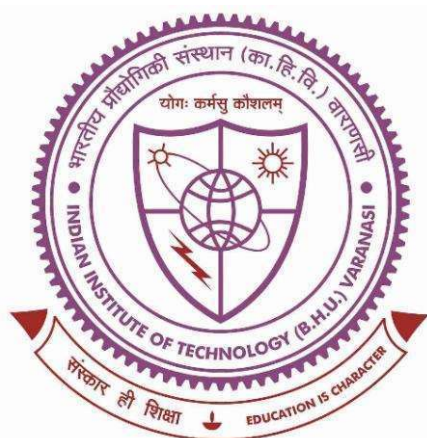


***Synthesis and Characterizations of Modified Y-Type
Hexaferrite Materials for Potential Applications in
Various Fields***



**A thesis submitted in partial fulfillment for the
Award of Degree
Doctor of Philosophy**

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JULY 2022

CHAPTER 9

CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

In brief, the present research explains the investigations regarding the structural and magnetic properties of substituted cobalt-based Y-type barium hexaferrites ($\text{Co}_2\text{-Y}$), synthesized using the nitrate-based sol-gel auto combustion method, and explores in five different applications. The nitrate-citrate sol-gel auto combustion process provides well-homogenized nanocrystalline hexaferrite powders. The multiple substitutions are performed within $\text{Co}_2\text{-Y}$ hexaferrite (at both barium and iron sites) and are in good agreement with earlier reported works. The tuning within the structural and magnetic parameters is correlated with the size of the substituting ions and their possible occupancies. The substituting ions are performed their desired function within the system and enhance the properties according to the expected outcomes. Compared to the earlier utilized ferrite materials, the substituted hexaferrites prove their excellency within a particular or specified application. Overall, the work can be concluded as follows:

- The Ce^{3+} substituted $\text{Co}_2\text{-Y}$ hexaferrite having a general formula of $\text{Ba}_{2-x}\text{Ce}_x\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ ($x = 0.0, 0.1, 0.2, \& 0.3$) is synthesized successfully and studied their structural and magnetic properties. The results suggest an overall volumetric contraction within the unit cell & increasing value of both saturation magnetization (from 30.58 to 38.03 emu/g) and coercivity (16.97 to 116.75 Oe). The as-prepared hexaferrite demonstrates excellent catalytic performance within the oxidation of styrene. It is found that 20 mg of $\text{Ba}_{1.8}\text{Ce}_{0.2}\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ hexaferrite provides total conversion of styrene & 71% isolated yield for benzaldehyde at 120°C of reaction temperature for 24 hrs. The higher selectivity for benzaldehyde can be explained due to the presence of oxygen vacancies over the catalytic surface, high surface area, and optimum dispersity, which provides additional active sites for the reaction with the presence of trifluoroacetic acid (TFA) as an oxidant. The as-obtained

hexaferrite material can be utilized as a heterogeneous catalyst for large-scale production of benzaldehyde due to its easy and cost-effective preparation, stability against the corrosive and harsh chemical environment, mild reaction conditions, better phase stability against thermal agitations, magnetically separable, and better reusability. Finally, it can be proposed as a promising material to be utilized as a heterogeneous catalyst in various oxidation reactions.

