

REPORT OF THE PROJECT PROPOSAL SANCTIONED UNDER RUSA 2.0

TITLE: Nano crystalline/bulk 3d metal based mixed metal oxides synthesized by different combustion methods: Magnetic and catalytic properties

NAME OF THE TEACHER: Prof. Devinder Singh Sambyal

DEPARTMENT: Chemistry

The seed money received under RUSA 2.0 has been utilized for research work proposed in the project proposal. The progress of the research work done so far is outlined as follows:

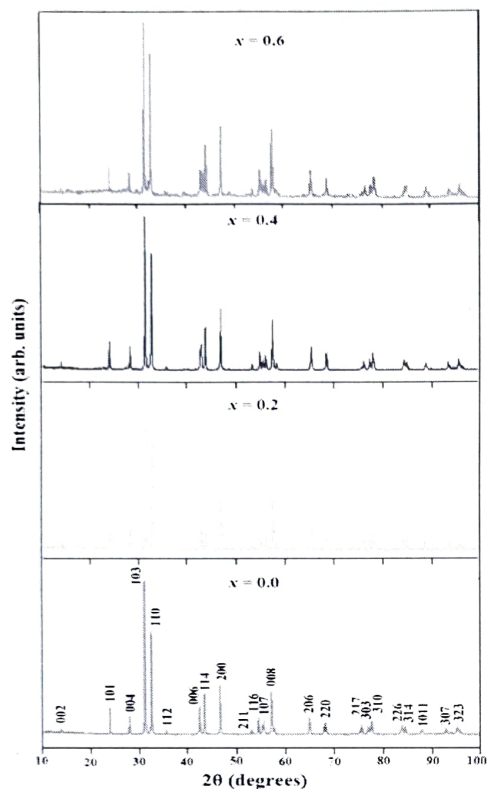
1. Synthesis of nanostructured NiCrFeO_4 was done via combustion method by using different fuels such as glycine, urea, and PVA (polyvinyl alcohol). The prepared phases were given heat treatment at $500\text{ }^\circ\text{C}$ and were used for characterization by various physical techniques. XRD and Rietveld refinement confirms the formation of nanocrystalline ferrite phases without any other impurity peak corresponds to spinel cubic structure with $Fd\bar{3}m$ space group. The crystallite sizes were calculated using Debye-Scherrer equation and found to be 43.31, 30.13 and 3.9 for samples prepared with glycine, urea and PVA as a fuel respectively. Furthermore, PL studies shows that recombination rate of photogenerated electron and hole pairs follows the order glycine > urea > PVA. The values of optical band gap, obtained from DRS technique, lie in visible region range (1.50-1.60 eV). Magnetic studies displayed superparamagnetic character of NiCrFeO_4 prepared with PVA while some antiferromagnetic interactions in the other two samples. All nanocatalysts were used for the reduction of nitroarenes and the photocatalytic degradation of various cationic (RhB, MB) and anionic (MO) dyes and their mixtures. The results of photocatalytic activity have shown that the degradation efficiency of NiCrFeO_4 prepared with PVA shows excellent results which follows the order RhB > MB > MO in their unitary solution. Furthermore, in case of mixture of dyes, it showed enhanced photocatalytic degradation for cationic dyes (RhB and MB) compared to that of anionic dye (MO). In addition to this, nitrobenzene and its various analogues were efficiently reduced using NiCrFeO_4 as catalyst and sodium borohydride



