

Effect of Ca Doping on the Structural, Morphological, and Optical Properties of Nano-crystalline MnFe_2O_4 Spinel Ferrite

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Abstract: In the present study, undoped and 3% Ca-doped MnFe_2O_4 nanoparticles were synthesized via the sol-gel auto-combustion method and characterized using XRD, Raman spectroscopy, FESEM, and UV-Vis spectroscopy. XRD confirmed the formation of a single-phase cubic spinel structure, while Ca doping induced crystallite size reduction and increased lattice strain. Raman spectra exhibited a shift of characteristic vibrational modes toward lower wavenumbers, suggesting modifications in the local bonding environment and cation distribution. FESEM observations revealed a reduction in particle size upon Ca incorporation. Optical studies showed a significant decrease in the band gap upon Ca incorporation, attributed to defect-induced electronic states and altered metal-oxygen interactions. The observed crystallite size reduction, strain enhancement, Raman band shift, and band-gap narrowing demonstrate that low-level Ca doping effectively tailors the physicochemical properties of MnFe_2O_4 , highlighting its potential for advanced photocatalytic and optoelectronic applications.

Key words: MnFe_2O_4 nanoparticles, Ca-doping, Spinel ferrite, Sol-gel auto-combustion.

1 Introduction

Spinel ferrites are a fascinating group of magnetic oxide materials, generally represented by the formula $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$. In these materials, A^{2+} and B^{3+} cations settle into the tetrahedral (A) and octahedral (B) sites of a cubic lattice, each playing a unique role. The way these cations are arranged and how many of each type are present can greatly influence the material's structural, magnetic, electrical, and optical behavior. By carefully swapping out different cations, scientists can fine-tune spinel ferrites to meet the needs of a wide range of technologies [1], [2].

MnFe_2O_4 , one of the spinel ferrites, has drawn a lot of interest because it's stable, affordable, and has a variety of useful properties. The way it's structured and its magnetic and optical traits depend heavily on how it's made and the arrangement

of its cations. This is why researchers are exploring how adding different ions to its framework can tweak its crystal structure and enhance its performance for various applications [3], [4].

Doping of alkaline earth metal ions into ferrite lattices has emerged as an effective strategy for tuning their functional properties. In particular, Ca^{2+} ions are expected to induce significant modifications in the structural and magnetic behaviour of MnFe_2O_4 owing to their larger ionic radius compared with Mn^{2+} ions. Calcium substitution can influence lattice parameters, crystallite size, cation redistribution, and magnetic exchange interactions, thereby altering the overall performance of the material. Previous studies have demonstrated that Ca incorporation can effectively modify the magnetic and catalytic properties of manganese ferrites [5], [6].

Among the various synthesis techniques

available for ferrite nanoparticles, the sol-gel method is widely preferred because of its simplicity, low processing temperature, excellent compositional homogeneity, and ability to produce nanoparticles with controlled size and morphology. Therefore, in the present work, $\text{Mn}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ nanoparticles were synthesized using the sol-gel route, and the influence of Ca substitution on their structural, morphological, and optical properties was systematically investigated [7], [8].

2 Experimental

2.1 Synthesis

Nano-crystalline $\text{Mn}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x = 0.00$ and 0.03) spinel ferrites were prepared via citric acid-assisted sol-gel auto-combustion method. For the preparation of 5 g of undoped MnFe_2O_4 sample, 5.55 g of manganese(II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 50 ml of deionized water and magnetically stirred at room temperature until a homogeneous solution was obtained. In parallel, 17.87 g of iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and 12.56 g of citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were each dissolved separately in 100 ml of deionized water under continuous stirring at room temperature to obtain homogeneous solutions. The separately prepared homogeneous solutions were mixed and subsequently heated at 90°C under continuous magnetic stirring, leading to gradual solvent evaporation and the formation of a uniform viscous gel. The obtained gel was heated in an oven at 110°C until the initiation of auto-combustion. The resulting product was gently ground using a mortar and pestle to obtain fine and uniform MnFe_2O_4 nano powder.

