Investigation of structural and dielectric properties of Co-Zr doped Barium M-type Hexaferrites

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Abstract: The Samples of Cobalt-Zirconium doped Barium nano-hexagonal ferrites of chemical formula BaFe12-2x(Zr-Co)xO19 (x = 0.5, 0.9) are prepared employing Microwave assisted Sol-gel auto-combustion Route, in which the ferrite materials were generated by providing continuous heat in microwave oven. The precursors in the form of nitrates are taken accompanied with urea as a fuel, supply energy to initiate exothermic reaction during the formation of materials. Uniform heating in the microwave leads to the ultrafast morphological transformations giving rise to a nano-scale particle size of the synthesized samples. The derived ferrites powders being analyzed for their structural and morphological characteristics with the help of X-ray diffraction techniques (XRD) and Transmission Electron Microscopy (TEM). Lattice constants ‘a’ and ‘c’, porosity (p) of the prepared materials were determined. Their d-values are counter checked and (h k l) planes were specified. TEM analysis confirmed the nano-scale particle size of the synthesized samples. The materials have been assessed with Impendence Analyzer for electrical resistivity (ρ). The obtained results suggest that the synthesized samples belong to the family of hexagonal M-type ferrites. A structural observation has verified that the space group symmetry of the prepared materials is P63/mmc. The ferrites samples show high resistivity of the order 107 (Ω-m). Such types of nano-sized ferrite materials with high resistivity are helpful especially for various microwave absorbing applications.

Key words: Ba-hexaferrites, Microwave induced synthesis, Nanocrystalline, Porosity, Resistivity, XRD, and TEM, etc.

1. Introduction
Magnetic ions in ferrites, which are a part of a magnetic oxide, are arranged to achieve spontaneous magnetization even as preserving strong electrical and magnetic properties in ferrite. The most important feature of the hexaferrites is the prospect of tailoring the magneto-electric behavior depending upon the application, which can be achieved by the biased replacement of trivalent, simultaneous substitution of divalent-tetravalent metal ion, and other compatible combinations for Iron (Fe) in the parent hexaferrite matrix [1,2]. Cost effectiveness, simple processing and fascinating electrical and magnetic properties make hexagonal ferrite one of the most significant materials that have drawn tremendous exposure within an area of technical purposes [3, 4]. The process of synthesis, sintering temperature, etc. shall, in
particular, specify the particle size upon which electrical and magnetic characteristics of the substance rely. [5]. In present research module, the novel method of Microwave assisted Sol-Gel Auto-Combustion process is utilized to fabricate zirconium-cobalt substituted barium nano-hexaferrite samples with the general formula BaFe\(_{12-2x}\)(Zr\(_x\)Co\(_x\))O\(_{19}\) (x=0.5, 0.9) [6, 7]. This section aims to characterize the structural and Electrical behavior of the synthesized substituted barium nano-hexaferrites materials. The structural and morphological characteristics of the synthesized ferrites powder are studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Impedance analyzer is employed to study for the electrical measurements of synthesized hexaferrite powder.

2. Experimental Procedure

For the synthesis of ferrites, a significant number of preparatory methods like Solid-state reaction, Coprecipitation, Hydrothermal synthesis, Glass crystallization, etc. had previously been documented. The documented Sol-gel assisted auto combustion route had several benefits to prepared doped M-type hexagonal ferrites owing to its high degree of simplicity in the process, lower anneal or calcine temperature, and, short reaction time [6]. Besides, the Sol-Gel auto-combustion method produces an ultra-fine nano powder with a substantial distribution of particle sizes, outstanding chemical uniformity and the probability of creating a unified single domain structure.

The Co-Zr doped BaM nano-hexagonal ferrites materials are processed by Microwave induced Sol-gel auto combustion route, where the microwave is replaced in the place of conventional furnace, to assure the continual heating of the materials through the combustion method. AR grade nitrates likes Ba(NO\(_3\))\(_2\), Ferric Nitrates, Cobalt Nitrates, Zirconyle Nitrates and Urea in proper stoichiometric proportion were liquefy with double filtered distilled water at 50\(^\circ\)C temperature and kept for 20 minutes. Initiate an exothermic reaction with adequate energy available from the fuel as Urea. The generated gel is then stored at room temperature for an hour and then put inside the digitally operated 2.54GHz microwave for 10 min for thermal decomposition. The gel is thermally decomposed and eventually transformed into a loose, foamy, uniform nanocrystalline ash powder. After that the synthesized hexaferrite powder was grinded in pestle mortar for four hour with gradually slow cooling rate maintained at 50 \(^\circ\)C / minute, with further grinding for four hours.

