Structural and magnetic properties of YFe$_{1-x}$Co$_x$O$_3$ (0.1 $\leq x \leq$ 0.5) perovskite nanomaterials synthesized by co-precipitation method

Nguyen Anh Tien$^1$, Chau Hong Diem$^1$, Nguyen Thi Truc Linh$^1$, V.O. Mittova$^2$, Do Tra Huong$^3$, I.Ya. Mittova$^4$

$^1$Ho Chi Minh City University of Education, Ho Chi Minh City, Vietnam
$^2$Burdenko Voronezh State Medical University, Voronezh, 394036, Russia
$^3$Thai Nguyen University of Education, Thai Nguyen University, Vietnam
$^4$Voronezh State University, Voronezh, 394018, Russia

anhtienhcmup@gmail.com, hongdiem.chau@gmail.com, linhhttn2811@gmail.com, vmittova@mail.ru, dotrahuong@gmail.com, imittova@mail.ru

Keywords: nanomaterial, co-doped YFeO$_3$, perovskite, co-precipitation.

PACS 75.50.Cc, 81.07.Wx DOI 10.17586/2220-8054-2018-9-3-424-429

YFe$_{1-x}$Co$_x$O$_3$ (0.1 $\leq x \leq$ 0.5) perovskite-type nanomaterials were successfully synthesized by the chemical co-precipitation method via the hydrolysis of Y(III), Fe(III) and Co(II) cations in boiling water using 5 % aqueous KOH solution as a precipitating agent. Along with the increase of cobalt ion concentration ($x$ values, from 0.1 to 0.5), there was an increase in the crystallite size nanomaterials (from 25.68 to 22.89 nm), as well as in the lattice constants ($a = 5.5781$ – 5.5217 Å; $b = 5.2732$ – 5.2177 Å; $c = 7.5902$ – 7.5009 Å; $V = 223.26$ – 216.11 Å), but there was an increase in the magnetic parameters including coercive force ($H_c = 88.86$ Oe), remnant magnetization ($M_r = 0.031$ – 0.268 emu/g), saturation magnetization ($M_s = 0.413$ – 1.006 emu/g) and maximum energy product ((BH)$_{\text{max}}$ = 0.413 – 1.006 emu/g).

1. Introduction

In general, ABO$_3$ perovskite-type materials are dielectric antiferromagnetic, which can be changed to ferromagnetic by doping it with impurity ions [1–4], especially, in the case of the perovskite-type materials that have rare-earth elements (R) at A sites and Fe(III) ions at the B sites. The reason is the magnetic moment of iron in RFeO$_3$ is shifted slightly. When transition metals, which have the changed ionic radius at the variable oxidation states, are doped in the structure of RFeO$_3$, it may cause an exchange interaction and indirectly lead to ferromagnetic properties. As a ferromagnetic material, perovskites can have interesting properties such as thermoelectric effect, giant magneto-caloric effect (GMCE), giant magneto-resistance (GMR) or spin glass state at low temperature. Thus, perovskite-type materials, particularly at the nano scale, can be applied in the fields of catalysts, solid-oxide fuel cells (SOFCs), chemical sensors, semiconductors, etc. [5–7]. Recently, Co-doped YFeO$_3$ materials have attracted extensively studying thanks to their interesting magnetic properties that may be changed because of the variable oxidation and spin states of cobalt, as well as its concentration in the solid solution [8].

There are numerous methods to synthesize RFeO$_3$ nanomaterials such as sol-gel combustion, sol-gel citrate or thermal hydrolysis, etc. [2–4, 9–11]. However, the preparation of the nanomaterials having RFeO$_3$ single phase by the mentioned methods requires the investigation of many factors including heating temperature and retention time, pH, stoichiometric ratio between the components, etc. As a result, the optimal conditions were difficult to be determined, and the formation of impurity phases such as Fe$_2$O$_4$, YFe$_2$O$_4$ or Y$_3$Fe$_5$O$_{12}$ [12, 13] might have a negative impact on the quality of the obtained materials. In our previous research [14–16], the perovskite nanomaterials were successfully synthesized by co-precipitation method via the hydrolysis of transition metal ions in boiling water. This paper presents the results of the structural and magnetic properties of Co-doped YFeO$_3$ nanomaterials prepared by co-precipitation method via the hydrolysis of Y(III), Fe(III) and Co(II) cations in boiling water using 5 % aqueous KOH solution as a precipitating agent.

