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Effect of Zn substitution on the structural and magnetic properties of densely packed Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ Nanowires

S. A. Seyyed Ebrahimi$^1$ · A. Pirouzfar$^1$ · S. M. Masoudpanah$^2$

Abstract In this study, Zn substituted cobalt ferrite (Co$_{1-x}$Zn$_x$Fe$_2$O$_4$, $x = 0, 0.125, 0.25, 0.375, 0.5$) nanowires were synthesized by an optimized sol–gel route using anodized aluminum oxide (AAO) template. The structure and distribution of cations in octahedral and tetrahedral sites of spinel structure were determined by X-ray diffraction technique. Furthermore, the morphology and magnetic properties of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires were investigated by electron microscopy and vibrating sample magnetometry. The coercivity of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires decreased from 1150 to 170 Oe with Zn$^{2+}$ substitution while the saturation magnetization initially increased from 69.6 to 80.9 emu/g up to $x = 0.125$ and then decreased to 47 emu/g for $x = 0.5$.

Keywords Nanowire · Cobalt ferrite · Zn substitution · Magnetic anisotropy

1 Introduction

In recent years, considerable interest has been drawn towards nanocrystalline spinel ferrites due to their potential applications in permanent magnets, microwave absorbers, chemical sensors, high density recording systems, ferrofluid technology, imaging and high-frequency devices, and also in biomedical applications (El-Dek 2010; Wang 2003; Anderson et al. 2004). The spinel ferrites have the general formula of MFe$_2$O$_4$ (where M: Fe, Co, Ni, Zn, etc.) and their unit cell contains 32 O atoms in cubic close packing with eight tetrahedral (A) and 16 octahedral (B) occupied sites (Nikam et al. 2015; Li et al. 2004). The electrical and magnetic properties of spinel ferrites are highly sensitive to the several factors, such as chemical composition, synthesis method, annealing temperature, and cation distribution at tetrahedral (A) and octahedral (B) sites (Jeng and Guo 2002).

Among spinel ferrites, cobalt ferrite (CoFe$_2$O$_4$) has received a special attention for its large magnetocrystalline anisotropy ($K_1 = 270 \times 10^3$ $J/m^3$, $K_2 = 300 \times 10^3$ $J/m^3$), moderate saturation magnetization (80 emu/g), high Curie temperature (793 K), remarkable chemical stability and mechanical hardness; which make it an ideal material for giant magnetoresistance devices (Rani and Sharma 2012; Ayyappan et al. 2009). However, the physical properties of cobalt ferrite can be strongly tuned by the substitution of the divalent/trivalent and magnetic/ diamagnetic cations, e.g., Zn$^{2+}$, Mn$^{2+}$, Bi$^{3+}$, etc. (Richter 2009; Kavas et al. 2009; Roongato et al. 2014). For example, the addition of nonmagnetic ions such as Zn$^{2+}$ influences the cation distribution in A and B sites, electrical and magnetic properties of the cobalt ferrite nanoparticles depending on the amount of used cations (Richter 2009; Gore et al. 2015).

In the recent decade, more and more attempts have been made to synthesize nanowires of cobalt ferrite because of their wide applications in high density storage media, sensors, ferrofluids, etc. Several methods have been applied for fabrication of CoFe$_2$O$_4$ nanowires, such as hydrothermal (Vaidyanathan and Sendhilnathan 2007), electrodeposition (Gajbhiye and Srivastava 2010; Wang and Liu...
and carbon nanotubes (Hua and Chen 2007; Ersen and Begin 2008; Keller and Huu 2004). However, the highly ordered magnetic nanowires arrays can only be obtained by template assisted sol–gel method (Pham-Huu and Keller 2002; Xu et al. 2009; Yuan and Zhao 2009; Chen et al. 2013).

Despite many investigations on Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles, not very much attempts have been done to synthesize their nanowires. In our previous work (Chen et al. 2013), we have successfully used sol–gel method to fabricate highly ordered CoFe$_2$O$_4$ nanowires by an AAO template and applying mechanical vacuum suction. In this work, we studied the effect of zinc substitution in the structural and magnetic properties of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.0, 0.125, 0.25, 0.375$ and $0.5$) nanowires.

2 Experimental procedures

The AAO templates used in this study were Whatman Anodisc $^\circledR$ 25 supported membrane disks with mean thickness of 60 μm. To prepare Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.125, 0.25, 0.375, 0.5$) by sol–gel method, Fe(NO$_3$)$_3$ 9H$_2$O, Co(NO$_3$)$_2$ 6H$_2$O, Zn(NO$_3$)$_2$ 6H$_2$O and citric acid (C$_6$H$_8$O$_7$) were first dissolved in a minimum amount of deionized water, at which the molar ratio of (cobalt + zinc) nitrate to ferric nitrate and citric acid was 1:2:3. During homogenization at 80 °C, the pH was also adjusted to 1. While the appropriate viscosity of gel was obtained during heating, suction with 60 torr vacuum was applied to draw the gel into AAO nanochannels. The AAO template filled with the solution was dried and then calcined in air at 600 °C for 1 hour to form spinel Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires. The heating and cooling rates of 5 °C/min were applied to prevent cracking of the nanowires.