- The Ce^{3+} substituted $\text{Co}_2\text{-Y}$ hexaferrite having a general formula of $\text{Ba}_2\text{Co}_2\text{Fe}_{12-x}\text{Ce}_x\text{O}_{22}$ ($x = 0.0, 0.1, 0.2, \& 0.3$) is synthesized successfully and studied their structural and magnetic properties. The results confirm an overall volumetric expansion within the unit cell & decreasing the value of saturation magnetization (from 33.63 to 30.37 emu/g) and increasing coercivity (21.72 to 35.51 Oe). The as-prepared hexaferrite demonstrates excellent catalytic performance within the reduction of nitro benzene. It is found that 100 mg of $\text{Ba}_2\text{Co}_2\text{Fe}_{11.80}\text{Ce}_{0.20}\text{O}_{22}$ hexaferrite provides total conversion of nitrobenzene & 73% of aniline selectivity in the presence of 2 mmol hydrated hydrazine, utilizing water as a solvent at 100 °C of reaction temperature for 12 hrs. The superior performance of the $\text{Ba}_2\text{Co}_2\text{Fe}_{11.8}\text{Ce}_{0.2}\text{O}_{22}$ ferrite is attributed to the maximum presence of Co^{3+} ion concentration, largest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, increased surface area, and oxygen vacancy concentration. The as-obtained hexaferrite material can be utilized as a heterogeneous catalyst for both large-scale wastewater treatment by degrading aromatic nitro compounds or industrial manufacturing of aniline due to its ease of synthesis, better thermochemical stability, mild reaction conditions, utilization of hydrated hydrazine as a hydrogen source instead of using several harmful sources, magnetically separable, and better reusability. Finally, it can be proposed as a

promising candidate to be utilized as a heterogeneous catalyst in various reducing organic reactions.

- The Ti^{4+} substituted $\text{Co}_2\text{-Y}$ hexaferrite having a general formula of $\text{Ba}_2\text{Co}_2\text{Fe}_{12-x}\text{Ti}_x\text{O}_{22}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ & 0.5) is synthesized successfully and studied their structural and magnetic properties. The results suggest an overall volumetric expansion within the unit cell & decreasing the value of both saturation magnetization (from 43.39 to 36.81 emu/g) and coercivity (160.84 to 120.66 Oe). The UV-visible spectrum analysis supports the increasing visible light absorption and decreasing bandgap values by increasing the substitution level of Ti^{4+} ions within the sample. The as-prepared hexaferrite demonstrates excellent photocatalytic performance within the degradation of methyl orange from its aqueous solution (4.6 mg/L). It is found that 0.05 mg/ml catalytic loading of $\text{Ba}_2\text{Co}_2\text{Fe}_{11.6}\text{Ti}_{0.4}\text{O}_{22}$ can completely degrade the methyl orange in the presence of H_2O_2 as a scavenger with an apparent rate constant of $1.9 \times 10^{-2} \text{ min}^{-1}$ and turn over frequency of $3.93 \times 10^{-6} \text{ mole g}^{-1} \text{ min}^{-1}$. This enhanced photocatalytic activity can be attributed to the fine crystallite size, the presence of active Ti^{3+} species promoting 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 results recommend that it can be proposed as a promising candidate for the photocatalytic degradation of several non-biodegradable organic compounds from wastewater without any hazardous footprint on the environment.
- The La^{3+} and Mg^{2+} substituted $\text{Co}_2\text{-Y}$ hexaferrite having a general formula of $\text{Ba}_{2-x}\text{La}_x\text{Co}_{2-x}\text{Mg}_x\text{Fe}_{12}\text{O}_{22}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ & 0.5) is synthesized successfully

and studied their structural and magnetic properties. The results suggest an overall volumetric contraction within the unit cell & decreasing values of saturation magnetization (from 38.53 to 33.71 emu/g) and increasing values of coercivity (94.17 to 213.30 Oe). The as-prepared hexaferrite demonstrates excellent microwave absorption performance within the Ku band frequency. It is found that $\text{Ba}_{1.5}\text{La}_{0.5}\text{Co}_{1.5}\text{Mg}_{0.5}\text{Fe}_{12}\text{O}_{22}$ shows the greatest reflection loss and total shielding effectiveness among all synthesized samples. The EMI shielding effectiveness is dominated by the absorption mechanism within the scanned frequency range. The improved shielding effectiveness for the $\text{Ba}_{1.5}\text{La}_{0.5}\text{Co}_{1.5}\text{Mg}_{0.5}\text{Fe}_{12}\text{O}_{22}$ hexaferrite sample can be proposed as an excellent microwave absorber material within the Ku-band (12.5 to 17.5 GHz) of the frequency with a moderate reflection loss ($R_L < -10\text{dB}$) at a sample thickness of 5 mm. The results propose that it can be proposed as a promising candidate to be utilized as radar absorbing materials (RAMs) or microwave absorbing materials (MAMs) vastly being applied to forbid the EM reflections from planes, tanks, and other military equipment.