2. Materials and methods

2.1. Materials

In this research, Y(NO$_3$)$_3$·6H$_2$O (Merck, > 99 %), Fe(NO$_3$)$_3$·9H$_2$O (Merck, ≥ 99 %), Co(NO$_3$)$_2$·6H$_2$O (Merck, ≥ 99 %), KOH (Merck, 99 %) were used for the synthesis of YFe$_{1-x}$Co$_x$O$_3$ (0.1 $\leq x \leq$ 0.5) perovskite-type nanomaterials.
2.2. Methods

Co-doped YFeO$_3$ were prepared via the process shown in Fig. 1. A mixture of Y(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_2$·6H$_2$O salts with the stoichiometric ratio of Y(III) : Fe(III) : Co(II) = 1 : (1 – x) : x (x = 0.1; 0.15; 0.2; 0.25; 0.3 and 0.5) was dissolved in distilled water. This solution was added to a glass vessel containing hot water (t$^\circ$ > 90$^\circ$ C) and stirred continuously. And then, the obtained mixture was cooled down to the room temperature (25 – 30$^\circ$ C), slowly added an excess KOH 5 % solution until the pH greater than 7. The mixture was stirred continuously for 30 mins, and settled for 15 mins. The precipitate was separated from the solution by filtration, washed with distilled water, left to dry at the room temperature and ground into powder.

![Flow chart for synthesis of Co-doped YFeO$_3$ by co-precipitation method](image)

All precipitates were converted to perovskite-type materials by annealing at 800$^\circ$ C for 1 hour with a heating rate of 10 K/min. The annealing condition was determined according to the previous results [14,17].

Phase composition of the synthesized samples was identified by powder X-ray diffraction (XRD) with a D8-ADVANCE diffractometer (Germany) using CuK$\alpha$ radiation ($\lambda$ = 0.154056 nm), 2$\theta$ = 20 – 80$^\circ$, a scan rate of 0.02$^\circ$ s$^{-1}$. Average size (nm) of crystal phase was calculated by Debye–Scherrer formula:

$$D_{XRD} = \frac{k \lambda}{\beta \cos \theta},$$

where $k$ is the shape factor (for the orthorhombic structure, $k$ = 0.9); $\lambda$ is the X-ray wavelength (nm); $\beta$ is the full width at half maximum (rad) and $\theta$ is the position of the diffraction peak.

Lattice constants $a$, $b$, $c$ and the unit cell volume $V$ were determined thanks to the X’pert High Score Plus 2.2b software.

Particle size and morphology of YFe$_{1-x}$Co$_x$O$_3$ nanomaterials were determined by transmission electron microscopy (TEM) with a JEOL-1400 microscope (Japan). Elemental composition of the samples was determined by energy-dispersive X-ray spectroscopy (EDX) with a FESEM S-4800 spectrometer (Japan). Magnetic parameters of the samples (coercive force $H_c$, remnant magnetization $M_r$, saturation magnetization $M_s$) were carried out at room temperature by a vibrating sample magnetometer (VSM) MICROSENE EV11 (Japan).
3. Results and discussion

3.1. Crystal structure

Figure 2 presented the XRD patterns of \( \text{YFe}_{0.8}\text{Co}_{0.2}\text{O}_3 \) nanomaterial and component oxides which were prepared via the process shown in Fig. 1 (after annealing at 800 °C for 1 hour). The results showed that \( \text{YFe}_{0.8}\text{Co}_{0.2}\text{O}_3 \) nanomaterial was pure perovskite-type, particularly, the peaks of \( \text{YFeO}_3 \) and Co-doped \( \text{YFeO}_3 \) were coincident with those of \( \text{YFeO}_3 \) orthoferrite phase (Card no. 00-039-1489 [18]). The diffraction peaks of oxide impurities cannot be identified in the XRD results. Noticeably, Co\( _3\text{O}_4 \) oxide was obtained instead of CoO because Co\( (\text{OH})_2 \) hydroxide can be oxidized and decomposed after annealing at high temperature [19]:

\[
6\text{Co(OH)}_2 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{H}_2\text{O}.
\]

This result indicated that Co ions existed in both (II) and (III) oxidation states in the crystal lattice of \( \text{YFeO}_3 \).

