

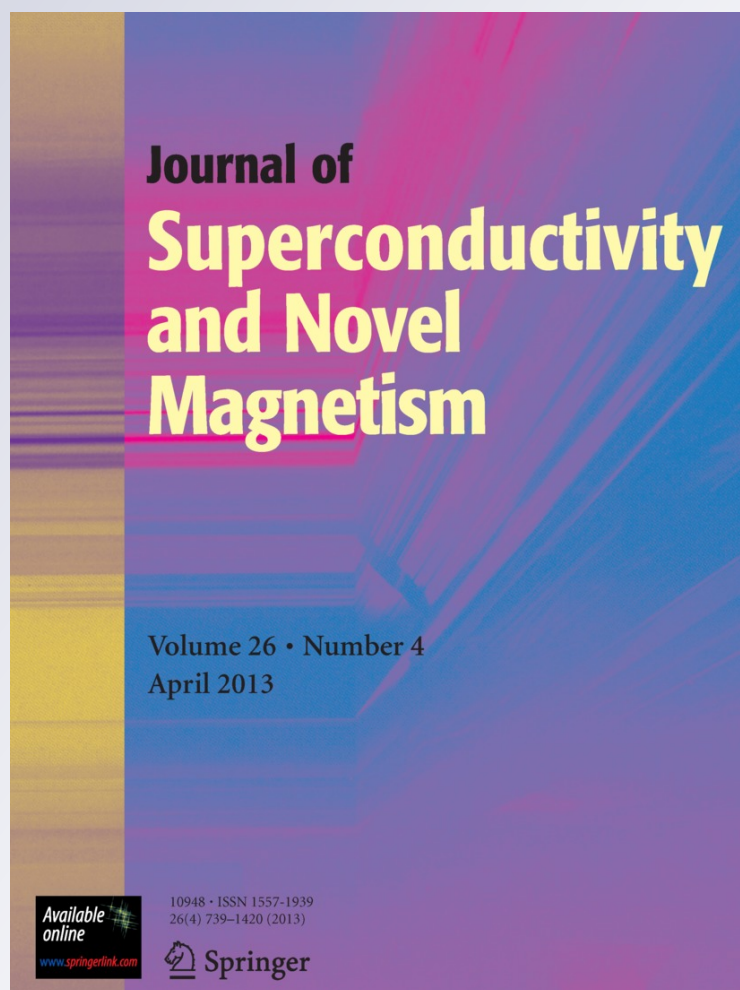
# *Effect of Ce Doping on the Magnetic Properties of NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles*

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# Effect of Ce Doping on the Magnetic Properties of NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles

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**Abstract** In the present work, effect of different concentration of Ce ions on the magnetic properties of nickel ferrite nanoparticles is discussed. A series of NiCe<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> ( $x = 0.0-0.10$ ) samples were prepared by a chemical route. XRD patterns show that all the samples are in pure spinel phase except that with  $x = 0.10$ . This indicates that rare earth ions have limited solubility in the spinel lattice. Magnetic properties are studied by electron paramagnetic resonance spectroscopy (EPR) and the results are explained in terms of a magnetic moment obtained by a vibrating sample magnetometer. Mössbauer spectroscopy was performed to have an idea about the distribution of ions between the tetrahedral and octahedral sites. Magnetic moment is found to decrease after doping with Ce ions. It was found that the samples show mixed spinel nature rather than the pure inverse character. Doping with Ce ions reduces the EPR linewidth of pure nickel ferrite, which indicates that eddy current losses are reduced.

**Keywords** Nickel ferrite · EPR · XRD · Magnetic resonance

## 1 Introduction

Systems with particle size in the nanometric scale expand their scope for use in device applications [1]. Ferrite nanomaterials exhibit interesting magnetic properties like high

mechanical hardness, high electrical resistivity, and chemical stability [2, 3]. The properties of ferrites are influenced by the distribution of metal atoms at the tetrahedral (A) and octahedral (B) lattice positions, method of synthesis, and particle size [4]. It has been reported that electromagnetic properties of ferrites could be modified by substituting Fe<sup>3+</sup> ions with the rare earth elements [5, 6]. Therefore, we are reporting here the effect of Ce ions on the magnetic behavior of nickel ferrite nanoparticles. Nickel ferrite is a typical soft ferromagnetic material, which crystallizes in inverse spinel structure with all the nickel ions located at the B site and the iron ions at both the A and B sites. It is a superior candidate for applications in telecommunications, transformers, aircraft, computer components, magnetic recording, microwave devices, and sensors, etc. [7] because of its high resistivity and moderate magnetisation.

