The effect of chelating/combustion agent on catalytic activity and magnetic properties of Dy doped Ni–Zn ferrite

P. Samoila a, T. Slatineanu a, P. Postolache b, A.R. Iordan a, M.N. Palamaru a, * 

a Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, 11 Carol I Boulevard 700506, Romania 
b Faculty of Physics, Alexandru Ioan Cuza University of Iasi, 11 Carol I Boulevard 700506, Romania

ABSTRACT

The spinel ferrite Ni0.8Zn0.2Fe1.98Dy0.02O4 was prepared by sol–gel low temperature auto-combustion method using four different chelating/combustion agents: citric acid, tartaric acid, urea and cellulose. Infrared spectroscopy (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) specific surface area measurement, the catalytic H2O2 decomposition and the magnetic behavior were employed to investigate the influence of the combustion agents on structural characteristics, catalytic activity and magnetic properties. Spinel-type phase in the nano-scale domain was accomplished during sol–gel synthesis and was confirmed by XRD and IR. The best catalytic activity is belonging to the sample obtained using urea, which shows the smallest grain size (SEM), the highest specific surface area (BET measurements) and DyFeO3 phase (XRD), while ferrimagnetic behavior prevails for all the samples independently of fuel agent.

ARTICLE INFO

Article history:
Received 22 December 2011
Received in revised form 13 June 2012
Accepted 26 June 2012

Keywords:
Nanostructures 
Fourier transform infrared spectroscopy 
X-ray diffraction 
Electron microscopy 
Magnetic properties

1. Introduction

Spinel ferrites M1−xM′xFe2−xRExO4, where M and M′ are bivalent metals (e.g. cobalt, manganese, nickel, zinc) and RE is a rare earth metal, are technologically attractive due to their promising magnetic properties. Thereby the ferrospins find extensive application in microwave devices [1], radar [2], ferro-fluids [3] or catalysis [4].

Furthermore, spinel ferrites are well known catalysts for various processes like the oxidative dehydrogenation of hydrocarbons [5], the decomposition of alcohols [6], the selective oxidation of carbon monoxide [7] and the decomposition of hydrogen peroxide [8]. Thereby, the isomorphic substitutions of the cations in the spinel structure plays a significant role both in magnetic properties and in tuning the catalytic properties of the material.

Applications of these mixed oxides depends on the high-quality powder synthesized by various methods like solid-state reaction [9], sol–gel [10], hydrothermal [11], thermal decomposition [12], vapor deposition [13], arc discharge [14], sonolysis [15] or co-precipitation [16] were reported in the literature. Among these
methods, sol–gel and its variants, including sol–gel auto-combustion, are often cited as novel synthesis techniques for advanced applications. The chelating/combustion agents frequently used in sol–gel auto-combustion method for the synthesis of spinel-type ferrite are citric acid [17,18], glycine [18,19], tartaric acid [20], urea [18,19], sucrose [21] and hydrazine [22].

Among the spinel ferrites, nickel substituted zinc ferrites have attracted considerable attention in recent years, especially due to their versatility in electrical and magnetic properties. Hence, in a previous work [10] we studied the magnetic properties of the Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ (NZFDy) nanoparticles, obtained by sol–gel auto-combustion method. It was shown that the magnetic properties of the nanoparticles demonstrate increased values of saturation magnetization with the increase in Ni substitution with a maximum performance for Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$. Previously, the solution proposed to make further improvements on the magnetic properties was the doping with rare earths of the nickel–zinc ferrites [23].

The decomposition of H$_2$O$_2$ is often used as a test reaction for ferrites catalyst, knowing that different parameters like chemical composition, crystal structure, electronic, electrochemical, topo-chemical, and microstructural factors have been found to contribute to the overall activity of these compounds [24].

The present work reports a study on the effects of four different chelating/combustion agents (citric acid, tartaric acid, urea and cellulose) used for the synthesis of a rare earth substituted Ni–Zn ferrite prepared by sol–gel low temperature auto-combustion method. Structural characteristics, magnetic properties and catalytic efficiency in the decomposition of hydrogen peroxide are reported. The synthesis of the spinel with Ni$_{0.8}$Zn$_{0.2}$Fe$_{1.98}$Dy$_{0.02}$O$_4$ formula it is reported for the first time and considered the target material for our investigation.

