parameter, X-ray density values etc.

Proposed cation distribution is confirmed by IR and XRD experimental data concerning structural characteristics, length of metal-oxygen bonds from both sublattices, theoretical lattice parameter values being close to those determined from XRD study.

SEM micrograph for $Zn_{0.4}Ni_{0.6}Fe_2O_4$ compound confirms the formation of spherical particles in the nanometer range.

Study of magnetic properties at room temperature of $Zn_{1-x}Ni_xFe_2O_4$ series confirms elevated magnetizației specific coercive field and permeability with increasing Ni content.

Nevertheless, $Zn_{0.2}Ni_{0.8}Fe_2O_4$ compound owns the magnetic behavior performance (M_s = 63 emu/g şi H_c = 79 Oe) which was confirmed also in terms of magnetic permeability at room temperature as a function of frequency.

 $NiFe_2O_4$ and $Zn_{0.2}Ni_{0.8}Fe_2O_4$ compounds can be good candidates for microwave frequency applications, while $Zn_{0.6}Ni_{0.4}Fe_2O_4$ and $Zn_{0.4}Ni_{0.6}Fe_2O_4$ compounds can be used properly in radio frequency applications.

The evaluation at room temperature of dielectric permittivity vs. frequency for Zn_{1-x}Ni_xFe₂O₄ series led to the establishment of performance as semiconductors. In general, increasing Ni content in the sample leads to an increase in electrical conductivity. However. $Zn_0 Ni_0 PFe_2O_4$ and $Zn_{0.6}Ni_{0.4}Fe_2O_4$ compounds are characterized by typical dielectric behavior, the remaining samples showing abnormal behavior due to possible lattice deffects confirmed by low values of ionic packing coefficient calculated theoretically (P_A) .

Furthermore, for $Zn_{0.2}Ni_{0.8}Fe_2O_4$ compound with performances as a magnetic material we have been concerned to study the structural and properties effects when doping with Dy^{3+} . Thus, we synthesized and analyzed $Ni_{0.8}Zn_{0.2}Fe_{1.98}Dy_{0.02}O_4$ compound using sol-gel autocombustion method and four different chelating-combustion agents: citric acid, tartaric acid, cellulose and urea.

From IR spectra and X-ray patterns of the four synthesized samples was noticed that tartaric acid, citric acid and cellulose favored, during combustion process, Dy^{3+} addition within spinel-type matrix, whilst urea favored DyFeO₃ segregation at the particles surface due to an intense and rapid combustion process.

Significant catalytic activity for hydrogen peroxide decomposition was noticed in the case of the sample obtained with urea as fuel. This sample was charaterized by the smallest value of particle diameter (52.2 nm) and the highest specific surface (20 m²/g), among all the samples, as a consequence of DyFeO₃ secondary phase which prevented the crystallites agglomeration process during thermal treatments.

Saturation magnetization high values were recorded for assynthesized monophase ferrite using citric acid and cellulose (\approx 62 emu/g). Coercivity values are influenced by fuel agent as an effect of secondary phases and particle size, the smallest value (67 Oe) being estimated for the sample sintesized with urea.

Cellulose and tartaric acid, respectively, influenced the dielectric behavior of Ni-Zn-Dy ferrite particles. These samples revealed the lowest dielectric loss values.

 $Zn_{1-x}Mg_xFe_2O_4$ ($0 \le x \le 1$ with a step of 0.2) series was successfully obtained by sol-gel autocombustion method with tartaric acid as fuel. Voluminous Mg^{2+} ions have tendency to replace Fe^{3+} from octahedral sites of spinel-type lattice which leads to an increase of wavenumber value of v_1 -type vibration from IR spectra, as a function of Mg content and thermal treatments.