For the preparation of 5 g of

$\text{Mn}_{0.97}\text{Ca}_{0.03}\text{Fe}_2\text{O}_4$ sample, 5.39 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.16 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved separately in 50 ml of deionized water. In addition, 17.91 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 12.58 g $\text{C}_6\text{H}_8\text{O}_7$ were individually dissolved in 100 ml of deionized water. The resulting solutions were then processed following the same sol-gel synthesis procedure employed for the preparation of the undoped MnFe_2O_4 sample.

The obtained samples were calcined at 400°C for 3 h to improve crystallinity, followed by grinding into fine powders for subsequent characterization.

2.2 Characterization details

The structural properties of the undoped and 3% Ca-doped MnFe_2O_4 were investigated using Bruker AXE D8 X-Ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The obtained diffraction patterns were used to determine phase purity, crystallite size, and lattice parameters.

The vibrational properties and phase confirmation of $\text{Mn}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x = 0.00$, and $x = 0.03$) samples were examined using an HR 800 Jobin-Yvon spectrometer equipped with a 50X objective.

The surface morphology and microstructural features of both samples were examined using Field Emission Scanning Electron Microscopy (FESEM, SIGMA 300 of Carl Zeiss Microscopy, Hamburg, Germany).

The optical properties were evaluated using UV-Visible spectroscopy (SHIMADZU UV-1800 Spectrometer).

3 Results and discussion

3.1 Structural analysis

undoped and Ca-doped manganese ferrite, $\text{Mn}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x = 0.00$ and 0.03), recorded in the 2θ range of 15° – 80° , are shown in Fig. 1.

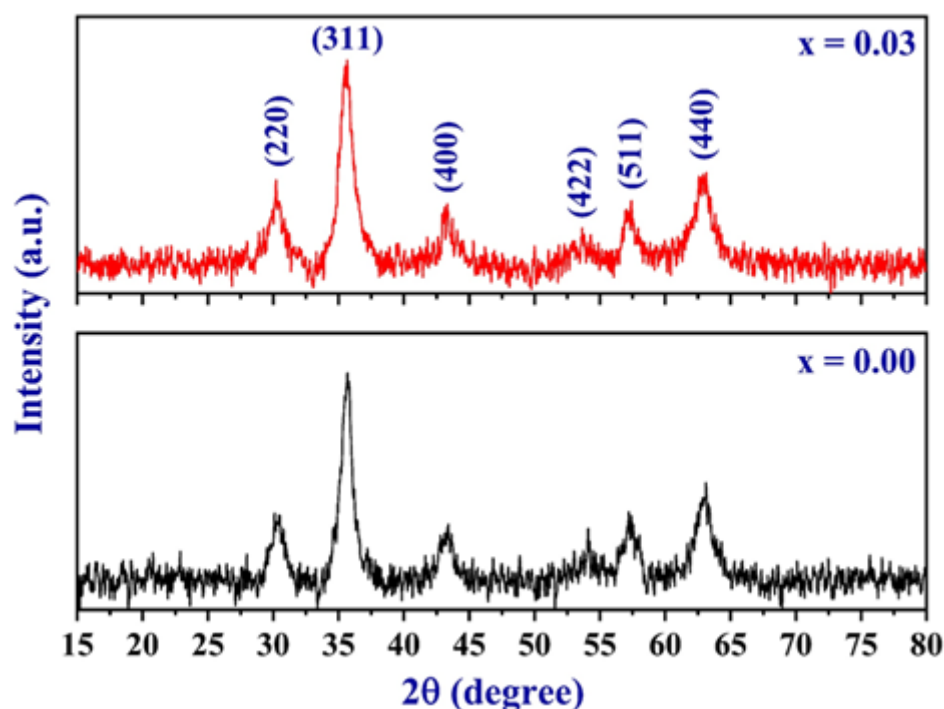


Figure 1: XRD patterns of undoped and 3% Ca-doped MnFe_2O_4 nanoparticles.