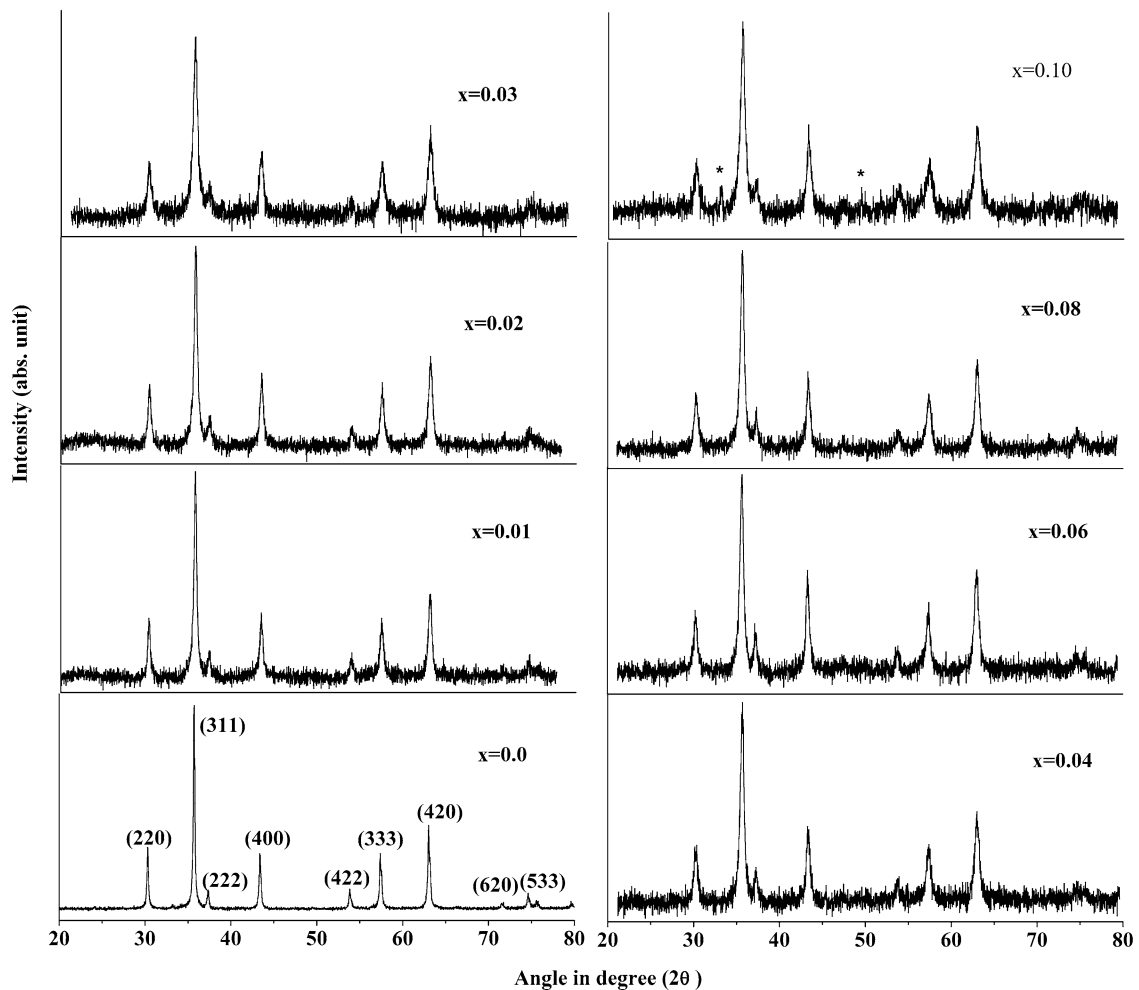
## 2 Experimental Details

Nanoparticles of NiCe<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> ( $x = 0.0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.10$ ) were prepared by the chemical route using the nitrates of nickel, iron, and cerium along with citric acid as the host matrix [8]. The obtained nanoparticles of NiCe<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> were characterized by XRD using the Cu-K $\alpha$  source for the confirmation of phase and structure. To study the magnetic properties, the samples were characterized by electron paramagnetic resonance (EPR) spectroscopy (Bruker EMX) at X-band (9.44 GHz). The distribution of cations between tetrahedral and octahedral sites was determined by <sup>57</sup>Fe Mössbauer spectroscopy in transmission geometry at room temperature using <sup>57</sup>Co- in Rh as the source.

