Synthesis, Structural and Electrical Investigations of Ba$_{0.9}$Mn$_{0.1}$Fe$_{12}$O$_{19}$ Hexaferrite NPs

Sandip K. Fasate$^{1,a}$, R.R. Parlikar$^{2,b}$, Shakti N. Bajaj$^{3,c}$, S.A. Rode$^{1,d}$, A.V. Raut$^{4,e}$, S.T. Alone$^{5,f}$

$^1$Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, INDIA
$^2$Department of Physics, Yogeshwari Mahavidyalay, Ambejogai, INDIA
$^3$Department of Physics, Pratishthan Mahavidyalaya, Paithan Aurangabad, INDIA
$^4$Department of Physics, Vivekanand Arts and Sardar Dalipsing Commerce and Science College, Aurangabad, INDIA
$^5$Department of Physics, Rajarshi Shahu Art's, Commerce and Science College, Pathri, Aurangabad, INDIA
$^a$Corresponding author: fasate2sandip@gmail.com; $^b$rrparlikar2015@gmail.com; $^c$prashanthahuja1986@gmail.com; $^d$rodesantosh97@gmail.com; $^e$nano9993@gmail.com; $^f$drureshtalone@gmail.com

Abstract: The family of barium hexaferrite BaFe$_{12}$O$_{19}$ stand out for the magnetic catalytic applications as it has an absorbance magnitude to a whole range in the visible light; chemical stability, magnetic properties and magnetodielectric characteristics as well. In this work, we have prepared pared BaFe$_{12}$O$_{19}$ hexaferrite, doped with a divalent Mn$^{2+}$ ion via sol-gel auto-combustion method using C$_6$H$_{12}$O$_7$ as a fuel. The synthesized Ba$_{0.9}$Mn$_{0.1}$Fe$_{12}$O$_{19}$ hexaferrite nanoparticles were characterized by XRD, Infra-Red spectroscopy (IR) approach for the structural investigation and phase purity. The XRD pattern scrutiny confirms the formation of a single-phase M-type hexagonal crystal structure of Ba$_{0.9}$Mn$_{0.1}$Fe$_{12}$O$_{19}$. The lattice constant ($a$), lattice constant ($c$), and unit cell volume ($V$) was resolved using unique XRD data. The crystallite size was obtained through Debye-Scherrer’s formula indicates the nanocrystalline nature of the Ba$_{0.9}$Mn$_{0.1}$Fe$_{12}$O$_{19}$ hexaferrite. IR spectra shows the formation of two main absorption bands near 574.79 cm$^{-1} $; 574.07 cm$^{-1}$ and 425.86 cm$^{-1}$ which are characterized to the formation of Ba$_{0.9}$Mn$_{0.1}$Fe$_{12}$O$_{19}$ nanoparticles. DC-electrical resistivity was in well correlation with the reported literature to explain the electrical properties of Mn$^{2+}$ loaded barium hexaferrite NPs.

INTRODUCTION

Now a days, M-type barium hexaferrite (BaFe$_{12}$O$_{19}$) are been outstretched as a permanent magnets, magnetic recording media, and magnetodielectric property [1]. The major consequential applications of hexaferrite also carry antenna, tunable filters and microwave, EMV stripes on credit cards [2] etc.. It is blooming that M-type barium hexaferrite possess large coercive force; conglomerate magneto-plumbite structure, higher saturation, better dielectric properties magnetocrystalline anisotropy; Curie temperature (Tc) and excellent chemical stability [3, 4]. A barium hexaferrite with general chemical prescription BaFe$_{12}$O$_{19}$ with space group P6$_3$/mmc [4] has a complex hexagonal crystal construction, in which 24 Fe$^{3+}$ ions take up 5 distinct crystallographic sites; (octahedral [B]-site, tetrahedral (A)-site and trigonal bipyramidal). The documents have suggested that the loading of various divalent cations significantly affect the permittivity and permeability of BaM. Many researchers are aggravating their best to obtain pure and substituted mono-domain particles of BaFe$_{12}$O$_{19}$. We address the structural parameters of Mn$^{2+}$ loaded BaFe$_{12}$O$_{19}$. Various synthesis technologies have been tried by the researchers such as the sol-gel auto-combustion technique [5], ceramic method, micro-emulsion method [6], co-precipitation, hydrothermal reaction [7],
etc. We have followed the bottom-up approach of synthesis for the fabrication of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$, and selected sol-gel auto-combustion technique for yielding nano-size powder of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$.

