

Tuning of Optical Properties in RFeO₃ Perovskites: Role of Structural Distortion, Doping, and Nanostructuring

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Abstract

The optical properties of RFeO₃ perovskite oxides are highly sensitive to structural and electronic modifications, making them promising candidates for advanced functional applications. This chapter explores the combined influence of structural distortion, doping, and nanostructuring on the optical behavior of RFeO₃ compounds. Distortion of FeO₆ octahedra significantly alters Fe–O bond geometry, thereby modifying Fe 3d–O 2p orbital overlap, which governs the electronic bandwidth and band gap. Increased distortion leads to band gap widening and reduced carrier mobility, while lower distortion enhances orbital interaction and optical absorption. Doping strategies at both A-site and B-site effectively tailor the band structure by introducing defect states and mid-gap energy levels, resulting in improved visible light absorption and enhanced photocatalytic efficiency. Furthermore, nanostructuring introduces size-dependent effects such as quantum confinement and increased surface area, which contribute to superior light–matter interaction and charge separation. Optical transitions in RFeO₃ are primarily dominated by charge transfer processes, while intrinsic defects such as oxygen vacancies introduce localized states within the band gap, enabling sub-band-gap absorption. Owing to these tunable optical characteristics, RFeO₃ materials exhibit significant potential in photocatalysis, solar energy conversion, sensing, and optoelectronic device applications.

2.1 Introduction to Perovskite Oxides

Perovskite oxides in the field of condensed matter physics and materials science, perovskite oxides (general chemical formula ABO₃) are a highly important category of functional materials based on their remarkable structural versatility and their broad spectrum of physicochemical characteristics [1,2]. Perovskite has an ideal structure, which is cubic with the A-site cation at the corners of the cube, the B-site cation at the center of the body and oxygen anions at the centers of the faces forming a network of corner-sharing BO₆ octahedra [3, 4]. In practical systems, however, the lack of a perfect cubic symmetry can arise because of the sizes of the ions, resulting in deformed structures, e.g., orthorhombic, rhombohedral or tetragonal phases [5,6].

Larger cations (rare-earth ions (La³⁺, Y³⁺, Bi³⁺), alkaline-earth ions (Sr²⁺, Ca²⁺, Ni³⁺)) usually occupy the A-site, and smaller transition metal ions (Fe³⁺, Mn³⁺, Co³⁺, Ni³⁺) occupy the B-site

The cation variety enables the structural parameters including lattice constants, bond lengths and bond angles to be determined accurately and directly affect the electronic band energy and the exchange interactions [7-11]. An important parameter that controls structural stability is the Goldschmidt tolerance factor (t) which is:

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)}$$

represent ionic radii of A-site, B-site, and oxygen ions, respectively. Tilting and structural distortion of the octahedra caused by deviation of t of unity is crucial in defining the characteristics of octahedra functionalities of the perovskite materials [12,13].

Perovskite oxides have an impressive variety of properties such as:

- 🚦 Ferroelectricity (e.g., spontaneous polarization of electrics in Bi-based).
- 🚦 Magnetism (antiferromagnetic, ferromagnetic or weak ferromagnetic order).
- 🚦 Electronic transport behavior and semiconducting behavior.
- 🚦 Catalytic activity (of environmental and energy applications).
- 🚦 Tunability of the band gap and optical absorption.

This is due to the fact that lattice, charge, spin, and orbital degrees of freedom are strongly coupled leading to these materials being of great interest in high-tech applications like sensors, actuators, energy storage systems, spintronic systems, etc [14,16].

Out of the wide range of perovskite oxides, rare-earth orthoferrites (RFeO_3) have received a significant amount of research attention because of their special traits of structural distortion combined with magnetic ordering. They are usually crystallized in an orthorhombically distorted perovskite structure (space group: Pnma) with the octahedra of FeO_6 being tilted significantly because of the relatively smaller ionic radius of the R^{3+} ions [7]. This deformation results in change in the Fe-O-Fe bond angle, which have a vital influence on the strength of superexchange interactions among Fe^{3+} ions. The RFeO_3 compounds are G-type antiferromagnetism with each spin of the Fe^{3+} being antiparallel to the closest neighbors. Nevertheless, with the antisymmetric exchange interaction (Dzyaloshinskii–Moriya interaction), there is a slight canting of spins leading to weak ferromagnetism. Furthermore, there are spin reorientation transitions in some of the members of this family, which makes it interesting in magnetic switching [8].

