Structural and Magnetic Properties of Sn$^{4+}$ Doped Strontium Hexaferrites Prepared via Sol–Gel Auto-Combustion Method

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Sn–Zn–Co-substituted strontium M-type hexaferrite SrZn$_x$Co$_{1-x}$Sn$_{2x}$Fe$_{12-4x}$O$_{19}$ ($x = 0.0, 0.3, 0.5,$ and $0.7$) was synthesized via modified sol–gel auto-combustion method. A microwave device was used to obtain the finest particles and to complete the combustion process. By substitution of tetravalent and divalent cations instead of iron, magnetic and structural properties of M-type hexaferrite were changed. So, the effects of Sn$^{4+}$, Zn$^{2+}$, and Co$^{2+}$ doping on the structure and magnetic characterization of M-type hexaferrite were investigated. The Fourier transform infrared spectroscopy revealed bands at 430 and 590 cm$^{-1}$, related to the stretching vibrating bonds of Fe–O. The X-ray diffraction analysis showed that all samples prepared were of P6$_3$/mmc symmetry and average crystal size of 68 nm. Field emission scanning electron microscopy analysis revealed the hexagonal platelet-like shape of all samples. Vibrating sample magnetometer results showed that by increasing the dopants content, coercivity ($H_c$), and saturation magnetization ($M_s$) changed drastically. Saturation magnetizations decreased during dopants displacement and then reach to the highest value (65.46 emu/g) at $x = 0.5$ then increasing of dopants to $x = 0.7$, cause the reduction of $M_s$ (56.13 emu/g). Coercivity diminished by dopant substitution and the semi-hard samples were received as an alternative to the hard hexaferrite.

Index Terms—Coercivity ($H_c$), M-type hexaferrite, saturation magnetization ($M_s$), sol–gel auto-combustion.

I. INTRODUCTION

M-TYPE hexagonal ferrites with high coercivity, high Curie temperature, high electrical resistivity, and large magnetocrystalline anisotropy along the c-axis are beneficial materials [1]–[4]. The usage of these materials as a permanent magnet, data recording media, super capacitors, and magnetic recording electron microscopy (SEM), and vibrating sample magnetometer (VSM) analysis.

II. EXPERIMENT

High purity Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$, Co(NO$_3$)$_2$, Zn(NO$_3$)$_2$, SnCl$_4$, and citric acid (as a fuel) were used without any further purification. Stoichiometric amounts of salts are dissolved in deionized water. An appropriate quantity of citric acid (molar ratio of citric acid/salts 1.5/1) was used. Ammonium solution was added dropwise under vigorous stirring to adjust pH value to 7. The solution was heated up to 110 °C while converting to gel. For gel ignition and gaining the finest particle size, a microwave device was utilized. The gel ignited, and a black and puffy powder was obtained. The products were calcined at 500 °C for 5 h and then calcined at 800 °C for 2 h. The schematic process of SrZn$_x$Co$_{1-x}$Sn$_{2x}$Fe$_{12-4x}$O$_{19}$ ($x = 0.0, 0.3, 0.5,$ and $0.7$) synthesis is depicted in Fig. 1.

III. CHARACTERIZATION

The FTIR analysis was performed using a Bruker-Tensor 27. The XRD characterizations were performed by Philips X-ert diffractometer using CuK$_\alpha$ line radiation at 2$\theta$ scanning 20–80 with the step size of 0.05°. The morphology of the product was studied by scanning electron microscopy (SIGMA VP-500, ZEISS model). Magnetic properties of the compounds were investigated by VSM ZVK, R&S.
IV. RESULTS AND DISCUSSION

A. FTIR Investigation

For asserting the formation of product bonds, FTIR studies were done (Fig. 2). For M-type hexagonal ferrites, two main bands at 430 and 590 cm\(^{-1}\) were observed which corresponds to the stretching vibrating bonds of Fe-O in tetrahedral and octahedral sites [17]–[19]. The vibrational modes of tetrahedral clusters are higher than octahedral one due to the shorter bond length of tetrahedral clusters. By increasing the dopant concentration, FTIR spectrum showed a red shift to the lower wavenumbers (580.7–594.5 cm\(^{-1}\)) because Sn\(^{4+}\) is heavier than Fe\(^{3+}\) [20].

