Mg\textsubscript{x}Zn\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} nanoparticles prepared by spray pyrolysis method using inorganic precursors with an inert component

Valentin Natarov, Dzmitry Kotsikau, Elena Petrova, Vladimir Pankov
Belarussian State University, 220030, Minsk, Belarus. val.natarov@gmail.com

ABSTRACT: The aim was to prepare non-agglomerated Mg\textsubscript{x}Zn\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} (x = 0.25, 0.5, 0.7) spinel-type nanoparticles and to characterize their structural features and magnetic properties. The ferrite particles were synthesized by spray pyrolysis of inorganic precursors at 600 °C in nitrogen atmosphere. The process was carried out in the presence of NaCl as an inert component providing the separation of the generated nanosized particles during the synthesis and further thermal treatment. The well-crystalline nature and single-phased spinel structure of the as-prepared ferrites were confirmed by X-ray diffraction and infrared spectroscopy. Scanning electron microscopy demonstrated the formation of NPs with diameters of 10–20 nm. The magnetic measurements shown very small remanence and coercivity at 5 and 300 K, which indicates a superparamagnetic behaviour of the ferrites. The saturation magnetization of the synthesized ferrites measured at 5 K lies in the range from 53 to 58 A·m\textsuperscript{2}·kg\textsuperscript{-1}, while at 300 K it ranges from 22 to 26 A·m\textsuperscript{2}·kg\textsuperscript{-1}. The developed nanomaterials can be potentially used for biomedical applications and electronics.

Keywords: Mg–Zn-ferrites; aerosol spray pyrolysis; superparamagnetic nanoparticles.

1 INTRODUCTION

Recently, the potential biomedical applications (contrast agents for magnetic resonance imaging, drug-targeting, magnetic bioseparation) of ferrite superparamagnetic nanoparticles (NPs) have focused the attention of many research workers on this kind of materials (Pedro T. et al., 2003; Khot S.S. et al., 2011). Ferrites also traditionally have a wide range of applications in catalysis, microwave and computer technologies.

Many synthetic methods have been proposed to obtain ferrite NPs, among them are co-precipitation, sol-gel and microemulsion synthesis (Pedro T. et al., 2003). The spray pyrolysis method applied here ensures a homogeneous distribution of the components over the product, since the formation of ferrite structure proceeds within microscopic droplets of the reacting mixture.

The Mg–Zn ferrite was chosen due to a low toxicity of Mg and Zn as compared to other typically applied metals (Ni, Co, Mn), which is important for biomedical applications (Khot S.S. et al., 2011; Diagle A. et al., 2011).

The aim of this study is to synthesize nanocrystalline nanoparticles of magnetic Mg–Zn ferrite by spray pyrolysis method, and to characterize their structural features and magnetic properties.

2 EXPERIMENTAL

A water solution of Zn (II), Mg (II), Fe (III) nitrates and NaCl (85 wt. %) was used as a precursor. The nitrates have been taken in the corresponding stoichiometric proportion to obtain Mg\textsubscript{x}Zn\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} with x = 0.25, 0.5, 0.7. NaCl was used in the pyrolysis process as an inert component to prevent an agglomeration of the ferrite NPs. An ultrasonication-derived aerosol of the precursor solution was delivered into a reaction zone by using nitrogen as a carrier gas. The reaction zone was represented by a quartz tube in a furnace heated to 600 °C. The produced powder was collected on an electrostatic precipitator heated to 200 °C. The obtained ferrite powders were washed several times with distilled water and dried at 60 °C.

The grain size and morphology of the powders were estimated by scanning electron
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microscopy (SEM) on a Hitachi S-4800 instrument. The X-ray diffraction (XRD) analysis was performed on a DRON-2.0 diffractometer with CoKα radiation. Infrared spectra were recorded on an AVATAR-330 spectrometer. Magnetic measurements were carried out on a Cryogenic Ltd system.

3 RESULTS AND DISCUSSIONS

The XRD patterns of the synthesized composite oxides shown in Figure 1. The reflexes diffracts only the allowed planes of cubic spinel-type structure. No reflexes of magnesium, zinc or iron oxides were found in the patterns, which indicates the formation of a single-phased structure for all the compositions. The diffraction lines are broad and diffuse, which is typical of nanocrystalline powders.