Due to a dinamic cation distribution within spinel-type lattice, increasing Mg content for $\mathbf{Zn}_{1-x}\mathbf{Mg}_x\mathbf{Fe}_2\mathbf{O}_4$ series involves differences between some structural investigated features. Thus, the calculated values of crystallite size (39 ÷ 25 nm), interplanar distance (2.530 ÷ 2.520 Å), lattice parameter (8.427 ÷ 8.369 Å), X-ray density (5.416 ÷ 4.532 g/cm3) decrease quasi-monotonous from large value for Zn ferrite to low values for Zn-Mg and Mg ferrite, respectively.

Our proposed cation distribution (mixt spinel-type for Zn ferrite and Zn-Mg ferrite, respectively, and invers spinel-type for Mg ferrite) was in agreement with IR şi DRX data concerning structural characteristics.

 $Zn_{0.8}Mg_{0.2}Fe_2O_4$ and $Zn_{0.2}Mg_{0.8}Fe_2O_4$ compounds shows a high packing degree with minimum cation vacations within spineltype lattice against the other $Zn_{1-x}Mg_xFe_2O_4$ series compounds. Electrical properties (resistivity vs. temperature) and dielectric properties (dielectric permittivity vs. frequency at room temperature) investigation led to the conclusion that, among all the other chemical compositions, $Zn_{0.8}Mg_{0.2}Fe_2O_4$ compound shows the highest resistivity at room temperature, high dielectric constant and low dielectric loss, proper qualities for energy storage applications.

The study of magnetic permeability vs. frequency at room temperature highlighted that $Zn_{0.2}Mg_{0.8}Fe_2O_4$ and $MgFe_2O_4$ compounds can be good materials for microwave applications due to low values of energy loss in the magnetic field and high resonance frequency.

 $Zn_{1-x}Co_xFe_2O_4$ series was successfully synthesized by solgel autocombustion method with tartaric acid as fuel.

By IR technique it was observed an increase of wavenumber value for v_1 -type vibrations with Co content, which reveals the fact that Fe cations replace Zn cations within tetrahedral site and modify the metal-oxygen bond strentgh.

It was proved the influence of Co content in Zn-Co ferrite concerning structural characteristics: interplanar distance $(2.548 \div 2.532 \text{ Å})$, lattice parameter $(8.451 \div 8.397 \text{ Å})$, X-ray density $(5.304 \div 5.263 \text{ g/cm}^3)$ values which are high for Zn ferrite and low for Zn-Co and Co ferrite, respectively.

The smallest crystallite size was calculated for $Zn_{0,4}Co_{0,6}Fe_2O_4$ compound (48 nm) and the highest one for $CoFe_2O_4$ compound (68 nm) as a consequence of induced effects of both chemical composition and thermal treatments.

The proposed cation distribution (mixt spinel for Zn and Zn-Co ferrite, respectively, inverse spinel for Co ferrite) was in agreement with IR and XRD data.

 $ZnFe_2O_4$ and $Zn_{0.8}Co_{0.2}Fe_2O_4$ compounds show values close to unit for ionic packing coefficient (P_A) which suggests minimum cation vacations against the other terms of the Zn-Co ferrite series. Furthermore, $Zn_{0.2}Co_{0.8}Fe_2O_4$ compound has optimal dielectric behavior with high dielectric constant and low dielectric loss, which are proper qualities for energy storage at high frequency (1 MHz) applications.

Magnetic behavior study at room temperature revealed that $ZnFe_2O_4$ and $Zn_{0.8}Co_{0.2}Fe_2O_4$ compounds exibit paramagnetic behavior, whilst $Zn_{0.6}Co_{0.4}Fe_2O_4$, $Zn_{0.4}Co_{0.6}Fe_2O_4$, $Zn_{0.2}Co_{0.8}Fe_2O_4$, $CoFe_2O_4$ compounds show ferrimagnetic behavior. $Zn_{0.8}Co_{0.2}Fe_2O_4$ compound is characterized by optimal magnetic parameters, high saturation magentization (87 emu/g) and low coercivity (174Oe). $ZnFe_2O_4$, $Zn_{0.2}Co_{0.8}Fe_2O_4$, $Zn_{0.8}Co_{0.2}Fe_2O_4$, $CoFe_2O_4$ compounds show small values of energy loss in the magnetic field and high resonance frequency which recommends them for microwave applications.

