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It is certified that the work contained in the thesis titled **"*Synthesis and characterizations of modified Y-type hexaferrite materials for potential applications in various fields*"** by **"Mukesh Suthar"** has been carried out under our joint supervision, and this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of a Ph.D. degree.


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# DECLARATION BY THE CANDIDATE

I, **Mukesh Suthar**, am certified that the work embodied in this Ph.D. thesis is my own bonafide work and carried out by me under the joint supervision of **Dr. P. K. Roy** and **Dr. S. K. Mishra** for a period from **July 2016** to **July 2022** at the "**Department of Ceramic Engineering**", Indian Institute of Technology (BHU), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports, dissertations, thesis, etc., or available on websites and have not included them in this thesis and have not cited as my own work.

**Date :** 11th July 2022

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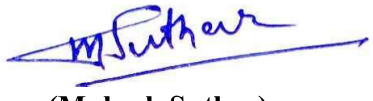
I hope I have not overlooked anyone, but if I have, it is not for lack of appreciation. In case of any omission, I sincerely beg my pardon, and I truly believe that it is purely incidental on my part.



**(Mukesh Suthar)**

# Dedicated

# To

# My Beloved Parents

*Electricity and Magnetism are those forces of nature by which people who know nothing about electricity and magnetism can explain everything.*

*Egon Friedell*

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# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| $Co_2$-Y | Cobalt based Y-type barium hexaferrite |
| EMI | Electromagnetic interference |
| UHF | Ultrahigh-frequency |
| emu | Electromagnetic unit |
| NB | Nitrobenzene |
| UV | Ultraviolet |
| min | Minutes |
| MO | Methyl orange |
| mM | Millimolar |
| mg | Milligram |
| MB | Methyl blue |
| DB122 | Direct black 122 |
| GHz | Gigahertz |
| FMR | Ferromagnetic resonance |
| GPS | Global positioning system |
| DNA | Deoxyribonucleic acid |
| MHz | Megahertz |
| NPR | Novolac phenolic resin |
| dB | Decibel |
| MRI | Magnetic resonance imaging |
| SLP | Specific loss power |
| SAR | Specific absorption rate |
| AC | Alternating current |
| ILP | Intrinsic loss power |
| LRT | linear response theory |
| SLP | Specific loss power |
| kHz | Kilohertz |
| CFO | Cobalt ferrite |
| HA | Hydroxyapatite |
| GR | General reagent |
| DGG | Discontinuous grain growth |

| | |
|---|---|
| M | Molar mass |
| hrs | Hours |
| PVA | Polyvinyl alcohol |
| mm | Millimeter |
| MPa | Megapascal |
| XRD | X–ray diffraction |
| IR | Infrared |
| FTIR | Fourier-transform infrared spectroscopy |
| cm | Centimetre |
| ATR | Attenuated total reflection |
| STP | Standard temperature and pressure |
| nm | Nanometer |
| NMR | Nuclear magnetic resonance |
| SEM | Scanning electron microscopy |
| SE | Secondary electrons |
| BSE | Back-scattered electrons |
| EDS | Energy-dispersive X-ray spectroscopy |
| DC | Direct current |
| VSM | Vibrating sample mode |
| SQUID | Superconducting Quantum Interference Device |
| QLS | Quasi-elastic light scattering |
| PCS | Photon correlation spectroscopy |
| DLS | Dynamic light scattering |
| PDI | Poly-dispersion index |
| XPS | X-ray photoelectron spectroscopy |
| μm | Micrometer, |
| VNA | Vector network analyzer |
| SWR | Standing wave ratio |
| DUT | Device under test |
| TFA | Trifluoroacetic acid |
| TLC | Thin-layer chromatography |
| NMR | Nuclear magnetic resonance |
| JCPDS | Joint committee on powder diffraction standards |