The composition and crystalline structure of the Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires were analyzed by Philips X’pert Pro prefix powder X-ray diffractometer using monochromatic CuKα radiation. The average crystallite size of the samples was calculated using Scherrer formula:

$$D = \frac{(0.9\lambda)}{(\beta \cos \theta)}$$

where $D$ is the mean crystallite size after correction for the instrument error, $\lambda$ is the wavelength of radiated X-ray, $\theta$ is the corresponding Bragg diffraction angle and $\beta$ is the full width of (311) main peak at half of its maximum (in radians). The morphology and microstructure of the nanowires were observed by Hitachi S-4160 field emission scanning electron microscope (FESEM) and Philips CM200 transmission electron microscope (TEM) at 200 kV. Selected area electron diffraction (SAED) pattern was also taken on TEM. To study the structure and morphology of the as-prepared nanowires, AAO template was dissolved in 6 M NaOH and then washed several times with distilled water to release the Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires from the template. A vibrating sample magnetometer (Meghnatis Daghigh Kavir Kashan Co., Iran) with the maximum field of 10 kOe was also employed to measure the magnetic properties of the samples at room temperature.

3 Results and discussion

Figure 1a shows the XRD patterns of the Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires as a function of Zn substitution. The amorphous background is due to the anodized aluminum oxide template. All the peaks were indexed as (220), (311), (400), (422), (511) and (440) are characteristics of single phase cubic spinel structure withFd3m space group (JCPDS card no. 22-1086). The cation distribution formula, crystallite size, experimental lattice parameter (aexp), theoretical lattice parameter (ath) and oxygen positional parameter of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires are presented in Table 1. The crystallite size decreased from 25 to 17 nm when the partial substitution of zinc increased. Table 1 also shows that the experimental lattice parameter increased from 0.8384 to 0.8423 nm with the Zn$^{2+}$ additions, because of its different ionic radii. The ionic radius of Zn$^{2+}$ ion (0.74 Å) is larger compared to Co$^{2+}$ ion (0.72 Å) (Pirouzfar and Seyyed Ebrahimi 2014). It can also be confirmed by the observed shift of (311) peak to small diffraction angles with the Zn$^{2+}$ additions (Fig. 1b).

The cation distribution in Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires can be obtained from the XRD analysis by the Bertaut method (Shannon 1976). The Bertaut method is based on a comparison between observed diffraction intensities and those theoretically calculated. The resultant cation distribution in Table 1 shows that the Co$^{2+}$ ions prefer to occupy the octahedral sites [B] while the Zn$^{2+}$ ions always occupy tetrahedral (A) site due to their favorable fit of charge distribution (Skolnick et al. 1958). The cation distribution can be further confirmed by the agreement between ath and aexp (Table 1). The O$^{2-}$ ions in the spinel structure are not generally located at the exact positions of the fcc sublattice. Their detailed positions are determined by $u$, which reflects adjustments of the structure to accommodate the cations with different radii ratio in the (A) and [B] sites. The $u$ parameter has the values of 0.375 for an ideal close-packed arrangement of O$^{2-}$ ions for origin at 43 m (Mane et al. 2011). The ideal situation is almost never realized, and the $u$ value for the vast majority of the known spinels is greater than 0.375, as can be seen in Table 1. The difference of the $u$ values from the ideal one can be explained by a small displacement of anions due to the expansion of the tetrahedral sites (Valenzuela 1994).
Figure 2a is a SEM planar-view of the empty AAO template. The corresponding view of the same AAO template filled with Co$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ nanowires in which the template dissolved partly by NaOH are shown in Fig. 2b. It can be seen that nanowires maintained an aligned morphology even in the absence of the AAO template support. TEM image of a single Co$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ nanowire is shown in Fig. 2c. It can be seen that the mean diameter of the nanowires is around 150 nm. Furthermore, the ring SAED patterns are related to the diffraction of the single phase zinc substituted cobalt ferrite with nanocrystalline structure. HRTEM image of the same nanowire is shown in Fig. 2d. from which individual crystal size is near to 20 nm. The observation is in consistence with the crystallite size calculated from XRD patterns by Scherrer formula (Table 1).

