Effect of pH on Magnetic Properties of Doped Barium Hexaferrite

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Abstract
In the present work, La-Ni doped barium nano hexaferrites (BaM) are synthesized via sol gel citrate precursor method. The effect of pH on the properties of the synthesized nano hexaferrites have been investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Vibrating Sample Magnetometer (VSM). The XRD study shows the formation of hexagonal structure of doped nano hexaferrites (BaLa_{0.5}Ni_{0.5}Fe_{19}O_{19}) with particle size lying between 33 nm to 38 nm. It is found that particle size of the doped barium nano hexaferrite decreases with increase in pH. The presence of the bands in the 375-600 cm\(^{-1}\) range FTIR spectra confirms the formation of hexagonal ferrites. The VSM analysis of the samples showed that with increase in pH value, coercivity, saturation magnetization, remanentivity and anisotropy factor increases.

Keywords
Barium Nano Hexaferrite, VSM, Coercivity, Anisotropy

I. Introduction
M type hexaferrites are considered to be the main magnetic materials in future electromagnetic devices which show the good enhancements in the properties at nanostructure level [1]. It has been studied extensively by the physicists, chemists and material researchers in the previous decade due to their extensive applications in technology for sensors, permanent magnets, transducers, loud speakers, energy storage systems, data storage, communication systems and microwave devices [2-3]. BaM is a hard ferrite with a hexagonal magneto-plumbite structure belonging to space group P63/mmc. It is important material due to its high Saturation Magnetization (M\(_s\)), High Coercivity (H\(_c\)) and High magnetic anisotropy [4]. Magnetic properties of BaM can be enhanced by using rare earth metals. La can replace Ba ion which has less ionic radii than barium. This substitution can cause Fe\(^{3+}\) ions to Fe\(^{2+}\) ions on 2a crystallographic sites. Fe\(^{2+}\) causes increase in magneto crystalline anisotropy. So, doping of rare earth metals can enhance the magnetic properties [5].

A. Experimental Procedure
A.R grade barium nitrate, lanthanum nitrate, nickel nitrate, citric acid and ferric nitrate are taken and the aqueous solution of iron and metal salts are prepared separately in stoichiometric proportions by dissolving them in double distilled water and then mixed together with constant magnetic stirring. Aqueous solution of citric acid is added to the salt solution with cation to citric acid molar ratio of 1:2. Then ammonium hydroxide solution is added dropwise to attain the pH of 0.29, 4 and 8. The solution is then heated at 80°C-85°C for 2 hours with continuous stirring using magnetic stirrer. After evaporation of water the liquid gets converted into a homogenous brown colored gel. The viscous solution is dried over hot plate at 400°C to form the precursor material. Then the precursor material is heated at 800°C for 3hrs in the muffle furnace.

II. Results and Discussions

A. XRD Study
Sol gel citrate precursor method assist in the formation of single phase structure of M type La-Ni doped barium hexaferrites that can be seen from XRD patterns of doped barium hexaferrites. The X-ray diffraction measurements were carried out using Cu-K\(_\alpha\) radiation (\(\lambda = 1.54060 \text{ Å}\)) with a Pananalytical X-ray diffraction unit (X’Pert pro). The XRD patterns of the synthesized hexaferrite materials are shown in Fig.1. The sharp peak shows that the synthesized nanoparticles are highly pure. The diffraction patterns consist of peaks corresponding to crystallographic planes (114), (107), (110), (200), (203), (205), (208), (217), (220), (304), (1011) and (2011) in samples having pH variations (0.29, 4 and 8).

![XRD Pattern](image.png)

Fig. 1: XRD Pattern of BaFe_{11}Ni_{0.5}La_{0.5}O_{19} nano-ferrite obtained after 3hr heating at 800°C

This provides a clear evidence for the formation of hexagonal structure in doped barium hexaferrite [6-7]. The grain size ‘D’ is calculated using the Scherrer formula [8] i.e.

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

where, \(\lambda\) is the X-ray wavelength and is equal to 1.54060 Å, \(\beta\) is the half peak width, \(\theta\) is the Bragg’s angle and \(k\) is the shape factor that is equal to 1 for hexagonal system. The average grain size is found to be 38 nm, 34 nm and 33 nm (Table 1). It is observed that pH does not affect the value of X-ray density. There is a little effect of pH (0.29, 4, and 8) on the values of lattice parameters.

