

Structural, Morphological, Optical and Magnetic Studies of Ce^{3+} Doped Zinc Spinel Nanoferrites for Photocatalytic Application

R.P. Panbude* and A.R. Bansod

Dr. Ambedkar College Deekshabhoomi, Nagpur, India

*Corresponding Author E-mail: rupalippanbude@gmail.com

K. G. Rewatkar

Vidya Viaks College, Samudrapur, India

E-mail: kgrewatkar@gmail.com

S. J. Dhoble

PGTD of Physics, RTM Nagpur University, Nagpur, India

E-mail: sjdhoble@gmail.com

(Received June 14, 2025, Accepted July 05, 2025)

Abstract: The present paper reports the effects of cerium (Ce) doping on structural, morphological, optical and magnetic properties of $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ ferrite nanoparticles (NPs) prepared via a microwave-assisted sol-gel technique. The crystalline structure, surface morphology, chemical composition, optical and magnetic features were characterised by powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray (EDAX), Fourier transform infrared spectroscopy (FT-IR), UV-visible (UV-vis) spectroscopy and vibrating sample magnetometer (VSM) individually. XRD patterns reveal the existence of single-phase cubic spinel structure with Fd-3m space group. Crystallite size of nanoferrites was calculated using Debye Sherrer formula, which was found to be in the range of 40-28nm. The Fourier transform infrared spectroscopy study showed the Fe-O stretching vibration in the range of $(400-700) \text{ cm}^{-1}$, confirming the formation of metal oxide. The change in optical band gap from 1.8 eV to 1.85 eV is due to the increased concentration of Ce content. Magnetic hysteresis (M-H) loops of samples were studied to determine saturation magnetization (M_s), remnant magnetization (M_r), Coercivity (H_c) values to study the magnetic nature of ferrite nanoparticles. The Photocatalytic activity against methylene blue is found to have 71% efficiency for ($x = 0.04$) Ce doped $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$. The synthesized samples are excellent photocatalytic agent against MB and are applicable in water treatment.

Keywords: Ferrites nanoparticles, Microwave assisted sol gel technique, magnetic properties.

1. Introduction

Currently, water pollution has emerged as a new environmental issue with the developing industrialization causing hazardous health effect on human-being and water bodies. Over the once many decades, numerous people used conventional natural and physical ways to remove the poisonous effluents present in wastewaters. But those ways proved to be hamstrung due to the generation of secondary adulterants and high energy consumption¹. Photocatalysis is visible light driven advanced oxidation, efficient, ecofriendly and cost-effective process and has attracted the researchers towards the photocatalyzed degradation of organic pollutants to a great extent². Photocatalysis technology has a huge potential in solving the water pollution problems because it is ecofriendly as it uses solar light, consume low energy, and show moderate catalytic efficiency. Nanotechnology has a potential for application in the field of environmental science and highly developed materials at nanoscale which can be used for the waste water treatment³.

Currently, ferrites have emerged as a new era in nanoscience and nanotechnology for their boundless effort in waste water treatment enhancing the photocatalytic activity. On the whole, ferrites are highly stable, cost-efficient and easily recyclable which is performing fine in photocatalytic methods on reducing dye concentration⁴. Normally, ferrites doped with transition metal like (Ni, Co, Zn, Cu, Mn) ferrites semiconducting materials enhance the photo-responsive behaviour⁵. Zinc ferrite has a narrow bandgap of ~ 1.9 eV and electronic structure which is distinctive in its all properties like electrical, magnetic, stability, physico-chemical and photo-response abilities that has been stated to exhibit a normal spinel structure, with Zn^{2+} occupying tetrahedral position and Fe^{3+} at octahedral sites, respectively⁶. Further to increase the visible light active properties, various factors like doping agent, sintering temperature, PH value, catalyst amount, experimental conditions are modified⁷.

Rare-earth-substituted ZnFe_2O_4 is a capable nanomaterial as a photocatalyst among all the materials. Keerthana et al synthesized Sm doped ZnFe_2O_4 by simple Coprecipitation method and showed better stability⁸ of removal of MB dye about 65%. P. Annie Vinosha et al synthesized recyclable Dysprosium (Dy) doped Zinc Ferrite (ZnFe_2O_4) by a facile co-precipitation technique and shown removal of MB dye with a 97.3% efficiency after 45

min⁹. Rare earth doping with the partial divalent substitution mostly improve magnetic and spinel catalytic performance¹⁰. Optimizing the substitution of rare earth metals like Cerium (Ce) enhance surface properties and create more active sites for catalyst to react with photons, develop electrical, optical, visible light-responsive and magnetic behaviour of host material¹¹. Our intent is to synthesize and characterize resultant Ce substituted ZnFe_2O_4 , further to explore the effect of Ce substitution enhanced photocatalytic dye degradation property for waste water treatment.

