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Spinel oxide compounds based on magnesium

SUMMARY

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The doctoral thesis entitled “Spinel oxide compounds based on magnesium” is structured as follows:

CONTENT

Keywords:

Sol-gel auto-combustion method, Ferrite, FTIR, XRD, SEM, Dielectric properties, Magnetic properties

In this summary are presented the results of personal research to Chapter 7 to entitled “Synthesis and characterization of magnesium substituted copper ferrite”, general conclusions and an extract of bibliography. Was maintained the numbering of tables and figures included in the thesis.

HISTORICAL

The name spinel is an ancient name who originally referred to the red gemstone. Origin of the name may derive from the Latin spina meaning "little spin", a reference to the sharp ends of crystals [1].

Based on historical sources, Badakhshan mines were the source of many of the most beautiful red rubies and spinels which can be found in the collections of jewelry from around the world such as the crown jewels of Iran, Topkapi in Istanbul Tower of palace of the Kremlin in Russia and the Tower of London in England [7].

Until now, the list of compounds recognized as having crystal structure of spinel is impressive.

The thesis is divided into two parts: the first part contains a study of the literature with reference to ferrites with spinel structure and the second part contains the synthesis and the study of some ferrites. The first part of the thesis is composed of four chapters.

Chapter 1 contains an overview of the crystalline structure of oxides with spinel structure. For binary oxides, which have the general formula $A_xB_yO_z$, meet three types of structures, namely: spinel structure, ilmenite structure and perovskite structure. Spinel crystal structure contains anions placed in conventional cell cubic lattice with compact packaging 96 interstices occupied by chemical species (32 anions O^{2-}, 16 cations B^{3+}, 8 cations A^{2+} and 40 vacation).

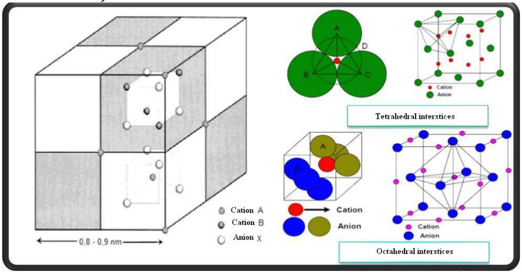


Figure 4. Spinel cell [15]

Chapter 2 describes the main methods of synthesis of oxide compounds with spinel structure focusing on the sol-gel self-combustion. This method combines the advantages of two methods: sol-gel method and combustion method and has the following advantages: good stoichiometric control, producing nano-sized particles and a uniform distribution for low temperature and short time synthesis.

Chapter 3 was assigned to describe the properties of oxides with spinel structure.

In **Chapter 4** we present physico-chemical methods for the characterization of oxides with spinel structure.

The second part of the thesis is composed on 6 chapters and includes personal contributions on the synthesis and study of classes of compounds.

In **Chapter 5** we have indicate several goals and strategies related to synthesis and characterization of compounds with spinel structure based on magnesium. The research in this paper have the following objectives:

- Optimization of the conditions of synthesis for obtaining the magnesium ferrite by the sol-gel auto-combustion method, using a variety of chelating/combustion agents and optimum setting of synthetic agent;
- Obtaining magnesium ferrite substituted with copper cation using chelating/combustion agent optimal;
- Obtaining magnesium ferrite substituted with cobalt cation;
- Obtaining magnesium ferrite dual substituted with cobalt and copper cations;
- Structural characterization of the obtained compound by infrared absorption spectroscopy, X-ray diffraction and scanning electron microscopy;
- Study of magnetic properties and their correlation with method of synthesis for obtained compounds;
- Study of electrical properties and their correlation with method of synthesis for obtained compounds;
- Establishment of structure - properties of the compounds obtained.

Chapter 6 of the thesis covers the study of the influence of chelating/combustion agents used to synthesis, structure and properties of magnesium ferrite unsubstituted. Nano-sized powder of magnesium ferrite was prepared by sol-gel auto-combustion with various complexing/combustion agents such as: citric acid (CA), tartaric acid (TA), cellulose (C), urea (U), glycine (Gly) and hexametilentetraamine (HA). Influence of chelating/combustion agents can be seen on the following parameters: the values of self-ignition flame temperature, crystallite size, the lattice parameter and grain porosity.

IR spectra recorded at different stages of synthesis have been used to follow the disappearance of organic and inorganic residues as well as the appearance of spinel phase.

The structure of compounds and crystallite size was analyzed using X-ray diffraction showed the formation of the spinel structure after heat treatment at 500°C. Subsequent heat treatment is necessary to obtain a complete conversion of the reactants to final products single phase. It was observed that with increasing calcination temperature increases the particle size.

Scanning electron microscopy confirmed the formation of particles with a uniform distribution. Histograms of samples analyzed, demonstrating a distribution of grain and nanometer size, which is consistent with the XRD results.

The highest saturation magnetization of the sample is in the synthesis was used as chelating/ combustion agent citric acid and for the same sample showed the lowest dielectric loss. This behavior leads to the use of these compounds in the field of electrical engineering.

In **Chapter 7** we described the synthesis and characterized the magnesium ferrite substituted with copper ions and this chapter will be described in more detail in this summary.

Chapter 8 contains data about the synthesis and characterization of magnesium ferrite substituted with cobalt ions. There were obtained the compounds of the series $Mg_{1-x}Co_xFe_2O_4$ (x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84, 1.00) by sol-gel auto-combustion using glycine as chelating/combustion agent. I used the chelating/combustion agent because I noticed from previous studies that is most suitable to obtain pure compounds.

Analysis by IR spectroscopy revealed that the stage of auto-combustion samples with $x \geq 0.17$ are chemically pure and spinel structure occurs in all samples of the series.

XRD data confirms the formation of spinel single structure of all samples after heat treatment at 900°C. Crystallite size values obtained for all samples are below 85nm.

Dielectric constant and dielectric loss decreases with increasing frequency and tends to a constant value at high frequencies, so the samples synthesized develop normal dielectric behavior. Dielectric loss factor values for the samples at higher frequencies falls within the 0.01 to 0.11. These features are very important for the manufacture of various electrical and electronic devices that may be used in a wide range of frequencies.

In **Chapter 9** we present the synthesis and characterized the magnesium ferrite double-substituted with copper and cobalt ions. Were synthesized nanopowders compounds with formula $Mg_{0,50}Co_{0.50-x}Cu_xFe_2O_4$ with x = 0.15, 0.25 and 0.35 by sol-gel auto-combustion method using glycine as chelating/combustion agent.

By IR spectroscopy, synthesis method used for proper monitoring has shown that any pure chemical compounds at the stage of self-combustion and spinel structure arise at this stage.

XRD patterns confirm the formation of single spinel structure with space group *Fd-3m* for all the samples after heat treatment at 900°C. The degree of substitution of ions of Cu^{2+} ions of Co^{2+} affect the lattice parameters and crystallite size. It was established that the lowest value of the crystallite size and the lattice parameter value is sample $Mg_{0,50}Co_{0,35}Cu_{0,15}Fe_2O_4$ (42 nm, 8.391 Å).