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**Fig. 1** XRD pattern of  $\text{NiCe}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles

**Table 1** XRD parameters for  $\text{NiCe}_x\text{Fe}_{(2-x)}\text{O}_4$

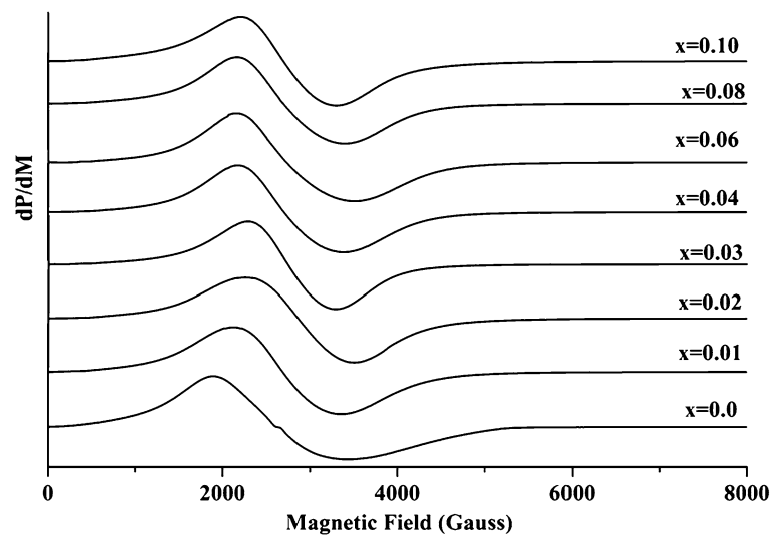
Ce ion concentration $x$	Crystallite size $D$ (nm)	Lattice parameter $a(\text{Å}) \pm 0.01$	Strain ( $\times 10^{-3}$ )
0.0	$57 \pm 12$	8.33	$0.95 \pm 0.33$
0.01	$28 \pm 7$	8.33	$1.47 \pm 0.83$
0.02	$20 \pm 1$	8.33	$0.54 \pm 0.19$
0.03	$19 \pm 2$	8.33	$1.45 \pm 0.62$
0.04	$11 \pm 1$	8.33	$2.72 \pm 0.10$
0.06	$19 \pm 2$	8.33	$0.89 \pm 0.37$
0.08	$20 \pm 2$	8.32	$1.23 \pm 0.45$
0.10	$17 \pm 5$	8.32	$2.27 \pm 0.14$

### 3 Results and Discussion

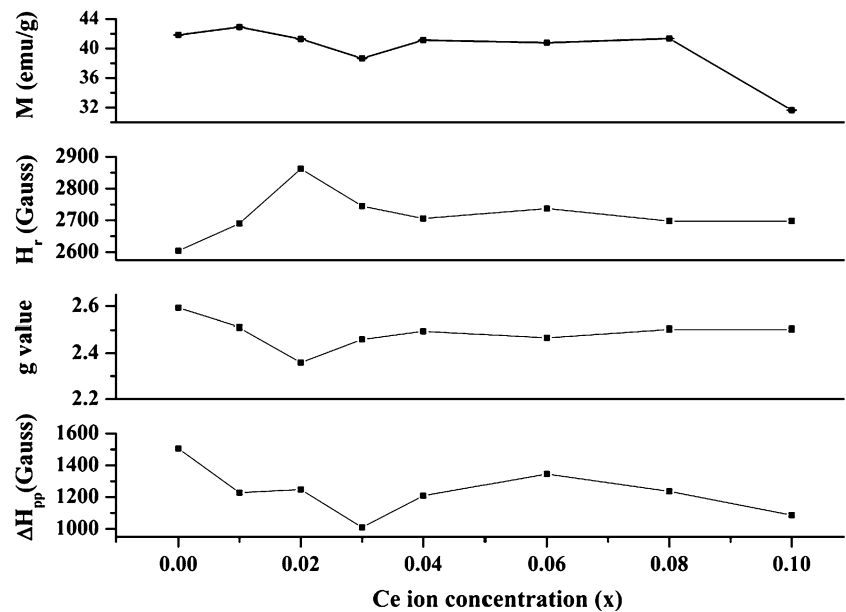
XRD patterns of  $\text{NiCe}_x\text{Fe}_{(2-x)}\text{O}_4$  nanoparticles show a pure spinel phase (Fig. 1). However, a peak of  $\text{CeO}_2$  appears in the sample corresponding to  $x = 0.10$ . This shows that the rare earth ions have limited solubility in the spinel lattice. XRD parameters such as crystallite size and strain were es-