The patterns exhibit well-defined and sharp diffraction peaks at 2θ values of approximately 30.33° , 35.62° , 43.25° , 54.11° , 57.32° , and 62.96° , which can be indexed to the (220), (311), (400), (422), (511), and (440) crystallographic planes of the

cubic spinel structure. All the observed reflections are in close agreement with the standard JCPDS card no. 74-2403 [4], [9], confirming the formation of single-phase MnFe_2O_4 without any detectable secondary phases.

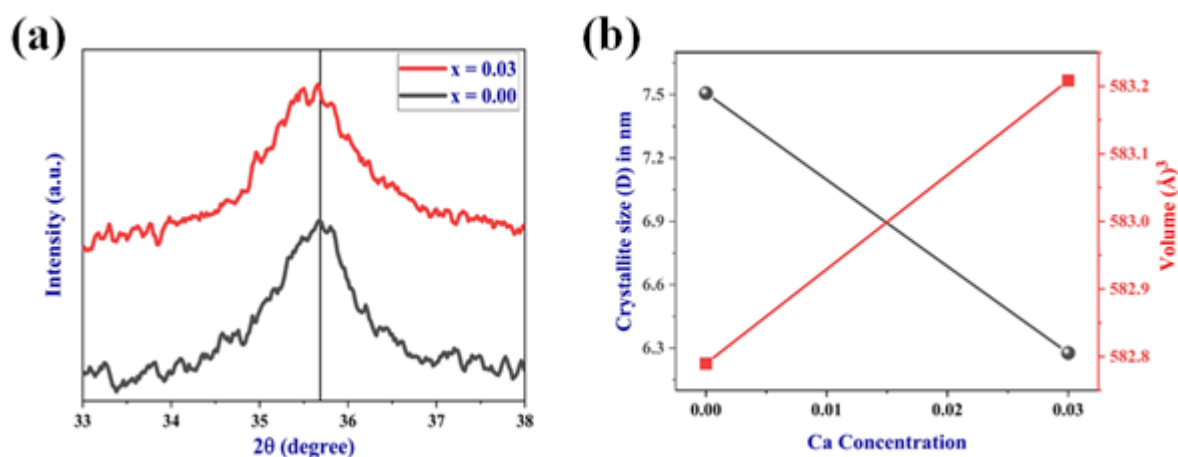


Figure 2: (a) Shift of the most intense diffraction peak, (b) crystallite size and unit cell volume of undoped, and 3% Ca-doped MnFe_2O_4 nanoparticles.

Furthermore, as shown in Fig. 2, the most intense diffraction peak corresponding to the plane (311) exhibits a slight shift towards the lower 2θ values in the Ca-doped sample compared to the undoped one. This shift confirms the successful incorporation of Ca into the spinel lattice without altering the overall crystal structure.

The average crystallite size was calculated using the Debye–Scherrer formula.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the average crystallite size (nm), k is the shape factor (≈ 0.9), λ is the X-ray wavelength of Cu-K α radiation (1.5406 Å), β represents the full width at half maximum (in radians), and θ is the Bragg diffraction angle.

The interplanar spacing (d) was calculated by using Bragg's law:

$$d = \frac{\lambda}{2\sin\theta} \quad (2)$$

The lattice parameter a of the cubic spinel structure was calculated using the relation:

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (3)$$

The unit cell volume (V) for the cubic spinel structure was calculated using the relation:

$$V = a^3 \quad (4)$$

The microstrain (ε) present in the crystal lattice was calculated using the relation:

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (5)$$

Table 1: XRD-derived structural parameters for undoped and Ca-doped MnFe₂O₄ nanoparticles.