The last goal of this research study was to synthesize by sol-gel autocombustion method $Zn_{1-x}Mg_xFe_2O_4$ series supported on Al_2O_3 . Catalytic activity for hydrogen peroxide decomposition reveal that the compound with x=0.8 shows significant performance against the other series terms. This is a consequence of structural characteristics studied by IR, DRX and AFM techniques.

Further studies on as-synthesized Zn nanoferrite powders will include ZFC (zero field cooling) and FC (field cooling) measurements to show off superparamagnetic behavior, magnetic and dielectric behavior vs. temperature of as-synthesized series.

Our collaboration with Faculty of Physics and with "Prof.Dr.N.Oblu" Emergency Clinique Hospital from Iasi will consider the possible biomedical applications of as-synthesized nanoferrite series as contrast agents or hyperthermia agents.

Selective bibliografy

[Ahmed, 2004]	M.A. Ahmed, N. Okasha, M. Gabal, Transport and
	magnetic properties of Co-Zn-La ferrite, Materials
	Chemistry and Physics 83 (2004) 107.
[Ahmed, 2009]	M.A.Ahmed, A.A.EL-Khawlani Enhancement of the
	crystal size and magnetic properties of Mg-substituted
	Co ferrite, Journal of Magnetism and Magnetic
	Materials 321(2009)1959.
[Ajmal, 2007]	M. Ajmal, A. Maqsood, AC conductivity, density
	related and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$
	ferrites with the variation of zinc concentration, Mater.
	Lett. 62 (2007) 2077.
[Albuquerque,	A. S. Albuquerque, M. V.C. Tolentino, J. D. Ardisson,
2012]	F. C.C. Moura, Nanostructured ferrites: Structural
-	analysis and catalytic activity, Ceramics International
	38 (2012) 2225.
[Amer, 2011]	M.A. Amer, A.Tawfik, A.G.Mostafa, A.F.El-Shora,
	S.M.Zaki, Spectral studies of Co substituted Ni-Zn
	ferrites, Journal of Magnetism and Magnetic Materials
	323 (2011) 1445.
[Amiri, 2011]	Gh.R. Amiri, M.H. Yousefi, M.R. Abolhassani, S.
. ,	Manouchehri, M.H. Keshavarz, S. Fatahian
	Magnetic properties and microwave absorption in Ni–
	indesite properties and interoritie dosorphon in th