2. Experimental Details

a) Materials and Synthesis:

Ce substituted $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ where ($x=0, 0.02, 0.04, 0.06, 0.08, 0.1$) were synthesized by employing microwave assisted sol-gel method. Analytical grade metal nitrates were utilized. The ferrite materials were synthesized using the stoichiometric proportion of precursors, such as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACS, 98%), $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and urea in the form of fuel. Firstly, the metal nitrates were dissolved in minimum amount of distilled water separately. After that, the mixture of all the metal nitrates was heated up continuously for 4 Hrs on a hot plate until a gel formed. The prepared gel fired for 3 minutes in Microwave oven to have powered ash and crushed for 3 hrs. Calcination at constant temp of 800°C in muffle furnace for 4 hrs and further crushing for 2 hrs will give resultant brown product.

b) Characterisations studies:

Structural studies of spinel ($\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ where ($x=0, 0.02, 0.04, 0.06, 0.08, 0.1$) samples were executed using a Bruker AXS D8 Advance X-ray diffractometer (XRD) with $\text{CuK}\alpha$ radiation at $\lambda = 1.54060 \text{ \AA}$. Magnetic estimations were carried out at room temperature using a Lake Shore 7400 series model vibrating sample magnetometer (VSM) equipped with 1 T magnet. Morphological studies and energy dispersive X-ray analysis have been carried out with a Jeol 6390LA/OXFORD XMX N scanning electron microscope (SEM) equipped with electron dispersive X-ray (EDX) for elemental chemical analysis.

c) Photocatalytic studies:

In this study, Methylene Blue (MB) was used as target pollutant to assess the photocatalytic potential of as-synthesized ferrite samples. Hence, the degradation reaction for the removal of pollutant dye was carried out in a wooden box, containing the $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0, 0.02, 0.04, 0.06, 0.08, 0.1$) nanoparticles and MB dye, when exposed to visible light (using a 200Watt bulb). In the experiment, 100 mL of MB deionized solution (10 ppm) was

mixed with 0.1 g of catalyst. Adsorption- desorption equilibrium condition was attained by continuous stirring the mixed solution of catalyst and stock amount of dye using magnetic stirrer. After every 30 min of irradiation time interval, a 5ml of aliquot was removed. following equation was being used for the calculation of photocatalytic efficiency.

(1) Degradation efficiency(D%) = $\frac{Co-C}{Co} \times 100$

where Co and C are the concentration of MB dye at the time 0 and t time interval.

3. Results and discussion

a) XRD analysis

XRD patterns showed that $ZnCe_xFe_{2-x}O_4$ (x= 0,0.02,0.04,0.06,0.08,0.1) had cubic spinel structures, which is in agreement with the values reported in the database of $ZnFe_2O_4$ (JCPDS 22-1012). The nanocrystalline nature of the synthesized materials are shown by XRD graph. The average crystallite size, DXRD, for each sample was estimated from the most intense peak (311) as shown in fig 1 using Debye Scherrer’s formula

(2) $D = \frac{0.9\lambda}{\beta Cos\theta}$

where λ , k, β and θ wavelength of the X-ray (0.15060 nm), the Scherrer’s constant (k = 0.89), the full width at half maximum observed in radians and the maximum intensity peak’s diffraction angle. For evaluating the lattice constant (a) the formula was being used as

(3) $a = d (h^2 + k^2 + l^2)^{1/2}$

where d is the distance between h, k, l planes are Miller indices. The average crystallite size was found to decrease from 42 nm to 28 nm with increasing Ce^{3+} substitution. Retwield refinement for standard $ZnFe_2O_4$ material shows chi square value of 1.79 confirmed the formation of Zinc Ferrites.