Mn _{1-x} Ca _x Fe ₂ O ₄	β (rad)	Crystallite size, D (nm)	d -spacing (Å)	Lattice parameter, $a = b = c$ (Å)	Volume, a^3 (Å ³)	Microstrain, ε
$x = 0.00$	0.0194	7.507	2.5185	8.3529	582.7897	0.015096
$x = 0.03$	0.0232	6.277	2.5191	8.3549	583.2083	0.018059

Ca substitution in MnFe₂O₄ leads to a noticeable increase in FWHM and microstrain, accompanied by a reduction in crystallite size and an increase in unit cell volume. The decrease in crystallite size suggests that Ca substitution suppresses crystal growth due to lattice distortion. The observed increase in lattice parameter and corresponding unit cell volume arises from the substitution of Mn²⁺ ions (ionic radius ≈ 0.83 Å) by larger Ca²⁺ ions (≈ 1.00 Å), leading to expansion of the spinel lattice. This lattice expansion is consistent with the shift of diffraction peaks towards lower 2θ values in accordance with Bragg's law [10], [11]. Furthermore, the increase in microstrain reflects the presence of significant lattice distortion arising from the ionic size mismatch between Ca²⁺ and Mn²⁺ ions. The substitution of larger Ca²⁺ ions induces

local strain fields and structural imperfections within the spinel lattice, which contribute to peak broadening and an increase in defect density.

The combined effects of lattice expansion, reduced crystallite size, and enhanced strain clearly demonstrate that Ca incorporation alters the structural characteristics of MnFe₂O₄ by introducing lattice distortion and suppressing crystallite growth, without altering the fundamental cubic spinel framework.

3.2 Raman analysis

Fig. 3 shows the Raman spectra in the wavenumber range of 175 to 700 cm⁻¹ at room temperature of samples Mn_{1-x}Ca_xFe₂O₄ ($x = 0.00$ and $x = 0.03$), fitted using Lorentzian functions.

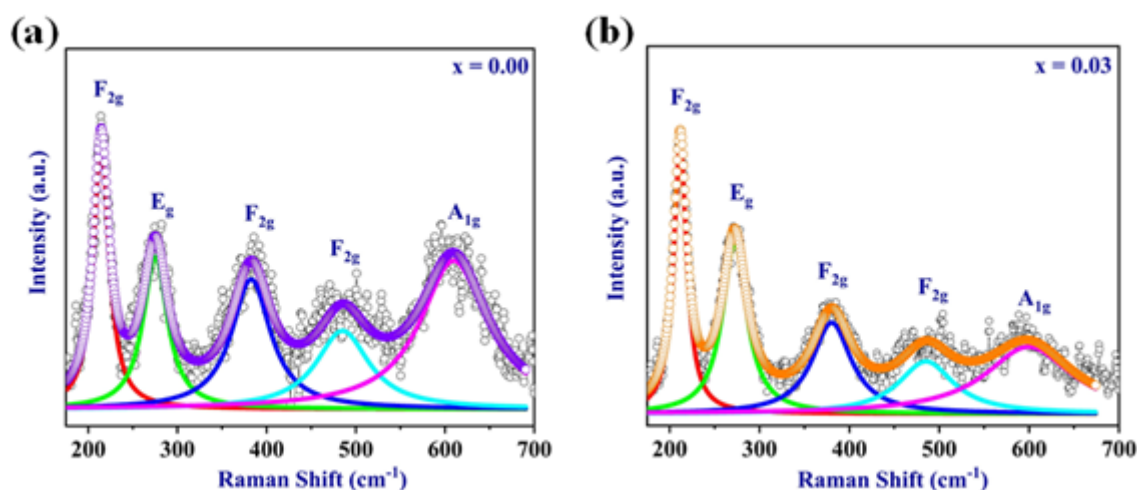


Figure 3: Raman spectrum of (a) undoped and (b) 3% Ca-doped MnFe_2O_4 nanoparticles.

The Raman spectra of both samples exhibit five well-defined vibrational peaks, which are characteristic of the spinel ferrite structure with Fd-3m space group, corresponding to A_{1g} , E_g , and $3F_{2g}$ Raman-active modes [12], [13], [14].