The great sensitivity of the properties of RFeO_3 systems to the type of the rare-earth ion (R) is another significant feature of these systems. For instance:

- 🚦 The bigger ions such as La^{3+} result in less distorted structures and a higher conductivity.

- ✚ Smaller ions such as Y^{3+} increase the distortion of structure and anisotropy of the magnetism.
- ✚ Electrons in Bi^{3+} are lone pairs, which cause ferroelectricity that contributes to the multiferroic behavior.

These properties have rendered $RFeO_3$ compounds good candidates in multifunctional applications which include [12]:

- ✚ Sensing gases and environmental scanning.
- ✚ Photocatalysis and conversion of solar energy.
- ✚ Magnetically and spintronic devices.
- ✚ Systems of dielectric and energy storage.

In this way, A-site substitution enables the control of structural distortion, electronic structure, and magnetic interactions, making perovskite oxides, especially $RFeO_3$ systems, a versatile system to design next-generation multifunctional materials [9].

2.2 Crystal Structure of $RFeO_3$ Perovskites:

Rare-earth orthoferrites ($RFeO_3$) are a type of distorted perovskite oxide where the cubic symmetry is distorted by a lattice instability caused by the ionic size mismatch. The compounds are mainly found in an orthorhombic structure with a $Pnma$ space group that is the product of cooperative rotations and distortions of the octahedra of FeO_6 to form perovskite [17].

With the $RFeO_3$ structure, Fe^{3+} ions are located in the center of the oxygen octahedra, creating an overall network of corner-linked FeO_6 units. The interstitial A-sites are filled with the rare-earth ions (R^{3+}), and are surrounded by twelve oxygen ions in a distorted coordination environment. This structural distortion is not isolated but a systematic structure that is based on steric effects and electrostatic interactions among constituent ions. An effective method to comprehend the breakage of cubic symmetry is via the principle of lattice strain due to the variation of the ionic size. As the radius of the R^{3+} ion is reduced, the lattice adjustment of this mismatch is through a greater tilting in FeO_6 octahedra. The internal energy is reduced by this structural adjustment but at the same time, the basic parameters like bond lengths and bond angles are changed. This leads to the Fe-O-Fe bond angle not being linear, thus, affecting the overlap between Fe-3d and O-2p orbitals [18].

Crystallographically, $RFeO_3$ distortion can be explained by octahedral tilt systems, in which the alternate rotation of FeO_6 octahedra are performed along various crystallographic directions. This results in a lattice with anisotropy and less symmetry than the perfect cubic phase. The orthorhombic nature of such compounds is proven by such distortions being directly reflected in X-ray diffraction patterns by splitting and shifting of peaks [19].