Table1. showing different xrd parameter analysed from xrd graph and band gap from UV graph:

Sample ($ZnCe_xFe_{2-x}O_4$)	Crystallite size D (nm)	Lattice parameter a (Å)	dhkl	Band gap (eV)
$ZnFe_2O_4$	41.06	8.4129	2.53724	1.85
$ZnCe_{0.02}Fe_{1.98}O_4$	42.68	8.411	2.53611	1.83
$ZnCe_{0.04}Fe_{1.96}O_4$	36.12	8.422	2.53934	1.80
$ZnCe_{0.06}Fe_{1.94}O_4$	42.06	8.409	2.53552	1.82
$ZnCe_{0.08}Fe_{1.92}O_4$	39.21	8.414	2.53715	1.82
$ZnCe_{0.1}Fe_{1.9}O_4$	28.35	8.4189	2.53842	1.83

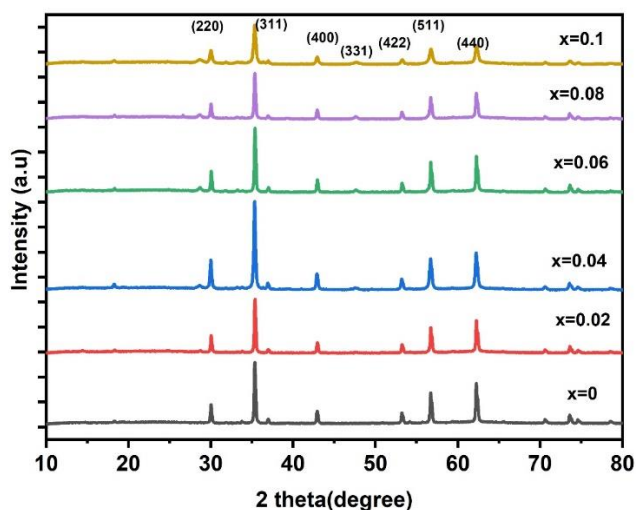


Figure 3.1: XRD analysis of $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ for ($x=0, 0.02, 0.04, 0.06, 0.08, 0.1$)

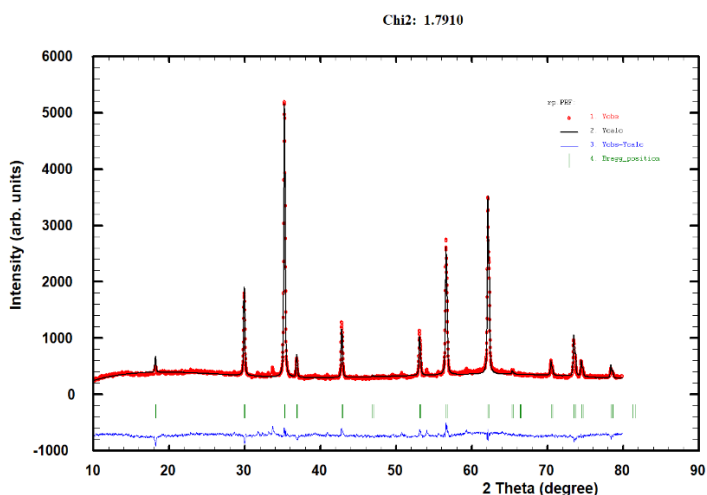


Figure 3.2: XRD graph and Rietveld refinement of ZnFe_2O_4 ($x=0$)

b) FTIR Analysis:

The FTIR spectra of Ce doped Zn ferrite magnetic nanoparticles are shown in Fig.3. Chemical structural changes occurring in the materials and the ionic positions can be investigated by Fourier transform infra-red spectroscopy. The synthesized Zinc ferrite magnetic nanoparticles exhibit two main vibration bands at 525–674 (ν_1) and at 382–394 (ν_2) cm^{-1} correlate with stretching vibration of M-O bond in tetrahedral and octahedral sites¹².