Microgafiile SEM shows that the substitution of copper ions with cobalt ions, increase the particle size.

Dielectric constant and dielectric loss decreases with increasing frequency tends to a constant value at high frequencies, so developing a normal dielectric behavior. Maximum dielectric constant is obtained for $Mg_{0,50}Co_{0,15}Cu_{0,35}Fe_2O_4$. For frequencies above 1 MHz, the dielectric loss factor values fall within the 0.007 to 0.014, which makes them great for electrotechnical applications.

In the last chapter, namely **Chapter 10** are presentet general conclusions.

Chapter 7. Synthesis and characterization of magnesium-substituted copper ferrite

7.1. Introduction

According to our literature data, no report has been made about the effect of Mg substitution for Cu on the dielectric properties of magnesium ferrite. Note that there are several studies focusing on the effect of metal ion substitution such as Ni [117, 118] and Zn [100] on the structure and magnetic properties of $MgFe_2O_4$. Therefore, our main objective was to synthesize pure nanocrystalline powders with general formula $Mg_{1-x}Cu_xFe_2O_4$ ($0.00 \leq x \leq 1.00$) by sol–gel auto-combustion method [119] using glycine as chelating/combustion agent and to investigate the effect of Cu^{2+} substitution in $MgFe_2O_4$ on the structural characteristics and electric properties. This method was chosen because it presents indisputable benefits: good stoichiometric control of reagents and obtain nanoparticles in a short time and at a low temperature synthesis [42], [120]. The energy released from the process auto-combustion using glycine as chelating/combustion agent is higher than in the case of use of urea and citric acid, which leads to pure compounds [121]. Chelating/combustion agent serves to maintain homogeneity among the constituents and also lower the sintering temperature. A further advantage of use glycine as chelating/combustion agent is the forming of polynuclear complexes with metal ions establish, which leads to increasing the solubility and preventing the selective precipitation of the metal ions during the evaporation of water [122]. Due to this fact are obtained oxide powders with a homogeneous composition in a short time.

7.2. Synthesis of substituted copper-magnesium ferrite

Nanoparticles of $Mg_{1-x}Cu_xFe_2O_4$ (x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84, 1.00) were prepared by sol–gel auto-combustion method. The following notations will be used for the samples synthesized: MFO for x = 0.00; MCuFO 0.17 for x = 0.17; MCuFO 0.34 for x = 0.34; MCuFO 0.50 for x = 0, 50; MCuFO 0.67 for x = 0.67; MCuFO 0.84 for x = 0.84; CuFO for x = 1.00. The reactants, of analytical purity, used are: magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$, copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$, iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ and glycine $C_2H_5NO_2$ was solubilized in the minimum volume of distilled water and mixed in the appropriate stoichiometric ratio sample synthesized and the molar ratio of cations: glycine was preserved in all cases the ratio 1: 3. The solution formed was heated at 75°C on a hotplate under continuous magnetic stirring for several hours, during which the dehydration process occurs by the xerogel formation. Dried gels were thermally treated on the sand bath at 100°C for 2^{30}, when auto-combustion occurs. Auto-combustion lasted about 10 seconds for each synthesis. Due to this fact, it obtain a fluffy powder, brown-reddish. The obtained powder was mortar and thermally treated on sand bath to a temperature at 350°C, with heating step by 50°C/h The samples obtained were subjected to heat treatment of 500°C/5h, 700°C/7h and 900°C/9h to remove organic and inorganic remains and to complete the crystalline structure of the sample.

The monitoring solid phase chemical reactions and the study of disappearance of the organic and inorganic phase were accomplished by IR spectroscopy using a Bruker

TENSOR TM27 with ATR cell, with 2 cm^{-1} resolution. The IR spectra ware recorded at room temperature in range 4000 - 400 cm^{-1}.

Analysis of crystalline structure (crystallite size, lattice parameter) and identification of spinel phases were performed by means of X-ray diffraction technique (XRD), using a Bruker ASX D8 Advance diffractometer with Cu K_α (λ = 0,15406 nm) radiation, for 2θ ranging between 20° and 80°, at a scanning speed of 0.02°/s.

The morphology and particle size distribution of the powders heated at 900°C were investigated by scanning electron microscopy (SEM) using a Hitachi S2600N mycroscope.

The frequency dependence of dielectric permittivity and dielectric losses were studied using a Agilent 4292-1 device, in the range of 40 Hz – 10^7 MHz. The pellets were pressed into a cylindrical disk at 400 kPa/cm^2, without subsequent calcinations and were inserted between two electrodes.

7.3. Structural characterization of magnesium-substituted copper ferrite

7.3.1. IR spectra interpretation

Chemical and structural changes which occur during the heat treatment was monitored by infrared absorption spectroscopy. IR spectra were recorded in the 4000 - 400 cm^{-1}wavenumber, at room temperature. IR spectra obtained after combustion of the samples are shown in Figure 22.

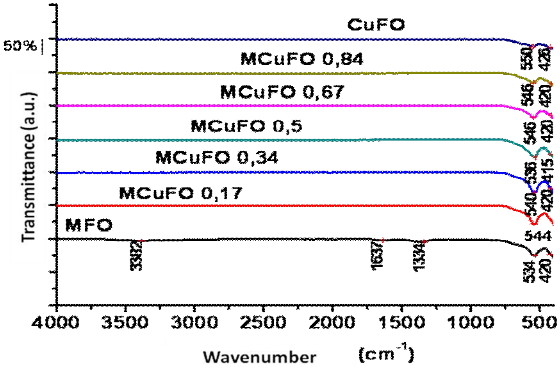


Figure 22. IR spectra of $Mg_{1-x}Cu_xFe_2O_4$ after auto-combustion proces

In the case of magnesium ferrite sample unsubstituted (MFO), after auto-combustion, the maximum of absorbtion characteristic stretching vibration of hydroxyl group at 3382 cm^{-1} [123]. Absorption bands at 1637 cm^{-1} and 1334 cm^{-1} corresponding to the vibration of carboxyl and antisymmetric nitrate group [48]. All these levels are gradually removed with increasing of temperature [99]. In addition to these absorption bands can be seen the appearance of peaks characteristic to the spinel structure that occur below the 600 cm^{-1} [87].

In the case of MCuFO 0.17, MCuFO 0.34, MCuFO 0.50, MCuFO 0.67, MCuFO 0.84 and CuFO samples, can bee observed that IR spectra do not show the characteristic absorption peaks of hydroxyl, carboxyl and nitrate groups, where we draw concluded that the organic phase and nitrate involved in the reaction for obtaining the ferrite substituted with copper ions has been completely removed.

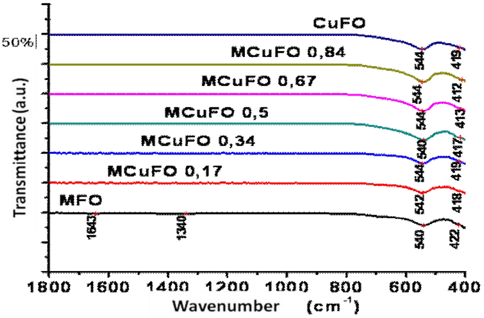


Figure 23. IR spectra for $Mg_{1-x}Cu_xFe_2O_4$ treated at 350°C

In Figure 23 are showed the IR spectra in the range 1800 cm^{-1} - 400 cm^{-1} for ferrites synthesized and heated at 350°C.