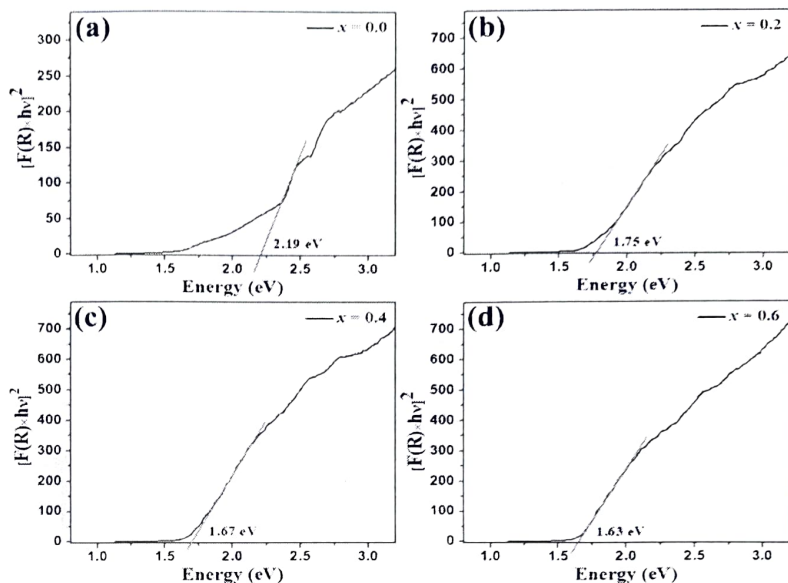
as reducing agent at room temperature in quick time 10 min. In conclusion, among all the prepared nanocatalysts sample prepared with PVA shows higher efficiency towards the degradation of dyes and reduction of nitroarenes owing to its higher surface area and lower band gap. This work is published in the **ACS Omega journal (Impact Factor: 3.512); DOI: doi.org/10.1021/acsomega.2c01616**.

2. The synthesis of new $n=1$ Ruddlesden-Popper oxides, $\text{LaSrFe}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.0, 0.2, 0.4$ and 0.6) was carried out using glycine-nitrate combustion method. The Rietveld refinement analysis confirms the formation of the prepared samples and indicates that all the phases crystallize in the tetragonal symmetry with space group $I4/mmm$. The diffuse reflectance spectra (DRS) spectra of the parent phase LaSrFeO_4 shows a band edge at 502 nm which further shifts towards higher wavelength side, indicating a red shift with the increase in the Cr^{3+} doping concentration. The optical band gap value decreases from 2.19 eV for $x = 0.0$ to 1.63 eV for $x = 0.6$ phase, attributed to the increase in Cr^{3+} substitution. The magnetic studies results revealed that dominant anti-ferromagnetic (AFM) interactions exist in all the phases and weak ferromagnetic (FM) interactions appears with Cr^{3+} substitution. The results are discussed by considering the increase in $\text{Fe}^{3+}-\text{O}-\text{Cr}^{3+}$ FM interaction in addition to the $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ and $\text{Cr}^{3+}-\text{O}-\text{Cr}^{3+}$ AFM super-exchange interactions induced due to random distribution of Fe^{3+} and Cr^{3+} ions at the octahedral site. The photocatalytic degradation of a Rhodamine B dye pollutant model was successfully done to check for the applicability of the photocatalytic activity of the prepared samples. The addition of Cr^{3+} substitution resulted in increased photocatalytic activity. The results show ~99% degradation for $x = 0.6$ while only ~76% degradation is shown for $x = 0.0$ sample in 40 min under visible light irradiation. The research work is communicated in the **Journal of Alloys and Compounds, and is currently under revision.**