The XRD patterns of \( \text{YFe}_{1-x}\text{Co}_x\text{O}_3 \) (0.1 ≤ \( x \) ≤ 0.5) samples (Fig. 3) showed the structures of the samples were single-phase perovskites, particularly, they were in the orthorhombic structure with space group \( Pnma \), No. 62. This proved that Fe(III) was partly substituted by Co(II)/Co(III). When the concentration of Co ions increased, XRD peaks shifted toward a higher 2\( \theta \) (right shift) and gradually broadened while the intensity of peaks decreased. Consequently, there was a decrease of lattice parameters and crystal size (Fig. 4A and Table 1). The similar results were published in the previous researches [1,16,17].

The results shown in Table 1 showed that lattice parameters of \( \text{YFe}_{1-x}\text{Co}_x\text{O}_3 \pm \delta \) samples decreased in parallel of the increase of the dopant concentration. The substitution of Fe\( ^{3+} \) ions \( (r_{\text{Fe}^{3+}} = 0.65 \text{ Å} [19]) \) by smaller Co\( ^{3+} \) ions \( (r_{\text{Co}^{3+}} = 0.55 \text{ Å} [19]) \) led to the reduction of unit cell parameters following to Vergard’s law for ideal solid solution.

Crystal sizes of \( \text{YFe}_{1-x}\text{Co}_x\text{O}_3 \pm \delta \) samples calculated by Debye–Scherrer formula (1) were in the range of 22 to 26 nm. The decrease in the values of crystal size in parallel of the increase of Co concentration can be explained by the substitution of Fe\( ^{3+} \) ions by Co\( ^{3+} \) ions, which led to the lattice distortion, the higher internal stress and the limitation of growing of crystalline.

3.2. Elemental composition

EDX spectra showed that the compositions of \( \text{YFe}_{1-x}\text{Co}_x\text{O}_3 \) samples included Y, Fe, Co and O, without impurity element. The empirical formulas obtained from the elemental analysis were in excellent agreement with the suggested formulas (Table 2).
3.3. Morphology

TEM images of YFe$_{1-x}$Co$_x$O$_3$ samples ($x = 0.1; 0.3$ and $0.5$) (Fig. 5) showed that the shape and size of nanoparticles synthesized were quite homogeneous. Particularly, the particles were in spherical or slightly angular shapes, with an average size of $30 – 50$ nm.

3.4. Magnetic properties

The magnetic parameters of the samples proved that Co substitution impacted not only on the structure but also on magnetic properties of the nanoparticles synthesized (Fig. 5B and Table 2). When the amount of Co ions in YFeO$_3$ crystal lattice increased, the magnetic parameters including $H_c$, $M_r$ and $M_s$ increased, and were significantly higher than those of the original YFeO$_3$ material [14, 17]. This can be explained by the increase of magnetocrystalline anisotropy because the substitution of Co into the sites of Fe. Besides, Co substitution also
Table 1. Lattice parameters and the values of crystal size of YFe\(_{1-x}\)Co\(_x\)O\(_3\) ±\(\delta\) nanomaterials