	Zn and Mn–Zn ferrite nanoparticles synthesized by low-temperature solid-state reaction, Journal of Magnetics and Magnetic Materials 323 (2011)730
[Arulmurugan]	R. Arulmurugan, B. Jevadevan, G. Vaidvanathan, S.
2005]	Sendhilnathan. Effect of zinc substitution on Co-Zn and
	Mn–Zn ferrite nanoparticles prepared by co-
	precipitation, Journal of Magnetism and Magnetic
	Materials 288 (2005) 470.
[Atassi, 2006]	Y. Atassi, M.Tally, Low Sintering Temperature of Mg-
	Cu-Zn Ferrite Prepared by the Citrate Precursor
	<i>method</i> , Journal of the Iranian Chemical Society 3 (2006) 242.
[Birajdar, 2012]	A.A. Birajdar, Sagar E. Shirsath, R.H. Kadam, S.M.
	Patange, K.S. Lohar, D.R. Mane, A.R. Shitre, Role of
	Cr^{3+} ions on the microstructure development, and
	magnetic phase evolution of Ni _{0.7} Zn _{0.3} Fe ₂ O ₄ ferrite
	nanoparticles, Journal of Alloys and Compounds 512
	(2012) 316.
[Bragg, 1915]	W.H. Bragg, The structure of magnetite and the
ID 10201	<i>spinels</i> , Nature 95 (1915) 561.
[Brunauer, 1938]	S. Brunauer, P. H. Emmett, E. Teller, Adsorption of
	Gases in Multimolecular Layers, J. Am. Chem. Soc.
[Căltur 2000]	OE Coltun Egrita de cobalt magnatostrictiva Ed
[Califull, 2009]	Univ Alevandru Ioan Cuza Jasi 2009
[Calvin 2002]	S Calvin F.F. Carpenter, V.G. Harris, S.A. Morrison
[Currin, 2002]	Multiedge refinement of extended x-ray-absorption
	fine structure of manganese zinc ferrite nanoparticles.
	Phys. Rev.B 66 (2002) 224405.
[Cedighian, 1966]	S. Cedighian, Ferite, Ed. Tehnică, București, 1966.
[Cha, 2009]	KS. Cha, HS. Kim, BK. Yoo, YS. Lee, KS.
	Kang, CS. Park, YH. Kim, Reaction characteristics
	of two-step methane reforming over a Cu-ferrite/Ce-
	ZrO ₂ medium, International Journal of Hydrogen
	Energy 34 (2009) 1801.
[Chatterjee, 1993]	A.Chatterjee, D.Das, S.K.Prahdan, D.Chakravorty
	Synthesis of nanocrystalline nickel-zinc ferrite by sol-
10(2)	<i>gel method</i> , J. Magn. Magn.Mat.127 (1993) 214.
[Colleu, 1963]	J. Colleu, J. Meximain, Structure et aspect physico-
	520
[Costa 2008]	ACEM Costa APA Diniz AGB de Melo
[Costa, 2000]	RHGA Kiminami DR Corneio AA Costa L
	Gama Ni–Zn–Sm nanopowder ferrites: Morphological
	aspects and magnetic properties. Journal of
	Magnetism and Magnetic Materials 320 (2008) 742.
[Costa, 2010]	A.C.F.M. Costa, V.J. Silva, C.C. Xin, D.A. Vieira,

	D.R. Cornejo, R.H.G.A. Kiminami, <i>Effect of urea and</i> elvcine fuels on the combustion reaction
	synthesis of Mn–Zn ferrites: Evaluation of morphology
	and magnetic properties, Journal of Alloys and
	Compounds 495 (2010) 503.
[Deraz, 2003]	NA. M. Deraz, The formation and physicochemical
	characterization of Al ₂ O ₃ -doped manganese ferrites,
	Thermochimica Acta 401 (2003) 175.
[Deraz, 2011]	N.M. Deraz, Fabrication, characterization and
	magnetic behaviour of alumina-doped zinc ferrite
	nano-particles, Journal of Analytical and Applied
	Pyrolysis 91 (2011) 48.
[Dionne, 2009]	Gerald F. Dionne, <i>Magnetic Oxides</i> , Ed. Springer, US 2009
[Divit 2012]	G Divit I P Singh R C Srivastava H M Agrawal
[DIAR, 2012]	Magnetic resonance study of Ce and Gd doped
	$NiFe_2O_4$ nanoparticles. Journal of Magnetism and
	Magnetic Materials 324 (2012) 479.
[Goldman, 2006]	A. Goldman, <i>Modern Ferrite Technology</i> , Ed.
	Springer, 2006.
[Hu, 2011]	P. Hu, D. Pan, X. Wang, J. Tian, J. Wang, S.Zhang,
	A.Volinsky, Fuel additives and heat treatment effects
	on nanocrystalline zinc ferrite phase composition,
	Journal of Magnetism and Magnetic Materials 323
	(2011) 569.
[Huang, 2006]	Y. Huang, Y. Tang, J. Wang, Q. Chen, Synthesis of
	$MgFe_2O_4$ nanocrystallites under mild conditions,
	Materials Chemistry and Physics 97 (2006)
HI 2 0003	394.
[Huo, 2009]	Huo, M. Wei, Characterization and magnetic
	properties of nanocrystalline nickel ferrite
	Synthesized by hydrothermal method, Motorials Latters 62 (2000) 1182
[Jacobs 1004]	Materials Letters 05 (2009) 1165.
[Jacobs, 1994]	Donac H H Brongersma The Surface of Catalytically
	Active Spinels Journal of Catalysis 147 (1994) 294
[Jadhay 2010]	S S Iadhay S E Shirsath S M Patange K M
[5441147, 2010]	Iadhay Effect of Zn substitution on magnetic
	properties of nanocrystalline cobalt ferrite. Journal of
	applied physics 108 (2010) 093920.
[Jang, 2009]	J. S. Jang, S. J. Hong and J. S. Lee, Synthesis of Zinc
-	Ferrite and Its Photocatalytic Application under
	Visible Light, Journal of the Korean Physical Society
	54 (2009) 204.
[Laokul, 2011]	P. Laokul, V. Amornkitbamrung, S. Seraphin, S.
	Maensiri, Characterization and magnetic properties of
	nanocrystalline $CuFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ powders

