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SYNTHESIS OF $Mn_{0.5}Cu_{0.5}Fe_2O_4$ BY SOL-GEL AUTOCOMBUSTION METHOD

Corina RADU[1], Anca Mihaela DUMITRESCU*, Alexandra Raluca IORDAN*,
Ionel HUMELNICU[1], Mircea Nicolae PALAMARU[1]

Abstract. *Nanocrystalline* $Mn_{0.5}Cu_{0.5}Fe_2O_4$ *ferrite powders were successfully synthesized using the sol–gel autocombustion method, by using nitrates as cations source and cellulose and urea as chelating/fuel agents. Reaction advancement was observed by means of IR absorption spectroscopy, by monitoring two characteristic bands for the spinel compounds at around 550 and 400 cm−1, respectively. X-ray diffraction studies reveal the formations of single phase cubic spinel structure.*

Keywords: *Ferrites, Sol–gel method, Nanopowders, X-ray diffraction, Spinel structure.*

Introduction

Ferrites are advanced materials generally characterized by high magnetic permeability, high saturation magnetization and low power losses.

Magnesium ferrite ($MgFe_2O_4$) is one of the most important ferrites. It has a cubic structure of normal spinel-type. This ferrite is a soft magnetic n-type semiconducting material, which finds a number of applications in heterogeneous catalysis, adsorption, sensors, and magnetic technologies. (Verma et. al., 2004) Recently, nanostructures of magnetic materials have received more and more attention due to their novel material properties that are significantly different from those of their bulk counterparts. (Busca et al., 1996, Shimizu et al., 1985, Machera et al., 2002, Franco et al., 2009

Magnesium ferrite with diamagnetic substitution for Mg^{2+} and Fe^{3+} ions has attracted attention of a number of research workers who attempted to explain magnetic properties on the basis of the distribution of only magnetic ion Fe^{3+} in tetrahedral (A) and octahedral [B] sites, which makes the analysis reliable. (Chhaya et al., 2004)

Physical and chemical properties of magnesium ferrites substituted or non-substituted, depend upon the cation distribution, which in turn is a complex function of processing parameters and preparation method of the material. (Pavlovič et al., 2009)

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[1] Faculty of Chemistry, “Alexandru Ioan Cuza” University of Iasi, Carol I Boulevard, 700506 Iasi, Romania
* Corresponding authors : Anca Mihaela Dumitrescu: +40232201341, ancamihadumi@yahoo.com
Alexandra Raluca Iordan: +40232201341, alexandra.iordan@uaic.ro

According to literature, no many report has been made about the effect of Mg substitution for Cu on the electric properties of $MgFe_2O_4$. In previous research we studied the influence of the substitution of magnesiun with copper ions in magnesium ferrite obtained by sol–gel auto-combustion method using glycine as chelating/fuel agent. A decrease in the dielectric loss has been found on Cu substitution, which is useful for power application of these ferrites. (Druc et al., 2013)

In the present paper, our research concerning the influence of the chelating/fuel agent on the crystal structure of the magnesium ferrite in which half of magnesium ions have been replaced with copper ions are presented.

Experimental details

$Mn_{0.5}Cu_{0.5}Fe_2O_4$ was synthesized sol–gel autocombustion method using cellulose and urea as chelating/fuel agent. A detailed description of the methodology used to prepare powder ferrite by sol–gel autocombustion method has been described elsewhere. (Dumitrescu et. al., 2013)

All analytical reagents (Aldrich) were used without further purification. Stoichiometric amounts of manganese nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot$ 3H2O) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) solutions were mixed for a molar ratio Mg:Cu:Fe = 0.5:0.5:2. At the nitrate solutions containing the cations mixture was added the chelating/fuel agent, cellulose (CL) or urea (U) solution respectively. The mass ratio ferrite:CL = 1:1.8 and molar ratio ferrite:U = 1:3. Each of two systems, cations solution - chelating/fuel agent, were transformed into gels, at 348K under continuous stirring, according to the synthesis prtocol described in Figure 1.