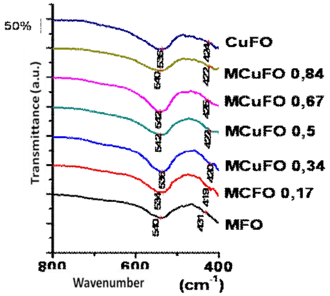


Figure 24. IR spectra for $Mg_{1-x}Cu_xFe_2O_4$ trated at 500°C

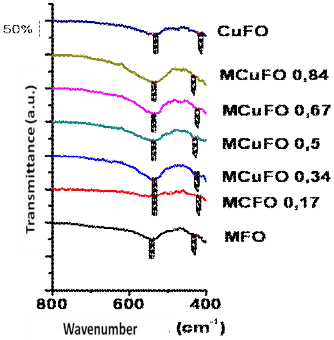


Figure25. IR spectra for $Mg_{1-x}Cu_xFe_2O_4$ trated at 700°C

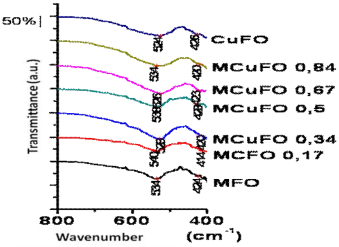


Figure 26. IR spectra for $Mg_{1-x}Cu_xFe_2O_4$ treated at 900°C

Figures 24, 25 and 26 are shown IR spectra of the synthesized ferrite in range 800 cm^{-1} - 400 cm^{-1}. It should be noticed that the peak attributable to hidroxyl, nitrate and carboxyl groups are absent from the IR spectra of samples heated at temperatures greater than 500°C, which means that reactions had taken place completely. In this domaine there is two main absorption bands, $\bar{\upsilon}_1$ and $\bar{\upsilon}_2$, which are typical for the spinel structure. This is in agreement to Waldron [87], who said that the strongest absorption peak, $\bar{\upsilon}_1$, observed in the range of 600 cm^{-1} – 500 cm^{-1}, is caused by intrinsic vibrations of bonds between metal ions from tetrahedral positions and oxygen ions $M^{2+} - O^{2-}$ ($M^{2+} = Mg^{2+}$, Cu^{2+}), while the weakest absorption peak, $\bar{\upsilon}_2$, observed in the range of 500 cm^{-1} – 400 cm^{-1}, may be assigned to the stretching vibrations of bonds between metal ions from octahedral sites and oxygen ions $Fe^{3+} - O^{2-}$[48]. There is an small variation in the bands position at wavenumbers $\bar{\upsilon}_1$ and $\bar{\upsilon}_2$, by increasing Cu content, caused by the decrease in length of metal – oxygen bond. Also, increasing amount of Cu^{2+} ions with larger ionic radius [124] ($r_{Cu}{}^{2+} = 0.73$ Å; $A_{Cu} = 63.55$; $r_{Fe}{}^{3+} = 0.645$ Å, $A_{Fe} = 55.85$) leads to pushing Fe^{3+} ions in tetrahedral positions.

7.3.2. Structural characterization by X-ray diffraction

Spinel phase formation and crystaline structure were performed by means of X-ray diffraction (XRD).

The XRD diffraction patterns of MFO, MCFO 0.17, MCFO 0.34, MCFO 0.50, MCFO 0.67, MCFO 0.84 and CFO powders heated at 900°C are illustrated in Figure 27.

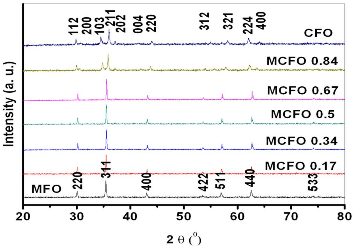


Figure 27. XRD diffraction patterns for $Mg_{1-x}Cu_xFe_2O_4$ heated at 900°C

From X-ray diffraction patterns, it can be seen that all samples present a single spinel phase without any secondary phases of α-Fe_2O_3 [79-1741 ICDD, 2002 JCPDS], MgO [77-2364 ICDD, 2002 JCPDS] and CuO [80-1916 ICDD, 2002 JCPDS].

Also, the presence of diffraction peak from (3 1 1) around 35.5°, confirms the formation of cubic spinel ferrite with *Fd-3m* space group for unsubstituted magnesium ferrite [73-2211 ICDD, 2002 JCPDS].

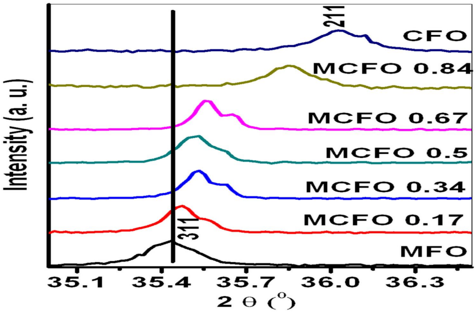


Figure 28. XRD diffraction patterns of $Mg_{1-x}Cu_xFe_2O_4$ heated at 900°C (2θ = 35°-36.5°)

It can be seen that once whit introduction of Cu^{2+} ion in the ferrite structure, take place a shift of the (3 1 1) diffraction peak to a higher 2θ (figure 28) characteristic for the tetragonal structure with $I4_1/amd$ space group [34-0425 ICDD, 2002 JCPDS]. These structure can be obtained by slow cooling from high temperature to room temperature. Metastable cubic phase can be obtained by rapid cooling from high temperature to room temperature [125].

The transition from cubic structure of MFO to tetragonal structure of CuFO can be explained by Jahn-Teller effect. For most transition metal oxides, octahedral symmetry positions (O_h), become tetragonal (D_{4h}) symmetry, because the local lattice distortions, due to an increase of M-O length outside of the plan and bond M-O reduction in the plan (figure 29 (a)) [126].

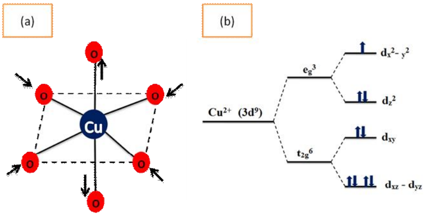


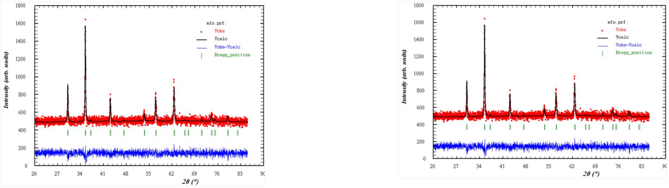
Figure 29. Tetragonal distorsion of CuO_6 and 3d orbital energy splitting of Cu^{2+} (d^9) ion

Cu^{2+} ion (electronic structure $1s^22s^22p^63s^23p^64s^23d^9$) of CuFO has in octahedral position configuration ($t_{2g}^{\,6}$)$e_g^{\,3}$. The 6 electrons with antiparallel spin degenerate triple ranks as the 3 orbital electrons in e_g are distributed as shown in Figure 29 (b). It is therefore expected to take place Jahn-Teller distortion ($O_h \rightarrow D_{4h}$) with values reported between cell parameters *c* and *a* greater than 1 (Table 13).

