X-ray Diffraction and Infrared Characterization of NiFe$_2$O$_4$ Nanoparticles (NFNPs) Prepared using Dextrose Assisted Sol-Gel Auto-Combustion Technique

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Abstract: In the current work, we comprehensively focused upon the synthesis of NiFe$_2$O$_4$ nanoparticles (NFNPs) via the sol-gel auto-combustion method. Particularly in the present investigation, we deployed dextrose (C$_{12}$H$_{22}$O$_{11}$) as an organic compound that works as a fuel in the sol-gel synthesis of NFNPs. The as-prepared samples of NFNPs were characterized for structural properties through XRD. The crystallite size (t), the lattice constant (a), unit cell volume (V), and X-ray density $d$ of NFNPs was determined using XRD data. Crystallite size was obtained through Debye-Scherrer’s formula indicates the nanocrystalline nature of the prepared NFNPs sample. The infrared spectroscopy (IR) was carried out for investigating the presence of phases and the function group analysis in the NFNPs. The IR has confirmed the formation of ferrite phase in dextrose assisted sol-gel synthesized NFNPs as we report the intrinsic vibrations belongs to the tetrahedral and octahedral sites.

INTRODUCTION

The ferrite with the general formula (Me$^{2+}$)$_{1-x}$Fe$^{3+}$$_x$)[Me$^{2+}$$_{x-1/3}$Fe$^{3+}$$_{2/3}$]O$_4$, and the proportion of Fe$^{3+}$ ions occupying tetrahedral (A) sites is called the degree of inversion. NiFe$_2$O$_4$ is a soft ferrite with space group Fd$_{3m}$O$_{6}$; inverse spinel, cubic structure [1]. In the nickel ferrite structure, 8 tetrahedral voids (A)-sites are occupied by Fe$^{3+}$ ions, and 16 octahedral voids [B]-sites are occupied by Fe$^{3+}$ and Ni$^{2+}$ ions in an equal proportion [2]. In pure NiFe$_2$O$_4$ degree of inversion is 1, and the inverse spinel structure of nickel ferrite changes partially concerning the change in the degree of inversion employing a change in composition. NFNPs is famous for spinel magnetic material with moderate coercivity and saturation magnetization in its bulk form [3]. It is now has been proven by researchers that the physical and chemical properties of nanosized materials differ from bulk counterparts [4]. The nanosize of the ferrites makes them special in the field of technological applications. NFNPs has a wide range of applications in various fields based on its physical and chemical properties. Some of the important applications include medical diagnosis tools [5], circulators [6], memory devices [7], electrical power equipment [8], Ni-based batteries [9], sensors, isolators, phase shifters, microwave magnetic resonance imaging [10], spintronics [11], etc. Researchers are always to take out the good output from the investigated materials. To improvise the applicability of these ferrites and to get new results, various synthesis techniques have been developed for research and commercial purpose. Some of these synthesis methods are the solid-state reaction method [12], sol-gel [13], ultra-fast pyro-synthesis [14], electro-deposition method [15], chemical co-precipitation method [16], micro-emulsion [17] and so on.
Nowadays, the focus has been given to the chemical methods in the bottom-up approach [18], to attain the nanocrystalline and new results satisfying the needs of the industries. We employed the sol-gel auto-combustion method for the synthesis of NFNPs in this investigation to find out the structural and infrared characteristics of the target sample. It is frequently noticed that in the preparation of nickel ferrite via the sol-gel auto-combustion method, glycine, urea, citric acid, dextrose, etc. were used as fuel [19]. The crucial role played by the fuel in the reaction reflects on the quality of the material and the properties of the final product. However, the dextrose played synthesis of NFNPs via sol-gel auto-combustion was not discussed so far in detail by the researchers. We aimed to set an example of a different route and improved techniques in dextrose assisted sol-gel synthesis of NFNPs. The preparation conditions, initial ingredients of the reaction, physical parameters like temperature, reaction time, etc. have huge effects that can tune the physical and chemical properties of the synthesized material [20]. The motivation for the trials taken for the synthesis of new materials comes from the idea of reducing the toxic pollutants and enormous gases exhausted during the reaction and the receded impurities incorporated during the reaction.

EXPERIMENTAL

Raw Materials

Analytical Reagent (AR) grade, Nickel nitrate hexahydrate [Ni(NO_{3})_{2}.6H_{2}O], ferric nitrate nonahydrate [Fe(NO_{3})_{3}.9H_{2}O], and dextrose C_{6}H_{12}O_{6}.H_{2}O as fuel were used as an initial starting material for the synthesis process of spinel structured NFNPs. Ammonia compound of nitrogen and hydrogen with the formula NH_{3} was considered for maintaining the pH of NFNPs.