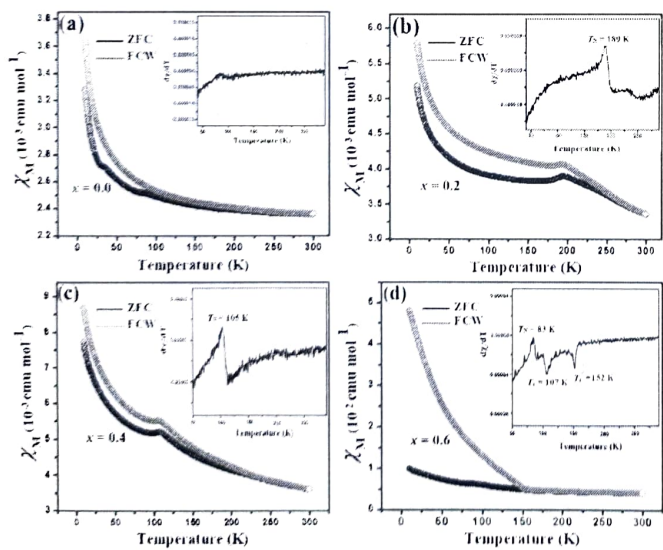




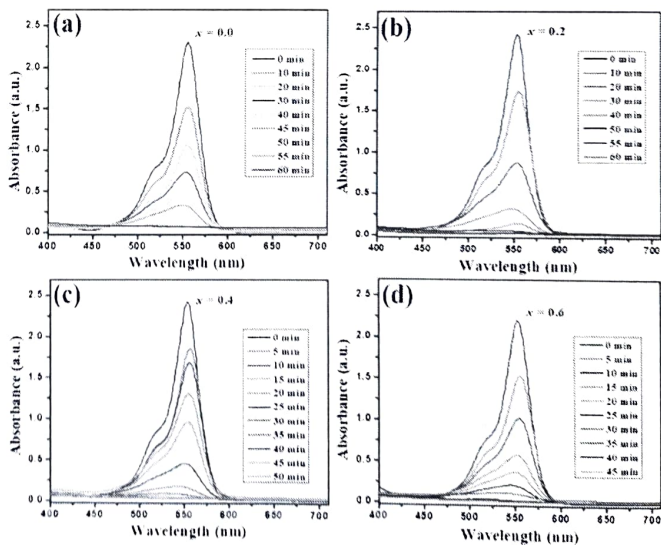
X-ray powder diffraction patterns of $\text{LaSrFe}_{1-x}\text{Cr}_x\text{O}_4$ phases.



Tauc plot transformation of diffuse reflectance spectra of $\text{LaSrFe}_{1-x}\text{Cr}_x\text{O}_4$ phases.



Plot of ZFC and FCW molar magnetic susceptibility (χ_M) versus temperature of $\text{LaSrFe}_{1-x}\text{Cr}_x\text{O}_4$ phases (Inset shows the $d\chi/dT$ vs T ZFC plot).

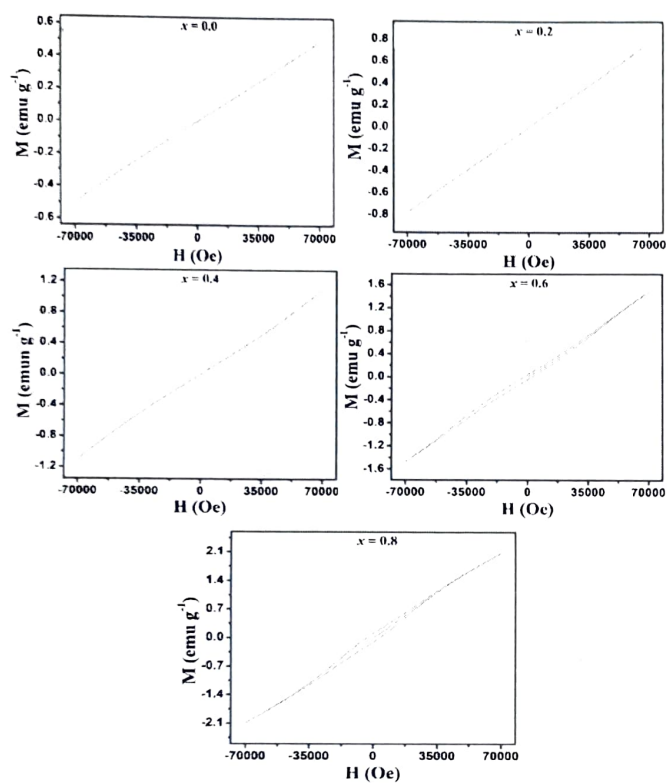


Time dependent UV-vis absorbance spectrum of RhB dye by $\text{LaSrFe}_{1-x}\text{Cr}_x\text{O}_4$ catalyst.