**EXPERIMENTAL**

High quality AR grade; barium nitrate (Ba(NO$_3$)$_2$.6H$_2$O), Manganese nitrate tetrahydrate (Mn(NO$_3$)$_2$.4H$_2$O), and ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O) were used as an initial ingredients for the sol-gel auto-combustion method. Citric acid ($C_6H_8O_7$.H$_2$O) was used as a fuel with the nitrate to citrate ratio 1:3. Initially, the selected metal nitrates were liquefying in the desired amount of de-ionized water. The blended solution was stirred on a magnetic stirrer for better homogenation. After a formation of a clear blended solution, the beaker was mounted on a magnetic-hot-plate stirrer for heating (80 $^\circ$C for 5 h) and stirring to carry out the evaporation of water. An addition of NH$_3$ solution was executed to restrict the pH value of the mixed solution to 7. The reactive metal nitrates were initially hydrolyzed, which were followed by condensation process and polymerization process. A ‘gel’ formation was occurred after evaporation of excess water. ‘dry-gel’ was self-ignite along with the exost of large gases, and the auto-burning of fuel assisted mixed metal-nitrates started. This high-temperature auto-combustion resulted in lightweight; voluminous; nano-sized; fluffy; loose powder of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$ as a yield product of the reaction.

**RESULTS AND DISCUSSIONS**

**X-ray diffraction analysis of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$ NPs**

The scrutiny of the XRD pattern for $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$ barium hexaferrite nanoparticles is demonstrated in Fig 1; which revealed the formation of M-type hexagonal structure of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$ nanoparticles [8]. X-ray diffraction peaks (006), (110), (008), (107), (114), (200), (203), (116), (205), (206), (1011), (209), (300), (217), (2011), (2012), (220), (2014), (228), (317), (403) affirms the standard pattern barium hexaferrite (JCPDS 84-0757) [9]. Very small quantity of impurity was detected in the XRD pattern illustrating the formation of $\text{Fe}_2\text{O}_3$ (JCPDS# 73-2234).

![X-ray diffraction patterns of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$ NPs](image_url)

**FIGURE 1.** X-ray diffraction patterns of $\text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19}$ NPs

The lattice constants (a) and (c) was calculated using the following equation [10];

$$\frac{1}{a^2_{Kl}} = \frac{4}{3} \left( \frac{h^2 + kk + k^2}{a^2} \right) + \frac{1^2}{c^2} \quad (1)$$
Where \( d_{hkl} \) is the crystal face distance, \( (a) \) is the lattice constant, and \( (hkl) \) is the miller indices of each plane. The lattice parameter \( a = 5.877401 \text{ Å} \), and \( c = 23.35858 \text{ Å} \). The \((006)\), \((110)\), \((008)\) plane in the Bragg’s reflections stands impressive for the hexagonal arrangement and the \((110)\), \((200)\), \((300)\), \((220)\) footprints the spinel structure. Both in combination represent the formation of hexagonal ferrite. The unit cell volume \((V)\) of \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) hexaferrite nanoparticles was calculated using the relation \( V= 0.866a^2c \).

### Table 1. Lattice constant \( (a) \), Lattice constant \( (c) \), ratio \( c/a \) and Unit cell volume \( (V) \) of \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) NPs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( a ) (Å)</th>
<th>( c ) (Å)</th>
<th>( c/a )</th>
<th>( V ) (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ba}<em>{0.9}\text{Mn}</em>{0.1}\text{Fe}<em>{12}\text{O}</em>{19} )</td>
<td>5.87741</td>
<td>23.35858</td>
<td>3.974304</td>
<td>699.4167</td>
</tr>
</tbody>
</table>

The average crystallite size obtained from XRD data is 47.09 nm, indicating the nanocrystalline nature of the present samples. X-ray density \( (\rho) \) of \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) NPs was calculated by using the relation \([11]\):

\[
d_X = \frac{ZM}{N_Aa^2 \cdot c}
\]

where \( Z \) is the number of formula units in the unit cell \((Z = 2)\), \( M \) is the molecular mass of the sample and \( N_A \) is the Avogadro’s number.

