Synthesis, characterization and optical properties of rare earth doped barium hexaferrite nano particles

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Abstract. In this work we have prepared a series of BaFe$_{12}$O$_{19}$ :xEu$^{3+}$ (x=0 to 2 mol %) samples by combustion method. The prepared samples were characterized by PXRD, TEM and FTIR. The structural analysis of PXRD pattern affirms that the specimens have space group p6/mmc and hexagonal structure. The TEM micrographs show hexagonal plate like structure and the FTIR spectra show vibration between the 4f$_1$ and 4f$_2$ crystallographic sites of the ferric ions. The absorption spectra of the prepared specimen were obtained from UV-vis spectroscopy. The calculated band gap values range from 3.99 eV to 2.29 eV.

1. Introduction

Ferrite materials have attracted the attention of technologists, physicists and chemists because of their fascinating magnetic and electromagnetic properties [1]. Ferrites are further subdivided into three types such as spinel ferrite, garnet, and magnetoplumbite/hexagonal ferrite depending on their crystal structure. Now a day’s hexagonal ferrites (hexaferrites) grabbing greater attention due to their high Curie temperature, high saturation magnetization, large uniaxial magnetic anisotropy, high coercivity, low dielectric loss and good chemical stability. Barium hexaferrites (BaFe$_{12}$O$_{19}$/BaM) are widely used in various devices such as multimeter devices, sound devices, perpendicular magnetic recording devices etc [2-9]. The crystal structure of BaM is described by the space group p6/mmc. The unit cell of BaM consists of two structural blocks ‘R’ and ‘S’ with stacking sequence RSR*S*, ordered along the direction of hexagonal c-axis. The S and R blocks have spinal and hexagonal structure respectively. The S* and R* are the rotated blocks obtained by 180° rotation of S and R block along the c-axis respectively [10]. The synthesis technique of BaFe$_{12}$O$_{19}$ plays a vital role in determining the structural, electrical and optical properties. Various synthesis methods were reported for the synthesis of high purity BaFe$_{12}$O$_{19}$ powders such as sol-gel method [11], hydrothermal synthesis [12], combustion method [13] etc.

In this work undoped and europium doped barium hexaferrite powders were prepared using combustion synthesis technique due to its low cost and less time consumption.
2. Synthesis Technique
The BaFe\(_{12-x}\)Eu\(_x\)O\(_{19}\)(x=0, 1, 1.25, 1.5, 1.75, 2) samples were prepared by combustion technique. Iron nitrate, europium nitrate, barium nitrate and citric acid were used as initial reactants. These reactants were taken according to their stoichiometric ratio and mixed in distilled water. The mixture was placed on a magnetic stirrer, when the temperature of the stirrer reaches 85\(^\circ\)C combustion process occurs and after that we get the combusted powder. The combusted powder was finely crushed and calcined for 3 hour at 1250\(^\circ\)C in a furnace. After calcination the final product was again ground finely and then subjected to various characterizations.

3. Result and Discussion

3.1 Structural Analysis
Figure 1 represents PXRD pattern for the BaFe\(_{12}O_{19}:x\)Eu\(^{3+}\)(x=2 mol\%) sample which was recorded using the PANalytical X-ray diffractometer. PXRD pattern analysis confirms formation of hexagonal phase of prepared powder sample. The diffraction peaks present in the PXRD pattern were indexed with respect to their hkl value. The crystallite size was calculated by Debye Scherrer formula \(D=\frac{k\lambda}{\beta\cos(\theta)}\) where \(\lambda\) is X-ray wave length, \(\beta\) is the Bragg’s diffraction angle and \(k\) is constant, and is found to be 38.15nm approximately.

![Figure 1. PXRD pattern for the BaFe\(_{12}O_{19}:x\)Eu\(^{3+}\)(x=2 mol\%) sample.](image)

3. TEM Analysis
TEM micrographs of the 2 mol % Eu\(^{3+}\) doped hexaferrite sample were recorded using Hitachi H- 600 TEM Analyzer. Figure 2a and 2b show the TEM micrographs of the hexaferrite sample which indicate that the prepared sample shows plate like structure [14].
3.3 FTIR Analysis

FTIR analysis was performed to get information about the molecular bands, functional groups etc. Figure 6 shows FTIR spectra of the prepared hexaferri te samples in the range from 400-500 cm$^{-1}$. The strong absorption between 420 cm$^{-1}$ to 480 cm$^{-1}$ indicates the vibration of the 4f$_1$ and 4f$_2$ crystallographic sites of the ferric ion corresponding to the octahedral vibration mode (A$_{2u}$) [15].

![Figure 3. FTIR spectra of the prepared hexaferri te samples.](image)
3.4 UV-Visible Spectroscopy

The UV visible spectra of BaFe$_{12-x}$Eu$_x$O$_{19}$ (x = 0 to 2) samples were shown in figure 4 (a-f). Due to the transition between CB (conduction band) and VB (valence band) we get UV-visible spectrum of the samples. The band gap of the hexaferrite samples were calculated by plotting Tauc plot using the equation $\alpha h\nu = A(h\nu - E_g)^n$ [16]

where $h\nu$ is the photon energy, $E_g$ is the energy band gap, $\alpha$ is the absorption coefficient, $A$ is a constant and $n$ is the characteristics constant for different transitions. For undoped and doped samples the observed values are ranging from 3.99eV to 2.29 eV. From the figures it is clear that with increase in europium ions concentration, the band gap value decreases. As the europium ions concentration increases the number of lattice defects increases which results in formation of intermediate electronic levels in the forbidden band gap therefore resulting the decrease in the band gap value [17].
1.5
2.0
2.5
3.0
3.5
4.0
4.5

0.0
0.5
1.0
1.5
2.0
2.5
3.0

(hvα)^2

3.11 ev

1.5
2.0
2.5
3.0
3.5
4.0
4.5

0.00
0.02
0.04
0.06
0.08
0.10
0.12

(hv)^2

2.29 ev

Figure 4. UV-visible spectra for the BaFe_{12-x}Eu_xO_{19} (x = 0 to 2 mol %) samples.

4. Conclusion
Europium ions doped and undoped barium ferrite nano particles were prepared by combustion synthesis technique and the structure of the prepared nano particles is hexagonal as confirmed by PXRD pattern analysis. TEM micrographs confirm the formation of plate like structure. Vibration between the crystallographic sites (4f_1 and 4f_2) of ferric ions of the prepared samples were observed in FTIR analysis. The prepared samples show semiconducting behaviour as confirmed by Uv-vis analysis.

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