<table>
<thead>
<tr>
<th>YFe(_{1-x})Co(_x)O(_3)</th>
<th>θ (121), °</th>
<th>D(_{\text{XRD}}), nm</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>V, Å(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.1</td>
<td>33.1913</td>
<td>25.68</td>
<td>5.5781</td>
<td>5.2732</td>
<td>7.5902</td>
<td>223.26</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>33.2616</td>
<td>25.67</td>
<td>5.5694</td>
<td>5.2625</td>
<td>7.5758</td>
<td>222.04</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>33.2792</td>
<td>24.44</td>
<td>5.5648</td>
<td>5.2619</td>
<td>7.5708</td>
<td>221.68</td>
</tr>
<tr>
<td>x = 0.25</td>
<td>33.3330</td>
<td>24.18</td>
<td>5.5575</td>
<td>5.2580</td>
<td>7.5551</td>
<td>220.77</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>33.3668</td>
<td>23.96</td>
<td>5.5524</td>
<td>5.2505</td>
<td>7.5482</td>
<td>220.05</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>33.5797</td>
<td>22.89</td>
<td>5.5217</td>
<td>5.2177</td>
<td>7.5009</td>
<td>216.11</td>
</tr>
</tbody>
</table>

Table 2. EDX results and magnetic properties of YFe\(_{1-x}\)Co\(_x\)O\(_3\) materials

<table>
<thead>
<tr>
<th>YFe(_{1-x})Co(_x)O(_3)</th>
<th>Nominal composition</th>
<th>Actual composition</th>
<th>(H_c), Oe</th>
<th>(M_r), emu/g</th>
<th>(M_s), emu/g</th>
<th>(BH)(_{\text{max}}), emu/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>YFeO(_3) [15]</td>
<td>YFe(<em>{0.02})O(</em>{3.32})</td>
<td>53.36</td>
<td>0.019</td>
<td>0.390</td>
<td>0.390</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>YFe(<em>{0.9})Co(</em>{0.1})O(_3)</td>
<td>YFe(<em>{0.88})Co(</em>{0.11})O(_{3.37})</td>
<td>88.86</td>
<td>0.031</td>
<td>0.413</td>
<td>0.413</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>YFe(<em>{0.8})Co(</em>{0.2})O(_3)</td>
<td>YFe(<em>{0.79})Co(</em>{0.21})O(_{3.28})</td>
<td>132.66</td>
<td>0.075</td>
<td>0.569</td>
<td>0.569</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>YFe(<em>{0.7})Co(</em>{0.3})O(_3)</td>
<td>YFe(<em>{0.69})Co(</em>{0.28})O(_{3.67})</td>
<td>352.16</td>
<td>0.207</td>
<td>0.825</td>
<td>0.825</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>YFe(<em>{0.5})Co(</em>{0.5})O(_3)</td>
<td>YFe(<em>{0.51})Co(</em>{0.51})O(_{3.43})</td>
<td>781.46</td>
<td>0.268</td>
<td>1.006</td>
<td>1.006</td>
</tr>
</tbody>
</table>

Fig. 5. TEM images of YFe\(_{1-x}\)Co\(_x\)O\(_3\) nanomaterials annealed at 800 °C for 1 h

led to a change in Fe–O–Fe angles, as well as an oxidation of a small amount of Fe\(^{3+}\) ions to Fe\(^{4+}\) ions to compensate the charge caused by the appearance of Co\(^{2+}\) at the sites of Fe\(^{3+}\). Similar results were mentioned by other authors [16,17,20].

Noticeably, with x ≥ 0.2, YFeO\(_3\) changed gradually from a soft magnetic material (\(H_c < 100\) Oe) to a hard magnetic material with high coercive force (\(H_c \gg 100\) Oe, especially with x = 0.5). This proved that magnetic properties of YFeO\(_3\) material can be changed by doping Co, thus the applicability of this material can be extended in many devices requiring the soft magnetic material (cores of transformers, electromagnets, magnetic conductors) and also the ones requiring the hard magnetic material (permanent magnets or recorders).

4. Conclusions

YFe\(_{1-x}\)Co\(_x\)O\(_3\) (0.1 ≤ x ≤ 0.5) perovskite-type nanomaterials were successfully prepared by the chemical co-precipitation method via the hydrolysis of cations in hot water (\(t^\circ \geq 90\) °C) with KOH 5 % as a precipitating agent. Along with the increase of Co doping, the values of crystal size and unit cell volume decreased from 26 nm to 22
References