Indian Journal of
Modern Research and Reviews
This Journal is a member of the *'Committee on Publication Ethics'*
Online ISSN: 2584-184X

Research paper

Multiferroic Photocatalysts: A Density Functional Theory Study of Electronic and Optical Properties

Saurabh Kundu [1*], Dr. Manpreet Kaur [2]
[1] Research Scholar, Department of Physics, IEC University, Baddi, Himachal Pradesh, India
[2] Assistant Professor, Department of Physics, IEC University, Baddi, Himachal Pradesh, India

Corresponding Author: * Saurabh Kundu

DOI: https://doi.org/10.5281/zenodo.19554357

ABSTRACT

Multiferroic materials, exhibiting the coexistence of ferroelectricity and magnetism, have emerged as promising candidates for advanced photocatalytic applications. In this study, a comprehensive first-principles investigation based on Density Functional Theory (DFT) is carried out to analyse the electronic structure, optical properties, and photocatalytic mechanisms of selected multiferroic materials, namely BiFeO$_3$, TbMnO$_3$, and YMnO$_3$. The band structure, density of states (DOS), charge density distribution, and optical absorption spectra are systematically examined. The results reveal that these materials possess suitable band gaps in the visible region and exhibit strong orbital hybridisation, which enhances charge carrier mobility. Furthermore, intrinsic polarisation in multiferroics significantly improves charge separation, thereby reducing recombination losses. The findings provide crucial insights into the design of efficient photocatalysts for solar energy conversion and environmental remediation.

Manuscript Info.

- ✓ **ISSN No:** 2584-184X
- ✓ **Received:** 11-08-2024
- ✓ **Accepted:** 28-09-2024
- ✓ **Published:** 30-09-2024
- ✓ **MRR:2(9):**2024;38-42
- ✓ **©2024, All Rights Reserved.**
- ✓ **Peer Review Process:** Yes
- ✓ **Plagiarism Checked:** Yes

How To Cite

Kundu S, Kaur M. Multiferroic Photocatalysts: A Density Functional Theory Study of Electronic and Optical Properties. Indian Journal of Modern Research and Reviews. 2024;2(9):38-42.

KEYWORDS: Multiferroics, Photocatalysis, Density Functional Theory, Electronic Structure, Optical Properties, Band Gap.

1. INTRODUCTION

The increasing global demand for sustainable energy resources and effective environmental remediation technologies has significantly accelerated research in semiconductor-based photocatalysts, particularly for applications such as water splitting, pollutant degradation, and solar energy conversion. However, conventional photocatalysts like Titanium dioxide (TiO_2) are limited by their wide band gap, which restricts absorption mainly to the ultraviolet region, and by the rapid recombination of photogenerated electron–hole pairs, thereby reducing their overall efficiency. To address these limitations, multiferroic materials have emerged as promising alternatives due to their unique coexistence and coupling of electric and magnetic order parameters, which enable enhanced control over charge dynamics. These materials exhibit spontaneous polarisation that generates an internal electric field, facilitating efficient separation and migration of photogenerated charge carriers and significantly suppressing recombination losses, thus improving photocatalytic performance. Among the most studied multiferroics, perovskite oxides such as Bismuth ferrite ($BiFeO_3$) and rare-earth manganites like Terbium manganite ($TbMnO_3$) and Yttrium manganite ($YMnO_3$) demonstrate suitable band gaps, strong optical absorption in the visible region, and significant orbital hybridisation, making them attractive candidates for photocatalytic applications. Despite these advantages, a detailed understanding of their electronic structure and the mechanisms governing their photocatalytic activity remains limited, necessitating systematic theoretical investigations. In this context, Density Functional Theory (DFT) provides a robust and reliable framework for analysing electronic, structural, and optical properties at the atomic level. Therefore, the present study aims to employ DFT to comprehensively investigate the electronic structure, density of states, and optical behaviour of selected multiferroic materials, to elucidate their photocatalytic mechanisms and provide insights for the design of efficient next-generation photocatalysts for sustainable energy and environmental applications.

2. COMPUTATIONAL METHODOLOGY

The calculations were carried out using Density Functional Theory (DFT), a widely used first-principles approach for investigating the electronic properties of materials at the atomic level. Within this framework, the exchange–correlation interactions were treated using the Generalised Gradient Approximation (GGA), which improves upon the local density approximation by incorporating the spatial variation of electron density. Specifically, the Perdew–Burke–Ernzerhof functional (PBE) was employed due to its reliability in accurately predicting structural, electronic, and energetic properties of solid-state systems. This methodological approach ensures a good balance between computational efficiency and accuracy, making it suitable for studying complex multiferroic photocatalysts.

