Study of bismuth doped cobalt ferrite nanoparticles using different spectroscopic techniques

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Various concentration of Bismuth doped Cobalt ferrite nanoparticles having chemical composition CoBixFe2-xO4 (x=0.0,0.05,0.1) has been prepared by sol-gel auto combustion method followed by annealing at 600˚C for 3 hours. Present work demonstrates a detail study of structural, electrical and magnetic transport properties of CoBixFe2-xO4 nanoparticles. Investigation of structural and morphological properties of the synthesized samples have been carried out using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS), Raman spectroscopy, Transmission electron microscopy (TEM), Field emission scanning electron microscopy (FESEM) and Atomic force microscope (AFM). Obtained results confirm the presence of single phase spinal structure in all the specimens having space group Fd3m. In addition, FT-IR spectra of parent cobalt ferrite revealed two strong absorption peaks at 393 cm⁻¹ and 596 cm⁻¹ respectively that have been shifted afterwards towards the higher frequency side with the addition of Bi³⁺ ion. Presence of spherical grains having diameters ranging from 20-30 nm has been detected through the FESEM and TEM micrographs. The surface roughness of all the specimens has been measured through AFM. Further, Mossbauer study was conducted to observe the distribution of the cobalt and bismuth in the spinel ferrite.
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Plan of presentation

1. Introduction to Ferrites
2. Classification of Ferrites
3. Structure of Ferrites
4. Advantages
5. Synthesis process for Cobalt ferrites
6. Multiferroic
7. Different ways for characterization of Bi doped CoFe$_2$O$_4$
   i. XRD
   ii. TEM
   iii. FESEM
   iv. FTIR
   v. RAMAN
   vi. AFM
   vii. Mossbauer
8. Conclusion
What are Ferrites?

- Magnetite (Fe₃O₄), also called loadstone, is a genuine ferrite and was the first magnetic material known to the ancient people.

- The general chemical formula of a ferrite molecule is \((\text{M}^{2+}\text{Fe}^{3+}\text{O}_4^{2-})\), where \(\text{M}^{2+}\) represents a divalent metal ion such as Co²⁺, Zn²⁺, Mg²⁺, Mn²⁺, Cd²⁺ etc. The term ferrite is commonly used to describe a class of magnetic oxide compounds that contain iron oxide as a principal component.

- Ferrimagnetic Materials are called Ferrites.

- Ferrites are the modified structures of iron with no carbon and are composed of two or more sets of different transition metals (d-block elements; transition metals).
Spontaneous domain formation

Ferromagnetism
- Moments of individual atoms aligned

Antiferromagnetism
- Moments alternating from atom to atom

Ferrimagnetism
- Unequal moments alternate

Paramagnetism
- No long-range order; alignment with applied field

Diamagnetism
- No long-range order; alignment opposes field
Ferrites crystallize in the form of a *cubic* structure. Each corner of a ferrite unit cell consists of a ferrite molecule.

The small filled circles represent metal ions, the large open or shaded circles represent oxygen ions: (a) tetrahedral or A sites; (b) octahedral or B sites; and (c) one-fourth of the unit cell of a cubic ferrite. A tetrahedron and an octahedron are marked.
Two types of sites
- Tetrahedral sites \((\text{AO}_4)\)
- Octahedral sites \((\text{BO}_6)\)

\[[\text{Co}_{1-x}\text{Fe}_x]_A [\text{Co}_x\text{Fe}_{2-x}]_B\]

Where \(x\) is the invariability, \(A\) and \(B\) represent tetragonal and octahedral sites.

- If \(x=0\), Normal spinel
- If \(x=1\), Inverse spinel
- If \(0<x<1\), partial inversion
Classification of Ferrites

- **Spinel**
  - $\text{MFe}_2\text{O}_4$ (where, M is the divalent cations like Co, Ni, Zn, Cd)

- **Hexagonal**
  - $\text{MFe}_{12}\text{O}_{19}$ (where, M = Ba, Sr, Pb etc.)