În figure 30 are represented the XRD patterns observed that simulated for MFO, MCFO 0.17, MCFO 0.34, MCFO 0.50, MCFO 0.67, MCFO 0.84 and CFO powders thermally treated at 900ºC.

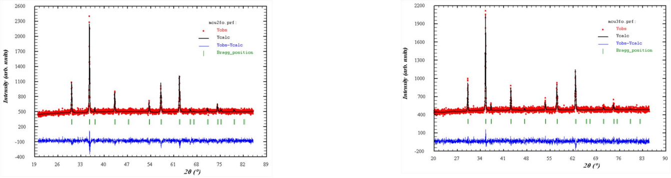
As can be sen from figure 30, calculated XRD diffraction for all samples are in agreement with the observed X-ray diffraction.

The grain size was estimated using the program FullProf 2000 [127], by profile fitting, with a peak shape modeled by a Voigt function using the Thomson Cox Hastings model [128].



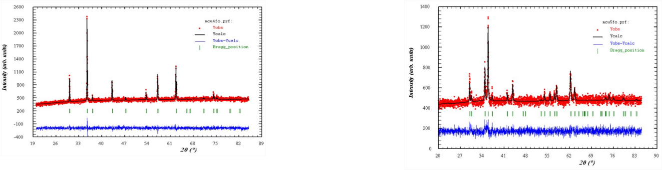
a. MFO

b. MCuFO 0.17



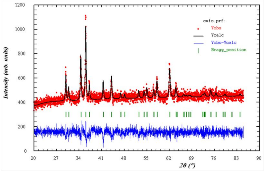
c. MCuFO 0.34

d. MCuFO 0.50



e. MCuFO 0.67

f. MCuFO 0.84



g. CuFO

Figure 30. (a-g) XRD powders of $Mg_{1-x}Cu_xFe_2O_4$ (calculated and observed) heated at 900ºC

The value of lattice parameter (*a*, *c*), crysalite size (*D*) and the cell volume (*V*) was determinated from simulated diffractograms and are represented in Table 13.

Table 13. Lattice parameter (*a*, *c*), cell volume (*V*), crystalite size (*D*) obtained for all samples trated at 900°C using FullProf programe

Compound	MFO	MCFO 0.17	MCFO 0.34	MCFO 0.5	MCFO 0.67	MCFO 0.84	CFO
Space group	*Fd-3m*	*Fd-3m*	*Fd-3m*	*Fd-3m*	*Fd-3m*	$I4_1/amd$	$I4_1/amd$
a (Å)	8.391	8.383	8.378	8.378	8.375	8.597	8.707
c (Å)	8.391	8.383	8.378	8.378	8.375	5.847	5.812
c/*a*	1.00	1.00	1.00	1.00	1.00	1.432	1.498
V (Å^3)	590.9	589.1	588.0	588.1	587.5	294.0	294.2
D (nm)	42	75	85	85	144	51	26

From table 13, it can be seen the increasing of crystallite size with increasing Cu content until the appearance of tetragonal structure for $Mg_{0,16}Cu_{0,84}Fe_2O_4$ sample, when it starts to decrease down to 26 nm. Value of lattice parameter and cell volume are in agreement with literature data [117]. The lattice parameter ***a*** decrease with increase of Cu content, which is due to replace of Fe^{3+} ion with Cu^{2+}ion which shows larger radius ($r_{Cu}{}^{2+}$ = 0.73 Å ; A_{Cu} = 63.55 ; $r_{Fe}{}^{3+}$ = 0.645 Å, A_{Fe} = 55.85) [124]. Decreasing of cell volume usually results in diminution of the diffusion path, leading to a decrease in the cation interdiffusion rate in the solid solution [129].

7.3.3. Morphological study by Scanning Electron Microscopy

The SEM micrographs for MCFO 0.17, MCFO 0.50, MCFO 0.84 and CFO samples heated at 900°C are shown in Figure 31 (a-d). Figure 32 (a-d) shows that all samples have small nanometric particles.

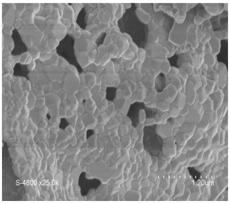


Figure 31.a. SEM image of MCuFO 0.17 treated at 900°C for 9 ore

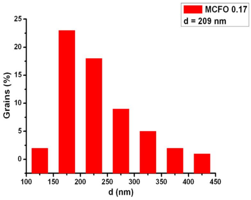


Figure 32.a. Grains distribution of MCuFO 0.17 treated at 900°C for 9h

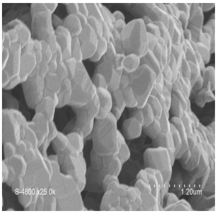


Figure 31.b. SEM image of MCuFO 0.50 treated at 900°C for 9 ore

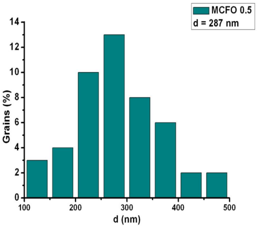


Figure 32.b. Grains distribution of MCuFO 0.50 treated at 900°C for 9h

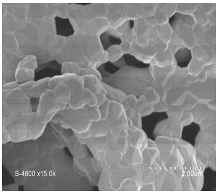


Figura 31.c. SEM image of MCuFO 0.84 treated at 900°C for 9 h

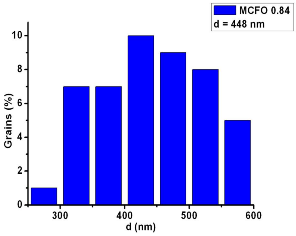


Figura 32.c. Grains distribution of MCuFO 0.84 treated at 900°C for 9h

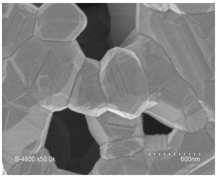


Figura 31.d. SEM image of CuFO treated at 900°C for 9h

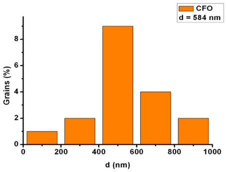


Figura 32.d. Grains distribution of CuFO treated at 900°C for 9 h

In figures 31 a and b it can be observed spherical shape particles of $Mg_{0,83}Cu_{0,17}Fe_2O_4$ and $Mg_{0,50}Cu_{0,50}Fe_2O_4$. For the $Mg_{0,16}Cu_{0,84}Fe_2O_4$ and $CuFe_2O_4$ samples can be seen aglomerated particels with hexagonal shapes. Voids and holes visible in Figures 31 (a-d) can be caused by the effect of different amounts of released gases during the auto-combustion process.