B. FTIR Study
During the FTIR study, all the samples are, first of all, grinded with mortar and pestle into a mixture with KBr at approximately 1:10 mass ratio. After that, the mixture is pressed to make thin pallets. The spectra of the samples are collected in the range of 4000-400 cm\(^{-1}\) with IR prestige- 21FTIR (model-8400S).
The bands in the range 3200–3700 and 1600 cm\(^{-1}\) (Fig. 2) are assigned to the hydroxyl and carboxyl groups of citric acid, respectively. The significant bands at about 1350 and 1445 cm\(^{-1}\) are attributed to nitrate ion and barium carbonate, respectively. Burnt powders show also some bands at below the 600 cm\(^{-1}\) which belong to magnetite. The spectrum of precursor indicates the anti-symmetrical and symmetrical stretching vibration bands of RCOO\(^-\) related to the organic acid are located at 1614 and 1444 cm\(^{-1}\) while the characteristic absorbing band for the C-O vibration is around 1725 cm\(^{-1}\). A set of band appear at 1381 and 848 cm\(^{-1}\), which are attributed to the N-O stretching and bending vibrations of NO\(_3^-\) respectively.

Table 1: Average Particle Size, Lattice Constant ‘a’, ‘c’, V\(_{\text{cell}}\) and X-ray density of BaLa\(_{0.5}\)Ni\(_{0.5}\)Fe\(_{11}\)O\(_{19}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Variation</th>
<th>Average grain size (D) (nm)</th>
<th>Lattice Constant (a) Å</th>
<th>Lattice Constant (c) Å</th>
<th>V(_{\text{cell}}) = 0.866025 a(^2)*c Å(^3)</th>
<th>X-ray density g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.29</td>
<td>38</td>
<td>5.87</td>
<td>23.24</td>
<td>693.49</td>
<td>5.26</td>
</tr>
<tr>
<td>B</td>
<td>4.00</td>
<td>34</td>
<td>5.87</td>
<td>23.15</td>
<td>690.80</td>
<td>5.28</td>
</tr>
<tr>
<td>C</td>
<td>8.00</td>
<td>33</td>
<td>5.80</td>
<td>23.23</td>
<td>676.76</td>
<td>5.39</td>
</tr>
</tbody>
</table>

C. VSM Study

To understand the magnetic properties of nano-hexaferrites, it is characterized using Vibrating Sample Magnetometer (VSM). (Model PAR 155, from Princeton Applied Research USA). Saturation magnetization, retentivity and coercivity have been calculated from the hysteresis loop and shown in the Table 2. The value of anisotropy constant increases with increase in pH of the samples B and C from 0.12 to 0.19 (Fig. 3). The value (for B and C samples) of saturation magnetization, retentivity and coercivity increases and grain size decreases with increase in pH indicates that the average magnetic domain size of the particles is increasing and atomic spins are getting more and more aligned with the direction of the applied magnetic field [9].

Table 2: Average Particle Size, Saturation Magnetization, Retentivity, Coercivity and Anisotropy of BaLa\(_{0.5}\)Ni\(_{0.5}\)Fe\(_{11}\)O\(_{19}\).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Variation</th>
<th>Average grain size (D) (nm)</th>
<th>Saturation Magnetization M(_s) (emu/g)</th>
<th>Retentivity M(_r) (emu/g)</th>
<th>Coercivity H(_c) (Oe)</th>
<th>Anisotropy K</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4.00</td>
<td>34</td>
<td>44.41</td>
<td>26.17</td>
<td>4379.46</td>
<td>0.12</td>
</tr>
<tr>
<td>C</td>
<td>8.00</td>
<td>33</td>
<td>60.73</td>
<td>36.55</td>
<td>4996.21</td>
<td>0.19</td>
</tr>
</tbody>
</table>
III. Conclusion
The present study shows that the sol gel citrate precursor method is an efficient method for synthesizing La-Ni doped barium hexaferrites nanoparticles. The XRD results of these studies confirmed the presence of hexagonal structure in the samples which is further confirmed by FTIR. It is found that coercivity, saturation magnetization, remanent and anisotropy factor depend on pH of the reaction mixture.

References
[4] Ying liu, Michael G. B. Drew, Yue Liu, Jingping Wang, Milin Zhang,“Preparation, Characterization and magnetic properties of the doped barium hexaferrites $\text{BaFe}^{12-2x}_{12} \text{Co}^{x/2} \text{Zn}^{x/2} \text{Sn}^{x} \text{O}_{19}$ $\text{X}=0.0-2.0$”, Journal of Magnetism and Magnetic Materials, Vol. 322, 2010, pp. 814-818

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