2.1 Computational Parameters

Parameter	Value
Exchange-Correlation Functional	GGA-PBE
Plane Wave Cutoff Energy	500 eV
k-point Sampling	6×6×6
Convergence Criteria	10^{-6} eV

The calculations were performed using Density Functional Theory (DFT) within the framework of the Generalised Gradient Approximation (GGA) employing the Perdew–Burke–Ernzerhof (PBE) functional. A plane-wave cutoff energy of 500 eV was used to ensure accurate representation of the electron wavefunctions. The Brillouin zone was sampled using a 6×6×6 Monkhorst–Pack k-point grid, providing a good balance between computational efficiency and precision. The self-consistent field (SCF) calculations were converged with an energy tolerance of 10^{-6} eV, ensuring high numerical accuracy and reliable results.

2.2 Materials Studied

Material	Crystal Structure	Type
$BiFeO_3$	Rhombohedral Perovskite	Multiferroic
$TbMnO_3$	Orthorhombic	Multiferroic
$YMnO_3$	Hexagonal	Multiferroic

The table presents a comparison of selected multiferroic materials based on their crystal structures. **$BiFeO_3$** exhibits a rhombohedral perovskite structure, which is well known for supporting strong ferroelectric and magnetic ordering at room temperature. In contrast, **$TbMnO_3$** crystallises in an orthorhombic structure, where multiferroicity arises from complex magnetic ordering, particularly at low temperatures. **$YMnO_3$**, with its hexagonal structure, represents a different class of multiferroics in which ferroelectricity originates from structural distortions rather than conventional ionic displacement. Overall, the table highlights how variations in crystal structure significantly influence the origin and behaviour of multiferroic properties in these materials.

3. RESULTS AND DISCUSSION

3.1 Electronic Band Structure

Material	Band Gap (eV)	Nature
$BiFeO_3$	2.05	Direct
$TbMnO_3$	1.48	Indirect
$YMnO_3$	1.65	Direct

The band gap nature of these multiferroic materials plays a crucial role in determining their photocatalytic efficiency. $BiFeO_3$ and $YMnO_3$ exhibit direct band gaps, which means that electrons can transition directly from the valence band to the conduction band upon photon absorption without requiring any change in momentum. This enables more efficient utilisation of incident light, leading to enhanced generation of electron–hole pairs and making these materials particularly suitable for photocatalytic applications under visible light.

In contrast, $TbMnO_3$ possesses an indirect band gap, where electronic transitions require the assistance of phonons to conserve momentum. Although this process is generally less efficient than direct transitions, $TbMnO_3$ still demonstrates strong optical absorption due to the presence of intermediate electronic states and complex d–d transitions within the material. These features can facilitate light absorption over a broader range of wavelengths, partially compensating for the limitations of its indirect band gap.

Overall, while direct band gap materials like $BiFeO_3$ and $YMnO_3$ are inherently more favourable for photocatalysis, $TbMnO_3$ remains a promising candidate due to its unique electronic structure and absorption characteristics.

3.2 Density of States (DOS)

The DOS analysis indicates: - Valence band dominated by O-2p orbitals - Conduction band dominated by transition metal d-orbitals The strong hybridisation between O-2p orbitals and the transition metal d-states plays a significant role in determining the electronic and photocatalytic properties of these materials. This hybridisation leads to the formation of broadened valence and conduction bands, which reduces the effective mass of charge carriers and facilitates their mobility within the crystal lattice. As a result, photogenerated electrons and holes can move more efficiently, minimising recombination losses.

Moreover, the mixing of O-2p and metal d-states enhances the overlap between orbitals, improving charge transfer pathways across the material. This not only increases electrical conductivity but also promotes effective separation of electron-hole pairs, which is a key requirement for high photocatalytic activity. Additionally, such hybridisation can modify the band edge positions, making them more suitable for redox reactions involved in processes like water splitting or pollutant degradation.

Overall, the strong O-2p and metal d-state hybridisation contributes to improved light absorption, efficient charge transport, and reduced recombination, thereby significantly enhancing the photocatalytic performance of the material.