B. XRD Patterns

The XRD diffraction patterns of compounds are shown in Fig. 3. All the specimens are matched with the ICSD 00-024-1207, which exactly indicate the structure of Sr-hexagonal ferrite. The peaks with Miller indices of (110), (107), (114), (108), (203), and (205) revealed the formation of strontium hexagonal ferrite [21]. Calcination at 800 °C caused the formation of orthorhombic \(\alpha\)-Fe\(_2\)O\(_3\) phase, which could be eliminated by the temperature increase. During the calcination process, local combustion occurs which is responsible for the existence of \(\alpha\)-Fe\(_2\)O\(_3\) impurity [22], [23]. At \(x = 0.5\), the orthorhombic phase disappeared, which may be related to the synthesis process but it needs further studies.

Based on Bragg’s law, the crystal plane distance and diffraction angle are in reverse relation. So, due to the increase of dopants, the peaks shifted to lower angles because of the enlargement of the structure. The lattice parameters and the cell volume were calculated from the following equations [24]:

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{1}
\]

\[
V = \frac{\sqrt{3} a^2 c}{2} \tag{2}
\]
Fig. 3. XRD diffraction patterns of SrZn$_x$Co$_x$Sn$_2$Fe$_{12-4x}$O$_{19}$.(a) $x=0$. (b) $x=0.3$. (c) $x=0.5$. (d) $x=0.7$.

where $d$ is the crystal plane distance, $a$ and $c$ are lattice parameters, $h$, $k$, and $l$ are Miller indices, and $V$ is the cell volume. By increasing the dopants content, the lattice parameters $a$ and $c$ increased and consequently the cell volume increased (Table I).

The reason for this observation lies under the higher ionic radius of dopants in comparison with iron. Ionic radius of dopants are Sn$^{4+} = 0.69$, Zn$^{2+} = 0.74$, and Co$^{2+} = 0.74$ Å, which are bigger than Fe$^{3+} = 0.64$ Å. The dopants radii are higher than iron; therefore, the lattice parameters $a$ and $c$ are enhanced by dopants content. The ratio of $c/a$ in all samples was about 3.95, which is in accordance with the value of all hexaferrites [25].

The average crystallite size estimated by Scherer’s equation $D = (k\lambda/\beta \cos \theta)$ is 68 nm. In this equation, $k$ (0.89) is constant, $\lambda$ (1.540 Å) is the wavelength of the X-ray radiation, $\theta$ is the diffraction angle, and $\beta$ is the full-width at half maxima.

C. FESEM Analysis

Morphology of the SrZn$_x$Co$_x$Sn$_2$Fe$_{12-4x}$O$_{19}$ ($x = 0.3$, 0.5, and 0.7) powder is displayed in Fig. 4. It can be observed from the micrographs that all the samples are in the form of hexagonal platelets. The average sizes for $x = 0$, 0.3, 0.5, and 0.7 are about 170.04, 143, 63.04, and 136 nm, which are smaller than the critical size of 650 nm. So, it can be estimated that all products have single-domain-wall structures [26]. Because of the magnetic attributes of the hexaferrite, agglomeration of specimens is clearly observed.

<table>
<thead>
<tr>
<th>samples $x$</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>$c/a$</th>
<th>$V$(Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0$</td>
<td>5.87</td>
<td>23.09</td>
<td>3.93</td>
<td>690.24</td>
</tr>
<tr>
<td>$x=0.3$</td>
<td>5.88</td>
<td>23.17</td>
<td>3.93</td>
<td>694.42</td>
</tr>
<tr>
<td>$x=0.5$</td>
<td>5.90</td>
<td>23.25</td>
<td>3.94</td>
<td>700.90</td>
</tr>
<tr>
<td>$x=0.7$</td>
<td>5.88</td>
<td>23.31</td>
<td>3.96</td>
<td>698.51</td>
</tr>
</tbody>
</table>

Fig. 4. SEM images of SrZn$_x$Co$_x$Sn$_2$Fe$_{12-4x}$O$_{19}$. (a) $x = 0.0$. (b) $x = 0.3$. (c) $x = 0.5$. (d) $x = 0.7$. 