| | |
|---|---|
| $M_W$ | Molecular weight |
| mL | Milliliters |
| MeOH | Methanol |
| PTSA | p-Toluenesulfonic acid |
| eV | Electron volt |
| NO | Nitrogen monoxide |
| CO | Carbon monoxide |
| mmol | Millimole |
| DMF | Dimethylformamide |
| IPA | Isopropyl alcohol |
| EtOH | Ethanol |
| BE | Binding energy |
| ppm | Parts per million |
| DI water | Deionized water |
| NCCS | National center for cell science |
| DMEM | Dulbecco's modified eagle medium |
| FBS | Fetal bovine serum |
| RH | Relative humidity |
| EDTA | Ethylenediaminetetraacetic acid |
| mT | Millitesla |
| UC | Un-coated |
| OC | Oleic acid-coated |
| OD | Optical density |
| CI | Confidence interval |
| $T_{sp}$ | Spin transition temperature |
| $T_c$ | Curie temperatures. |
| $M_s$ | Saturation magnetization |
| $H_c$ | Coercivity |
| $M_r$ | Magnetic retentivity |
| $S_R$ | Squareness ratio |
| $K_1$ | Magnetic anisotropy constant |
| $\lambda$ | Wavelength |
| $\theta$ | Bragg's angle |

| | |
|---|---|
| $d$ | Inter-planer spacing |
| n | Diffraction order |
| $k_s$ | Sherrer's constant |
| $D_m$ | Crystallite size |
| $W_{hkl}$ | Full width at half maxima |
| $W_{hkl}^{measured}$ | Full width at half maxima of measured peak |
| $W_{hkl}^{instrumental}$ | Instrumental broadening |
| $a$ and $c$ | Lattice parameters |
| h k l | Miller index |
| $V_{uc}$ | Unit cell volume |
| $D_x$ | X-ray density |
| $Z_e$ | Effective number of formula units |
| $N_a$ | Avogadro's constant |
| $\varepsilon$ | Lattice strain |
| $L_b$ | Bond length |
| F | Force constant |
| Å | Angstrom |
| $\upsilon_{wn}$ | Wavenumber |
| $c_{vl}$ | Speed of light |
| $\mu_{em}$ | Effective mass of bonded atoms |
| $M_1$ and $M_2$ | Atomic weights of bonded atoms |
| $P_g$ | Gas pressure |
| $\theta_{fs}$ | Surface area with monolayer adsorption |
| $X$ | Weight of adsorbed nitrogen at a relative pressure of $(P/P_o)$ |
| $X_m$ | Volume required to achieve monolayer adsorption of gas at STP |
| $S_a$ | Sample surface area |
| $A_m$ | Cross-sectional area |
| $M_v$ | Molar volume |
| $^1H$ | Proton |
| K | Kelvin |
| H | Magnetic field |
| $\chi$ | Susceptibility at higher field |
| $H_a$ | Anisotropy field |

| | |
|---|---|
| $\mu_o$ | Free space permeability |
| $f$ | Frequency |
| W | Watt |
| $C_d$ | Specific heat capacity of the dispersant |
| $M_{np}$ | Mass of magnetic nanoparticles |
| $H_{AC}$ | AC magnetic field strength |
| $I_0$ | Initial intensity of light and |
| $I$ | Outgoing intensity through the sample |
| $C_M$ | Molar concentration of material within the solvent |
| $P_L$ | Path length through which the radiation has to interact with the sample |
| $\varepsilon_{MA}$ | Molar absorptivity of that material |
| $D_{Bulk}$ | Bulk density |
| $P_{\%}$ | Percentage porosity |
| $W_D$ | Dry weight |
| $W_S$ | Soaked weight |
| $W_A$ | Suspended weight |
| $E_{binding}$ | Energy of an electron attached to the nucleus, |
| $E_{photon}$ | Energy of the X-ray photons dependent on the X-ray source |
| $E_{kinetic}$ | Kinetic energy of the emitted electron |
| $\Delta$ | Work function |
| $S_{21}$, $S_{12}$, $S_{11}$, $S_{22}$ | Scattering parameters |
| $\chi''$ | Imaginary part of susceptibility |
| $\rho_m$ | Mass density |
| $P_d^{LRT}$ | Power dissipation from linear response theory |
| $\chi_0$ | Susceptibility value at equilibrium |
| $\tau$ | Neel-Brown relaxation time |
| $k_B$ | Boltzmann constant |
| $V_p$ | Volume of particle |
| $V_{opt}$ | Optimum volume |
| DMF | Dimethylformamide |
| T | Tesla |
| ZFC | Zero-field-cooled |