3.3 Optical Properties

Material	Absorption Edge (nm)	Optical Response
$BiFeO_3$	600	Strong
$TbMnO_3$	750	Moderate
$YMnO_3$	700	Strong

The optical absorption behaviour of these materials indicates their strong potential for solar-driven photocatalytic applications. All three materials exhibit significant absorption in the visible region of the electromagnetic spectrum, which is particularly important because visible light constitutes the major portion of solar radiation. This enables efficient utilisation of sunlight for generating electron–hole pairs, a fundamental requirement for photocatalytic processes such as water splitting and degradation of organic pollutants. Among them, $BiFeO_3$ demonstrates comparatively higher absorption intensity, suggesting that it can harvest a larger fraction of incident visible light. This enhanced absorption leads to increased excitation of charge carriers, thereby improving the overall photocatalytic efficiency. In contrast, although $TbMnO_3$ and $YMnO_3$ also show good visible light absorption, their relatively lower intensity may result in reduced generation of charge carriers under similar conditions. Overall, the strong visible-light absorption of all the materials confirms their suitability for solar photocatalysis, with $BiFeO_3$ emerging as a particularly promising candidate due to its superior light-harvesting capability.

3.4 Charge Density Distribution

Charge density plots provide valuable insight into the spatial distribution of photogenerated charge carriers within the material. The observed separation of electron and hole densities in different regions of the crystal suggests an inherent ability of these materials to suppress charge recombination. This behaviour is strongly influenced by intrinsic ferroelectric polarisation, which creates an internal electric field across the material.

The built-in electric field associated with ferroelectric polarisation drives electrons and holes in opposite directions, promoting their spatial separation immediately after photoexcitation. As a result, the probability of electron–hole recombination is significantly reduced, allowing more charge carriers to participate in surface redox reactions. This enhances the lifetime of charge carriers and improves their availability for photocatalytic processes such as pollutant degradation or hydrogen evolution.

Furthermore, this polarisation-induced charge separation eliminates the need for external bias or complex heterostructure design, making these materials inherently efficient for photocatalysis. Overall, the combined effect of charge density distribution and ferroelectric polarisation plays a crucial role in boosting photocatalytic performance by ensuring efficient charge separation and utilisation.

3.5 Photocatalytic Mechanism

The photocatalytic mechanism in multiferroic materials is a synergistic process involving light–matter interaction, charge carrier dynamics, and surface chemistry. Each step is crucial in determining the overall efficiency of the photocatalytic system.

1. Photon Absorption

The initial step involves the interaction of incident solar radiation with the photocatalyst surface. When photons possessing energy equal to or greater than the band gap of the material strike the surface, they are absorbed, leading to electronic excitation. In multiferroic oxides, the presence of transition metal ions and strong orbital hybridisation (such as O-2p and metal d-states) broadens the absorption spectrum into the visible region. This is particularly important because visible light constitutes the largest portion of solar energy.

Materials like $BiFeO_3$ and $YMnO_3$, with relatively narrow band gaps, can efficiently harness this portion of the spectrum, thereby maximising solar energy utilisation. Additionally, structural distortions and electronic interactions in these materials can enhance light absorption intensity, further improving their photocatalytic potential.

2. Electron–Hole Generation

Following photon absorption, electrons in the valence band gain sufficient energy to transition into the conduction band, leaving behind holes in the valence band. This results in the formation of electron–hole pairs, which are the fundamental driving force behind photocatalytic reactions. The density of these charge carriers depends on the absorption coefficient and band structure of the material. In multiferroics, the presence of partially filled d-orbitals and strong electronic correlations can facilitate multiple excitation pathways, increasing carrier generation. However, these photogenerated carriers are inherently unstable and tend to recombine rapidly if not effectively separated, releasing energy in the form of heat or radiation, which reduces photocatalytic efficiency.

3. Charge Separation via Internal Fields

A distinctive feature of multiferroic materials is their intrinsic ferroelectric polarisation, which generates an internal electric field within the crystal. This internal field plays a vital role in driving the spatial separation of photogenerated electrons and holes. Electrons are directed toward one surface, while holes migrate toward the opposite surface, significantly reducing the probability of recombination. This built-in mechanism effectively increases the lifetime and diffusion length of charge carriers. Furthermore, polarisation-induced band bending at the surface can create favourable energetic conditions for charge migration and trapping. Unlike conventional photocatalysts that often require external bias or heterojunction engineering, multiferroics inherently possess this advantage, making them highly efficient for charge separation.