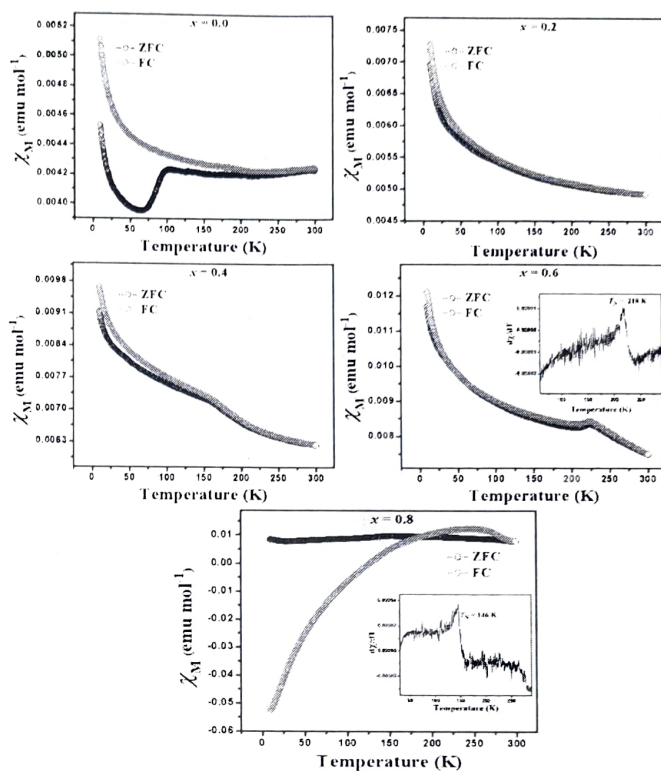
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3. $\text{La}_2\text{SrFe}_{2-x}\text{Cr}_x\text{O}_7$ ($x = 0.0, 0.2, 0.4, 0.6$ and 0.8) phases belonging to the $n=2$ member of the Ruddlesden-Popper oxides, have been prepared via Sol-gel Pechini method. The effect of Cr^{3+} doping on the crystal structure, optical and the magnetic properties of the, $\text{La}_2\text{SrFe}_2\text{O}_7$ phase has also been systematically explored via different characterization techniques. Rietveld refinement analysis indicates a decrease in the lattice parameters a and c , as well as the unit cell volume V , is observed with the increase in Cr^{3+} doping. The magnetization versus applied field curves shows the appearance of weak ferromagnetism at higher Cr concentration in otherwise dominant anti-ferromagnetic interaction. The phenomenon of magnetization reversal (MR) is observed for $x = 0.8$ phase. Here the χ_{M-FC} curve on cooling shows a maximum value at $T_{max} \sim 246$ K and becomes zero at $T_{comp} \sim 127$ K, where the magnetization reversal begins and the value becomes negative on further decreasing the temperature. The photocatalytic degradation of a Rhodamine B dye pollutant model was carried out to check for the photocatalytic applicability of the prepared samples. The best result was achieved by the $x = 0.2$ phase, which showed a $\sim 99\%$ dye degradation in 30 minutes, followed by $\sim 83\%$, $\sim 75\%$, $\sim 64\%$, and $\sim 61\%$ in the same time span by the $x = 0.4, 0.0, 0.8,$ and 0.6 phases respectively. This trend has been explained on the basis of recombination of charge carriers in the prepared samples and are in good agreement with the results of Photoluminescence (PL) emission intensity spectra obtained. This research work is communicated in the **Ceramics International Journal, and is currently under revision.**

