Facile Synthesis, Structure and Infrared Properties of CoFe$_2$O$_4$ Ferrite Nanoparticles (CFN)

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Abstract: In this investigation, CoFe$_2$O$_4$ ferrite nanoparticles (CFN) were successfully synthesized by a simple and cost-effective sol-gel auto-combustion method using citric acid (C$_6$H$_8$O$_7$) as a fuel. The sol-gel synthesized CFN samples were characterized for microstructural and physic-chemical properties through X-ray diffraction (XRD) and infrared analysis. The crystallite size (\(d\)), the lattice constant (\(a\)) \(a = b = c\), and X-ray density \(\rho\) of CFN were calculated using X-ray diffraction data. Crystallite size was obtained through Debye-Scherrer’s formula indicates the nanocrystalline nature of the prepared sample. The functional group analysis of CFN was carried out by infrared spectroscopy which confirmed the presence of M-O stretching vibrations in the investigated samples. The IR analysis confirmed the formation of the ferrite phase in the CFN samples.

INTRODUCTION

Nowadays, spinel ferrite materials have attracted researchers due to their unique physical and chemical properties which makes them technologically very important in the range of fields [1]. The semiconducting behavior of some magnetic ferrite materials deserves the leader place in the industrial, research, biomedical applications compared to the other competent materials [2]. The spinel ferrites belong to the space group \(Fdd\) \(O_8\) having the general formula of \(AB_2O_4\) [3]. These ferrites can be described as a cubic closed-pack arrangement of oxygen ions with an equal distribution of cations at tetrahedral (A)-site and octahedral (B)-sites in the lattice structure [4]. Magnetic ferrites are of great interest owing to their dynamic magnetic properties, catalytic activity, and improvable electrical properties [5]. They are specially designed molecular crystalline structures which decides the dynamicity of enormous properties lies within. These ferrites have comparatively high Curie temperature \(T_C\) [6], a high magnetic coercive force, high anisotropy field, and considerably good chemical stability [7, 8]. They possess corrosion resistivity useful as coating materials at a very cheap cost [9]. CFN is commonly used in numerous applications such as magnetic resonance imaging (MRI) [10], magnetic recording media [11] such as cassettes and CD’s, the magnetic stripes in electronic cards, and Rfid magnetic sheet used for digital transactions [12]. The advanced level of applications of CFN included biomedical drug delivery, medical appliances, biological implants in the biological structure, nanorobotic applications, and complex algorithmic technologies in various modern research and development [13]. CFN also fascinated the world with numerous applications like magnetic fluids [14], micro and nanoelectronic chips used in mobile and computer technologies, gas sensing devices [15], microwave communication [16], transformers, transducers [17], nano-electronic switches, electric motors and dynamos [18]. To meet this application pyramid a dynamic desired product could be continuously designed over the various traditional and new modern synthesis techniques. Among the range of synthesis techniques viz. ceramic method [19], auto-
clayle method [20], micro-emulsion method [21], wet-chemical method [22], hydrothermal method [23], spray pyrolysis technique, a salt-melt technique [24], etc. Efforts have been made to improve the performance and designs in the CFN by the scientists and researchers throughout the world. We aimed to synthesize the cobalt ferrite nanoparticles via bottom-up approaches using the sol-gel auto-combustion method.

EXPERIMENTAL

Raw Materials used for the synthesis of CFN

Analytical Reagent (AR) grade, cobalt nitrate hexahydrate [Co(NO$_3$)$_2$.6H$_2$O], ferric nitrate nonahydrate [Fe(NO$_3$)$_3$.9H$_2$O], and citric acid C$_6$H$_8$O$_7$.H$_2$O as fuel were used as an initial starting material for the synthesis process of CFN samples. Ammonia compound of nitrogen and hydrogen with the formula NH$_3$ was considered for maintaining the pH of CFN mixed solution.