Dextrose (C_{6}H_{12}O_{6})

Dextrose is the name of simple sugar that is derived from the Latin word ‘dexter’ which means ‘right’, as, in an aqueous solution of sugar, the plane of linearly polarized light is turned to the right [21]. Dextrose is made from corn and is chemically identical to glucose [22]. Dextrose or glucose is also known as monosaccharide which is approximately 30% less sweet than that of pure or refined sugar [23]. Dextrose is widely available at an affordable price, so it is a commonly used ingredient in packaged or processed food [24]. A dextrose is a form of glucose derived from starches. Biochemically nature of glucose is a form of sugar found in blood and dextrose is a form of sugar found in plants [25]. It's like a natural sugar that can be used as a sweetener, thickener, and texturizing agent, extracted from monosaccharides starch sources [26]. The dextrose is commercially manufactured from corn starch in the United States and Japan, from potato [27]. It is also produced from wheat starch in European countries and tapioca starch in some of the tropical areas. The production of dextrose is made by hydrolysis technique using pressurized steaming at controlled pH in a jet which is further processed via enzymatic depolymerization.

Synthesis of NFNPs

Sol-gel processing has been known for a long time for the synthesis of ferrite nanoparticle fabrication line of materials. Drastic developments in the sol-gel synthesis techniques were undertaken from the last few decades. All these modernization in the sol-gel synthesis techniques were accelerated as of the growing organic and hybrid-organic-inorganic compound role in the preparation techniques. The selected metal nitrates for the aimed synthesis has been dissolved in a beaker with a minimum quantity of de-ionized water. All the mixed nitrates were stirred on the magnetic hot plate stirrer for several minutes to attain homogeneity. Then the homogeneous mixture of the solution was kept on a magnetic hot plate stirrer with a set temperature 80°C for evaporation of water. The metal nitrate to the dextrose (C_{6}H_{12}O_{6}.H_{2}O) ratio was taken as 1:2. The pH value of the mixed solution was maintained by adding drop by drop ammonia. With the evaporation of water, the ‘gel’ formation was executed with an exhaust of some gasses from the ingredients in the beaker. Suddenly at a particular temperature waterless ‘gel’ get ignited and form large quantity release of gasses. Now, the reaction goes into the self-ignition mode and powder form of NFNPs was obtained. This powder is used for characterization purposes.
CHARACTERIZATION

X-Ray Diffraction of NFNPs

X-ray diffraction pattern of nanocrystalline NFNPs was taken by using Cu-kα radiation (λ = 1.5406 Å) on Bruker X-ray diffractometer. The XRD parameters were characterized at room temperature operated at 40 mA current 40 Kv voltage. The entire X-ray diffraction pattern was recorded in the 2θ range of 20° to 80° with a scanning rate of 2 deg/min and the major Bragg’s reflections of nanocrystalline NFNPs were recorded for the analysis of structural parameters.

Infrared spectroscopy of NFNPs

The functional group analysis of the dextrose assisted sol-gel synthesized NFNPs sample was carried out by IR spectroscopy. From the IR spectra, we have reported the formation ferrite phase and the presence of various 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 NFNPs

The dextrose assisted sol-gel synthesized NFNPs sample was characterized for a structural parameter analysis by Bragg’s X-ray diffractometry. The Bragg’s reflections occur at (220), (310), (311), (222), (400), (422), (511), (440) and (533) within the range of 20° to 80° without any extra reflections representing the single-phase, cubic spinel structure of NFNPs sample [28]. The XRD data helps in determining the phase purity, the crystallite size (t), and lattice constant (a) of NFNPs. XRD data was useful for the determination of various other structural parameters like porosity (P%), unit cell volume (V), etc. on using the related formulas. Table 1 represents the values of hopping length L_A, L_B, tetrahedral bond d AX, octahedral bond d BX tetra edge d AXE octa edge d BXE and octa edge unshared d BXEu of nanocrystalline NFNPs calculated from XRD data.

<p>| Table 1. Hopping length L_A, L_B, tetrahedral bond d AX, octahedral bond d BX tetra edge d AXE octa edge d BXE and octa edge unshared d BXEu of nanocrystalline NFNPs |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>NFNPs</th>
<th>L_A (Å)</th>
<th>L_B (Å)</th>
<th>d AX (Å)</th>
<th>d BX (Å)</th>
<th>d AXE (Å)</th>
<th>d BXE (Å)</th>
<th>d BXEu (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6048</td>
<td>2.9433</td>
<td>1.8889</td>
<td>2.0325</td>
<td>3.0846</td>
<td>2.8021</td>
<td>2.9450</td>
<td></td>
</tr>
</tbody>
</table>

Lattice constant (a) of NFNPs

The average lattice constants (α) in which $a = b = c$ for the cubic spinel structure of the NFNPs sample was calculated using the following equation;

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$  

(1)

Where $d_{hkl}$ the interplanar spacing of two planes, (a) is the lattice constant, and (hkl) is the miller indices of each plane. The lattice constants (α) of NFNPs calculated from the XRD data is $\alpha = 8.3753$ Å which is in good agreement with the literature value. The value of the lattice parameter calculated using the above equations is presented in Table 2.
Crystallite size (t) of NFNPs

The crystallite size (t) of dextrose assisted sol-gel synthesized NFNPs was calculated by using the Debye-Scherrer method taking (311) plane of maximum intensity, which is mentioned by eq. ;

\[ t = \frac{k\lambda}{\beta \cos \theta} \]  

(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 27.47nm, indicating the nanocrystalline nature of the NFNPs.