- **Garnets**
  - $\text{R}_3\text{Fe}_5\text{O}_{12}$ (R = Yttrium or rare earth ions like Gd, La etc.)
<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Parameter</th>
<th>Hexagonal</th>
<th>Garnet</th>
<th>Spinel</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Structure</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
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<tr>
<td>2</td>
<td>Molecular Formula</td>
<td>$M(\text{Fe}<em>{12}\text{O}</em>{19})$</td>
<td>$M_3(\text{Fe}<em>5\text{O}</em>{12})$</td>
<td>$M(\text{Fe}_2\text{O}_4)$</td>
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<tr>
<td>3</td>
<td>Space group</td>
<td>P6$_3$/mmc, D6h</td>
<td>Ia-3d</td>
<td>Fd 3m</td>
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<td>4</td>
<td>Interstitial sites</td>
<td>12k, 2a, 4f$_2$, 4f$_1$, 2b</td>
<td>a, c and d (A) &amp; [B]</td>
<td>(A) &amp; [B]</td>
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<tr>
<td>5</td>
<td>Lattice Constant (Å)</td>
<td>5.83</td>
<td>12.37</td>
<td>8.38</td>
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<tr>
<td>6</td>
<td>Curie Temp. (K)</td>
<td>673</td>
<td>553</td>
<td>668</td>
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<tr>
<td>7</td>
<td>Saturation Magn. (emu/gm)</td>
<td>66</td>
<td>26</td>
<td>63</td>
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<tr>
<td>8</td>
<td>Electrical Resistivity, (Ω - cm)</td>
<td>$1 \times 10^6$</td>
<td>$1 \times 10^{14}$</td>
<td>$1 \times 10^8$</td>
</tr>
<tr>
<td>9</td>
<td>Examples</td>
<td>$\text{CaFe}<em>{12}\text{O}</em>{19}$</td>
<td>$\text{Y}_3\text{Fe}<em>5\text{O}</em>{12}$</td>
<td>$\text{CoFe}_2\text{O}_4$</td>
</tr>
</tbody>
</table>
Normal Spinel Ferrite

Inverse Spinel Ferrite

[Co$_{1-x}$Fe$_x$]$_A$ [Co$_x$Fe$_{2-x}$]$_B$

Where $x$ is the invariability, $A$ and $B$ represents tetragonal and octahedral sites

- If $x=0$ Normal spinel
- $x=1$ Inverse spinel
- $0<x<1$ partial inversion

(A$^{ll}$)$_{tet}$ (B$^{lll}$)$_2$ $^{oct}$O$_4$

(B$^{lll}$)$_{tet}$ (A$^{ll}$B$^{lll}$)$_{oct}$O$_4$
Synthesis of Ferrites

Ferrite can be prepared by using various Conventional techniques which include:

- Wet chemical route
- Temperature-controlled co-precipitation method
- Sol–gel auto-combustion method
- Co-precipitation method
- Solid state route
### Application of ferrites

<table>
<thead>
<tr>
<th>Soft ferrites</th>
<th>Inductors</th>
<th>Transformer cores</th>
<th>Televisson</th>
<th>Communication</th>
<th>Convertors</th>
<th>Space Research</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard ferrites</td>
<td>Permanent magnets</td>
<td>Electric generator and motors</td>
<td>Tv Tubes</td>
<td>Small Dc Motors</td>
<td>Compact Torque Devices</td>
<td>Magnetic Latch</td>
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<tr>
<td></td>
<td>Rotators</td>
<td>Satellite</td>
<td>Phase Shifters</td>
<td>Memory Cores</td>
<td>Circulators</td>
<td>Radar</td>
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<td></td>
<td>Substrate for memory chips</td>
<td>Substrate For Bubble memories</td>
<td>Radio Frequency Coil</td>
<td>Magnetic Recording Media</td>
<td>Magnetic Recording Media</td>
<td>Computer Memory Chips</td>
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<td></td>
<td>Antennae rods</td>
<td>Noise Absorbing Cores</td>
<td>Metallurgy Application</td>
<td>Magnetic Switches</td>
<td>Magnetic Switches</td>
<td>Insulators</td>
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<td>Magnetic sensors</td>
<td>Magnetic Sensor</td>
<td>Magnetic Sensor</td>
<td>Humidity Sensitivity</td>
<td>Picture Tube Core</td>
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<td>Power transformer</td>
<td>Reactor Core</td>
<td>Fly Block Transformer Core</td>
<td>Radio Therapy</td>
<td>Cell Lebelling</td>
<td></td>
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<tr>
<td></td>
<td>Cancer therapy</td>
<td>Drug Delivery</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **High frequency applications**
- **Data storage devices**
- **Microwave application**
- **Magnetic sensors**
- **Biomedical applications**
- **Other applications**
Advantages Of Ferrites