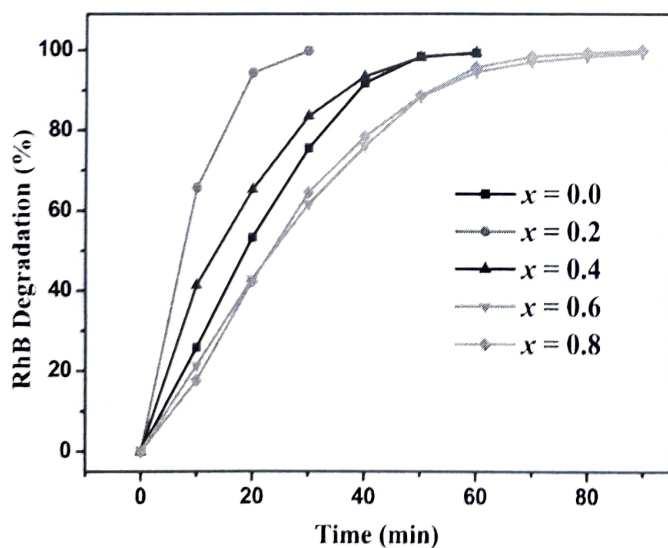




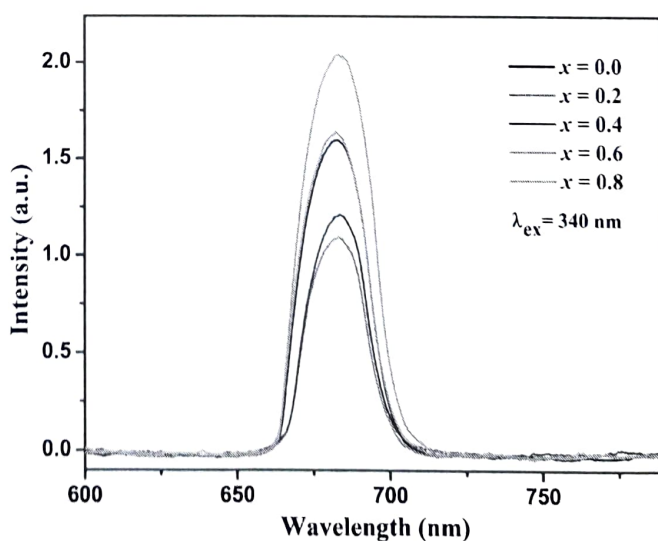
Variation of magnetization (M) as a function of applied magnetic field (H) for $\text{La}_2\text{SrFe}_{2-x}\text{Cr}_x\text{O}_7$ phases.



Plot of ZFC and FCW molar magnetic susceptibility (χ_M) versus temperature of $\text{La}_2\text{SrFe}_{2-x}\text{Cr}_x\text{O}_7$ phases (Inset shows the $d\chi/dT$ vs T ZFC plot).



Degradation percentage of RhB dye by $\text{La}_2\text{SrFe}_{2-x}\text{Cr}_x\text{O}_7$ phases.



Photoluminescence emission spectra of $\text{La}_2\text{SrFe}_{2-x}\text{Cr}_x\text{O}_7$ phases.

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4. Ni–Co ferrite materials with general chemical formula $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_{1.98}\text{R}_{0.02}\text{O}_4$ (R = La, Nd, Sm, Gd, Dy) were synthesized by Sol-gel Pechini method. All the ferrites possess the cubic symmetry in the space group $Fd\bar{3}m$. A very small change in the lattice parameter was observed with the rare earth (R^{3+}) doping. The cation distribution between the tetrahedral (A-site) and octahedral (B-site) sites, as estimated by X-ray diffraction analysis (XRD), showed that the R^{3+} , Co^{2+} and Ni^{2+} ions have migrated to the octahedral site. Magnetization results at room temperature, obtained from vibrating sample magnetometer (VSM) measurements, showed that the saturation magnetization of rare-earth-doped ferrites is strongly dependent on the magnetic moment of the rare-earth ion. The coercivity increases with increasing rare earth ion atomic number, which could be explained by the stability of the spin-orbit coupling that controls the magnetic anisotropy in ferrites. The results also indicate that the Curie temperature depends on the lattice parameter and thus on the interatomic distance between magnetic ions. This work was published in **Ceramics International (Impact Factor : 4.527) ; 47 (2021) 17510-17519** DOI: doi.org/10.1016/j.ceramint.2021.03.069 .

Based on the performance of the work done, a major research project has been submitted to JKDST.