X-ray density (\( d_x \)) of NFNPs

The X-ray density (\( d_x \)) of NFNPs was calculated by the following relation.

\[ d_x = \frac{8M}{N\alpha^3} \]  

(3)

Where \( M \) is molecular weight and \( N_A \) is the Avogadro’s number, \( \alpha \) is lattice constant. The X-ray density for NFNPs was obtained as 5.3961 (g/cm\(^3\)). The values of Lattice parameter \( \alpha \), X-ray density \( d_x \), Bulk density \( d_B \), Volume V, and Porosity P\%, and Crystallite size t of NFNPs are listed in Table 2.

<table>
<thead>
<tr>
<th>NFNPs</th>
<th>( \alpha ) (Å)</th>
<th>( d_x ) (g/cm(^3))</th>
<th>( d_B ) (g/cm(^3))</th>
<th>V (Å(^3))</th>
<th>P%</th>
<th>t (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.3250</td>
<td>5.3961</td>
<td>4.793</td>
<td>577.0</td>
<td>11.18</td>
<td>27.47</td>
</tr>
</tbody>
</table>

The values of the tetrahedral site radius (\( r_A \)) and octahedral site radius (\( r_B \)) of the nanocrystalline NFNPs are reported in table 3.

Infrared spectroscopy of NFNPs

IR spectroscopy is a common characterization technique used to confirm the functional group present in the ferrite materials among others [29]. This analysis confirms the phase formation and the bands associated with the ferrite structure. All characteristic peaks indicating the intrinsic vibrations within the phase are reflecting in the IR spectrum which confirms the formation of the ferrite phase and their values are depicted in table 3.

<table>
<thead>
<tr>
<th>NFNPs</th>
<th>( r_A ) (Å)</th>
<th>( r_B ) (Å)</th>
<th>( v_1 ) (cm(^{-1}))</th>
<th>( v_2 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5803</td>
<td>0.7236</td>
<td>550</td>
<td>391</td>
</tr>
</tbody>
</table>

We report the results obtained in the IR spectra based on studies carried out by Waldron. According to Waldron ferrites are considered s continuously bonded crystals [30]. Bonded crystals are the crystals in which the atoms in the lattice system form a complex bonding with all the nearest possible atoms employing ionic forces, co-valent, or
Van der Waals forces. The IR absorption bands of solids are assigned to the vibration of metal ions (M-O) 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 $\text{Fe}^{3+}-\text{O}^2$. We can observe in the IR spectra of the NFNPs sample as shown in figure 1.

**Figure 1.** Infrarred spectra of NFNPs sample

**CONCLUSIONS**

We report the successful preparation of nanocrystalline NFNPs by using dextrose assisted sol-gel auto-combustion method. The crystallite size (t) of the prepared NFNPs was recorded as 27.47 nanometers, witnessing the achievement of nano size NFNPs. From the XRD data, the values obtained and calculated according to the standard method. It is cleared that; the dextrose-assisted sol-gel synthesized NFNPs belongs to the inverse; single-phase; cubic spinel ferrite structure. The lattice constant $\alpha$ was reported as 8.3250 Å for NFNPs is in good agreement with the reported literature. X-ray density ($d_A$) was obtained as 5.3961 $(g/cm^3)$. Hopping length $L_A, L_B$, tetrahedral bond $d_{AX}$ octahedral bond $d_{BX}$ tetra edge $d_{AXE}$ octa edge $d_{BXE}$ and octa edge unshared $d_{BXXU}$ of nanocrystalline NFNPs were derived from the XRD data is following the reported range in literature. The values of the tetrahedral site radius ($r_A$) and octahedral site radius ($r_B$) are reported as per the calculations. The infrared spectroscopy (IR) has confirmed the ferrite phase formation in NFNPs as we report the $\nu_1 = 391 \text{ cm}^{-1}$ and $\nu_2 = 550 \text{ cm}^{-1}$ corresponds to the intrinsic vibrations belongs to the tetrahedral (A)-site and octahedral [B]-site.

**ACKNOWLEDGMENT**

One of the authors Rani D. Dudhal is thankful to Prof. K.M. Jadhav, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, INDIA for his fruitful discussion for this research work.

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