It can be seen that uniform grain size which are distributed over the entire surface has a tendency to decrease with increasing the amount of copper introduced. Average particle size samples obtained from SEM images, significantly increases with increasing concentration of copper because copper ion radius greater than the radius of the magnesium ion. This shows that each particle consists of a number of crystallites [130]. Average particle size obtained from SEM images are 209 nm for MCuFO 0.17, 287 nm for MCuFO0.50, 448 nm for McuFO 0.84 and 584 nm for CuFO.

7.4. Dielectric properties of magnesium ferrite substituted with copper

Variation of real (ε'), imaginary (ε'') parts of dielectric constant and dielectric loss tangent (tanδ) with frequency in the range 40 Hz – 10 MHz for MFO, MCuFO 0.17, MCuFO 0.34, MCuFO 0.50, MCuFO 0.67, MCuFO 0.84 and CuFO samples are showed in Figure 33 (a-c).

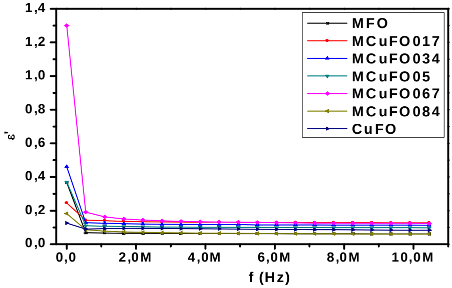


Figure 33 (a) The real part variation of the dielectric constant with frequency for $Mg_{1-x}Cu_xFe_2O_4$ heated at 900°C

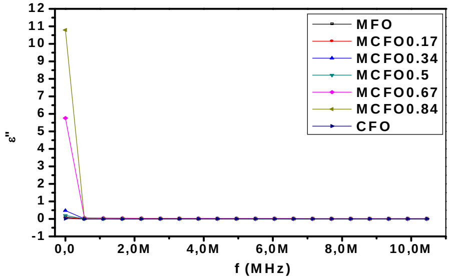


Figura 33 (b) The imaginary part variation of the dielectric constant with frequency for $Mg_{1-x}Cu_xFe_2O_4$ heated at 900°C

From figure 33 (a-b) it can be seen that dielectric constant varie with frequency wich means and can se poate observa că variaţia constantei dielectrice cu frecvenţa indicates a normal dielectric dispersion due to Maxwell-Wagner [131], [77] according to Koops theory [115].

It can be seen that value of dielectric constant decreases with increasing frequency and reach a constant value at high frequencies, according to Modelul Maxwell-Wagner model. This variation can be caused by oxygen vacancies, lattice defects, holes and by the electronic exchange $Fe^{2+} \leftrightarrow Fe^{3+}$ that cannot follow the alternating field because of the predominance of species such as Fe^{2+} ions.

At low frequencies dielectric constant increase in the range $0.0 \leq x \leq 0.67$, which means that there is a large number of polarizable Fe^{2+} ions in the octahedral sites, so that polarization increases. For the rest of samples polarization decreases, which means that the number of polarizable Fe^{2+} ions in the octahedral sites decreases.

In Figure 33 (c) are represented variation of dielectric loss factor (tan δ) with frequency, for all samples, measured at room temperature.

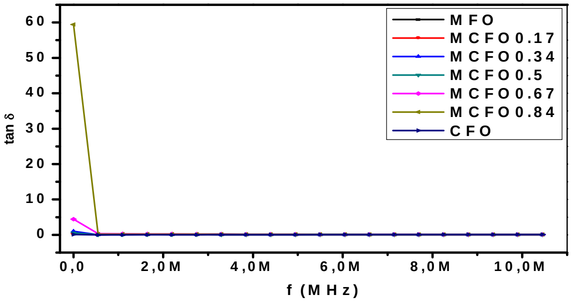


Figura 33 (c). Dielectric loss function on frequency for for $Mg_{1-x}Cu_xFe_2O_4$ heated at 900°C

It can be observed that all investigated samples show a normal dielectric behavior. Dielectric loss factor decreases with the increse of frequency, remain constant at higher value of frequency. The decrease of tanδ with increasing frequency can be explained on the basis of Koop's phenomenological theory [115]. In the frequency range 100 Hz – 1 MHz, all samples exhibit low dielectric constant values and and very low loss factors.

Figures 34 (a-g) show the complex constant plots of magnesium ferrite substituted with copper in the frequency range from 100 Hz to 100 MHz. The Cole–Cole plots [74]were obtained by plotting the imaginary part (ε'') of dielectric constant against the real part (ε').