### Infra-Red analysis of \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) NPs

The IR spectra carried out by model: SHIMADZU; in the specified range of 4000-250 cm\(^{-1}\) showing the various functional groups present in \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) NPs annealed at 950 °C is shown in Figure 2. The IR spectra shows two main absorption bands with the formation of hexaferrite phase with some additional bands indicating some changes in the position and intensity of the \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) bands, governing the site occupation of the doped ions.

![IR spectra of \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) NPs](image)

**FIGURE 2.** IR spectra of \( \text{Ba}_{0.9}\text{Mn}_{0.1}\text{Fe}_{12}\text{O}_{19} \) NPs

The stretching vibrations of C-H bonds of organic compounds can be studied close to band 2991.59 cm\(^{-1}\). The impressive bands at 574.79 cm\(^{-1}\); 574.07 cm\(^{-1}\) and 425.86 cm\(^{-1}\) are assigned to the vibrational bands which confirms the presence of the hexaferrite phase \([12]\).
DC-resistivity of Ba\textsubscript{0.9}Mn\textsubscript{0.1}Fe\textsubscript{12}O\textsubscript{19} NPs

The DC-electrical resistance was recorded by two probe method in the temperature range 1000-2000 (K\textsuperscript{-1}). The DC-resistivity was calculated by standard formula;

\[ \rho = \frac{RA}{t} \]  \hspace{1cm} (4)

Where, R is the resistance, t is the thickness of the sample; and A = (\pi r\textsuperscript{2}) is the area of the electrode in contact with the Ba\textsubscript{0.9}Mn\textsubscript{0.1}Fe\textsubscript{12}O\textsubscript{19} NPs sample. The logarithm of DC-resistivity versus 1000/T(K\textsuperscript{-1}) temperature of (Ba\textsubscript{0.9}Mn\textsubscript{0.1}Fe\textsubscript{12}O\textsubscript{19} NPs) is shown in figure 3; which revealed an immense resistive property and marked a fall in resistivity with hikeing temperature obeying the Arrhenius law[13].

![Graph showing DC-resistivity vs 1000/K](image)

An increasing temperature leads to the decrease in DC-resistivity, following the ordinary nature of semiconducting material. The trapping of electrical charges participated in the conduction mechanism, with decreasing the DC- resistivity; enhancing the drift mobility of the thermally activated electrons in ferrite materials is explained by the Verwey’s hopping mechanism [14, 15].

CONCLUSIONS

The citric acid assisted sol-gel auto-combustion method was used to prepared Ba\textsubscript{0.9}Mn\textsubscript{0.1}Fe\textsubscript{12}O\textsubscript{19} hexaferrite nanoparticles retaining the nitrate to citrate ratio at 1:3. The unique XRD pattern reveals the successful formation of M-phase hexagonal structure in as prepared Ba\textsubscript{0.9}Mn\textsubscript{0.1}Fe\textsubscript{12}O\textsubscript{19} nanoparticles. The lattice constant \( a = 5.87774 \) Å and \( c = 23.35858 \) Å were found to be well-matched with the reported values. Infrared spectra exhibit two distinct absorption bands near 574.79 cm\textsuperscript{-1}; 574.07 cm\textsuperscript{-1} and 425.86 cm\textsuperscript{-1} indicating the characteristic features of hexagonal ferrites phase. The logarithmic plot of DC-resistivity versus 1000/T(K\textsuperscript{-1}) temperature shows the semiconducting behavior for Ba\textsubscript{0.9}Mn\textsubscript{0.1}Fe\textsubscript{12}O\textsubscript{19}, and the conduction mechanism explained on the basis of Verwey’s hopping mechanism.

REFERENCE