![Figure 1: The XRD patterns of Mg₅Zn₁₋ₓFe₂O₄ powders with x = 0.7 (1), 0.5 (2) and 0.25 (3)](image)

The growth of the lattice parameter of the ferrites (Table 1) with increasing Zn²⁺ content is caused by its larger ionic radius (0.074 nm) as compared to Mg²⁺ (0.060 nm). After the removal of the inert component, all the particles have a nearly spherical shape with the diameter in the range of 10–20 nm (Figure 2, Table 1). Note that the particles are not sintered together and can be easily separated from each other due to the presence of NaCl in the precursor solution.

![Figure 2: The typical SEM micrograph of Mg₅Zn₁₋ₓFe₂O₄ powders](image)

Table 1. The grain size, lattice parameter and saturation magnetisation values of MgₓZn₁₋ₓFe₂O₄ ferrites

<table>
<thead>
<tr>
<th>x</th>
<th>d, nm</th>
<th>a, nm</th>
<th>Mₘₙₐₓ (5 K), A·m²·kg⁻¹</th>
<th>Mₘₙₐₓ (300 K), A·m²·kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>13–17</td>
<td>0.844</td>
<td>58</td>
<td>22</td>
</tr>
<tr>
<td>0.5</td>
<td>10–15</td>
<td>0.842</td>
<td>52</td>
<td>22</td>
</tr>
<tr>
<td>0.7</td>
<td>15–20</td>
<td>0.841</td>
<td>53</td>
<td>26</td>
</tr>
</tbody>
</table>

The infrared spectroscopy study confirms the formation of MgₓZn₁₋ₓFe₂O₄ single-phased powders with a uniform distribution of Zn and Mg ions over the ferrite crystalline lattice.

The specific magnetization curves of the powders are shown in Figures 3 and 4.

![Figure 3: The magnetization curves for MgₓZn₁₋ₓFe₂O₄ powders recorded at 5 K](image)

At both 5 and 300 K, the materials show no hysteresis behaviour, which indicates their
superparamagnetic state under these conditions. The superparamagnetic behaviour was expected for the ferrite prepared here since their particle size does not exceed 20 nm (see Table 1).

Some of the functional properties of MgZn-ferrites (electric conductivity, proton relaxation times in contrasting magnetic resonance images etc.) may depend on the Mg:Zn ratio. The saturation magnetization values of the ferrites are listed in Table 1. The highest magnetization of 26 A‧m⁻²‧kg⁻¹ (300 K) was shown by Mg₀.7Zn₀.3Fe₂O₄ composition. As expected, the magnetization of the MgZn-ferrite decreases with increasing Zn content.

There is a clear effect of the synthesis temperature on the magnetization of MgZn-ferrites (Khot S.S. et al., 2011; Daigle A. et al., 2011; Barbosa G.F. et al., 2013). The magnetization of samples prepared here at 600 °C ranges from 22 to 26 A‧m⁻²‧kg⁻¹ (300 K). However, the presence of NaCl in the as prepared samples allows tailoring their magnetic features by sintering the powders at high temperatures without noticeable agglomeration and increase in the grain size.

4 CONCLUSION

Nanocrystalline MgₓZn₁₋ₓFe₂O₄ (with x = 0.25, 0.5, 0.7) particles have been synthesized by SP method in nitrogen atmosphere at 600 °C. NaCl as a non-toxic inert additive was used to prevent the NPs from aggregation. Under these conditions, single-phased oxide solid solutions with particle sizes of 10–20 nm were formed. The magnetic measurements shown a superparamagnetic state of all the powders at 5 and 300 K. At 300 K, the highest saturation magnetization (26 A‧m⁻²‧kg⁻¹) corresponds to the composition with x = 0.7 (Mg₀.7Zn₀.3Fe₂O₄). The prepared MgZn-ferrite NPs can be potentially used as contrast agents for magnetic resonance imaging, magnetically controlled sorbents of biological molecules, materials for electronics and other applications.

REFERENCES