The magnetization curves of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanowires in the parallel direction of nanowire axis have been shown in Fig. 3. The magnetization and coercivity versus the Zn$^{2+}$ content are presented in Fig. 4. The saturation magnetization (Ms) strongly depends on the Zn concentrations and increased till $x = 0.125$ from 69.6 to 80.9 emu/g, and then decreased to 47 emu/g for $x = 0.5$. The magnetization of spinel ferrites originated from the difference in the net magnetic moment of the cations at the tetrahedral (A) and octahedral [B] sites (O’Neill and Navrotsky 1983; Chikazumi 1997). The non-magnetic Zn$^{2+}$ cations do not contribute to the overall magnetization. Therefore, the distribution of the magnetic Co$^{2+}$ and Fe$^{3+}$ cations in the (A) and [B] sublattices determines the magnetization. As zinc is substituted in cobalt ferrite, it pushed Fe$^{3+}$ cations from tetrahedral A sites to octahedral B sites because the Zn$^{2+}$ cations have a strong preference to occupy the tetrahedral A sites (Nikam et al. 2015; N’eel et al. 1950). Hence, the saturation magnetization increased on account of the reduction of the magnetic moment of the A site and the increasing of the magnetic moment of the B site. However, the saturation magnetization gradually decreases for $x>0.125$ which can be explained on the basis of the reduction of the A–B superexchange interaction (Chikazumi 1997).

The behavior of coercivity in the Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ spinel ferrite can be explained on the basis of Brown’s relation (Kambale et al. 2011):

**Table 1** Cation distribution, crystallite size and lattice parameter of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles

<table>
<thead>
<tr>
<th>$x$</th>
<th>Cation distribution</th>
<th>Crystallite size (nm)</th>
<th>$a_{exp}$ (nm)</th>
<th>$a_{th}$ (nm)</th>
<th>$U$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(Fe)$^6$[CoFe]$^{16}$O$_4$</td>
<td>25</td>
<td>0.8384</td>
<td>0.8422</td>
<td>0.385</td>
</tr>
<tr>
<td>0.125</td>
<td>(Zn$<em>{0.125}$Fe$</em>{0.875}$)$^6$[Co$<em>{0.875}$Fe$</em>{1.72}$]$_{16}$O$_4$</td>
<td>23</td>
<td>0.8391</td>
<td>0.8425</td>
<td>0.386</td>
</tr>
<tr>
<td>0.25</td>
<td>(Zn$<em>{0.25}$Fe$</em>{0.75}$)$^6$[Co$<em>{0.75}$Fe$</em>{1.75}$]$_{16}$O$_4$</td>
<td>20</td>
<td>0.8405</td>
<td>0.8429</td>
<td>0.387</td>
</tr>
<tr>
<td>0.375</td>
<td>(Zn$<em>{0.375}$Fe$</em>{0.625}$)$^6$[Co$<em>{0.625}$Fe$</em>{1.625}$]$_{16}$O$_4$</td>
<td>21</td>
<td>0.8412</td>
<td>0.8433</td>
<td>0.387</td>
</tr>
<tr>
<td>0.5</td>
<td>(Zn$<em>{0.5}$Fe$</em>{0.5}$)$^6$[Co$<em>{0.5}$Fe$</em>{1.5}$]$_{16}$O$_4$</td>
<td>17</td>
<td>0.8423</td>
<td>0.8436</td>
<td>0.388</td>
</tr>
</tbody>
</table>
Hc = 0.96K/Ms

where K is an anisotropy constant. The large value of coercivity of the unsubstituted CoFe2O4 originates from the anisotropy of cobalt cations at octahedral [B] site due to its important spin–orbit coupling. When Zn2+ cations enter in the spinel lattice, leading to disappearance of the spin–orbit coupling, that determines the magnetic anisotropy in the ferrites. Therefore, the magnetocrystalline anisotropy decreased by Zn substitution.

**Fig. 2**  
a FESEM planar-view of the empty AAO template,  
b FESEM image of Co0.75Zn0.25Fe2O4 nanowires after partial dissolution of AAO,  
c TEM image of a single Co0.75Zn0.25Fe2O4 nanowire (the inset is the SAED pattern) and  
d HRTEM image

**Fig. 3** Magnetization curves of the Co1-xZnxFe2O4 nanowires

**Fig. 4** Magnetization and coercivity as a function of composition

**4 Conclusions**

Single phase zinc substituted cobalt ferrite (Co1-xZnxFe2. O4) nanowire arrays were fabricated using sol–gel route on the AAO template after calcination at 600 °C. The XRD results confirm the substitution of Zn2+ with Co2+ in cobalt ferrite structure. The saturation magnetization initially increases up to x = 0.125 after substitution of Zn2+ and then decreases. The coercivity also decreases with Zn additions due to the reduction of magnetocrystalline anisotropy.
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