timated from the Williamson–Hall plot [9]. Lattice parameter is estimated by Bragg's law from the most intense peak (311) [10]. The estimated parameters are given in Table 1. The crystallite size reduces from  $(57 \pm 12)$  nm to  $(28 \pm 7)$  nm as the Ce concentration increases from  $x = 0.0$  to  $x = 0.01$  in nickel ferrite. This is because doping with

**Fig. 2** EPR spectra for  $\text{NiCe}_x\text{Fe}_{(2-x)}\text{O}_4$  nanoparticles



**Fig. 3** Variation of EPR parameters and magnetic moment for  $\text{NiCe}_x\text{Fe}_{(2-x)}\text{O}_4$  nanoparticles



rare earth ions restrains the grain growth [11]. With a further increase in Ce concentration, the crystallite size does not change significantly. Lattice parameter of nickel ferrite comes out to be  $(8.33 \pm 0.01) \text{ \AA}$  and it remains almost constant after doping with  $\text{Ce}^{+3}$  ions. This reveals that the cubic structure of nickel ferrite does not change after doping of  $\text{Ce}^{+3}$  ions. The EPR study of ferrites is important for investigating the magnetic properties at high frequency because the resonance originates from the interaction between spins and electromagnetic waves [12]. First derivative EPR spectra of the Ce doped nickel ferrite nanoparticles are shown in Fig. 2. The intensity of the spectra is normalized by the weight of sample. The spectra show single broad resonance peaks. The line shape of nickel ferrite ( $x = 0.0$ ) seems to be broadened and asymmetrical in comparison to that of Ce doped samples. EPR line shape is defined in terms of  $g$ -value and it is

estimated from the relation given in reference [13]. Figure 3 shows the variation of EPR parameters, the peak to peak line width ( $\Delta H_{pp}$ ), resonance field ( $H_r$ ) and the  $g$ -value. It is found that the value of  $\Delta H_{pp}$  is reduced from 1505 to 1228 G after doping with  $x = 0.01$  Ce ions. For a further increase in Ce concentration, the  $\Delta H_{pp}$  value decreases to a minimum value 1008 G for  $x = 0.03$  and then starts to increase up to  $x = 0.06$  (but still less than that of nickel ferrite). For  $x = 0.08$  and  $x = 0.10$ , it again decreases. Contrary to  $\Delta H_{pp}$ , the  $g$  value and  $H_r$  also do not show a regular trend with Ce concentration. The sample corresponding to  $x = 0.02$  shows minimum  $g$ -value 2.36 and highest  $H_r$  1325 G. For a higher value of  $x$ , the  $g$  value increases ( $H_r$  decreases) up to  $x = 0.04$  and then becomes almost independent of the Ce concentration. Reduction of the  $g$  value for nickel ferrite (2.59) after doping with Ce ions shows that