TABLE I

LATTICE PARAMETERS OF SrZn$_x$Co$_x$Sn$_2$Fe$_{12-4x}$O$_{19}$

($x = 0.3$, 0.5, AND 0.7)
at 800 °C [28]. In this temperature, nonmagnetic $\alpha$-Fe$_2$O$_3$, since the calcination temperature was set hexaferrite is lower (46.40 emu/g) than the usual reports magnets [27].

cations, for example, data recording media and permanent squareness ratio in hexaferrites is appropriate in various appli-
cations. As a result, the $M_s$ hexaferrite. As a result, the appeared as a secondary phase in addition to the strontium

was the formation of nonmagnetic $\alpha$-Fe$_2$O$_3$ phase and the sec-
dond was the introduction of dopants in the crystal structure.

In the structure of strontium hexaferrite, iron is responsible for magnetic properties of the whole lattice. Iron in the hexagonal structure occupies five different sites in tetrahedral 4f$_1$ ($\downarrow$), bipyramidal 2b ($\uparrow$), and three octahedral sites [12 K ($\uparrow$), 4f$_2$ ($\downarrow$), and 2a ($\uparrow$)] [29], [30]. According to other studies and especially Mossbauer results, Co$^{2+}$ is substituted for Fe$^{3+}$ in octahedral and 4f$_2$($\downarrow$) and 2a ($\uparrow$) sites [31]. Sn$^{4+}$ is preferred to substitute for Fe$^{3+}$ in bipyramidal 2b and tetrahedral 4f$_1$ sites. Due to the large radius, Sn$^{4+}$ cations choose to occupy octahedral sites for any predictable distortion. So, Sn$^{4+}$ prefers to occupy 2b position rather than 4f$_1$ sites [32], [33]. Consequently, the saturation magnetization decreased in comparison to the pure SrM. By increasing dopants and when $x = 0.5$, the $\alpha$-Fe$_2$O$_3$ phase disappeared, and Sn$^{4+}$ preferably occupied 4f$_1$ sites. Consequently, saturation magnetization ($M_s$) increased noticeably and reached the highest values (65.463 emu/g) [34].

Likewise, addition of dopants causes $\alpha$-Fe$_2$O$_3$ phase formation and saturation magnetization ($M_s$) decreases in comparison to $x = 0.5$ (from 65.46 to 56.13 emu/g). But the value of saturation magnetization is higher than $x = 0.3$ (40.15 emu/g) because, by increasing dopant, Sn$^{4+}$ preferred 4f$_1$ position. As a result, $M_s$ at $x = 0.5$ is smaller than $x = 0.7$. Zn$^{2+}$ occupied tetrahedral sites 4f$_1$ ($\downarrow$) which can increase the total magnetic moments. But because of the formation of $\alpha$-Fe$_2$O$_3$, the saturation magnetization did not enhance. For Co$^{2+}$, when the amount of substitution was less than 0.5, this cation can occupy the 2a site. Therefore, the saturation magnetization decreased. For the substitutions higher than 0.5, Co$^{2+}$ occupied 4f$_1$ sites, so the saturation magnetization decreased [35], [36].

On the whole, the effect of 4+ cation doping is more effectual than 2+ cation substitution in the variation of magnetic properties [37]. As a result, Sn$^{4+}$ doping is much more impressive than Co$^{2+}$ and Zn$^{2+}$.