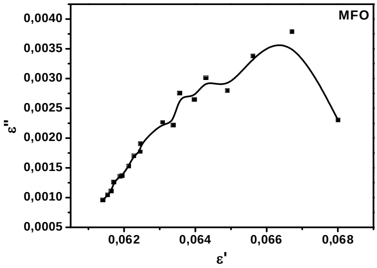


Figure 34 a. Cole-Cole plot for MFO treated at 900°C

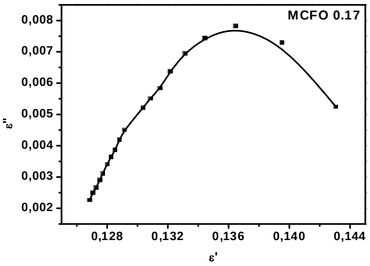


Figure 34 b. Cole-Cole plot for MCuFO 0.17 treated at 900°C

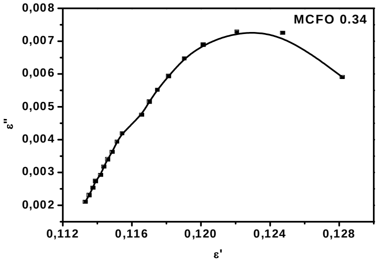


Figure 34 c. Cole-Cole plot for MCuFO 0.34 treated at 900°C

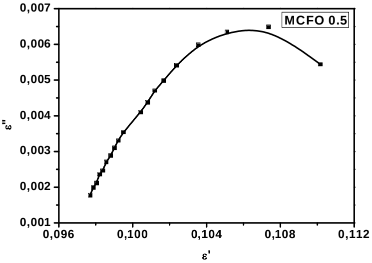


Figure 34 d. Cole-Cole plot for MCuFO 0.50 treated at 900°C

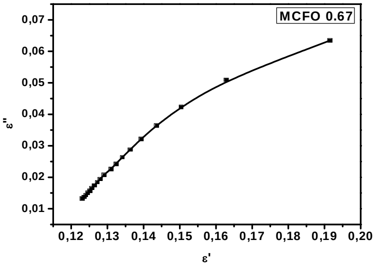


Figure 34 e. Cole-Cole plot for MCuFO 0.67 tratată termic la 900°C

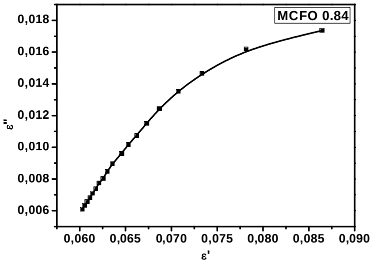


Figure 34 f. Cole-Cole plot for MCuFO 0.84 treated at 900°C

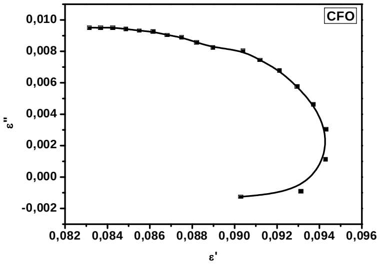


Figure 34 g. Cole-Cole plot for CuFO treated at 900°C

From the Cole-Cole plots it can be observed only a single semicircle is present for all samples. This means that the contribution of the grain boundary is predominant, while the contribution from the grain-bulk interior is not resolved for these samples. Otherwise, the contribution of the separation layer can not be separated from the contribution from electrical measurements grain. It also could be due to the presence of additional time constant, which occurred outside the measured frequency range [132]. From the variation of dielectric constant is clear that the values of grain boundary resistance increase together with Cu amount up $Mg_{0,33}Cu_{0,67}Fe_2O_4$ and then a decrease in the resistance is produced. It can be noted that the grain boundary resistance of examined samples is directly proportional to the polarizability.

Chapter 10. Final Conclusions

In this PhD thesis, we proposed to synthesize and study the properties of four series of compounds:

✓ Unsubstituted magnesium ferrite spinel structure synthesized by a number of chelating/combustion agents such as: glycine, hexametilentetraamine, urea, tartaric acid, citric acid, cellulose and a mixture of cellulose - citric acid;

✓ Magnesium ferrite substituted with copper cations with spinel structure and general formula $Mg_{1-x}Cu_xFe_2O_4$ with x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84 and 1.00;

✓ Magnesium ferrite substituted with cobalt cation with spinel structure and general formula $Mg_{1-x}Co_xFe_2O_4$ with x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84 and 1.00 ;

✓ Magnesium ferrite double substituted with copper and cobalt cation with spinel structure and general formula $Mg_{0.50}Cu_{0.50-x}Co_xFe_2O_4$ with x = 0.15, 0.25 and 0.35.

Oxide compounds studied were obtained using sol-gel auto-combustion method. In all syntheses as cation sources have been used nitrates. I used this method to synthesize due to the many advantages it offers:

- Obtaining homogeneous particle size in the nanometer range;
- Suppliers cheap cation;
- Simple apparatus;
- Terms of synthetic advantages over ceramic method: heat treatment is carried out at lower temperatures and the heat treatment time is reduced.

The main conclusions that can be drawn from research conducted in this PhD thesis were:

1) Influence of chelating/combustion agent on properties of magnesium ferrite. This study provides some useful information on optimizing the synthesis conditions. If magnesium ferrite main synthesis parameters influenced are:

- values of self-ignition flame temperature: 1200°C for MFO-Gly
- crystallite size: 76 nm for MFO-AC
- lattice parameter value: 8.404 Å for MFO-HA;
- cation distribution;
- saturation magnetization: $MgFe_2O_4$-CA (42.2 emu/g)
- dielectric properties:

$MgFe_2O_4$-HA > $MgFe_2O_4$-TA > $MgFe_2O_4$-CA/C > $MgFe_2O_4$-C > $MgFe_2O_4$-Gly > $MgFe_2O_4$–CA

2) Research conducted away from magnesium ferrite substituted with copper cation with spinel structure having the general formula $Mg_{1-x}Cu_xFe_2O_4$ with x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84 and 1.00 led to the following conclusions.

Seven samples were synthesized of magnesium ferrite substituted with copper cation using sol-gel auto-combustion method and glycine as chelating/combustion agent. We use this agent because it has the lowest ignition temperature of the six agents are using the previous syntheses. Another advantage of using this chelating/combustion agent is the temperature generated during the self-combustion process is very high and this helps to achieve uniform and clean particles from a cousin of phase from the low temperature. In this study we can draw the following conclusions:

- IR absorption spectroscopy, X-ray diffraction and scanning electron microscopy confirmed the formation of $Mg_{1-x}Cu_xFe_2O_4$ ferrite powders with x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84 and 1.00 spinel structure without secondary phases.
- X-ray diffraction revealed the transition of cubic structure of the magnesium ferrite in tetragonal structure of copper ferrite with increasing content of copper in the composition (x = 0.84).
- Study of dielectric properties for this series of compounds shows that the value of dielectric constant increases for samples with x in the range $0.00 \leq x \leq 0.67$, due to the large number of existing polarized ion Fe^{2+} in octahedral positions. For other samples polarization decreases due to lower number of Fe^{2+} ions polarize the octahedral positions. The values of dielectric constant and dielectric loss decreases with increasing frequency and reaches a constant value at high frequencies. These features are very important for the production of various electronic devices that can be used successfully in a wide range of frequencies.

3) The study of magnesium ferrite substituted by cobalt cations with spinel structure having the general formula $Mg_{1-x}Co_xFe_2O_4$ with x = 0.00, 0.17, 0.34, 0.50, 0.67, 0.84 and 1.00 revealed the following conclusions:

- use of sol- gel self- combustion method using glycine as chelating/combustion agent led to the formation of nano size particles.
- infrared absorption spectroscopy indicated the absence of organic phase and nitrate groups and the formation of spinel structure occurs immediately after the self-ignition.
- X -ray diffraction confirmed the formation of cubic spinel structure for all seven samples and the absence of secondary phases.
- The dielectric constant and dielectric loss decreases with increasing frequency and tends to a constant value at high frequencies, so the samples synthesized develop normal dielectric behavior. Maximum dielectric constant corresponds to compound $Mg_{0.33}Co_{0.67}Fe_2O_4$ and then decreases with increasing cobalt content.

4) Samples of magnesium ferrite double substituted with copper and cobalt cation with spinel structure having the general formula $Mg_{0.50}Co_{0.50-x}Cu_xFe_2O_4$ with x = 0.15, 0.25 and 0.35 were synthesized by sol - gel auto-combustion method and the conclusions are:

- IR indicated the spinel structure arise as soon as there is the self- combustion and absence of organic phase and of nitrate groups.
- X -ray diffraction confirms the spinel structure for all three samples and the crystallite size in the nanometer range.
- The analysis of the dielectric properties is observed that the values of dielectric constant and dielectric loss decreases with increasing frequency and tends to a constant value at high frequencies, to developing a normal dielectric behavior. The sample with the best results is to $Mg_{0.50}Co_{0.15}Cu_{0.35}Fe_2O_4$.
- The compounds obtained have dielectric properties superior comparative with magnesium ferrite unsubstituted, which calls for applications in the field of electrical technology.

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Annex I. The scientific activity

I.1. List of papers published in ISI

1. **A. C. Druc**, A. M. Dumitrescu, A. I. Borhan, V. Nica, A. R. Iordan, M. N. Palamaru, *Optimization of synthesis conditions and the study of magnetic and dielectric properties for* $MgFe_2O_4$ *ferrite*, Central European Journal of Chemistry, 11 (2013) 1330-1342.