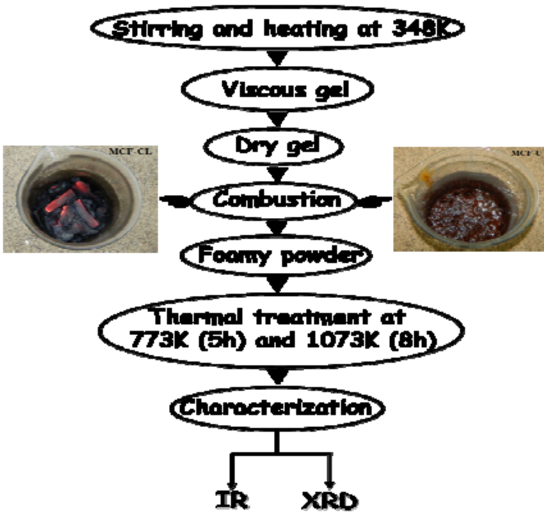

Figure 1. Flowchart of the powder preparation

Subsequently, the gels were heated on the sand bath up to 573K, until the combustion was clearly observed and foamy powder was obtained. Auto-combustion process unfolds differently depending on the chelating/fuel agent. When was used urea as chelating/fuel agent, the process occurs quickly (about 2 minutes), with the release of large quantities of gas and heat. In the case of cellulose, the process takes place over a long period of time (about 30 minutes). Table 1 illustrates temperatures during auto-ignition which were measured with an UT infrared thermometer for each synthesis. After the combustion process, the powders were ground and subjected to thermal treatments in two steps: at 773K and 1073K for 5h and 8h respectively in order to complete the spinel structure formation.

Table 1. Flame temperature for chelating/fuel agents

Chelating/fuel agent	Flame temperature (K)
Cellulose (CL)	923
Urea (U)	873

The overall reaction of the synthesis can be written as follows:

$$Mg(NO_3)_2 + Cu(NO_3)_2 + 4Fe(NO_3)_3 + \text{chelating/combustion agent} \rightarrow$$
$$\rightarrow 2\ Mg_{0.5}Cu_{0.5}Fe_2O_4 + \text{volatile compounds}$$

The samples were denoted according to the chelating/fuel agents, as follows: MCFCL and MCFU.

The phase formation of the $Mg_{0.5}Cu_{0.5}Fe_2O_4$ ferrite was checked by using a Fourier transform infrared (FTIR) spectra, recorded in the range 4000 cm^{-1} to 400 cm^{-1} with 2 cm^{-1} resolution on a Bruker spectrophotometer TENSORTM 27-type with Fourier transform (FTIR) equipped with an ATR cell. X-ray diffraction measurements at room temperature for to investigate the formation of the spinel phase in the powder were performed with a SHIMADZU XRD 6000 diffractometer using Ni-filtered CuKα radiation (λ = 1.5418 Å), with a scan step of 0.02° and a counting time of 1 s/step, for 2θ ranging between 20° and 80°.

Results

The study of infrared spectra is an important tool to monitoring the synthesis reactions. It helps to confirm the end of reaction and the formation of spinel structure in ferrite samples. Because in the IR spectra recorded for the two ferrites after the thermal treatment at 1073K (MCFCL and MCFU), there are no absorption bands characteristic of hydroxyl, nitrate or carbonate groups, in the figure 2 we presented only wavenumber region between 1000 – 400 cm^{-1}. (Pradeep et al., 2008) The absorption maxima at wavenumbers below 800 cm^{-1} are assigned to the stretching vibrations of bonds between the metallic cation and the oxygen anion (M-O). The absorption maximum within the range of 540- 520 cm^{-1}

is assigned to the intrinsic vibration (ν_1) of bonds between metal and oxygen ions in tetrahedral positions (A). The absorption maximum of lower intensity, about 420 cm^{-1}, corresponds to the stretching vibrations (ν_2) of bonds between octahedral metal [B] and oxygen ions (Mukherjee et al., 2010). These absorption maximum values, obtained for the two samples indicate the spinel structure formation, subsequently confirmed by XRD. According to Waldron (Waldron, 1955), the strongest absorption peak, observed in the range of 600 - 500 cm^{-1}, is caused by intrinsic vibrations of bonds between metal and oxygen ions in tetrahedral positions M^{2+}–O^{2-} ($M^{2+} = Mg^{2+}, Cu^{2+}$), while the weakest absorption peak observed in the range of 500 - 400 cm^{-1}, may be assigned to the stretching vibrations of bonds between octahedral metal and oxygen ions Fe^{3+} - O^{2-}. The slightly variation in bands position at wavenumbers $\overline{\nu}_1$ and $\overline{\nu}_2$ may be caused by the variation in the metal - oxygen bond length.

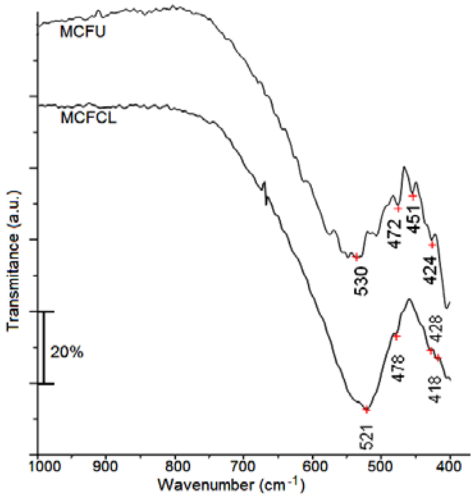

Figure 2. IR spectra of $Mg_{0.5}Cu_{0.5}Fe_2O_4$ powders heated at 1073K.