- High resistivity
- Wide frequency range (10kHz to 50MHz)
- Low cost
- Shape versatility
- Economical assembly
- Temperature and time stability
Superiority of ferrites over other materials

- Ferrites can be made a wide range of permeability.
- Squareness ratio is high.
- Ferrites are very hard compared to other materials.
- Shape versatility.
- Good tunability.
Comparative study of some ferrites

<table>
<thead>
<tr>
<th>S.No</th>
<th>Ferrite</th>
<th>Saturation magnetisation (kA m(^{-1}))</th>
<th>Net magnetic moment per formula unit (\mu=(x)\mu_m + 10(1-x))</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe(_3)O(_4)</td>
<td>360</td>
<td>4(\mu_B)</td>
</tr>
<tr>
<td>2</td>
<td>CoFe(_2)O(_4)</td>
<td>422</td>
<td>3(\mu_B)</td>
</tr>
<tr>
<td>3</td>
<td>MnFe(_2)O(_4)</td>
<td>386</td>
<td>5(\mu_B)</td>
</tr>
<tr>
<td>4</td>
<td>NiFe(_2)O(_4)</td>
<td>270</td>
<td>2(\mu_B)</td>
</tr>
<tr>
<td>5</td>
<td>CuFe(_2)O(_4)</td>
<td>135</td>
<td>1(\mu_B)</td>
</tr>
<tr>
<td>6</td>
<td>ZnFe(_2)O(_4)</td>
<td>122</td>
<td>0(\mu_B)</td>
</tr>
</tbody>
</table>
Cobalt ferrite (COF)

- Good thermal stability
- It has moderate saturation magnetization (for high density recording media)
- High coercivity (5400 Oe)
- High electrical resistance and low Eddy currents (high frequency devices, memory cores and recording media)
- Remarkable chemical stability
- At nano level it exhibits superparamagnetism
Crystal Structure of cobalt ferrite:

Inverse spinel Cubic Tetrahedral and actahedral sites
Ferrimagnetic behavior

Superparamagnetic behavior

\[ d_{cr} = 100 \text{ nm} \]

\[ d_{sp} = 10 \text{ nm} \]
Multiferroic Materials

- Discovered less than a century ago, ferroics relate to the ancient study of magnetism.

- Ferroic materials can be:
  - Ferroelectric
  - Ferromagnetic
  - Ferroelastic

- Multiferroics exhibit two or more of these properties simultaneously.
Ferroelectric materials possess a spontaneous, stable polarization that switches hysteretically in an applied electric field.
Ferroelectricity

- Polarization characteristics change when subjected to varying
  - Pressure
  - Temperature
  - Applied Voltage

- These unique properties make the material useful for many different applications
Synthesis procedure

- **Glycine (Fuel)**
- Iron nitrate, cobalt nitrate, bismuth nitrate
- Homogenous mixture
- Combustion
- Spinel ferrite
- Characterization

Steps:
- Hydrolysis
- Gelation
- Sintering
An X-ray diffractometer illuminates a sample with x-rays of known wavelength, moving the sample and detector in order to measure the intensity of the diffracted radiation as a function of beam and sample orientation. From the resulting intensity versus angle plot, one can infer about the phases present and structure of the material. It is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. When a monochromatic X-ray beam with wavelength $\lambda$ is projected onto a crystalline material at an angle $\theta$, diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number $n$ of wavelengths.