2. Experimental

Nanocrystalline particles of Ni–Zn ferrite doped with Dy with formula Ni$_{0.8}$Zn$_{0.2}$Fe$_{1.98}$Dy$_{0.02}$O$_4$ (NZFDy) were obtained by sol–gel auto-combustion method using as precursors nitrates of Fe$^{3+}$, Ni$^{2+}$, Zn$^{2+}$ and Dy$^{3+}$ and different chelating/combustion agents: citric acid (C$_6$H$_8$O$_7$·H$_2$O, Merck), tartaric acid (C$_4$H$_6$O$_6$, Merck), cellulose and urea (CH$_4$ON$_2$, Merck). The metal nitrate solutions were mixed in stoichiometric proportions. Zinc nitrate solution 1 M was obtained in situ from ZnO (Sigma–Aldrich) and nitric acid (Merck) 20% solution.

The molar ratio of metallic cations to fuel agent was 1:1 for tartaric acid and citric acid [25] respectively, 1:2 for urea [26], while the weight ratio between nitrates mixture and cellulose was 2.52:1.

The thermal dehydration and the gel formation took place by stirring and gradually heating the mixture on the water bath for several hours at 353 K. Then the gel was heated on the sand bath up to 623 K until the auto-ignition was clearly observed and the dark fluffy loose powder was formed.

The powders were subjected to thermal treatments in two steps: up to 773 K and up to 973 K, each for 7 h.

In order to achieve a pure spinel-phase formation the samples were supplementary heat treated for 9 h at 1173 K. Samples were denoted NZFDyCA, NZFDyTA, NZFDyCel, NZFDyU after as-used fuel agent (CA = citric acid, TA = tartaric acid, Cel = cellulose, U = urea).

The initiation and formation of spinel-type phase of NZFDy series was monitored by means of spectroscopy in the mid infrared range (4000–350 cm$^{-1}$) using a Bruker spectrophotometer TENSOR$^\text{TM}$ 27-type with Fourier transform (FTIR) with an ATR cell at a resolution of 2 cm$^{-1}$.

XRD patterns of the powder samples heat treated at 1173 K were recorded using a Shimadzu LabX 6000 diffractometer equipped with graphite monochromator and CuK$_\alpha$ ($\lambda = 0.15406$ nm) radiation. The specimens mounted in the reflection mode were analyzed in the ambient atmosphere with a scanning rate of 0.02° s$^{-1}$ over the 2$\theta$ = 20–80° range.

Using Vega Tescan-type scanning transmission electron microscope (SEM) was investigated the morphology and microstructure of ferrite samples sintered at 1173 K.

The specific surface area, $S_{\text{BET}}$, of as-obtained powders were calculated from nitrogen adsorption isotherm determined at 77 K using an Quantachrome Nova 2200 automated gas adsorption system after the samples were outgassed under vacuum at 473 K. The Brunauer–Emmet–Teller (BET) method was used to calculate the specific surface area.

The catalytic activities of Ni$_{0.8}$Zn$_{0.2}$Fe$_{1.98}$Dy$_{0.02}$O$_4$ spinels were investigated by decomposition of H$_2$O$_2$ using the conventional gasometric technique [24]. For this purpose, 5 mL H$_2$O$_2$ solution
The IR spectra of samples heat treated at 1173 K reveal only the specific bands for M−O stretching vibration from tetrahedral (A)-site in the range 542−554 cm$^{-1}$ and octahedral (B)-site in the range 359−370 cm$^{-1}$, respectively (Fig. 2). Shoulders detected in the range 467−474 cm$^{-1}$ could be attributed to the presence of Zn$^{2+}$ and Ni$^{2+}$ ions from A-site as a result of cation migration from B-site same with Dy$^{3+}$ insertion into spinel interstices [28]. Only for NZFDyU samples the shoulder around 470 cm$^{-1}$ is not so evident which could be explained by segregation of DyFeO$_3$ out of spinel matrix in agreement with XRD data.

### 3.2. XRD interpretation

Recorded XRD patterns for the samples heat treated at 1173 K are shown in the Fig. 3. It is noticed the influence of the combustion agent on pure spinel phase formation. Thus, in the case of NZFDyU and NZFDyTA samples could be observed the existence of different secondary phases, DyFeO$_3$ (orthorhombic system, 89−6645, ICDD, JCPDS 2002) for NZFDyU sample and Fe$_2$O$_3$ (rhombohedral system, 89-0599, ICDD, JCPDS 2002) for NZFDyTA sample, respectively. From XRD patterns one can notice the pure spinel phase achieved in the case of NZFDyCA and NZFDyCel, respectively.