2. **A. C. Druc,** A. I. Borhan, G. G. Nedelcu, L. Leontie, A. R. Iordan, M. N. Palamaru, *Structure-dielectric properties relationships in copper-substituted magnesium ferrites,* Materials Research Bulletin, 48 (2013) 4647-4654.

I.2. Abstract published in scientific papers

1. **A.C. Druc**, A.M. Dumitrescu, A.R. Iordan, M.N. Palamaru, *Influence of chelating/combustion agents on catalytic properties of the magnesium ferrite,* Scientific session of the students, masters and PhD students "Chemistry - frontier open to knowledge", edition II, Iasi, June 24, 2011, Acta Chemica Iasi SCSMD 2011, ISSN 2067-2438, pp. 59-59 (abstract published).

2. **A.C. Druc**, A.M. Dumitrescu, V. Nica, A.R. Iordan, M.N. Palamaru, *Influence of complexing/combustion agents on electric, magnetic and catalytic properties of magnesium ferrite,* Scientific session of the students, masters and PhD students "Chemistry - frontier open to knowledge", edition III, Iasi, Acta Chemica Iasi SCSMD 2012, ISSN 2067-2438, pp. 50-52 (abstract published).

3. **A.C. Druc**, A.I. Borhan, G.G. Nedelcu, L. Leontie, A.R. Iordan, M.N. Palamaru, *Structure-dielectric properties relationships in copper-substituted magnesium ferrite)*, Scientific session of the students, masters and PhD students "Chemistry - frontier open to knowledge", edition IV, Iasi, Acta Chemica Iasi SCSMD 2013, ISSN 2067-2438, pp. 12-13 (abstract published).

I.3. List of participations in national and international conferences

1. **A.C. Druc**, A.M. Dumitrescu, A.R. Iordan, M.N. Palamaru, *Optimization of synthesis conditions for* $MgFe_2O_4$ *ferrite using different complexation/combustion agents*, „International Conference of Applied Sciences, Chemistry and Chemical Engineering" Bacau 28-29 April 2011 – http://cisaconf.ub.ro/ (poster)

2. **A.C. Druc**, A.M. Dumitrescu, A.R. Iordan, M.N. Palamaru, *Influence of chelating/combustion agents on catalytic properties of the magnesium ferrite,* Scientific session of the students, masters and PhD students "Chemistry - frontier open to knowledge", edition II, Iasi, June 24, 2011, Acta Chemica Iasi SCSMD 2011, ISSN 2067-2438, pp. 59-59 – http://www.chem.uaic.ro/ro/manifestari/programul-sesiunii.html – (poster)

3. **A. C. Druc**, A. M. Dumitrescu, A. R. Iordan, M. N. Palamaru, *Influence complexing/combustion agents on catalytic properties of magnesium ferrite,* Scientific session occasioned university days, 28.10.2011, Iasi – http://www.chem.uaic.ro/files/File/2011-2012/zu-2011/program-zilele-universitatii-2011(10).pdf – (oral comunication).

4. **A.C. Druc,** A.M. Dumitrescu, A.R. Iordan, M.N. Palamaru, *Influence complexing/combustion agents on catalytic properties of magnesium ferrite,* „International Conference of Applied Sciences, Chemistry and Chemical Engineering",Sixth Edition – April 24-27/ 2012, Bacau, Romania – http://cisaconf.ub.ro – (poster).

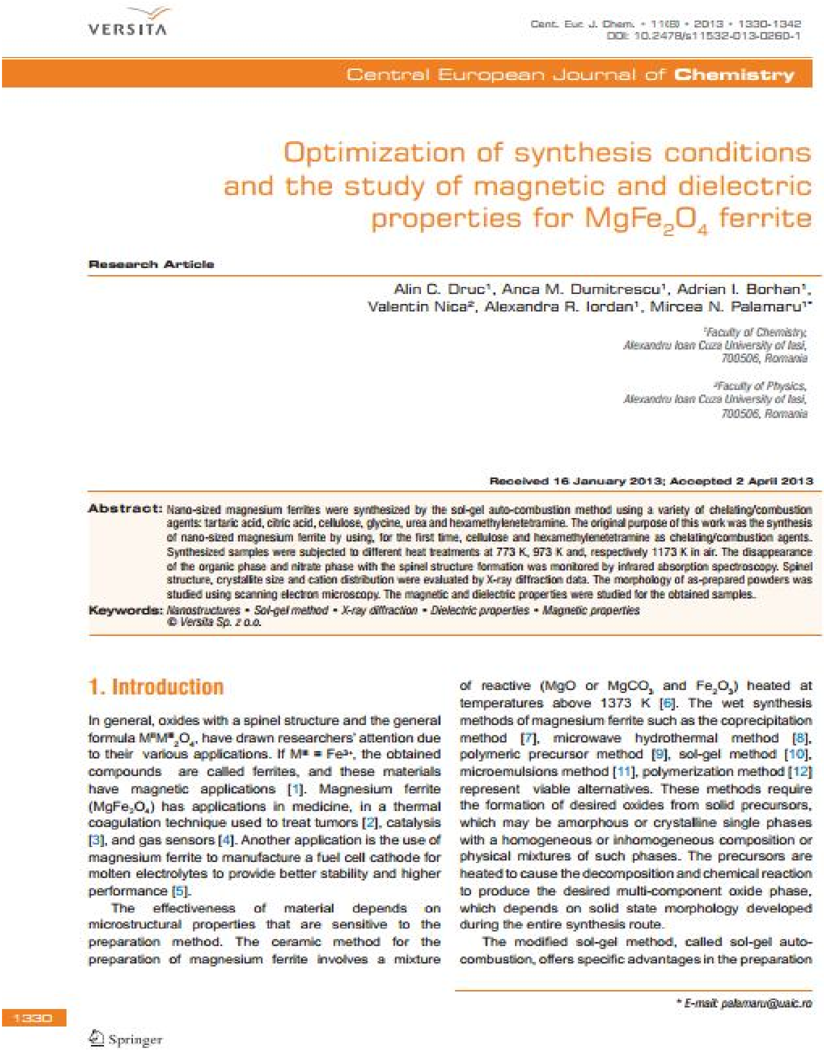
5. **A.C. Druc**, A.M. Dumitrescu, V. Nica, A.R. Iordan, M.N. Palamaru, *Influence of complexing/combustion agents on electric, magnetic and catalytic properties of magnesium ferrite,* Scientific session of the students, masters and PhD students "Chemistry - frontier open to knowledge", edition III, Iași, 26 mai 2012 - http://www.chem.uaic.ro/files/File/2011-2012/smd-26-mai-2012/program-final-conferinta-26-05-2012(3).pdf - (poster).