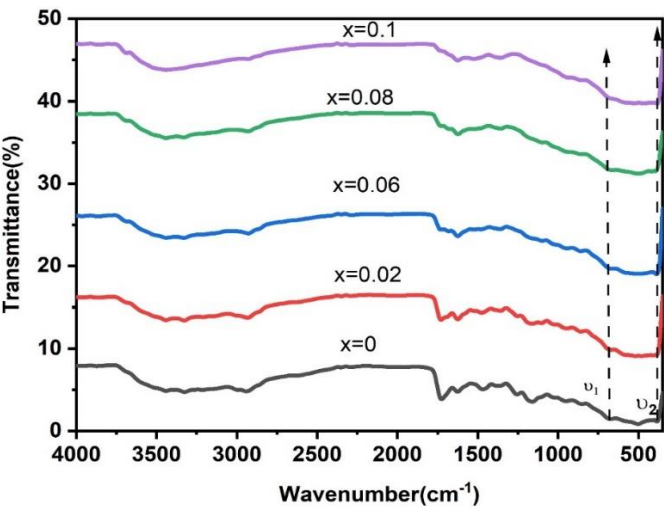
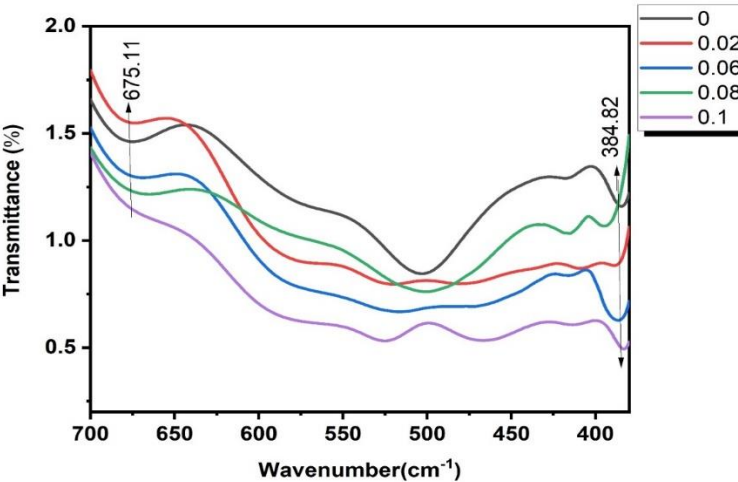


Figure 3.3: vibrational peaks of $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0$ to 0.1)



Figures 3.3 and 3.4: Vibrational peaks of $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0$ to 0.1)

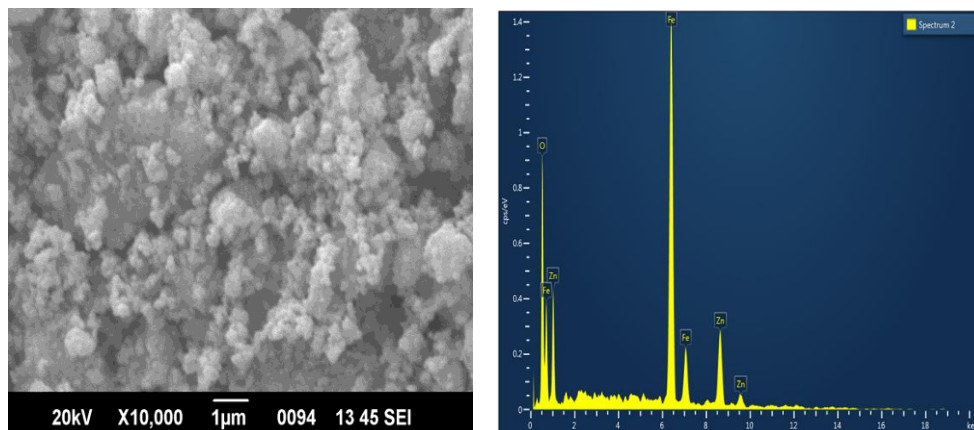
Table 2. showing different vibrational frequencies analysed from ftir graph:

Sample ($\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$)	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$
$(\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4)$	384.82	675.11
$\text{ZnCe}_{0.02}\text{Fe}_{1.98}\text{O}_4$	388.67	673.19
$\text{ZnCe}_{0.04}\text{Fe}_{1.96}\text{O}_4$	388.67	539
$\text{ZnCe}_{0.06}\text{Fe}_{1.94}\text{O}_4$	386.74	668
$\text{ZnCe}_{0.08}\text{Fe}_{1.92}\text{O}_4$	394.46	665.47
$\text{ZnCe}_{0.1}\text{Fe}_{1.9}\text{O}_4$	382.89	525.62