Different Fuel-Adopted Combustion Syntheses of Nano-Structured NiCrFeO₄: A Highly Recyclable and Versatile Catalyst for Reduction of Nitroarenes at Room Temperature and Photocatalytic Degradation of Various Organic Dyes in Unitary and Ternary Solutions

Sumit Singh, Shikha Sharma, Ujwal Manhas, Irfan Qadir, Amit Kumar Atri, and Devinder Singh*

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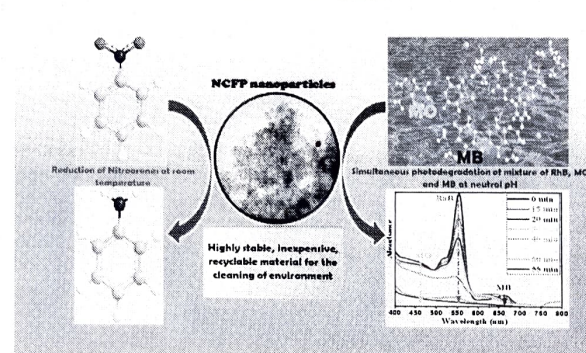
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ABSTRACT: As industrialization progresses, there is a large release of hazardous pollutants into the environment. These pollutants, which contain nitro compounds and organic dyes, are extremely dangerous due to their toxic and carcinogenic nature. An efficient, environmentally benign, and economical catalyst to degrade environmental pollutants or convert them into useful products has been of sustained interest in recent years. In this context, we report a simple and inexpensive combustion fabrication of NiCrFeO₄ using different fuels such as glycine, polyvinyl alcohol (PVA), and urea, showing tremendous catalytic and photocatalytic functionalities. Rietveld refinement and X-ray diffraction studies confirmed the formation of single-phase ferrites, with crystallite sizes ranging from 3.9 to 43.31 nm. The values of optical band gap, obtained from the diffused reflectance spectroscopy technique, lie in the visible region range (1.50–1.60 eV), and hence, all the synthesized ferrites can act as good photocatalysts in the presence of visible light. All the NCF nanocatalysts were utilized for the reduction of nitroarenes and photocatalytic degradation of various cationic (RhB and MB) and anionic (MO) dyes and their mixture. NCF displayed excellent activity for the reduction and oxidation reactions owing to its large surface area and low optical band gap. Furthermore, the photo-oxidative degradation by NCFP was also enhanced due to its low recombination of charge carriers as confirmed by the photoluminescence (PL) spectroscopy. NCFP efficiently reduces nitrobenzene to aminobenzene with 95% yield using sodium borohydride as the reducing agent in methanol medium at RT in 10 min. The results of photocatalytic activity have shown that the degradation efficiency of NCFP follows the order RhB > MB > MO in their unitary solution. Furthermore, in the case of the mixture of dyes, NCFP showed enhanced photocatalytic degradation for cationic dyes (RhB and MB) compared to that of anionic dye (MO). From the performance point of view, this catalyst can be useful in industrial application because of its high stability, greater catalytic efficiency, and cost-effectiveness.



1. INTRODUCTION

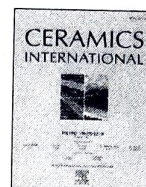
In the past several years, magnetic nano-ferrites have been mostly investigated because of their enormous features, which are superior in contrast to their corresponding bulk counterparts,^{1,2} like super-paramagnetism, high surface area, large surface to volume ratio, being smoothly separable under external magnetic field, and strong adsorption ability. One of the most interesting and important properties of nano-sized magnetic ferrites is catalysis, which is turning out to be a tactical field because it expresses a new route to face the challenges of energy and sustainability. Green and environment-friendly procedures of synthesis and conditions for reaction have played a crucial role toward the purpose of transforming hazardous processes to proficient ones. Such processes reduce the usage of harmful reagents and solvents,

hard reaction conditions, and also complex as well as time-consuming separation of catalysts from reaction mixtures.^{3,4} Magnetic nano-ferrites have been proven to be in demand for carrying various tedious organic reactions.^{5–7} By altering the size, chemical composition, morphology, or oxidation state of the metals used in the ferrite catalyst, enhancement and control over the reaction can be achieved by nano-catalysis.