6. **A.C. Druc**, A.M. Dumitrescu, A.R. Iordan, M.N. Palamaru, *Synthesis and characterization of oxide compounds with general formula* $Mg_{1-x}Cu_xFe_2O_4$.- http://www.chem.uaic.ro/ro/manifestari/zu2012.html – (oral comunication)

7. **A.C. Druc**, A.I. Borhan, G.G. Nedelcu, L. Leontie, A.R. Iordan, M.N. Palamaru, *Structure-dielectric properties relationships in copper-substituted magnesium ferrites*, „International Conference of Applied Sciences, Chemistry and Chemical Engineering" Bacău 16-18 May 2013 – http://cisaconf.ub.ro/ (poster)

8. **A.C. Druc**, A.I. Borhan, G.G. Nedelcu, L. Leontie, A.R. Iordan, M.N. Palamaru, *Structure-dielectric properties relationships in copper-substituted magnesium ferrites,* Scientific session of the students, masters and PhD students "Chemistry - frontier open to knowledge", edition IV, Iasi, 2013, http://www.chem.uaic.ro/files/File/2011-2012/smd-26-mai-2012/program-final-conferinta-28-06-2013(3) (comunicare orală)

Annex II. The papers published or submitted for publication in ISI



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Central European Journal of **Chemistry**

Optimization of synthesis conditions and the study of magnetic and dielectric properties for $MgFe_2O_4$ ferrite

Research Article

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Abstract: Nano-sized magnesium ferrites were synthesized by the sol-gel auto-combustion method using a variety of chelating/combustion agents: tartaric acid, citric acid, cellulose, glycine, urea and hexamethylenetetramine. The original purpose of this work was the synthesis of nano-sized magnesium ferrite by using, for the first time, cellulose and hexamethylenetetramine as chelating/combustion agents. Synthesized samples were subjected to different heat treatments at 773 K, 973 K and, respectively 1173 K in air. The disappearance of the organic phase and nitrate phase with the spinel structure formation was monitored by infrared absorption spectroscopy. Spinel structure, crystallite size and cation distribution were evaluated by X-ray diffraction data. The morphology of as-prepared powders was studied using scanning electron microscopy. The magnetic and dielectric properties were studied for the obtained samples.

Keywords: *Nanostructures • Sol-gel method • X-ray diffraction • Dielectric properties • Magnetic properties*

1. Introduction

In general, oxides with a spinel structure and the general formula $M^{II}M^{III}_2O_4$, have drawn researchers' attention due to their various applications. If $M^{III} = Fe^{3+}$, the obtained compounds are called ferrites, and these materials have magnetic applications [1]. Magnesium ferrite ($MgFe_2O_4$) has applications in medicine, in a thermal coagulation technique used to treat tumors [2], catalysis [3], and gas sensors [4]. Another application is the use of magnesium ferrite to manufacture a fuel cell cathode for molten electrolytes to provide better stability and higher performance [5].

The effectiveness of material depends on microstructural properties that are sensitive to the preparation method. The ceramic method for the preparation of magnesium ferrite involves a mixture of reactive (MgO or $MgCO_3$ and Fe_2O_3) heated at temperatures above 1373 K [6]. The wet synthesis methods of magnesium ferrite such as the coprecipitation method [7], microwave hydrothermal method [8], polymeric precursor method [9], sol-gel method [10], microemulsions method [11], polymerization method [12] represent viable alternatives. These methods require the formation of desired oxides from solid precursors, which may be amorphous or crystalline single phases with a homogeneous or inhomogeneous composition or physical mixtures of such phases. The precursors are heated to cause the decomposition and chemical reaction to produce the desired multi-component oxide phase, which depends on solid state morphology developed during the entire synthesis route.

The modified sol-gel method, called sol-gel auto-combustion, offers specific advantages in the preparation

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Structure-dielectric properties relationships in copper-substituted magnesium ferrites

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ABSTRACT

Nanocrystalline powders of copper-substituted magnesium ferrites with general formula $Mg_{1-x}Cu_xFe_2O_4$ ($x = 0.00$, 0.17, 0.34, 0.50, 0.67, 0.84, 1.00) were prepared for the first time by sol–gel auto-combustion method, using glycine as fuel agent. Solid phase chemical reactions and the occurrence of spinel structure were monitored by using infrared spectroscopy. X-ray diffraction analysis confirmed the spinel single-phase formation. A shift from cubic structure to tetragonal structure starting with $x = 0.84$ was also observed. Microstructure of the samples was analyzed by scanning electron microscopy and particle size was estimated from the micrographs.

Analysis of dielectric properties revealed very low values of dielectric loss at frequencies over 10 MHz.

1. Introduction

Spinel ferrites, with general formula of AB_2O_4, where $B = Fe^{3+}$ is a trivalent cation from octahedral positions and $A = Mg^{2+}$, Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} is a divalent cation located in tetrahedral positions, are a very important class of materials, due to their electric [1] and magnetic properties [2]. These materials, which have significant features as low toxicity, high chemical and thermal stability, play a major role in many application areas. Spinel ferrites have applications in thermal coagulation technique used to treat tumors [3]. They are also used as chemical sensors [4], catalysts [5], magnetic carriers for drugs [6] in microwave devices due to high electric resistivity and low dielectric loss [7].

To obtain ferrites with desired characteristics, suitable for applications, several preparation methods have been developed, such as: ceramic method [8], co-precipitation method [9], hydrothermal method [10], Pechini method [11,12], sol–gel method [2] and combustion method [13].

According to our literature data, no report has been made about the effect of Mg substitution for Cu on the electric properties of $MgFe_2O_4$. Note that there are several studies focusing on the effect of metal ion substitution such as Ni [14] and Zn [15] on the structure and magnetic properties of $MgFe_2O_4$. Therefore, our main objective was to synthesize pure nanocrystalline powders with the general formula $Mg_{1-x}Cu_xFe_2O_4$ ($0.00 \leq x \leq 1.00$) by sol–gel auto-combustion method [16] using glycine as chelating/combustion agent and to investigate the effect of Mg/Cu^{2+} substitution in $MgFe_2O_4$ on the structural characteristics and electric properties. As is known, one important technique for the ferrite preparation is the sol–gel auto-combustion method, because this procedure allows control of the chemical composition, solid texture and particle size [17]. According to literature, glycine is cheaper than urea and citric acid, and the heat of combustion is lower (-13.54 kJ g^{-1}) compared to urea (-12.45 kJ g^{-1}) or citric acid (-11.53 kJ g^{-1}) [18]. Another advantage of using glycine as chelating/combustion agent is the formation of stable complexes with metal ions, which increases solubility and prevents selective precipitation of metal ions during water evaporation [19]. Glycine fuel is expected to yield finer-sized powders, exhibiting desirable powder characteristics.

2. Experimental

Nanoparticles of $Mg_{1-x}Cu_xFe_2O_4$ ($x = 0.00$, 0.17, 0.34, 0.50, 0.67, 0.84, 1.00), hereinafter denoted as MFO, MCFO 0.17, MCFO 0.34, MCFO 0.5, MCFO 0.67, MCFO 0.84 and CFO, where MFO represents $MgFe_2O_4$ and CFO is $CuFe_2O_4$, were prepared by sol–gel auto-combustion method. All analytical grade reactives (Aldrich) were used without further purification. Mixed oxide nanopowders were produced from aqueous solution containing ($[Mg(NO_3)_2 \cdot 6H_2O]$,

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