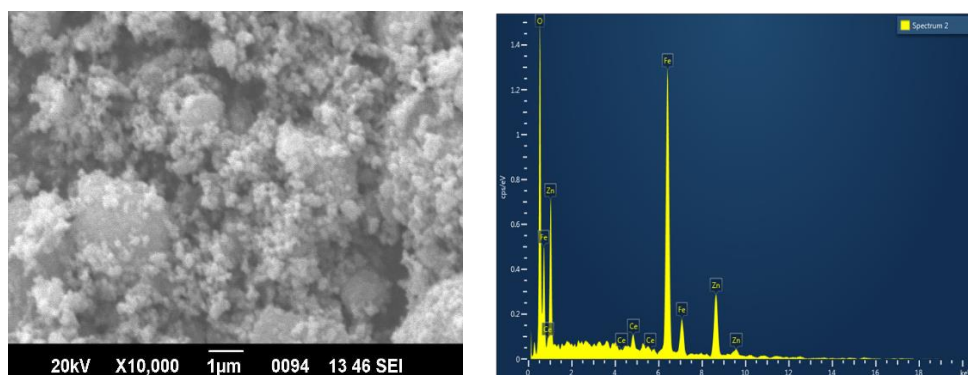
Impressions of Some peaks of metal-metal, H-O-H, also appeared in the FTIR Spectrum. The position and intensity of ν_1 and ν_2 tend for changing with increasing Ce^{3+} ions content. Lastly, the change of frequency confirms the presence of the Ce^{3+} ions which occupies the octahedral sites in the ferrites lattice. At last, the FTIR results confirmed the cubic spinel nature of ZnFe_2O_4 .

c) SEM-EDAX Analysis:

SEM images of spinel pure ZnFe_2O_4 and Ce doped $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.04$) NPs manufactured by microwave assisted sol gel technique as explained in the experimental part. Resulting products displays in self-assembled alongside forming regular aggregation demonstrated a spherical morphology and also shown coalescence and agglomerated grains. The agglomerated and spherical morphology were being observed in the different NPs. EDAX analysis confirms the elemental composition of Zn, Fe, O and Ce in the prepared resultant product.



Figures 3.5 and 3.6: SEM and EDAX images of $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles ($x=0$)



Figures 3.7 and 3.8: SEM and EDAX images of $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles ($x=0.04$)

d) UV Analysis:

The optical properties of the prepared series of Ce doped Zn Ferrite magnetic nanoparticles with different Ce^{3+} concentration was investigated by using UV-Vis spectroscopy.