Bragg's law \[ \sin \theta = n \lambda \]
RESULTS - XRD

- All the diffraction maxima correspond to the cubic spinel structure of CFO (JCPDS card no. 22-1086). The full width at the half-maximum (FWHM) of the (311) peak was used to calculate the average crystallite size by using the Scherrer formula.

\[ D_p = \frac{0.94\lambda}{\beta^{1/2} \cos \theta} \]

- The lattice parameter value obtained in all cases is 8.368 Å.
Characteristic technique: TEM

An electron microscope uses high energy electron beams for the illumination of samples, instead of light so that magnification to the tune of a million times (10,000,000 x) and sub-nanometer resolution can be achieved. Electron microscopes are essential tools for characterizing nanomaterials as they provide an array of information such as topography, morphology, composition and crystallographic information. In the nano-world, ‘believe what you see’ and electron microscopes such as TEM provides realistic images of nanomaterials. In fact, one of the major reasons for emergence of the field of nanotechnology is the invention of modern microscopes including the electron microscopes that have very high magnification and resolution in the nanometer length scales. In TEM, high energy electron beam passes through a very thin sample and constructs a two dimensional image of the sample. High resolution TEM can achieve atomic resolution.
The TEM results support the XRD findings and clearly shows the same trend of particle size variation. The lattice parameter value obtained in all cases is 8.378 Å, which is in good agreement with the value obtained from XRD pattern.
The FESEM facilitates ultra-high resolution microstructural characterization and analysis of ceramic and metallic samples. It combines advanced optics (including a two-mode final lens), SE/BSE (Secondary Electrons/ Backscattered Electrons) in-lens detection and beam deceleration. The Nova NanoSEM introduces a new suite of latest generation, high sensitivity retractable SE/BSE and STEM detectors, as well as versatile SE/BSE filtering capabilities, to optimize the information of interest. Intelligent scanning modes are available to minimize imaging artifacts.

Resolution: 1.4 nm @ 1 kV without beam deceleration
FESEM image of CoBi$_x$Fe$_{2-x}$O$_4$ (where x = 0.00, 0.05, 0.1) nano ferrite particles.

- A apparent growth in the particle size is observed which is due to Bi substitution.
- The particle size grows controllably from $\sim$40 nm in parent to $\sim$130 nm in Bi modified cobalt ferrite samples.
Infrared spectroscopy provides information about the vibrational and rotational modes of motion of a molecule. The IR spectrum of an organic compound provides a unique fingerprint, characteristic of the compound and its optical isomers. Fourier transform Infrared spectroscopy (FTIR), due to its enhanced resolution, is considered as one of the fundamental techniques for identification and characterization of organic or inorganic compounds.
RESULTS – FTIR

The above broad frequency range corresponds to O-H stretching, H-O-H bending vibration of water molecules and spinal structure with sub lattices respectively.

Prominent absorption bands are observed at around 585.7 and 448.5 cm\(^{-1}\) respectively for all the compositions. This reveals the development of single phase spinel structure comprising two sub lattices, i.e., tetrahedral (A-site) and an octahedral (B-site) absorption band observed within the specific range and confirms the existence of M-O stretching band in ferrite samples.
Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range.
In ferrites the modes below the 600 cm\(^{-1}\) belongs to octahedral vibrations (BO\(_6\) group) and above it belongs to tetrahedral vibrations (AO\(_6\) group) of the oxygen atoms. The most intense Raman peak in octahedral modes is 466 cm\(^{-1}\) and for tetrahedral site is 684 in cobalt ferrite.
Cobalt ferrite has inverse spinel structure constructed by cubic close packing of oxygen ions where cations (Co$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Co$^{3+}$) are distributed between the octahedral and tetrahedral sites.

The most intense Raman peak in octahedral modes is 474 cm$^{-1}$ and for tetrahedral site is 682 in cobalt ferrite but in our case we got the most intense peaks at 466 cm$^{-1}$ and 684 cm$^{-1}$. 