| | |
|---|---|
| FC | Field-cooled |
| α | Coefficient of absorption |
| $\nu$ | Incident photon frequency |
| $K_T$ | Energy-independent constant |
| $K_{arc}$ | Apparent rate constant or pseudo-first-order rate constant |
| $C_o$ | Initial concentration |
| N | Newtons |
| $(\varepsilon = \varepsilon' - i\varepsilon'')$ | Complex permittivity |
| $(\mu = \mu' - i\mu'')$ | Complex permeability |
| $\zeta$ | Extinction coefficient, |
| $R_L$ | Reflection loss |
| $SE_T$ | Total shielding effectiveness |
| $SE_A$ | Shielding effectiveness due to absorption |
| $SE_R$ | Shielding effectiveness due to reflection |
| $SE_M$ | Shielding effectiveness due to multiple reflective |
| $P_T$ | Power transmitted |
| $P_I$ | Power incident |
| $T_s$ | Transmissivity of incident radiation |
| R | Reflectivity of incident radiation |
| $\xi$ | Attenuation coefficient |
| $\sigma_{ac}$ | AC conductivity |
| S | Siemens |
| $\varepsilon_o$ | Permittivity of vacuum |
| *PBS* | Phosphate buffered saline |
| $K_{eff}$ | Effective magnetocrystalline anisotropy constant |

# ABSTRACT

The hexaferrites, which occupy a major class of oxides with significant magnetic properties, have been investigated and applied during the last 60 years. The applications of these materials encompass an impressive range extending from millimeter-wave integrated circuitry to intricate power handling transformers, simple permanent magnets to sophisticated reading heads, and many other remarkable technical involvements. Although all these applications belong to the basic properties of ferrites, a vast level of research has begun concentrating on tuning these basic parameters through elemental manipulations.

The Y-type hexaferrite ($Co_2$-Y), having the chemical formula ($Ba_2Co_2Fe_{12}O_{22}$), is a magnetoelectric multiferroic (type II) material. It has planar magnetic anisotropy at room temperature and is made up of alternating stacking of T ($Ba_2Fe_8O_{14}$) and S ($Co_2Fe_4O_8$) blocks with a corresponding rotation of 120$^o$ along the *c*-axis after each TS pair. The S block is responsible for the net magnetic moment for this ferrite system along the direction of $Fe^{3+}$ ions from the octahedral site. In contrast, the magnetic moments of the T block cancel out the contribution arising from the octahedral and tetrahedral site ions. The inherent properties such as better thermochemical stability, excellent mechanical hardness, wear and corrosion resistance, and higher value of Curie temperature associated with $Co_2$-Y hexaferrite may facilitate the adoption of this material to be utilized within the diverse field of applications.

The present research work includes several aspects of achieving a successful tunability of the concerned compound, i.e., Y-type barium hexaferrite ($Co_2$-Y), to overcome the flaws associated with earlier studied ferrite (especially spinel-type) systems within its real-time adoption by the industries. The thesis deals with exploring the

performance of substituted $Co_2$-Y hexaferrite, synthesized using the citrate-nitrate auto-combustion method, within five versatile fields, including i) heterogeneous catalysis for oxidation (conversion of styrene to benzaldehyde), ii) heterogeneous catalysis for reduction or hydrogenation (conversion of nitrobenzene compound to aniline), iii) heterogeneous photocatalysis for wastewater treatment (degradation of aqueous methyl orange ), iv) as a microwave absorbing material for EMI shielding application and v) as a biocompatible hyperthermia agent.

The cerium substituted nanocrystalline Y-type barium hexaferrite {$Ba_{2-x}Ce_xCo_2Fe_{12}O_{22}$ (x = 0.0, 0.1, 0.2, & 0.3)} can be selected as an industrially adoptable heterogeneous catalyst for the conversion of styrene to benzaldehyde. The as-prepared hexaferrite shows excellent catalytic performance due to its high surface area and large dispersity by providing additional active sites for the reaction. The optimum catalytic efficiency has been achieved by using 20 mg of $Ba_{1.8}Ce_{0.2}Co_2Fe_{12}O_{22}$ hexaferrite at a reaction temperature of 120°C for 24 hrs with trifluoroacetic acid (TFA) as an oxidant. It results in the 71% isolated yield for the concerned product (benzaldehyde) with a total consumption of styrene. The as-prepared catalyst is magnetically separable to reprocess. There is no remarkable loss of catalytic activity when it is reprocessed for five consecutive trials.