For the undoped MnFe_2O_4 sample ($x = 0.00$), these Raman-active modes are observed at 214 cm^{-1} (F_{2g}), 275 cm^{-1} (E_g), 382 cm^{-1} (F_{2g}), 486 cm^{-1} (F_{2g}), and 608 cm^{-1} (A_{1g}), which closely match the earlier reports on MnFe_2O_4 spinel structure, indicating the successful formation of the desired phase.

For the Ca-doped MnFe_2O_4 sample ($x = 0.03$), these modes are observed at 212 cm^{-1} (F_{2g}), 271 cm^{-1} (E_g), 380 cm^{-1} (F_{2g}), 485 cm^{-1} (F_{2g}), 597 cm^{-1} (A_{1g}). The Raman spectra of the Ca-doped MnFe_2O_4 sample exhibit a noticeable shift toward the lower wavenumber (red-shift) region compared to the undoped sample; however, the presence of all characteristic vibrational modes confirms that the fundamental crystal structure remains preserved upon Ca substitution.

In pure MnFe_2O_4 , a partially inverse spinel structure is formed, where Mn^{2+} ions predominantly occupy tetrahedral (A) sites, while Fe^{3+} ions are distributed between both tetrahedral and octahedral (B) sites. A small fraction of Mn^{2+} also resides at

B-sites due to partial inversion.

Upon Ca^{2+} substitution at the Mn site, a significant modification in cation distribution occurs due to the larger ionic radius of Ca^{2+} ($\sim 1.00 \text{ \AA}$) compared to Mn^{2+} ($\sim 0.83 \text{ \AA}$ in octahedral coordination). Due to its larger ionic radius and its preference for higher coordination, Ca^{2+} ions preferentially occupy the octahedral (B) sites rather than the tetrahedral sites. This results in a decrease in Mn^{2+} occupancy at B-sites and a relative increase in Fe^{3+} migration toward tetrahedral sites to maintain structural stability. The incorporation of Ca^{2+} induces lattice expansion and distorts the octahedral framework, weakening the metal-oxygen bonds and reducing the bond force constant. Consequently, the vibrational frequencies of the lattice decrease, giving rise to a systematic red shift in the Raman spectra without altering the fundamental spinel structure.

3.3 Surface morphological analysis by FESEM

The surface morphology of the undoped and 3% Ca-doped MnFe_2O_4 samples was examined using field emission scanning electron microscopy (FESEM). The corresponding FESEM micrographs in Fig. 4(a) and (b) exhibit significant differences in surface morphology between the two samples.

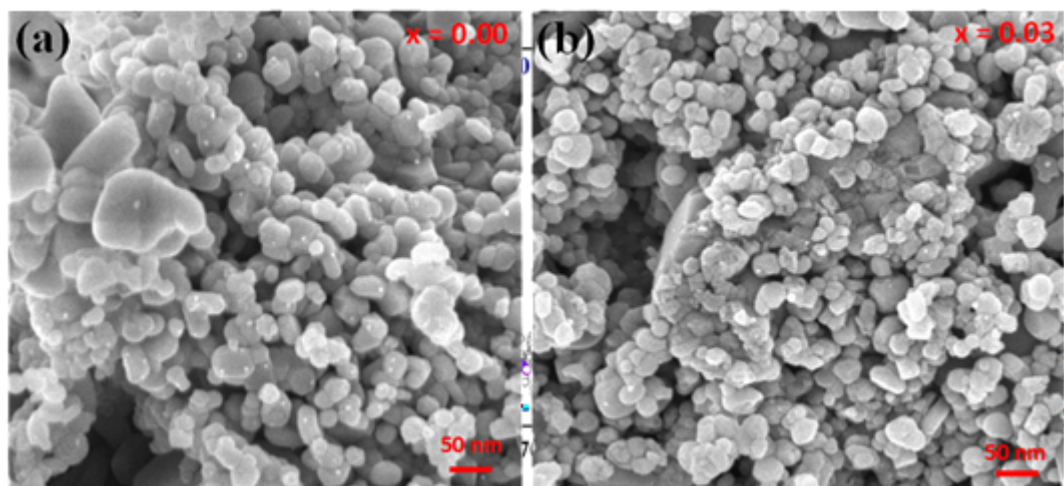


Figure 4: FESEM images of (a) undoped and (b) 3% Ca-doped MnFe_2O_4 nanoparticles.