Synthesis of CFN

The essential requirement for the initial mixed solution in the sol-gel synthesis was made possible by the addition of proportionally selected metal nitrates were dissolved in the desired amount of double-distilled water. This mixed solution was stirred well in a beaker and mounted on a magnetic stirrer for continuous stirring for 20 min to achieve homogeneity in the mixed nitrate solution. Citric acid was mixed in the same solution maintaining the ratio of 1:3. This beaker was placed on a hot plate magnetic stirrer so that an excessive amount of water can be evaporated. The continuous heating and stirring have been made for 5 h at the temperature of 80 °C. Meanwhile, drop by drop ammonia was added to the solution with the help of a burette to adjust the pH value of the mixed solution to 7. We witness the formation of gel over the evaporation of excess water throughout the solution. To speed up this exercise we increase the temperature level up to 110 °C at the end reaction, so that gel turns in to dry-gel releasing a good amount of gasses. In the climax stage of the sol-gel auto-combustion the reaction goes into the self-ignition mode. This leads to the high-temperature auto-combustion resulted in solidified, loose fluffy powder as an end product of the synthesis. A loose powder was annealed at 950 °C for 8 h to obtain CoFe$_2$O$_4$ ferrite powder which was used for further characterizations and analysis.

CHARACTERIZATION

X-Ray Diffraction of CFN

X-ray diffraction pattern of nanocrystalline CFN was taken by using Cu-ka radiation (λ = 1.5405 ˚) on Philips PW-1730 X-ray diffractometer. The XRD parameters were characterized at room temperature. The entire X-ray diffraction pattern was recorded in the 20 range of 20° to 80° with a scanning rate of 0.02 deg/s and the major Bragg’s reflections of nanocrystalline CFN ferrite nanoparticles were recorded for the analysis of structural parameters.

Infrared spectroscopy of CFN

The functional group analysis of the prepared CFN sample was carried out by infrared spectroscopy. From the infrared spectra, we have reported the formation of ferrite structure and the presence of stretching vibrations within the lattice structure. Infrared spectroscopy was recorded by Nicolet-MAGNA-550 spectrometer using KBr pellet at room temperature in the wavenumber range of 0 cm$^{-1}$ - 4000 cm$^{-1}$.

RESULTS AND DISCUSSIONS

Structural analysis of CFN

The prepared CFN sample was characterized by structural analysis by using Bragg’s X-ray diffractometry. The XRD data stands very crucial in determining the phase purity of the synthesized material, the crystallite size (t),
lattice constant \( (a) \), and various other structural parameters on employing the related formulas. In this characterization, Bragg’s reflections occur at (220), (311), (222), (400), (422), (511), (440), (620) and (533) [25] within the range of 20° to 80°. It can be seen in figure 1 that extra peak is reported in the XRD.

![X-ray diffraction pattern of CFN sample](image)

**Figure 1.** X-ray diffraction pattern of CFN sample

All these reflections represent the cubic spinel structure. Thus, it can be concluded from XRD data that, the prepared CFN sample possesses a single-phase cubic spinel structure. Table 1 represents the Miller indices \((hkl)\), Bragg’s angle \((2\theta)\), \(\sin \theta\), \(\sin \theta/\lambda\) interplanar spacing \((d)\), and the intensity of various reflections evolved in the XRD pattern.

<table>
<thead>
<tr>
<th>((hkl))</th>
<th>(2\theta)</th>
<th>(\theta)</th>
<th>(\sin \theta)</th>
<th>(\sin \theta/\lambda)</th>
<th>(d) (Å)</th>
<th>(a) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(220)</td>
<td>30.13</td>
<td>15.06</td>
<td>0.2599</td>
<td>0.1687</td>
<td>2.962</td>
<td>8.380</td>
</tr>
<tr>
<td>(311)</td>
<td>35.52</td>
<td>17.76</td>
<td>0.3050</td>
<td>0.1979</td>
<td>2.524</td>
<td>8.373</td>
</tr>
<tr>
<td>(222)</td>
<td>37.03</td>
<td>18.51</td>
<td>0.3175</td>
<td>0.2061</td>
<td>2.425</td>
<td>8.400</td>
</tr>
<tr>
<td>(400)</td>
<td>43.16</td>
<td>21.58</td>
<td>0.3678</td>
<td>0.2387</td>
<td>2.093</td>
<td>8.375</td>
</tr>
<tr>
<td>(422)</td>
<td>53.82</td>
<td>26.91</td>
<td>0.4526</td>
<td>0.2938</td>
<td>1.701</td>
<td>8.335</td>
</tr>
<tr>
<td>(511)</td>
<td>57.1</td>
<td>28.55</td>
<td>0.4779</td>
<td>0.3102</td>
<td>1.611</td>
<td>8.372</td>
</tr>
<tr>
<td>(440)</td>
<td>62.68</td>
<td>31.34</td>
<td>0.5201</td>
<td>0.3376</td>
<td>1.480</td>
<td>8.375</td>
</tr>
<tr>
<td>(620)</td>
<td>71.25</td>
<td>35.62</td>
<td>0.5825</td>
<td>0.3781</td>
<td>1.322</td>
<td>8.361</td>
</tr>
<tr>
<td>(533)</td>
<td>74.28</td>
<td>37.14</td>
<td>0.6038</td>
<td>0.3919</td>
<td>1.275</td>
<td>8.364</td>
</tr>
</tbody>
</table>