prepared	by	the	Aloe	vera	extract	solution,	Current
Applied F	hys	ics 1	11 (20	11) 1	01.		

- [Lavat, 2006] A.E. Lavat, E.J. Baran, *IR-spectroscopic* characterization of *NaLnIIITiO4* and *AgLnIIITiO4* oxides related to the K_2NiF_4 structural type, Journal of Alloys and Compounds, 419 (2006) 334.
- [Liu, 2007] C.-P. Liu, M.-W. Li, Z. Cui, J.-R. Huang, Y.-L. Tian, T. Lin, Comparative study of magnesium ferrite nanocrystallites prepared by sol-gel and coprecipitation methods, J. Mater. Sci. 4(2007)6133.

[Mitoşeriu, 1999] L.Mitoşeriu, V.Țura, *Fizica dielectricilor*, Ed. Universității "Al.I.Cuza" Iași, 1999.

 [Mohammed,
X.A. Mohammed, A.D. Al-Rawas, A.M.Gismelseed,
A.Sellai, H.M.Widatallah, A.Yousif, M.E. Elzain,
M.Shongwe, *Infrared and structural studies of Mg₁₋* ,*Zn*,*Fe*₂O₄ ferrites, Physica B 407(2012)795.

[Mukherjee, 2012] K. Mukherjee, S.B. Majumder, Synthesis process induced improvement on the gas sensing characteristics of nano-crystalline magnesium zinc ferrite particles, Sensors and Actuators B 162 (2012) 229.

[Palamaru, 2009] M.N. Palamaru, A.R. Iordan, Procedeul sol-gel de obținere a feritelor în Ferite de cobalt magentostrictive (O.F. Călţun coordinator), Ed.Universității "Al.I.Cuza" Iaşi, 2009

- [Patil, 2012] J.Y. Patil, M.S. Khandekar, I.S. Mulla, S.S. Suryavanshi, Combustion synthesis of magnesium ferrite as liquid petroleum gas (LPG) sensor: Effect of sintering temperature, Current Applied Physics 12 (2012) 319.
- [Peng, 2011] Z. Peng, X. Fu, H. Ge, Z. Fu, C. Wanga, L. Qi, H. Miao *Effect of* Pr^{3+} *doping on magnetic and dielectric properties of* Ni–Zn ferrites by "one-stepsynthesis", Journal of Magnetism and Magnetic Materials 323 (2011) 2513.
- [Plocek, 2003] J. Plocek, A. Hutlová, D. Nižňanský, J. Buršík, J.-L. Rehspringer, Z. Mička, Preparation of ZnFe₂O₄/SiO₂ and CdFe₂O₄/SiO₂ nanocomposites by sol-gel method, Journal of Non-Crystalline Solids 315 (2003) 70.

[Serktol, 2009] M. Sertkol, Y. Koseoglu, A. Baykal, H. Kavas, A. Bozkurt, M.S. Toprak, *Microwave synthesis and characterization of Zn-doped nickel ferrite nanoparticles*, J. Alloys Compd. 486 (2009) 325.