Raman spectra of $\text{CoBi}_{x}\text{Fe}_{2-x}\text{O}_4$ (where $x = 0.00, 0.05, 0.1$) nano ferrite particles
Characteristic technique: AFM

Scanning Probe Microscopy (SPM) stands for a group of techniques that are used for studying properties of surfaces at atomic level. All these microscopes work by measuring a local property, such as height, optical absorption, or magnetic property, with a probe or “tip” placed typically at a distance of a few angstroms or nanometers. The interaction between the sharp probe and the surface being studied provides 3D topographic image of the surface at atomic scale. To acquire an image, the microscope raster scans the probe over the sample while measuring the local property in question. The resulting image is projected on a television screen in the form of rows or lines of information placed one above the other.

Veeco/849-012-711, NIT Rourkela
AFM image of CoBi$_x$Fe$_{2-x}$O$_4$ (where $x = 0.00, 0.05, 0.1$) nano ferrite particles.

- The atomic force microscopy (AFM) technique was also carried out to see the particle size of the samples prepared. The complimentary information about the surface microstructure of prepared ferrites is obtained from three-dimensional images of AFM shown.

- These images lead to conclude that there is formation of small clusters with small degree of crystallinity which may be due to the moisture absorption factor.
Mössbauer spectroscopy is a versatile technique that can be used to provide information in many areas of science such as Physics, Chemistry, Biology and Metallurgy. It can give very precise information about the chemical, structural, magnetic and time-dependent properties of a material.

The Mössbauer effect which results in the resonant absorption/emission of gamma rays and gives us a means to probe the hyperfine interactions of an atom's nucleus and its surroundings.

A Mössbauer spectrometer system consists of a gamma-ray source that is oscillated toward and away from the sample by a “Mössbauer drive”, a collimator to filter the gamma-rays, the sample, and a detector.
A Mössbauer absorption spectrum of $^{57}$Fe

There are three types of nuclear interactions that are observed, isomer shift (or chemical shift), quadrupole splitting and hyperfine splitting (or Zeeman splitting).

**Isomer shift** ($\delta$) is a relative measure describing a shift in the resonance energy of a nucleus due to the transition of electrons within its s orbital.

**Quadrupole splitting** reflects the interaction between the nuclear energy levels and surrounding electric field gradient.

**Magnetic splitting** (hyperfine splitting) is a result of the interaction between the nucleus and any surrounding magnetic field.
Mossbauer spectra shows the distribution of the cobalt and bismuth in the spinel ferrite. The Mossbauer spectra illustrates a normal magnetic sextet due to Fe\(^{3+}\) at tetrahedral (A) site and another one due to Fe\(^{3+}\) at octahedral [B] sites which is classified on the basis of Isomer shift. The isomer shift (δ), quadrupole splitting (Δ), and hyperfine field (H\(_{f}\)) corresponding to various concentration of Bi are shown in fig. the s- electron distribution of Fe\(^{3+}\) ions is responsive to small amount of Bi\(^{3+}\) content doping in cobalt ferrite as can be observed from the δ value at both tetrahedral (A) site and octahedral [B] site. An increase in δ value is observed for x = 0.1 at (A) site and decrease in value is observed in [B] site.
Room temperature M-H loops of Bi$^{3+}$ substituted cobalt ferrite nanoparticles
Variation magnetic parameter for Bi$^{3+}$ substituted cobalt ferrite nanoparticles
CONCLUSIONS

On the basis of experimental results we can conclude the following:

• Bismuth doped cobalt ferrite nanoparticles have been successfully synthesized at a sufficiently low temperature by sol gel auto combustion technique.

• The single phase nature of the samples (CoFe2O4) was confirmed from X-ray diffraction data. Addition of bismuth in small amount doesn’t lead to formation of any secondary phase.

• FESEM and TEM data confirmed the formation of nano particles which is around 40nm to 130 nm.

• FTIR study revealed the development of single phase spinel structure comprising two sub lattices.

• AFM study showed the formation of small clusters with small degree of crystallinity.

• Raman spectra of the cobalt ferrite nanoparticles further confirmed the formation of CoFe₂O₄ nanoparticles.

• Mossbauer spectra showed the distribution of the cobalt and bismuth in the spinel ferrite.
Thank you...