**Average** 8.371

**Table 1.** Miller Indices \((hkl)\), Bragg’s angle \((2\theta)\), \(\sin \theta\), \(\sin \theta/\lambda\) interplanar spacing \((d)\), and Intensity of various reflections of nanocrystalline CFN

The calculated lattice constant \( a = (a = b = c) \) of CFN was calculated using the following equation [26];

\[
a = d_{hkl} \sqrt{h^2 + k^2 + l^2}
\]
Where $d_{hkl}$ is the interplanar spacing of two planes, $a$ is the lattice constant, and $(hkl)$ is the miller indices of each plane. The lattice parameters of CFN calculated from the XRD data for the spinel structure is $a = 8.371$ Å which is in good agreement with the reported values in the literature. The value of the lattice parameter calculated using the above equations is presented in Table 1.

**Crystallite size (t) of CFN**

The crystallite size (t) of CFN was calculated by using the Debye-Scherrer method taking (311) plane of maximum intensity, which is mentioned by eq. [16];

$$t = \frac{k\lambda}{\beta \cos \theta}$$

(2)

where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum, $\theta$ is the Bragg’s angle, and $k = 0.89$. The average crystallite size (t) obtained from XRD data is 26.78 nm. The crystallite itself indicating the nanocrystalline formation of the CFN. The FWHM (degree) value noted from the XRD pattern is given in table 2.

| Table 2. Lattice parameter $a$(Å), FWHM (degree) and Crystallite size (t) nm CoFe$_2$O$_4$ ferrite nanoparticles |
|-------------|--------|----------------|
| CoFe$_2$O$_4$ ferrite nanoparticles | $a$(Å) | FWHM (degree) | Crystallite size (t) nm |
| 8.371 | 0.3116 | 26.78 |

Figure 2. Infrared spectra of CFN sample

**Infrared spectra of CFN**

Infrared spectroscopy is a common characterization technique used to confirm the functional group present in the sample and the bands associated with the structure; particularly for ferrites. We can see the IR spectra of CFN sample in figure 2. All characteristic peaks near 390 cm$^{-1}$ and 554 cm$^{-1}$ in the IR spectrum were analyzed to confirm the formation of the ferrite phase. Waldron reported in his studies considering the ferrites as continuously bonded
crystals [27]. That means atoms within the lattice structure are bonded to all the nearest neighboring by equivalent forces like ionic forces, co-valent, or Van der Waals forces. The infrared absorption bands of solids are assigned to the vibration of metal ions in the crystal lattice. The high-frequency band \( \nu_1 = 390 \text{ cm}^{-1} \) correspond to the intrinsic vibration of the tetrahedral group complexes \( \text{Fe}^{3+} \)- \( \text{O}^2- \) and \( \nu_2 = 554 \text{ cm}^{-1} \) corresponds to the octahedral group complexes \( \text{Fe}^{3+} \)- \( \text{O}^2- \). The variance in the frequency of characteristic vibrations \( \nu_1 \) and \( \nu_2 \) can be attributed to the dynamic bond length of oxygen \( \text{O}^2- \) and metal ions \( \text{Fe}^{3+} \) at octahedral [B]-site and tetrahedral (A)-site.

**CONCLUSIONS**

We have successfully prepared nanocrystalline CFN by using the sol-gel auto-combustion method. The crystallite size \( t \) of the prepared CFN was recorded as 26.78 nm. From the XRD data values it is cleared that; the prepared CFN sample belongs to the single-phase; cubic structure; inverse spinel ferrite. Bragg’s angle \( (20) \) reflections are in very good agreement with the reported literature. The lattice constant \( \alpha \) was reported as is \( \alpha = 8.371 \text{ Å} \) for CFN and was recorded to be in good agreement. The infrared spectroscopy has confirmed the ferrite phase formation as we report the \( \nu_1 = 390 \text{ cm}^{-1} \) and \( \nu_2 = 554 \text{ cm}^{-1} \) corresponds to the intrinsic vibrations belongs to the tetrahedral (A)-site and octahedral [B]-site.

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**REFERENCE**