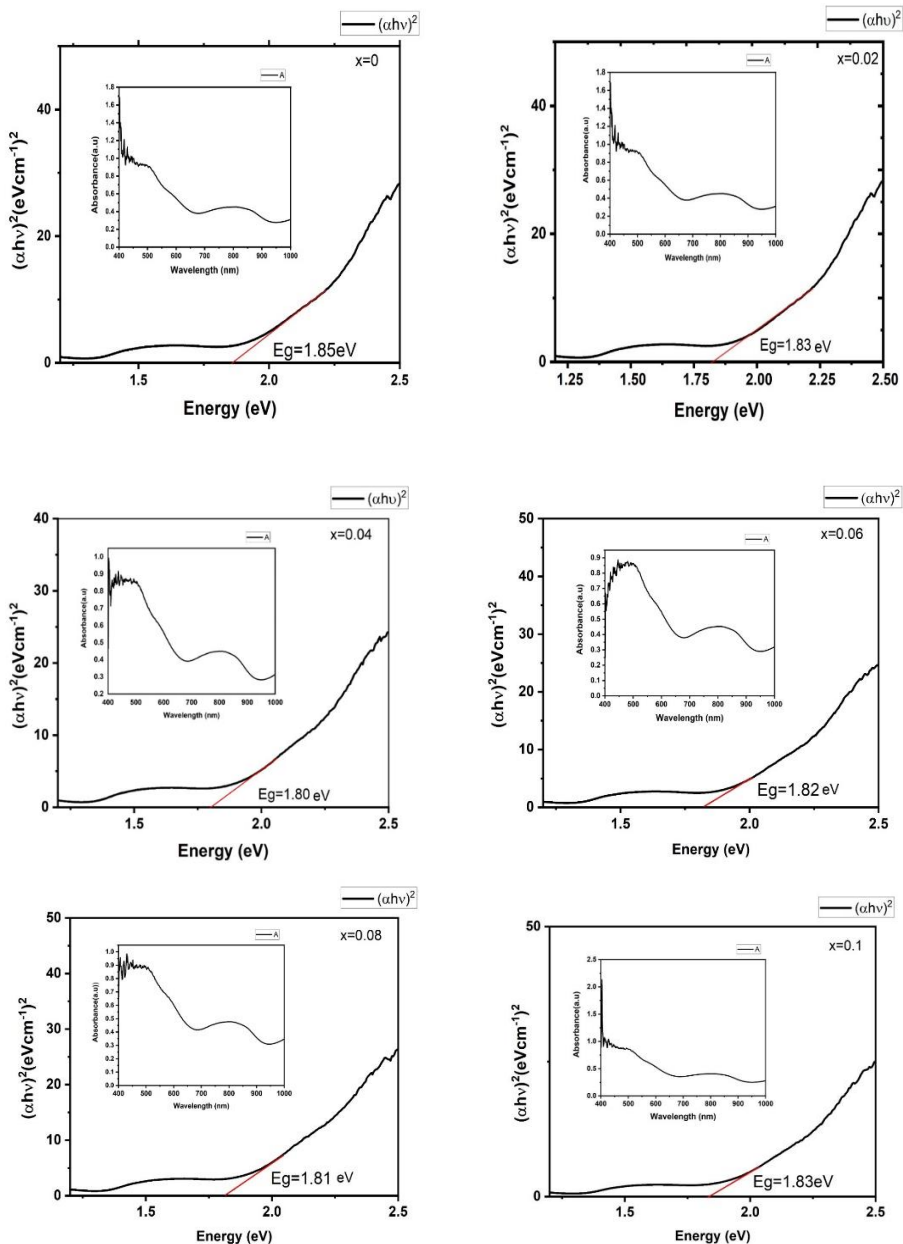


Figure 3.9: UV characterisation graphs for synthesised samples $\text{ZnCe}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0$ to 0.1)

UV spectroscopic absorbance data analysed and related Tauc plots were figure out, where X axis being interpreted as band gap E_g and $(\alpha h\nu)^2$ as Y axis. The samples were found to absorb visible light more efficiently. The bandgap (E_g) value of samples as prescribed in table1 characterized using Tauc plot¹³ is in the range (1.8-1.85) eV; a value of 1.85 eV was calculated for the pure an ZNF which is in close approximation to 1.9eV to act as a very good visible light active photocatalyst. Sample for $x = 0.04$ show comparably less value for energy band gap.

e) VSM Characterization:

Different magnetic parameters for $ZnFe_{2-x}O_4$ are calculated as shown in table (3), shows superparamagnetic nature with very low values of M_s , M_r , H_c and Squareness ratio¹⁴. All the parameters changes with a decreased order in some random manner. Very low calculated value of squareness ratio of less than 0.5 exhibit single domain nature.

Table 3: Analysis of magnetic parameters

Sample	M_s (emu/gm)	M_r (emu/gm)	H_c (Oe)	Squareness ratio
($x=0$)	4.058×10^{-2}	3.28×10^{-4}	55.51	0.00808
($x=0.02$)	4.43×10^{-2}	2.2×10^{-4}	48.38	0.00498
($x=0.04$)	4.68×10^{-2}	1.73×10^{-4}	41.79	0.00371
($x=0.06$)	4.09×10^{-2}	1.40×10^{-4}	42.48	0.00343
($x=0.08$)	2.46×10^{-2}	1.10×10^{-4}	61.64	0.00449
($x=0.1$)	2.99×10^{-2}	0.7×10^{-4}	27.33	0.00233

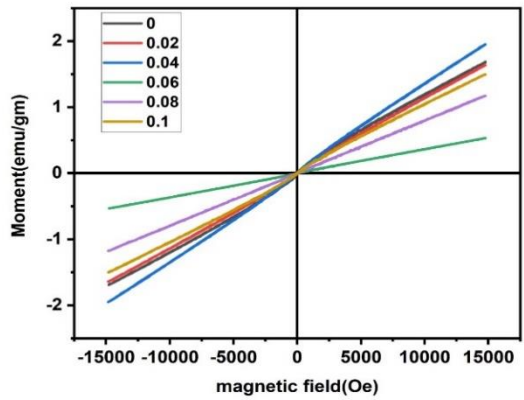


Figure 3.10: M-H Graph for VSM analysis

f) Photocatalytic Activity:

When $ZnFe_2O_4$ nanoparticles are doped with Ce^{3+} ions, their pollutant (MB) removal efficiency is enhanced. The higher photocatalytic performance at

higher Ce^{3+} introduced may be due to smaller crystallite sizes varying from 41 to 28 nm with increasing rare earth ions content. That would be increasing the surface area of the catalyst and number of active photocatalytic sites enhancing adsorption-desorption equilibrium process between catalyst and dye solution. Moreover, another effect is band gap energy value decreasing from 1.85 to 1.80 eV with increasing ions concentration, which aids the formation of hydroxyl (OH) active species at the surface of catalyst and stimulates oxidative degradation of dye molecules. The highest degradation efficiency and rate constant was found as 71% for sample $x = 0.04$. This phenomenon can rely on the combination of rare earth ions and metal ions in the crystal lattice of ferrite to generate the energy levels and the defects in crystal.