Table 1 shows the calculated values for lattice parameter, interplanar distance, mean crystallite size, X-ray density for as-obtained powders. From Table 1 one can see that the NZFDyTA sample presents the smallest crystallite size and lattice parameter values and the highest value of density. It was reported earlier the influence of rare earth metals on lattice parameter and density values of spinel-type ferrite [26]. These could be due to a compressive pressure exerted by Fe$_2$O$_3$ phase segregated at the grain boundaries which overcomes the dilatation effect of doped Dy$^{3+}$ larger ionic radius (0.912 Å) than Fe$^{3+}$ ion radius (0.645 Å) into the spinel matrix [29]. The values of crystallite size, interplanar distances and lattice parameter for NZFDyU sample are the highest among all the samples. These could be possible as an effect of urea behavior during combustion process which favors partially DyFeO$_3$ segregation at grain boundaries. Thus, the unit cell parameter values are close to those of NZFDyCA and NZFDyCel, respectively, where the doping effect of Dy$^{3+}$ with large ionic radius compared to Fe$^{3+}$ and Ni$^{2+}$ into spinel matrix could led to an increase of crystallite size, lattice parameter and interplanar distance values as found also in previous works [30].

### 3.3. SEM and BET surface area interpretation

The SEM images show the formation of spherical grains, a fine powder size and homogenous nanostructures for all the samples. The grain size was determined from various SEM pictures by means of histograms as illustrated in Fig. 4. For all as-obtained ferrospins it can be observed the presence of nanometric grains, a uniform grain size distribution and a low degree of agglomeration. Also, it should be noted that the grains size varies from 20 to 160 nm for

---

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ$_{2θ}$ (degrees)</th>
<th>a$^\ast$ (Å)</th>
<th>d$^\ast$ (Å)</th>
<th>D$^\ast$ (nm)</th>
<th>pc$_{cal}$ (g cm$^{-1}$)</th>
<th>D$^\parallel$ (nm)</th>
<th>S$_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>M$_s$ (emu g$^{-1}$)</th>
<th>H$^c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZFDyU</td>
<td>35.473</td>
<td>8.3862</td>
<td>2.5285</td>
<td>42</td>
<td>5.3572</td>
<td>52.2</td>
<td>20.7</td>
<td>59</td>
<td>67</td>
</tr>
<tr>
<td>NZFDyCel</td>
<td>35.495</td>
<td>8.3812</td>
<td>2.5270</td>
<td>36</td>
<td>5.3669</td>
<td>73.1</td>
<td>6.5</td>
<td>63</td>
<td>112</td>
</tr>
<tr>
<td>NZFDyTA</td>
<td>35.552</td>
<td>8.3682</td>
<td>2.5231</td>
<td>30</td>
<td>5.3920</td>
<td>72.3</td>
<td>11.8</td>
<td>57</td>
<td>108</td>
</tr>
<tr>
<td>NZFDyCA</td>
<td>35.483</td>
<td>8.3839</td>
<td>2.5278</td>
<td>41</td>
<td>5.3616</td>
<td>76.4</td>
<td>6.1</td>
<td>62</td>
<td>97</td>
</tr>
</tbody>
</table>

*Data from XRD.

Data from SEM.

Data from VSM.
Fig. 4. Scanning electron photomicrographs (a) and grain size distributions (b) of NZFDy samples annealed at 1173 K.
the NZFDyU, NZFDyTA, NZFDyCel samples, while the NZFDyCA sample shows some larger particles (220 nm).

Calculated data from Table 1 shows a significant influence of the chelating/combustion agent over the grain size of as-obtained ferrite samples. Therefore, urea leads to the smallest grains size of as-obtained samples, the particle diameter varying in the following order:

NZFDyCA > NZFDyCel > NZFDyTA >> NZFDyU

Specific surface areas, reported in Table 1, are in the range 6–21 m² g⁻¹. Among the analyzed samples, the highest Sₐ is exhibited by NZFDyU sample, followed by NZFDyTA, while for NZFDyCel and NZFDyCA powders the values are significantly lower, due to the different degrees of agglomeration. The obtained results are in good agreement with the SEM analysis and catalysis experimental results.

3.4. Catalysis interpretation

The catalytic activity of NZFDy powders using four different combustion agents was examined by the decomposition of H₂O₂. The hydrogen peroxide decomposition rates were monitored by measuring the volumes of liberated oxygen as a function of time, at intervals of 30 s for the first 5 min of reaction and of 60 s up to 3000 s at room temperature.