- [Shannon, 1976] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst. A 32 (1976)751.
- [Sickafus, 1999] K. E. Sickafus, J. M. Wills, Structure of spinel, J. Am.

	Ceram. Soc. 82 (1999) 3279.				
[Smart, 1954]	J.S. Smart, Cation distribution in mixed ferrites,				
	Phys. Rev. 94 (1954) 847.				
[Smit, 1961]	J. Smit, H.P.J. Wijn, Les Ferrites, Ed. Bibliotheque				
	Technique Philips, Eindhoven, p.251-260, 1961.				
[Verma, 2012]	K. Verma, A. Kumar, D. Varshney, Dielectric				
	relaxation behavior of $A_x Co_{1-x} Fe_2 O_4$ (A = Zn, Mg)				
	mixed ferrites, Journal of Alloys and Compounds 526				
	(2012) 91.				

Activitatea științifică Participări la conferințe, seminarii, simpozioane, sesiuni de comunicări la nivel național și internațional

1	T Clătingony A D	South said of Zu Ni E. O	Zilala Universității I-ai
1.	1. Slauneanu, A. K.	Synthesis of $Zn_{1-x}Ni_xFe_2O_4$	20.21 a stambrid 2000
	Ioruan, M. N. Palamaru,	<i>jerrites by autocombustion</i>	(Dester)
	L. Leonne, V. Galton, O.	metnoa	(Poster)
	F. Calțun		
2.	T.Slătineanu, M. N.	New routes for Zn ferrite	Zilele Universității, Iași,
	Palamaru, A. R. Iordan,	powder synthesis	30-31 octombrie 2009.
	L. Leontie, O. F. Călțun		(Poster)
2	T Clătingony A D	The influence of Ni content	Conforinto Internatională
5.	<u>I. Slatificaliti</u> , A. K.	The influence of Ni content	de Stiinte Aplicate
	L Leontie V Cafton O	On some properties of Mi-	Chimie și Inginerie
	E. Leonne, V. Ganon, O. E. Căltun	Zn jernies	Chimică (CISA) Slănic
	1. Calçan		Moldova-Bacău 8 - 11
			aprilie 2010 (Poster)
4.	T. Slătineanu. A. R.	The influence of Ni content	Conferintă Internationale
	Iordan, M. N. Palamaru,	on the electrical and	Materials for Electrical
	I. Dumitru, O. F. Călțun,	magnetic properties of Ni-	Engineering (IEEE-
	V. Gafton, L. Leontie	Zn ferrites	ROMSC), Iași, 6-8 iunie
		Publicație în volumul de	2010. (Poster)
		rezumate al conferinței.	
5.	<u>T. Slătineanu,</u>	Studiul comparativ al	Sesiunii Jubiliare de
	A.R.Iordan,	pulberilor nanocristaline de	Comunicări Științifice a
	M.N.Palamaru,	ferită de zinc obținute prin	Studenților,
	O.F.Călțun, L.Leontie	metoda sol-gel	Masteranzilor și
		Rezumat publicat în	Doctoranzilor "Chimia-
		Suplimentul revistei Acta	frontieră deschisă spre
		Chemica Iaşi, ISSN 2067-	cunoaștere"
		2438, UAIC Iasi.	(SJCSSMD), Iași, Ediția
			1, 2 tulie 2010. (SC)
6.	<u>1.Statineanu</u> , A.K.Iordan, M.N.Dalamaru	The influence of the	conferința Internațională
	IVI.IN.Palamafu,	compustion agent on zinc	ai societațiior de Chimie
	O.r.Caliun, L.Leonne,	Dublicatio în volumul de	uni țarne sud-est
	n.Apostolescu	rublicație în volumul de	Empresente chimie –
		rezumate ai comerinței.	Rucuresti 15 17
			sentembrie 2010
			(Poster)
7.	T.Slătineanu, A.R.Iordan.	The synthesis.	Conferinta Natională de
	M.N.Palamaru,	characterization and	Fizică (CNF), Iași, 23-25
	,		21