The cerium substituted nanocrystalline Y-type barium hexaferrite {$Ba_2Co_2Fe_{12-x}Ce_xO_{22}$ (x = 0.0, 0.1, 0.2, & 0.3)} can be designed as an industrially adoptable heterogeneous catalyst for the conversion of nitrobenzene to aniline. The as-prepared ferrite powder can be utilized in a large-scale wastewater treatment plant or industrial conversion of aromatic nitro compounds to the corresponding amine. The optimum catalytic efficiency has been attained by using 100 mg of $Ba_2Co_2Fe_{11.80}Ce_{0.20}O_{22}$ hexaferrite at a reaction temperature of 100°C for 12 hrs with 2 mmol of hydrated

hydrazine within the water as a solvent. It results in the 73% isolated yield for the concerned product (aniline) with a total consumption of nitrobenzene.

The Ti-substituted nanocrystalline Y-type barium hexaferrite $Ba_2Co_2Fe_{12-x}Ti_xO_{22}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 & 0.5) can be explored as a heterogeneous photocatalyst for the degradation of methyl orange from the wastewater. The UV-visible spectrum analysis supports the enhancement in visible light absorption and decreasing behavior for bandgap value by increasing the substitution level of $Ti^{4+}$ ions within the sample. The photocatalytic degradation study of aqueous MO solution in the presence of $H_2O_2$ suggests the superiority of $Ba_2Co_2Fe_{11.6}Ti_{0.4}O_{22}$ compared to pristine $Co_2$-Y barium hexaferrite with an apparent rate constant of 1.9 x $10^{-2}$ $min^{-1}$ and turn over frequency of 3.93 x $10^{-6}$ mole $g^{-1}min^{-1}$. This enhanced photocatalytic activity for sample $Ba_2Co_2Fe_{11.6}Ti_{0.4}O_{22}$ can be correlated to the fine crystallite size; the presence of active $Ti^{3+}$ species to promote the reactivity of catalyst surface; the presence of mixed $Fe^{3+}$ & $Fe^{2+}$ to slow down the recombination process by trapping the photogenerated electrons and holes; the existence of oxygen vacancy to enhance the visible light absorption and leads to narrowing the bandgap by creating an extra impurity level adjacent to the valence band.

The lanthanum and magnesium substituted nanocrystalline Y-type barium hexaferrite $Ba_{2-x}La_xCo_{2-x}Mg_xFe_{12}O_{22}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 & 0.5) can be employed as a microwave absorbing material for EMI shielding applications. The magnetic measurements reveal that the saturation magnetization decreases, and the coercivity increases with increasing $La^{3+}$ and $Mg^{2+}$ content. The optimum EMI shielding and microwave absorbance performance have been achieved by $Ba_{1.5}La_{0.5}Co_{1.5}Mg_{0.5}Fe_{12}O_{22}$ composition at a thickness of 5 mm with a moderate value of reflection loss ($R_L$<-10dB), resulting in 90% absorption of the incident microwave.

The chromium substituted cobalt-based nanocrystalline Y-type barium hexaferrite $Ba_2Co_2Fe_{12-x}Cr_xO_{22}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 & 0.5) can be applied as a biocompatible hyperthermia agent. The surface of the ferrite particles is functionalized using oleic acid to overcome the issue associated with ferrofluid stability and analyzed their biocompatibility using the MG-63 cell line. The optimum hyperthermic performance is accomplished by $Ba_2Co_2Fe_{11.7}Cr_{0.3}O_{22}$ ferrite under an applied AC magnetic field of 25 mT at a frequency of 114.1 kHz, resulting in the SAR value of 84.39 W/g and ILP value of 1.86 $nHm^2/Kg$ with excellent biocompatibility.

The enhanced performance of all these substituted $Co_2$-Y hexaferrite samples has been explained by the variations in structural, magnetic, morphological parameters and the presence of multivalence elemental states within the samples. This work indicates that the catalytic oxidation, catalytic reduction, photocatalytic degradation, microwave absorptivity, and the magnetic hyperthermia activity of the complex ferrites are not only limited to conventionally utilized soft ferrite materials but also can be explored to hard ferrites too. The substituted Y-type barium hexaferrite ($Co_2$-Y) proves its promising candidacy with several advantages such as ease of separation, better reusability, excellent thermochemical stability, total conversion of reactant, better selectivity for the desired product, lower value of band gap energy, total degradation of non-biodegradable dye, the optimum value of EMI shielding and microwave absorption, exceptional heating capability within AC magnetic field and excellent biocompatibility.

***Keywords:*** *Y-type barium hexaferrite; Sol-gel auto combustion; Heterogeneous catalyst; Oxidation; Reduction; Photocatalyst; Microwave absorption; Magnetic hyperthermia*