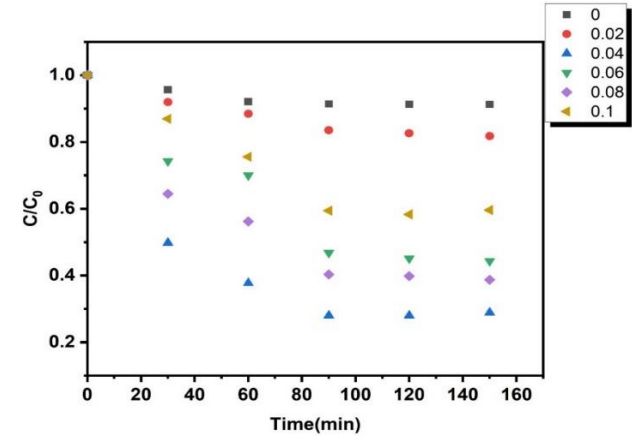


Figure 3.11: Graph of C/C_0 versus time of exposure(t) for $ZnCe_xFe_{2-x}O_4$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$)

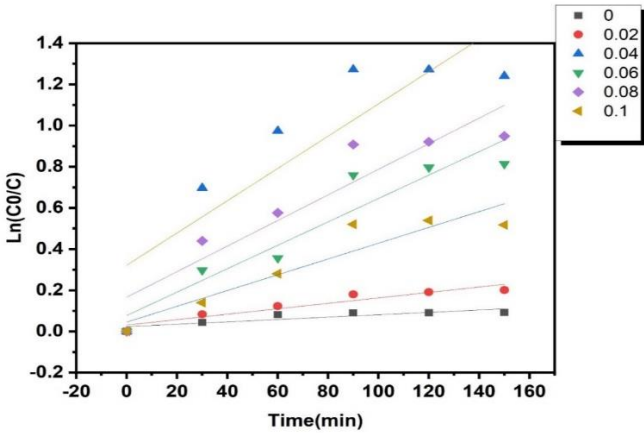


Figure 3.12: Graph of $\ln(C_0/C)$ versus irradiation time (t) for $ZnCe_xFe_{2-x}O_4$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1$)

Table 4: Degradation efficiency and pseudo first-order rate constant (k) for the photocatalytic degradation of MB in the presence of H₂O₂ 1% using ZnCe_xFe_{2-x}O₄

Sample (ZnCe _x Fe _{2-x} O ₄)	K (min ⁻¹)	R ²
x = 0	5.75688	0.75512
x = 0.02	0.00132	0.90233
x = 0.04	0.00383	0.88118
x = 0.06	0.00568	0.90057
x = 0.08	0.00621	0.86815
x = 0.1	0.00783	0.71689

4. Conclusion

Successful synthesis of Ce substituted ZnFe₂O₄ was completed using innovative microwave assisted sol gel technique. XRD confirmed the single-phase cubic spinel structure with highly intense plane peaked (2θ) at (311) for all the samples. SEM images displayed the agglomeration of the ferrite nanomaterials at nanoscale. FT-IR spectroscopy showed the stretching vibration of Fe and Zn metal ions at tetrahedral and octahedral sites which is consistent with spinel crystal structure of the synthesized ferrites. The present investigation highlighted the degradation of methylene blue dye using prepared Ce substituted zinc nanoferrites. Enhanced degradation efficiency was observed with an increase in the Ce concentration from (x = 0 to 0.1). Successful degradation of MB dye was adequately done at the rate of 0.00383min⁻¹ for x = 0.04 with a 71% efficiency at 150 min.

Acknowledgement: One of the authors RPB is thankful to the Mahatma Jyotiba Phule Research Fellowship, Government of Maharashtra, India (Ref. No. MAHAJYOTI/2022/Ph.D.Fellow/1002(814), dated 13/12/2022) for financial assistance and R.T.M. Nagpur University, Nagpur for constant encouragement.