	O.F.Călțun, L.Leontie	properties of zinc ferrite substituted with magnesium Publicație în volumul de	septembrie 2010. (Poster)
8.	<u>T. Slătineanu</u> , A. R. Iordan, M. N. Palamaru, O. F. Călțun, L. Leontie, V. Gafton	Synthesis and characterization of nanocrystalline Ni-Zn ferrite doped with Dy Publicație în volumul de rezumate al conferinței.	Conferinta Națională cu participare internațională - Materiale Nanostructurate Multifuncționale, Iași, 4- 5 noiembrie 2010. (Poster)
9.	<u>T. Slătineanu</u> , A. R. Iordan, M. N. Palamaru, O. F. Călțun, L. Leontie, I. Dumitru	Sinteza, caracterizarea și studiul proprietăților feritei de zinc substituită cu magneziu	Sesiunea de comunicări – Zilele Universității Ieșene, 12-13 noiembrie 2010, Iași. (SC)
10.	M.P. Samoilă, <u>T.</u> <u>Slătineanu</u> , A.R.Iordan, M.N.Palamaru	Studiul proprietăților catalitice ale feritelor de zinc substituite Zn _{1-x} M _x Fe ₂ O ₄ , unde M=Mg, Ni	Sesiunea de comunicări –Zilele Universității Ieșene, 12-13 noiembrie 2010, Iași. (Poster)
11.	M.P. Samoilă, <u>T.</u> <u>Slătineanu</u> , A.R. Iordan, M.N. Palamaru	The influence of the combustion agent on the structure and catalytic properties of nanocrystalline Ni _{0.8} Zn _{0.2} Dy _{0.02} Fe _{1.98} O ₄	CISA, Bacău, 28-30 aprilie 2011. (Poster)
12.	A.I. Borhan, <u>T.</u> <u>Slătineanu</u> , A.R. Iordan, M.N. Palamaru	Synthesis and structural characterization of Cr- substituted Zn ferrite	CISA, Bacău, 28-30 aprilie 2011, (Poster)
13.	<u>T. Slătineanu</u> , M.P. Samoilă, A.M Dumitrescu, A.R. Iordan, M.N. Palamaru	Effects of sintering temperature on catalytic properties for alumina- supported $Zn_{1-x}Mg_xFe_2O_4$ spinels Publicație în volumul de rezumate al conferinței.	The 10th International conference on colloids and surfaces chemistry, Galați, 9 – 11 iunie 2011. (Poster)
14.	A.I. Borhan, <u>T.</u> <u>Slătineanu</u> , A.R. Iordan, M.N. Palamaru	Aspecte noi în sinteza spinelilor pe bază de crom Rezumat publicat în Suplimentul revistei Acta Chemica Iași, ISSN 2067- 2438, UAIC Iasi.	SJCSSMD, Editia a II-a, Iași, 24 iunie 2011.
15.	M.P. Samoilă, <u>T.</u> <u>Slătineanu</u> , A.M Dumitrescu, A. Vasile, A.R. Iordan, M.N.	Catalytic oxidation of phenol over $Zn_{1-x}Mg_xFe_2O_4$ supported catalysts Publicație în volumul de	The 1 st Conference of Central and Eastern European Committee for Thermal Analysis and