3. Results and Discussions.

3.1. Structural Properties

The XRD diffract graph of fabricated materials were obtained by using Philips X’pert Diffractometer, with CuK\(\alpha\) radiation of wavelength \(\lambda=1.542(\text{Å})\). Fig.1.(a and b) present the x-ray intensity graphs of synthesized materials for x=0.5 and x=0.9 respectively. After matching the diffraction patterns with the JCPDS standard files, leveraging 2\(\theta\) values, the observed d-values and intensity differences, the d-value is being determined and the (h k l) planes were specified. With the help of interplaner spacing \(d_{h k l}\) corresponding to finalized planes the values of lattice parameters can be calculate employing relation

\[
d^2_{h k l} = \frac{3a^2}{h^2 + 2hk + k^2} + \frac{c^2}{l^2}
\]

The percentage Porosity is being calculated by

\[
P = \left(1 - \frac{D_{\text{bulk}}}{D_{\text{x-ray}}}\right) \%
\]

Where, P is porosity, \(D_n\) is bulk density and \(D_{\text{x-ray}}\) is x-ray density of formulated materials
Figure 1. Powder XRD of Ba\((\text{Co-Zr})_x\text{Fe}_{12-2x}\text{O}_{19}\) Hexaferrite for \(x=0.5\) and \(x=0.9\)

The value of lattice parameters affirms that the hexagonal ferrites with a single-phase is formed. Lattice constants ‘\(a\)’ and ‘\(c\)’ were observed to be 5.8256 (Å) and 23.124 (Å) independently for \(x=0.5\) and 5.8239 (Å) and 23.127 (Å) for \(x=0.9\) respectively. The space group symmetry of the formulated hexaferrites powder is found to \(P6_3/mmc\).

Table 1 summarizes the Lattice parameters, x-ray and bulk density, porosity and the electrical Resistivity of these hexaferrites samples [15-17] at concentrations \(x = 0.5\) and \(x = 0.9\).

| Conc. (\(x\)) | \(a\) (Å) | \(c\) (Å) | \(D_x\) (Å\(^3\)) | \(D_B\) (Å\(^3\)) | \(P\) (%) | \(\rho\) at 373K (Ω-m) |
|---------------|-----------|-----------|--------------------|--------------------|----------|-------------------|
| \(X= 0.5\)   | 5.8256    | 23.124    | 5.39               | 2.72               | 49.54%   | \(1.229*10^5\)    |
| \(X= 0.9\)   | 5.8239    | 23.134    | 5.60               | 2.81               | 49.86%   | \(1.788*10^4\)    |

Figure 2. Transmission Electron Micrographs of the prepared \(\text{Ba(Co-Zr})_x\text{Fe}_{12-2x}\text{O}_{19}\) materials, for \(x=0.5\) and \(x=0.9\).
3.2 Morphological Analysis.
Figure 2 displays TEM pictures of the prepared hexaferrites samples taken by TEM Philips Model CM 200. Micrographs showing hexagonal platelet structure with morphological homogeneity. Prominent grain boundaries are also observed.

TEM images of the samples are taken at nano-scale about 50nm, gives an idea about the particle size, which indicates the formation of the zirconium-cobalt substituted Barium nano- hexaferrite particles.

3.3 Electrical properties.
Precision impedance Analyser 6500B, Wayne kerr Electronics is used to study the electrical properties of synthesized materials. For regulated thermal variations, the material is housed inside the electric furnace operated digitally. Four probes techniques were utilized to calculate the electrical characteristics of prepared materials in palletized form. The electrical properties of ferrites termed phonon-assisted electron tunnelling can also be interpreted by the tunnelling of electrons among Fe^{2+} and Fe^{3+}. It is being noted that the electrons are closely bound to the lattice that participates in the Fe^{2+} ↔F^{3+} + e⁻ exchange mechanism and migrate from one lattice sites to other sites owing to the phonon-induced transfer process [8,9].

Table 1 indicates that with a rise in Co^{2+} and Zr^{4+} ions doped concentrations, the values of electrical resistivity at a normal temperature decreased from 1.229 x10⁵ Ωm to 1.788 x10⁴ Ωm, while the percentage porosity (P) increased from 49.54 % to 49.86 %. This might be attributed to the evidence that, as a result of a increase in porosity, the driving pathways are made harder for charge carriers to travel from grain to grain. A number of reasons, along with the development of other secondary phases and significantly larger porosity values, may be accountable for the comparatively high resistivity value of the order of 10⁵ Ωm. Separations in between grains are mostly attributed to increased porosity. And this separation can lead to difficulties in driving free electrons across grain boundaries [10].

4. Conclusion.
The series of Co^{2+} and Zr^{4+} doped Barium nano-hexaferrite of composition BaFe_{12-2x}(Zr-Co)_{x}O_{19} via "Microwave Assisted Sol-gel auto-combustion technique" synthesized successfully. The formation of hexaferrites is confirmed by XRD results and the values of lattice constant ‘a’ and ‘c’ of the processed materials support such assertion. The prepared materials have hexagonal symmetry with space group P6₃/mmc (No.194) which is confirmed by the structural study. From TEM analysis, the size of crystallites is being noticed in nano scale.

With high values of electrical resistivity of such synthesized nano-scale barium hexaferrite doped with Zr^{4+} and Co^{2+} can prove to be a promising material in the microwave absorbing, EMI shielding applications. Also, the nanosize of the particles helps to reduce the noise produced in magnetic data storage devices which occur due to the displacement of domain boundaries. The lowering of hexaferrites crystallite size to nano scale range allow us to enhance improve the previously described electrical properties.

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