In the case of MCFCL can be seen that the absorption maxima shift to smaller wavenumbers, indicating an elongation of the M - O bond that is consistent with the higher lattice parameter determined by XRD measurements.

The XRD patterns for the MCFCL and MCFU ferrites are shown in Figure 3. The strongest reflection peak at 2θ value around 35° was identified for each diffraction pattern of the samples and assigned to (3 1 1) XRD diffraction plan typical for the spinel phase. Thus, the XRD patterns confirm the formation of single-phase cubic spinel structure for the samples annealed at 1073 K. All the reflection peaks were identified and indexed in good agreement with the referred database of the International Centre for Diffraction Data (77-2211 ICDD, 2002 JCPDS). The broad XRD lines indicate that ferrite particles are in the nano-sized scale which was also confirmed by calculations. [Slatineanu_2011_Materials-Research-Bulletin]

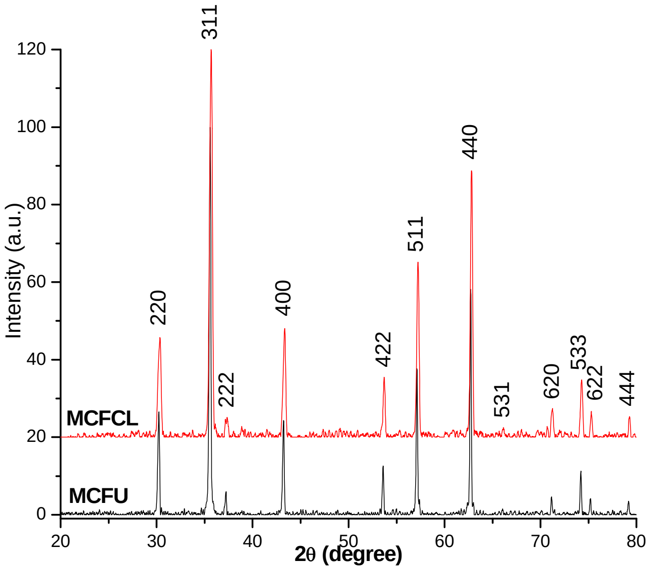

Figure 3. X-ray diffraction patterns of $Mg_{0.5}Cu_{0.5}Fe_2O_4$ powders heated at 1073K

[Borhan_2014_Polyhedron]The lattice was analyzed by means of line broadening of the most intense (311) diffraction peak. The calculated values of lattice parameter (a_{311}), crystallite size (D), and X-ray density (d_x) are presented in Table 2.

Table 2. Structural parameter of $Mg_{0.5}Cu_{0.5}Fe_2O_4$ powders: lattice constant (a_{311}), crystallite size (D), X-ray density (d_x)

Samples	a_{311} (Å) ± 0.2%	D (nm) ± 0.5%	d_x (g/cm^3)
MCFCL	8.369	75	4.84
MCFU	8.353	46	4.86

The lattice parameter a_{311} were determined according to Laue and Bragg equations for cubic lattice:

$$a_{311} = d_{311}(h^2 + k^2 + l^2)^{1/2}$$

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

with n = 1 for the cubic system.

The crystallite size (D) of the powders was determined by using the Debye-Scherrer formula:

$$D = 0.9\lambda/\beta_{1/2}\cdot\cos\theta$$

where D is the crystallites size, λ is the wavelength of X-ray source used (CuK_α = 1.5405 Å), $\beta_{1/2}$ (degree) is width at half-maximum intensity of the diffraction (311) peak and θ is the Bragg angle.

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

$$d_x = ZM / Na^3$$

where Z is the number of molecules per primitive unit cell (Z = 8), M is the molecular weight of the each compound, N is the Avogadro's number ($6.0223\cdot10^{23}$ particles/mol), and (a) is the lattice constant (cm). Obtained lattice parameters are in agreement with literature data [Pradhan et al., 2005].

Conclusions

This paper reports a study over the influence of two chelating/fuel agents on structure of the $Mg_{0.5}Cu_{0.5}Fe_2O_4$ spinel. For the first time, the successful synthesis of $Mg_{0.5}Cu_{0.5}Fe_2O_4$ nanopowder by sol–gel auto-combustion method using cellulose and urea was reported. For analyzed samples, IR spectra and XRD patterns confirm the pure spinel phase formation.

The difference of approximately 40% between the crystallites size of the two samples can be explained by the influence of chelating/fuel agent on the combustion process.

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