The undoped MnFe_2O_4 sample exhibits a comparatively larger particle size with a compact and clustered morphology. In contrast, the 3% Ca-doped sample shows a significant reduction in particle size along with a more porous and loosely packed structure. This variation in morphology can be attributed to the incorporation of Ca^{2+} ions, which induce lattice distortion and hinder the normal grain growth process during synthesis. Consequently, the suppression of particle growth leads to finer particles

and enhanced porosity, which in turn increases the effective surface area and the availability of active sites.

3.4 UV-Visible Absorption and Optical Band Gap Analysis

Fig. 5(a) displays the UV-Visible absorption spectra for undoped and 3% Ca-doped MnFe_2O_4 nanoparticles measured over the 200–1000 nm wavelength range. Fig. 5(b) presents the corresponding Tauc plots.

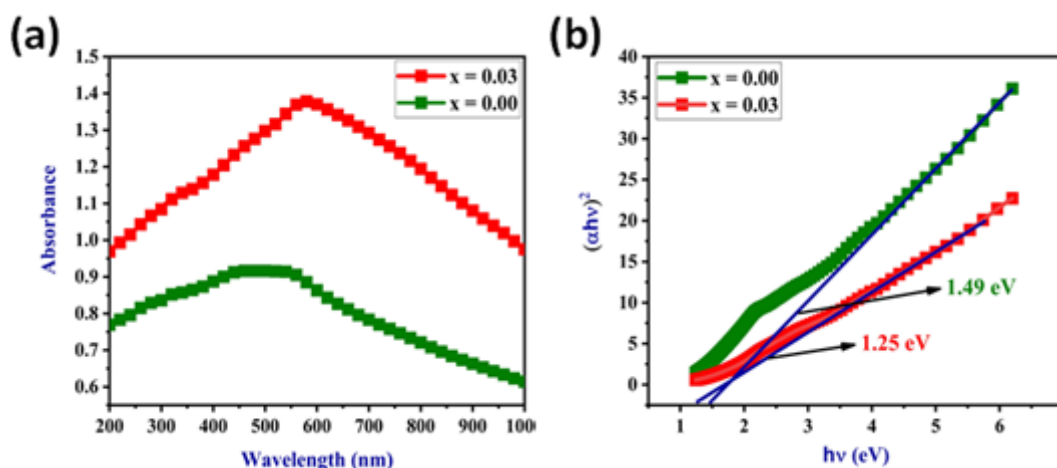


Figure 5: (a) UV-Visible absorption spectra and (b) corresponding Tauc plots of undoped and 3% Ca-doped MnFe_2O_4 nanoparticles.

Both samples exhibit strong absorption in the visible region, confirming their semi-conducting nature [15]. The Ca-doped sample shows a noticeable enhancement in absorption intensity, indicating higher photon absorption compared to the undoped sample. In MnFe_2O_4 , Mn^{2+} ions preferentially occupy the tetrahedral (A) sites, and their substitution by larger Ca^{2+} ions introduces lattice distortion and local structural disorder. This substitution modifies the $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ and $\text{Mn}^{2+}\text{-O}^{2-}\text{-Fe}^{3+}$ superexchange interactions, leading to changes in the electronic structure and enhanced charge transfer transitions. Consequently, the increased density of localized states and improved orbital overlap enhance the probability of photon-induced electronic transitions, resulting in stronger absorption.