Easy magnetization directions of SrFe$_{12}$O$_{19}$ hexaferrite was named uniaxial anisotropy which was along the c-axis. By substituting tetravalent and divalent cations such as Sn$^{4+}$, Co$^{2+}$, and Zn$^{2+}$ instead of Fe$^{3+}$, the uniaxial anisotropy along the c-axis improves and changed to the basal plane [38]. Consequently, $H_c$ decreased severely from 5778.19 to 414.65 Oe [39]. By further substitution of dopants at $x = 0.7$ (1507.51 Oe), $H_c$ increases according to the enhancement of the in-plane anisotropy [40].

### Table II

<table>
<thead>
<tr>
<th>samples</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
<th>$H_c$ (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=0</td>
<td>46.404</td>
<td>26.993</td>
<td>0.581</td>
<td>5778.19</td>
</tr>
<tr>
<td>X=0.3</td>
<td>40.151</td>
<td>13.134</td>
<td>0.327</td>
<td>602.45</td>
</tr>
<tr>
<td>X=0.5</td>
<td>65.463</td>
<td>19.008</td>
<td>0.290</td>
<td>414.65</td>
</tr>
<tr>
<td>X=0.7</td>
<td>56.137</td>
<td>32.894</td>
<td>0.585</td>
<td>1507.51</td>
</tr>
</tbody>
</table>

D. Magnetic Properties

The hysteresis loops of pure ferrite (Fig. 5) indicate that the sample is classified in the hard magnetic materials because of the large coercivity ($H_c$). Dopants addition considerably changed the magnetic properties and turned samples into semi-hard ferrites. The saturation magnetization ($M_s$), coercivity ($H_c$), the remanent magnetization ($M_r$), and squareness ratio ($M_r/M_s$) of substituted compounds are listed in Table II.

Squareness ratio ($M_r/M_s$) of the samples is in the range of 0.2–0.59. From the industrial point of view, different squareness ratio in hexaferrites is appropriate in various applications, for example, data recording media and permanent magnets [27].

The saturation magnetization ($M_s$) of pure strontium hexaferrite is lower (46.40 emu/g) than the usual reports (60.23 emu/g), since the calcination temperature was set at 800 °C [28]. In this temperature, nonmagnetic $\alpha$-Fe$_2$O$_3$ appeared as a secondary phase in addition to the strontium hexaferrite. As a result, the $M_s$ value decreased abruptly. By dopant addition, $M_s$ reduced because of two facts. The first was the formation of nonmagnetic $\alpha$-Fe$_2$O$_3$ phase and the second was the introduction of dopants in the crystal structure. In the structure of strontium hexaferrite, iron is responsible for magnetic properties of the whole lattice. Iron in the hexagonal structure occupies five different sites in tetrahedral 4f$_1$ ($\downarrow$),

![Fig. 5. Hysteresis loops of Sn–Zn–Co-substituted and pure strontium hexaferrite.](image)

V. Conclusion

A series of SrZn$_x$Co$_y$Sn$_{2x}$Fe$_{12-4y}$O$_{19}$ ($x = 0.0, 0.3, 0.5$, and 0.7) was synthesized successfully via sol–gel auto-combustion method. FTIR analysis showed the metal-oxygen bands at 430 and 590 cm$^{-1}$ frequency, which was related to the stretching vibrating bonds of Fe-O. The hexagonal structure of the samples with the secondary phase of $\alpha$-Fe$_2$O$_3$ was confirmed by XRD results. Lattice parameters $a$ and $c$ increased by substitution of large radius cations in comparison with iron.

FESEM micrographs revealed the hexagonal of all prepared products. In all samples, coercivity ($H_c$) decreased as a result of dopant addition, and the semi-hard magnetic products were produced rather than the hard strontium hexaferrite. Saturation magnetization ($M_s$) reduced at $x = 0.3$ because of the formation of nonmagnetic $\alpha$-Fe$_2$O$_3$ phase and the occupation...
of the crystal sites by dopants. At $x = 0.5$, no secondary phase is formed; as a result, $M_s$ increased to 65.46 emu/g. At $x = 0.7$, the secondary phase appeared, so saturation magnetization reduced as a result of the nonmagnetic phase formation.

REFERENCES


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