magnetic interaction is decreased. The observed results can be explained as follows: The factors that affect linewidth and resonance field are anisotropy, porosity, eddy currents, inhomogeneous demagnetization, and intrinsic properties [14]. Decrease in linewidth of Ce doped samples in comparison to pure nickel ferrite may be due to the decrease in magnetic dipolar interaction and decrease in particle size. Small value of line width is useful for an application point of view, as it reduces the eddy current losses at high frequency [15]. It has been reported that magnetization value plays a dominant role in the evaluation of the resonance field and the line widths [16]. Therefore, to observe the effect of magnetization M–H hysteresis curves were recorded at room temperature (not shown here) and the value of magnetization is plotted in Fig. 3. It is found that the magnetisation is reduced after doping with Ce ions. High magnetization for pure nickel ferrite indicates high internal field and, therefore, resonance occurs at low magnetic field. As the concentration of Ce ion increases, the magnetization, and hence internal magnetic field decreases. Consequently, a high field is required for the resonance up to  $x = 0.02$ . For a further increase in the concentration of Ce, the resonance field decreases because of a decrease in porosity [17]. It is reported that doping with rare earth ions decrease the porosity of the ferrites [18]. It can be observed from Table 1 that after  $x = 0.02$  the crystallite size does not change significantly, therefore,  $H_r$  becomes almost independent of the Ce concentration. The decrease in the  $g$  value is due to the decrease in particle size after doping with Ce ions up to  $x = 0.03$ . For a further increase in the Ce concentration, the particle size does not change significantly; therefore, the  $g$  value also remains almost constant. This suggests that microscopic magnetic interaction decreases as the particle size decreases. It is known that the effective  $g$ -value depends on the net average magnetic moment (net average spin per molecule) at the sublattices of ferrites. The reduction of  $g$  value shows that the total effective moment is reduced and this supports the result obtained by VSM. Moreover, the deviation of the  $g$ -value from the reported value for pure nickel ferrite (2.43) is caused by the deviation of the perfect inverted spinel structure [19]. It has been confirmed by Mössbauer spectroscopy. The room temperature Mössbauer spectrum shows (not shown here) presence of two sextets corresponding to tetrahedral and octahedral sites. The area ratio of these two sextets gives information about the occupancy of cations between two sites [20] considering that Ce ions being large in size go to B site. Table 2 shows the distribution of cations for all samples. It is found that some of the Ni ions have moved to A site from the B site leading the structure from pure inverse to a mixed spinel nature.

**Table 2** Mössbauer parameters for  $\text{NiCe}_x\text{Fe}_{(2-x)}\text{O}_4$ 

$x$	Structural formula
0.0	$[\text{Ni}_{0.08}\text{Fe}_{0.92}]_A[\text{Ni}_{0.92}\text{Fe}_{1.08}]_B\text{O}_4$
0.01	$[\text{Ni}_{0.01}\text{Fe}_{0.99}]_A[\text{Ni}_{0.99}\text{Ce}_{0.01}\text{Fe}_{1.0}]_B\text{O}_4$
0.02	$[\text{Ni}_{0.02}\text{Fe}_{0.98}]_A[\text{Ni}_{0.98}\text{Ce}_{0.02}\text{Fe}_{1.0}]_B\text{O}_4$
0.03	$[\text{Ni}_{0.03}\text{Fe}_{0.97}]_A[\text{Ni}_{0.97}\text{Ce}_{0.03}\text{Fe}_{1.0}]_B\text{O}_4$
0.04	$[\text{Ni}_{0.02}\text{Fe}_{0.98}]_A[\text{Ni}_{0.98}\text{Ce}_{0.04}\text{Fe}_{0.98}]_B\text{O}_4$
0.06	$[\text{Ni}_{0.1}\text{Fe}_{0.90}]_A[\text{Ni}_{0.90}\text{Ce}_{0.06}\text{Fe}_{1.04}]_B\text{O}_4$
0.08	$[\text{Ni}_{0.07}\text{Fe}_{0.93}]_A[\text{Ni}_{0.93}\text{Ce}_{0.08}\text{Fe}_{0.99}]_B\text{O}_4$
0.10	$[\text{Ni}_{0.11}\text{Fe}_{0.89}]_A[\text{Ni}_{0.89}\text{Ce}_{0.10}\text{Fe}_{1.01}]_B\text{O}_4$

#### 4 Conclusion

The chemical synthesis method shows that only up to  $x = 0.08$  Ce doped nickel ferrite nanoparticles shows pure spinel phase. The crystallite size is found to reduce after doping with Ce ions. Reduction in crystallite size and magnetization is responsible for the observed behavior of linewidth and resonance field. Low value of linewidth (1008 G for  $x = 0.03$ ) for Ce doped samples in comparison to that of pure nickel ferrite (1505 G) indicates that Ce doping reduces eddy current losses and makes them suitable for applications.

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