A typical reaction profile is shown in Fig. 5, which is similar for all studied the spinels in this work. It can be observed that the catalytic performances for the NZFDy samples depend on the combustion agent used during synthesis. Thus, the activity in hydrogen peroxide decomposition varies in the following order:

NZFDyU >> NZFDyTA > NZFDyCel > NZFDyCA

Also, it is important to observe that the catalytic results can be correlated with the grains diameters (Table 1) obtained from SEM and with the BET area values. Thereby, the grains size seems to be a determining parameter that induces a different catalytic behavior. The presence of small sizes grains (≈ 52 nm) is required for an optimal catalytic activity, largest grains being less active for this reaction. Specific surface area varies directly proportional with the average size of crystallites and inversely proportional to the degree of agglomeration (grain size) [31]. Hence, the higher catalytic activity of the NZFDyU sample, can be explained by a lower degree of agglomeration, and also by the presence of DyFeO₃ secondary phase which significantly enhances performance in the reaction of hydrogen peroxide decomposition.

3.5. VSM interpretation

The hysteresis curves registered at room temperature are shown in Fig. 6 and the corresponding values for Mₙ (specific magnetization) and Hₙ (coercivity) are listed in Table 1.

Could be noticed from M–H curves the ferrimagnetic behavior of all four samples. The influence of fuel agent on the crystallite size and the purity of the samples generates light different values for Mₙ and Hₙ. In the molecular environment rare earth ions are generally paramagnetic because the multiple lobes of the 4f orbital wavefunctions do not extend far enough for covalent bonding and magnetic exchange to be significant. The shielding of the 4f shell inside the 5s² and 5p⁶ outer shells of their core makes magnetically active electrons to be weak [32]. It is well-known the impact of rare earth ions (RE³⁺) on the magnetic behavior of spinel-type ferrites due to the weak magnetic exchange interaction RE³⁺–Fe³⁺ (3d—4f electron coupling) induced by the displacement of ferric ions with RE³⁺ in B-sites [31], though Dy³⁺ (4f⁵) has a higher magnetic moment value, 10.64 μB with respect to Fe³⁺ (3d⁵) 5 μB.

Thus, it is remarkable that the same value for Mₙ (63 emu g⁻¹) it was registered for Ni₀.₈Zn₀.₂Fe₂O₄ sample obtained by the same synthesis method (using tartaric acid) and reported elsewhere [10]. Single phase ferrite samples, NZFDyCel and NZFDyCA, respectively show almost the same Mₙ value as a consequence of a similar cation distribution when Dy³⁺ replace the same amount of Fe³⁺ from B-site. The fuel agents as well as a small quantity of Dy³⁺ are not affecting the magnetic properties of Ni–Zn ferrite.

Comparing Mₙ values for the ferrite samples with impurities (NZFDyTA and NZFDyU) one can see the similarity explained by the same cause of Fe³⁺ lacking in B-site when small amount of impurities were segregated.

The coercivity value is influenced by grain size. The smaller are grains the higher coercivity value is registered due to a high energy required by domain wall rotation influencing the contribution to magnetization and demagnetization process. Domain wall motion is governing the magnetization and demagnetization process for large grain size and requires low energy. This could be the main cause for differences between Hₙ values of NZFDyU and NZFDyCA.
samples [23]. On the other hand, the nature of impurities from NZFDyTA and NZFDyU samples go more or less against the displacement of domain wall resulting in larger or smaller coercivity.

4. Conclusions

This paper reports a study over the influence of four combustion agents on structure, morphology and properties of the Ni0.8Zr0.2Fe1.98Dy0.02O4 spinel prepared by sol–gel autocombustion method. From IR spectra and XRD patterns it was confirmed the spinel phase formation of Ni0.8Zr0.2Fe1.98Dy0.02O4 nanopowders by this technique.

Tartaric acid, citric acid and cellulose favored during combustion process the dissolution of Dy4+ into spinel matrix, while urea induced the segregation of DyFeO3. Nevertheless, the optimal catalytic activity among all the samples is belonging to the one obtained using urea, which is showing the smallest grain size, the highest specific surface area and DyFeO3 phase at grain boundaries. Ferrimagnetic behavior prevails for all the samples independently of fuel agent. Specific magnetization value is not affected by fuel agent when single spinel ferrite is accomplished. The highest value was registered for the pure samples obtained using citric acid and cellulose (=62 emu g⁻¹). Coercivity values are influenced by fuel agent in terms of impurities type and grain size differences, the smallest value (67 Oe) being found for the sample obtained using urea.

Acknowledgments

The authors are grateful to the financial support of POSDRU/89/1.5/S/49944 Project.

References