The optical band gap of undoped and 3% Ca-doped MnFe_2O_4 nanoparticles was determined using the Tauc relation

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (6)$$

Where α is the absorption coefficient, $(h\nu)$ is the photon energy, (A) is a constant, and (E_g) is the optical band gap. The (E_g) values were obtained by extrapolating the linear region of the $(\alpha h\nu)^2$ versus $(h\nu)$ plot to the photon energy axis. As shown in Fig. 5(b), the optical band gap decreases from 1.49 eV for the undoped MnFe_2O_4 sample to 1.25 eV for 3% Ca-doped MnFe_2O_4 sample, indicating that Ca incorporation modifies the electronic structure and narrows the band gap.

The presence of Ca^{2+} modifies the local electronic environment and promotes the formation of defect states within the band structure. These defect levels serve as intermediate energy states, thereby narrowing the energy gap between the valence and conduction bands. Additionally, cation redistribution between tetrahedral and octahedral sites alters the Fe-O-Fe and Mn-O-Fe superexchange interactions, further influencing the electronic band structure. As a result, the Ca-doped MnFe_2O_4 sample exhibits enhanced electronic transitions at

lower photon energies, leading to the observed decrease in optical band gap.

4 Conclusion

Undoped and 3% Ca-doped MnFe_2O_4 nanoparticles were successfully synthesized via the sol-gel auto-combustion method. Ca incorporation preserved the single-phase spinel structure while reducing the crystallite size from 7.507 to 6.277 nm and increasing the lattice strain from 0.015096 to 0.018059. The Raman red shift and FE-SEM results confirmed lattice distortion and particle-size reduction induced by Ca substitution. Furthermore, the significant decrease in optical band gap from 1.49 to 1.25 eV demonstrates effective band-gap engineering and enhanced visible-light absorption.