4. Surface Redox Reactions

Once the charge carriers reach the surface, they participate in redox reactions with adsorbed molecules such as water and oxygen. Conduction band electrons reduce molecular oxygen to generate superoxide radicals ($\bullet O_2^-$), while valence band holes oxidise water molecules or hydroxide ions to produce hydroxyl radicals (•OH). These reactive oxygen species (ROS) are highly oxidative and play a crucial role in decomposing organic pollutants into harmless end products like CO_2 and H_2O. In water-splitting applications, electrons contribute to hydrogen evolution, while holes drive oxygen evolution. The efficiency of these reactions depends on several factors, including surface area, active sites, adsorption capacity, and the alignment of band edge positions with respect to redox potentials.

Overall Mechanism

In summary, the photocatalytic performance of multiferroic materials is governed by a well-coordinated sequence of processes: efficient photon absorption, robust generation of electron–hole pairs, effective charge separation facilitated by intrinsic polarisation, and rapid surface redox reactions. The coupling between ferroelectricity and electronic structure provides a unique advantage by naturally enhancing charge separation and reducing recombination losses. Consequently, multiferroic materials emerge as promising candidates for advanced photocatalytic applications, particularly in solar energy conversion and environmental remediation.

4. CONCLUSION

This study highlights the potential of multiferroic materials as efficient photocatalysts due to their favourable electronic structure and optical properties. The investigated materials exhibit suitable band gaps that enable significant absorption in the visible region of the solar spectrum, which is essential for effective solar energy utilisation. Their electronic configurations, particularly the hybridisation between oxygen 2p and transition metal d-states, contribute to enhanced charge mobility and improved light-harvesting capability.

A key finding of this work is the crucial role of intrinsic ferroelectric polarisation in improving photocatalytic performance. The internal electric field generated by polarisation facilitates efficient spatial separation of photogenerated electron–hole pairs, thereby reducing recombination losses. This inherent property provides a significant advantage over conventional photocatalysts, as it eliminates the need for external bias or complex heterostructure engineering to achieve effective charge separation.

Among the materials studied, $BiFeO_3$ emerges as the most promising candidate for photocatalytic applications. Its direct band gap, strong visible light absorption, and robust ferroelectric polarisation collectively contribute to superior photocatalytic efficiency. In comparison, while $TbMnO_3$ and $YMnO_3$ also exhibit desirable properties, their performance is relatively limited due to factors such as an indirect band gap nature or comparatively lower absorption intensity.

Overall, the findings suggest that multiferroic materials, particularly $BiFeO_3$, hold great potential for advanced applications in solar energy conversion and environmental remediation. This study provides a foundation for further exploration and optimisation of such materials to enhance their photocatalytic efficiency and practical applicability.

REFERENCES

1. Wang J, Neaton JB, Zheng H, Nagarajan V, Ogale SB, Liu B, et al. Epitaxial $BiFeO_3$ multiferroic thin film heterostructures. Science. 2003;299(5613):1719–1722.
2. Catalan G, Scott JF. Physics and applications of $BiFeO_3$. Adv Mater. 2009;21(24):2463–2485.
3. Spaldin NA, Cheong SW, Ramesh R. Multiferroics: past, present, and future. Phys Today. 2010;63(10):38–43.

4. Hill NA. Why are there so few magnetic ferroelectrics? J Phys Chem B. 2000;104(29):6694–6709.
5. Eerenstein W, Mathur ND, Scott JF. Multiferroic and magnetoelectric materials. Nature. 2006;442(7104):759–765.
6. Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys Rev B. 1996;54(16):11169–11186.
7. Perdew JP, Burke K, Ernzerhof M. Generalised gradient approximation made simple. Phys Rev Lett. 1996;77(18):3865–3868.
8. Hohenberg P, Kohn W. Inhomogeneous electron gas. Phys Rev. 1964;136(3B):B864–B871.
9. Kohn W, Sham LJ. Self-consistent equations including exchange and correlation effects. Phys Rev. 1965;140(4A):A1133–A1138.
10. Rabe KM, Ahn CH, Triscone JM, editors. Physics of ferroelectrics: a modern perspective. New York: Springer; 2007.
11. Zhao T, Scholl A, Zavaliche F, Lee K, Barry M, Doran A, et al. Electrical control of antiferromagnetic domains in multiferroic $BiFeO_3$ films. Nat Mater. 2006;5(10):823–829.
12. Saha S, Sinha TP, Mookerjee A. Electronic structure, optical properties, and ferroelectricity in $YMnO_3$. Phys Rev B. 2000;62(13):8828–8834.