	Palamaru	rezumate al conferinței.	Calorimetry, Craiova, 7- 10 Septembrie 2011. (Poster)
16.	<u>T.Slătineanu</u> , A.R.Iordan, M.N.Palamaru, A. Doagă, O.F.Călțun, V. Nica	The influence of Co content on the nanocrystalline structure and magnetic properties of Co-Zn ferrites	20th Soft Magnetic Materials Conference, Kos, Grecia, 18-22 septembrie 2011. (Poster)
17.	C. P. Constantin, A. Doaga, A. Cojocariu, <u>T.</u> <u>Slatineanu</u> , O. F. Caltun	Ferrite nanoparticles as contrast agents in magnetic resonance imaging	20th Soft Magnetic Materials Conference, Kos, Grecia, 18-22 septembrie 2011. (Poster)
18.	E. Diana <u>, T.Slătineanu</u> , A.R.Iordan, N. Valentin, V.Oancea, M.N.Palamaru	Vibrational behavior, microstructure and morphology of Zinc Ferrite obtained with differing fuels Publicație în volumul de rezumate al conferinței.	XXIV Congresso Nazionale della Società Chimica Italiana, Lecce, Italia, 11-16 septembrie 2011. (SC)
19.	C. P. Constantin, A. Doaga, A. M. Cojocariu, T. Slatineanu, O. F.Caltun	Co and Ni Doped Zn ferrites as MRI contrast agents Publicație în volumul de rezumate al conferinței.	IEEE-ROMSC - Iasi, 17 octombrie, 2011.
20.	C. Constantin, A. Doaga, A. M. Cojocariu, <u>T.</u> <u>Slatineanu</u> , O. F. Caltun	Enhancement of the magnetic resonance images contrast	Symposium of Magnetic Measurements - Varsovia, Polonia, 17-19 octombrie 2011. (Poster)
21.	A.I. Borhan, <u>T.</u> <u>Slătineanu</u> , A.R. Iordan, M.N. Palamaru	Compuși oxidici de tip spinel pe bază de crom	Zilele Universitatii, Iasi, 28 octombrie 2011. (SC)
22.	A.I. Borhan, <u>T.</u> <u>Slătineanu</u> , A.R. Iordan, M.N. Palamaru	Effect of chromium ion substitution on the electromagnetic properties of zinc ferrites	CISA, Bacău, 24 –27 aprilie 2012. (Poster)
23.	C. P. Constantin, T. Slatineanu, M.N. Palamaru, F. Brânză, O. F.Caltun	Studiul seriei de ferită Ni _x Zn _{1-x} Fe ₂ O ₄ în contrastul RMN	Conferința Națională, Fizica și Tehnologiile Educaționale Moderne, Iași, 17-19 Mai 2012.

Lista de publicații în reviste/jurnale cotate ISI

- <u>T. Slătineanu</u>, A.R. Iordan, M.N. Palamaru, O.F. Călţun, V. Gafton, L. Leontie, *Synthesis and characterization of nanocrystalline Zn ferrites substituted with Ni*, Materials Research Bulletin 46 (2011) 1455-1460, Factor de Impact 2,145; Scor Relativ de Influență 1,33978.
- <u>T. Slătineanu</u>, E. Diana, V. Nica, V. Oancea, O.F. Călţun, A.R. Iordan, M.N. Palamaru, *The influence of the chelating/combustion agents on the structure and magnetic properties of zinc ferrite*, Central European Journal of Chemistry (Factor de Impact **0,991**; Scor Relativ de Influență **0,65569**), DOI: 10.2478/s11532-012-0098-y.
- P. Samoilă, <u>T. Slătineanu</u>, P. Postolache, A.R. Iordan, M.N. Palamaru, *The effect of chelating/combustion agent on catalytic activity and magnetic properties of Dy doped Ni-Zn ferrite*, Materials Chemistry and Physics, (Factor de Impact 2,234; Scor Relativ de Influență 1,48387) http://dx.doi.org/10.1016/j.matchemphys.2012.06.059.

ACKNOWLEDGEMENTS

This work was supported by the the European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectoral Operational Programme for Human Resources Development 2007-2013 [grant POSDRU/88/1.5/S/47646].

For the professional and personal support I would like to express my gratitude to all the colleagues and collaborators both from the Faculty of Chemistry and Physics, Alexandru Ioan Cuza University of Iasi.

With high appreciation, I would like to thank to Prof. Dr. Mircea Nicolae PALAMARU for his trust, for the material, moral and scientific support which were vital to carry out properly my research studies.

I would like to thank also to our working team (especially to Ms. Prof. Dr. Alexandra Raluca Iordan), guidance committee members, public thesis defense comission members who led my "steps" during the research work with professionalism, patience and devotion.