The synthesized Ca-doped MnFe_2O_4 nanoparticles show enhanced structural and optical properties, particularly a decreased optical bandgap that may improve visible-light absorption. These characteristics indicate that the material has potential for photocatalytic applications, such as the degradation of organic pollutants in wastewater. Further studies will be conducted to evaluate its photocatalytic performance.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] S. J. Salih and W. M. Mahmood, "Review on magnetic spinel ferrite (MFe₂O₄) nanoparticles: From synthesis to application," *Heliyon*, vol. 9, no. 6, p. e16601, Jun. 2023, doi: 10.1016/j.heliyon.2023.e16601.
- [2] T. Vigneswari and P. Raji, "Structural and magnetic properties of calcium doped nickel ferrite nanoparticles by co-precipitation method," *J. Mol. Struct.*, vol. 1127, pp. 515–521, Jan. 2017, doi: 10.1016/j.molstruc.2016.07.116.
- [3] S.-W. Lee, J.-G. Lee, K.-P. Chae, W.-H. Kwon, and C.-S. Kim, "Superparamagnetic Properties of MnFe₂O₄ Nanoparticles," *J. Korean Magn. Soc.*, vol. 19, no. 2, pp. 57–61, Apr. 2009, doi: 10.4283/JKMS.2009.19.2.057.
- [4] K. Islam, M. Haque, A. Kumar, A. Hoq, F. Hyder, and S. M. Hoque, "Manganese Ferrite Nanoparticles (MnFe₂O₄): Size Dependence for Hyperthermia and Negative/Positive Contrast Enhancement in MRI," *Nanomaterials*, vol. 10, no. 11, p. 2297, Nov. 2020, doi: 10.3390/nano10112297.
- [5] Z. Iqbal, S. Sadiq, M. Sadiq, M. Ali, K. Saeed, N. U. Rehman, M. Ilyas, S. Ullah, S. U. Jan, I. Ahmad, and M. H. Shah, "Synergetic Effect of Calcium Doping on Catalytic Activity of Manganese Ferrite: DFT Study and Oxidation of Hydrocarbon," *Crystals*, vol. 10, no. 4, p. 335, Apr. 2020, doi: 10.3390/cryst10040335.
- [6] R. G. D. Andrade, D. Ferreira, S. R. S. Veloso, C. Santos-Pereira, E. M. S. Castanheira, M. Côrte-Real, and L. R. Rodrigues, "Synthesis and Cytotoxicity Assessment of Citrate-Coated Calcium and Manganese Ferrite Nanoparticles for Magnetic Hyperthermia," *Pharmaceutics*, vol. 14, no. 12, p. 2694, Dec. 2022, doi: 10.3390/pharmaceutics14122694.
- [7] S. V. Bhandare, R. Kumar, A. V. Anupama, H. K. Choudhary, V. M. Jali, and B. Sahoo, "Annealing temperature dependent structural and magnetic properties of MnFe₂O₄ nanoparticles grown by sol-gel auto-combustion method," *J. Magn. Mater.*, vol. 433, pp. 29–34, Jul. 2017, doi: 10.1016/j.jmmm.2017.02.040.
- [8] S. E. Shirsath, S. S. Jadhav, M. L. Mane, and S. Li, "Ferrites Obtained by Sol–Gel Method," in *Handbook of Sol-Gel Science and Technology*, L. Klein, M. Aparicio, and A. Jitianu, Eds., Cham: Springer International Publishing, 2018, pp. 1–40. doi: 10.1007/978-3-319-19454-7_125-2.
- [9] A. Mary Jacintha, V. Umapathy, P. Neeraja, and S. Rex Jeya Rajkumar, "Synthesis and comparative studies of MnFe₂O₄ nanoparticles with different natural polymers by sol–gel method: structural, morphological, optical, magnetic, catalytic and biological activities," *J. Nanostructure Chem.*, vol. 7, no. 4, pp. 375–387, Dec. 2017, doi: 10.1007/s40097-017-0248-z.
- [10] S. D. Chhaya, M. P. Pandya, M. C. Chhantbar, K. B. Modi, G. J. Baldha, and H. H. Joshi, "Study of substitution limit, structural, bulk magnetic and electrical properties of Ca²⁺ substituted magnesium ferrite," *J. Alloys Compd.*, vol. 377, no. 1–2, pp. 155–161, Sep. 2004, doi: 10.1016/j.jallcom.2003.11.151.
- [11] M. Ustundağ and M. Aslan, "Electronic and Magnetic Properties of Ca-Doped Mn-Ferrite," *Acta Phys. Pol. A*, vol. 130, no. 1, pp. 362–364, Jul. 2016, doi: 10.12693/APhysPolA.130.362.
- [12] O. Yamashita and T. Ikeda, "Effect of polishing stress on Raman spectra of the Mn–Zn ferrite," *J. Appl. Phys.*, vol. 95, no. 4, pp. 1743–1748, Feb. 2004, doi: 10.1063/1.1641522.
- [13] Z. Ž. Lazarević, Č. Jovalekić, A. Recnik, V. N. Ivanovski, M. Mitrić, M. J. Romčević, N. Paunović, B. . Cekić, and N. Ž. Romčević, "Study of manganese ferrite powders prepared by a soft mechanochemical route," *J. Alloys Compd.*, vol. 509, no. 41, pp. 9977–9985, Oct. 2011, doi: 10.1016/j.jallcom.2011.08.004.
- [14] K. P. Remya, R. Rajalakshmi, and N. Ponpandian, "Development of BiFeO₃ /MnFe₂O₄ ferrite nanocomposites with enhanced magnetic and electrical properties," *Nanoscale Adv.*, vol. 2, no. 7, pp. 2968–2976, 2020, doi: 10.1039/D0NA00255K.
- [15] E. C. Devi and I. Soibam, "Structural and optical characterization of MnFe₂O₄ nanoparticles," *Adv. Mater. Proc.*, vol. 2, no. 2, pp. 93–96, Dec. 2021, doi: 10.5185/amp.2017/206.