- The Cr^{3+} substituted $\text{Co}_2\text{-Y}$ hexaferrite having a general formula of $\text{Ba}_2\text{Co}_2\text{Fe}_{12-x}\text{Cr}_x\text{O}_{22}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4 \text{ \& } 0.5$) is synthesized successfully and studied their structural and magnetic properties. The results suggest an overall volumetric contraction within the unit cell & decreasing values of saturation magnetization (from 39.06 to 33.50 emu/g) and increasing values of coercivity (86.87 to 281.84 Oe). The as-prepared hexaferrite demonstrates an improved magnetic heating capability along with excellent biocompatibility. The magnetic hyperthermia capability measured by applying an AC magnetic field of 25 mT at a frequency of 114.1 kHz suggests that oleic acid-coated $\text{Ba}_2\text{Co}_2\text{Fe}_{11.7}\text{Cr}_{0.3}\text{O}_{22}$ provide the uppermost value of SAR, i.e., 84.39 W/g, and ILP value of 1.86 nHm^2/Kg . The

biocompatibility analysis against the MG-63 cell line shows that both pristine and oleic acid-coated particles favor cell growth and proliferation at all the examined concentrations. The results propose that it can be proposed as a promising candidate to be utilized within various biomedical applications such as MRI cell tracking combined with hyperthermia due to its enhanced SAR, ILP, and biocompatibility properties.

As a conclusive remark, it can be proposed that the present work provides an enhanced performance within all five proposed applications, owing to the suitability of substituting elements for each series. Conclusively, this work explains that several sophisticated applications are not only limited to conventionally using soft ferrite materials but also can be applied to some hard ferrites.

9.2 Future scope

With the enhanced performances within discussed applications, this work can be further extended to other applications, which are being dominated or limited by soft ferrite materials only. In the future, the proposed material can be explored further within a few other important fields as mentioned below:

- (a) For photocatalytic, removal of other organic pollutants from wastewater bodies such as Bromophenol Blue, Chicago Sky Blue, Copper Phthalocyanine, Eosin Yellowish, Evans Blue, Naphthol Blue Black, Phenol Red, Poly B-411, Reactive Orange 16, Azo dye, Rhodamine B, Methylene Blue, Remazol Brilliant Blue, Ciprofloxacin, Bisphenol A, Chlorpyrifos, Naproxen, Congo red, etc.
- (b) As a heterogenous catalyst for catalytic oxidation reactions such as *oxidation* of carbon monoxide (CO) gas, oxidation of Dimethyl Ether, oxidation of sulfide to polysulfides, oxidation of thiols to disulfides, oxidation of sulfides to

sulfoxides, oxidation of formaldehydes, oxidation of methane, oxidation of alcohols for the preparation of carbonyl compounds, aerobic oxidation of cyclohexane compounds.

- (c) As a heterogenous catalyst for other complex reactions such as Carbon-carbon cross-coupling (Suzuki-Miyaura reaction for producing asymmetric biaryls by coupling aryl halides with arylboronic acids) and Carbon-oxygen bond formation reactions.
- (d) As a heterogenous catalyst within reduction reactions such as reduction of CO₂ to produce olefin, hydrogenation of 2,4-dinitrotoluene, reduction of furfural alcohol to furfuryl alcohol using 2-propanol and asymmetric hydrosilylation of ketones, etc.
- (e) As an adsorber for removal of heavy metals such as Cr(VI), Pb(II) and Cd(II), Ni(II), Cu(II), Fe(II), and Al(III) ions from wastewater.