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Sumit Singh



Rare-earth doped Ni–Co ferrites synthesized by Pechini method: Cation distribution and high temperature magnetic studies

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ABSTRACT

The present work was focused on the effect of rare earth doping on the structural and magnetic properties of Ni–Co ferrite materials with general chemical formula $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_{1.98}\text{R}_{0.02}\text{O}_4$ ($\text{R} = \text{La, Nd, Sm, Gd, Dy}$). All the ferrites, synthesized by the Pechini method, possess cubic symmetry with $Fd\bar{3}m$ space group. A very small change in lattice parameter has been observed with rare earth (R^{3+}) doping. The cation distribution between the tetrahedral (A-site) and octahedral sites (B-site), as estimated by X-ray diffraction analysis (XRD) revealed that the R^{3+} , Co^{2+} and Ni^{2+} ions have migrated to the octahedral site. Room temperature magnetization results, obtained from Vibrating Sample Magnetometer (VSM) measurements, showed that saturation magnetization of rare-earth doped ferrites is strongly dependent on magnetic moment of rare earth ion. The coercivity increases with increase in the atomic number of rare-earth ion, which could be justified on the grounds of the stability of spin-orbital coupling that controls the magnetic anisotropy in ferrites. The results further suggest that the Curie temperature is dependent on lattice parameter and hence inter-atomic distance between magnetic ions.

1. Introduction

Spinel ferrites have general formula $\text{MO}:\text{Fe}_2\text{O}_3$ where M is Ni^{2+} , Zn^{2+} , Co^{2+} , and so on in which the oxygen ions crystallize into a cubic closed packed arrangement. The cations are found to be present at two types of interstitial sites known as octahedral (B) site and tetrahedral (A) site. The site occupancy is usually represented by the chemical formula $(\text{M}_{1-\delta}^{2+}\text{Fe}_{\delta}^{3+})[\text{M}_{\delta}^{2+}\text{Fe}_{2-\delta}^{3+}]\text{O}_4$, where the brackets and square brackets represent A and B sites respectively, M designates a divalent cation, and δ is inversion parameter. Ferrimagnetic nickel ferrites have drawn growing recognition because of their extraordinary properties such as high permeability, large saturation magnetization, high resistivity, lower eddy currents, and are major candidates for magnetic elements such as resonators, tunable signal filters phase shifters, functional radio electronic devices, materials for electronics, and, for spintronics applications [1–14]. The above features make these materials distinctive in microwave appliances that need powerful electromagnetic signal-coupling. Magnetic spinel ferrite nanoparticles also have potential biomedical applications, especially in drug delivery for cancer therapy [15–17]. Cobalt ferrite, a renowned hard magnetic substance, is a prominent material for high-density recording media. It possesses high

magneto-crystalline anisotropy, giant coercivity, huge magnetostrictive coefficient, moderate saturation magnetization, mechanical rigidity, and chemical firmness [18]. CoFe_2O_4 , NiFe_2O_4 , and CuFe_2O_4 ferrites are used as cathode materials in lithium batteries [19,20]. Substitution of nickel in cobalt ferrite drives the decrement in dielectric constant [21]. The structural and magnetic properties of ferrites can be modified by doping rare earth metal ions which have attracted the attention of researchers. Spinel ferrites substituted with rare-earth ions have been reported by numerous research groups [22–30]. The magnetic properties, cation distribution and grain size of rare-earth (Gd, Pr, Dy, Ho, and Er) substituted CoFe_2O_4 crystallites have been reported [31–33]. The effect of La^{3+} substitution on the electrical, dielectric, and magnetic properties of cobalt ferrite produced via coprecipitation method has been explored [34] and lower values of dielectric constant, dielectric loss and magnetic loss could be associated with Fe ions concentration and better compositional stoichiometry. The structural and transport properties of Gd^{3+} exchanged cobalt ferrite nanoparticles were explored and these substances exhibit high resistivity, low loss and soft magnetic properties because of Gd^{3+} doping [35]. Substitution of Dy^{3+} or Gd^{3+} in ferrite structures results in constitutional deformities like an expansion in lattice boundary or microstrain because of ionic radii discrepancy [1,10,

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