References

1. A. Soufi, H. Hajjaoui, R. Elmoubarki, M. Abdennouri, S. Qourzal and N. Barka; Spinel ferrites nanoparticles: Synthesis methods and application in heterogeneous Fenton oxidation of organic pollutants - A review, *Applied Surface Science Advances*, 6, (2021). doi: 10.1016/j.apsadv.2021.100145
2. B. Ohtani; Revisiting the fundamental physical chemistry in heterogeneous photocatalysis: Its thermodynamics and kinetics, *Physical Chemistry Chemical Physics*, 16(5) (2014), 1788-1797. doi: 10.1039/c3cp53653j.
3. A. Rahman, M. F. Warsi, I. Shakir, M. Shahid and S. Zulfikar; Fabrication of Ce³⁺ substituted nickel ferrite-reduced graphene oxide heterojunction with high photocatalytic activity under visible light irradiation, *J Hazard Mater*, 394 (2020). doi: 10.1016/j.jhazmat.2020.122593.

4. T. Dippong, E. A. Levei, and O. Cadar; Recent advances in synthesis and applications of MFe_2O_4 (M = Co, Cu, Mn, Ni, Zn) nanoparticles, *Nanomaterials*, 11(6) (2021). doi: 10.3390/nano11061560.
5. A. Sutka, M. Millers, M. Vanags, U. Joost, M. Maiorov, V. Kisand, R. Pärna, and I. Juhnevica; Comparison of photocatalytic activity for different co-precipitated spinel ferrites, *Research on Chemical Intermediates*, 41(12) (2015), 9439-9449. doi: 10.1007/s11164-015-1969-6.
6. M. Qin, Q. Shuai, G. Wu, B. Zheng, Z. Wang and H. Wu; Zinc ferrite composite material with controllable morphology and its applications, *Materials Science and Engineering: B*, 224 (2017), 125-138. doi: 10.1016/j.mseb.2017.07.016.
7. L.T.T. Nguyen, L.T.H. Nguyen, N.C. Manh, D.N. Quoc, H.N. Quang, H.T.T. Nguyen, D.C. Nguyen and L.G. Bach; A facile synthesis, characterization, and photocatalytic activity of magnesium ferrite nanoparticles via the solution combustion method, *J Chem*, (2019). doi: 10.1155/2019/3428681.
8. S.P. Keerthana, R. Yuvakkumar, P.S. Kumar, G. Ravi and D. Velauthapillai; Rare earth metal (Sm) doped zinc ferrite (ZnFe_2O_4) for improved photocatalytic elimination of toxic dye from aquatic system, *Environ Res*, 197 (2021). doi: 10.1016/j.envres.2021.111047.
9. P.A. Vinosha, J.V.A. Vinsla, J. Madhavan, S. Devanesan, M.S. AlSalhi, M. Nicoletti and B. Xavier; Impact of dysprosium doped (Dy) zinc ferrite (ZnFe_2O_4) nanocrystals in photo-fenton exclusion of recalcitrant organic pollutant, *Environ Res*, 203 (2022). doi: 10.1016/j.envres.2021.111913.
10. S. A. Jadhav, S. B. Somvanshi, S. S. Gawali, K. Zakde and K. M. Jadhav; Rare earth-doped mixed Ni–Cu–Zn ferrites as an effective photocatalytic agent for active degradation of Rhodamine B dye, *Journal of Rare Earths*, 42-3 (2024), 488-496. doi: 10.1016/j.jre.2023.03.004.
11. K. N. Harish, H. S. Bhojya Naik, P. N. Prashanth Kumar and R. Viswanath; Optical and photocatalytic properties of solar light active Nd-substituted Ni ferrite catalysts: For environmental protection, *ACS Sustain Chem Eng*, 1-9 (2013), 1143-1153. doi: 10.1021/sc400060z.
12. D. Chahar, S. Taneja, S. Bisht, S. Kesarwani, P. Thakur, A. Thakur and P.B. Sharma; Photocatalytic activity of cobalt substituted zinc ferrite for the degradation of methylene blue dye under visible light irradiation, *J Alloys Compd*, 851 (2021). doi: 10.1016/j.jallcom.2020.156878.
13. P. Ajithkumar, S. Mohana and S. Sumathi; Synthesis, characterization, optical and photocatalytic activity of yttrium and copper co-doped zinc ferrite under visible light, *Journal of Materials Science: Materials in Electronics*, 31-2 (2020), 1168-1182. doi: 10.1007/s10854-019-02628-8.
14. T. Theivasanthi and M. Alagar; Innovation of Superparamagnetism in Lead Nanoparticles, *Physics and Technical Sciences*, 1(3) (2013), 39-45.