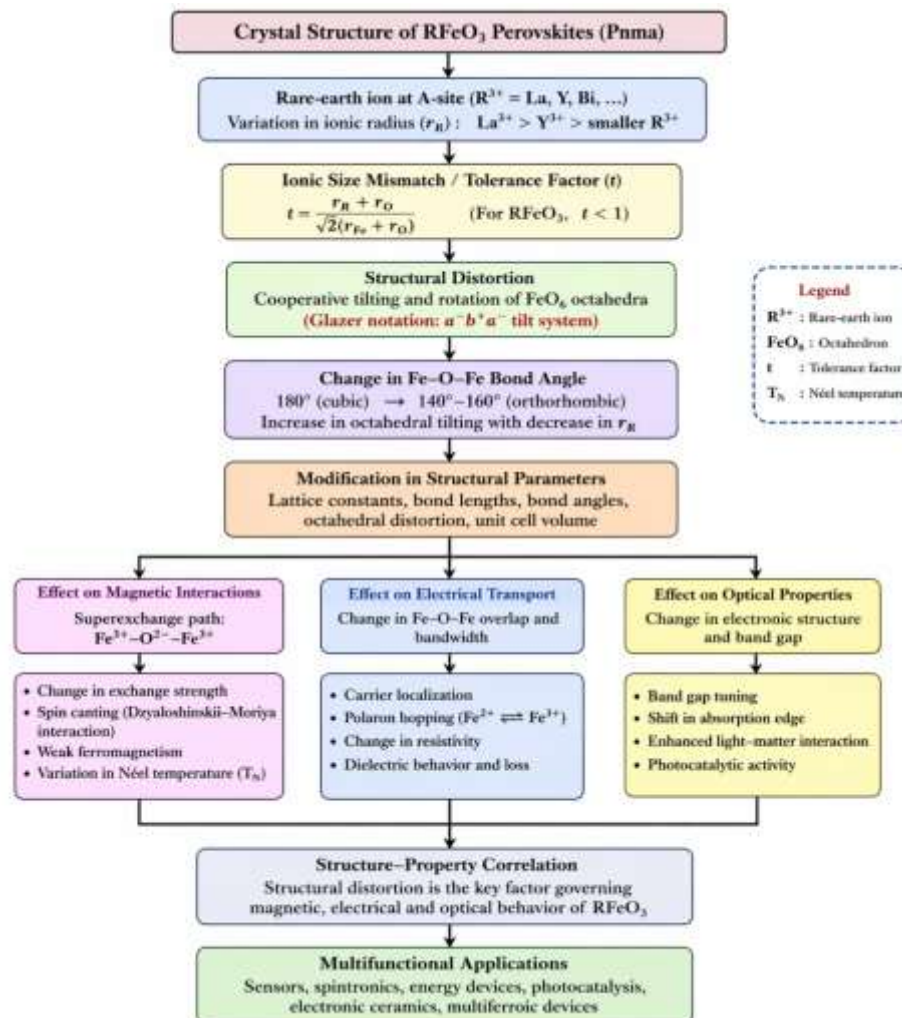


Fig. 2.1: Schematic representation of structure–property correlation in RFeO₃ perovskites.

There is a systematic trend in the series of rare-earths:

- ✚ Whereas compounds containing larger A-site ions (e.g., La³⁺) have rather less distorted structures of higher symmetry.
- ✚ Compounds of more reduced ions (e.g. Y³⁺ or other heavy rare earths) exhibit a greater lattice distortion and greater octahedral tilting.

Such a progressive evolution of structure greatly affects the electronic and magnetic properties of the substance. The decrease in the angle of Fe-O-Fe bonding dilutes the superexchange pathway, thus altering the magnetic ordering. Specifically, greater distortion enhances spin canting leading to weak ferromagnetism overlaid on the overlaying antiferromagnetic structure [20].

Besides the magnetic effects, there is also structural distortion that controls the electrical transport mechanism. Tilting causes a decrease in orbital overlap and results in localization of the charge carriers and an enhancement of resistive behavior. Therefore, materials that have a greater distortion tend to have lower electrical conductivity and increased dielectric dispersion. Raman and infrared spectroscopy are also techniques of vibrational spectroscopy that support the existence of structural distortion. The phonon modes that are observed are very sensitive to the lattice dynamics and give indirect evidence of the octahedron tilting. The differences in peak position, intensity as well as linewidth are evidence of changes in bond strength, lattice strain and reduced symmetry. The crystal structure of RFeO_3 is not just a geometrical structure of the ions but a dynamic structure which determines the interaction of the different physical characteristics. The strong dependence of structural parameters on the ionic radius of the rare-earth element highlights the importance of compositional control in tailoring material performance [17-20].

2.3 LaFeO_3 -Based Perovskites:

Among the most widely studied representatives of the rare-earth orthoferrite family is the lanthanum ferrite (LaFeO_3) because of its high physicochemical stability, low cost and non-toxic environment. It has become a model system to study structure-property correlations in perovskite oxides, especially with its crystalline structure, and strong magnetic ordering. LaFeO_3 is crystallized in an orthorhombically distorted perovskite form (space group: Pnma) with the Fe^{3+} ions coordinated by the oxygen atoms in an octahedrally coordinated form (FeO_6). These octahedra are joined corner-sharing together, and form a three-dimensional structure. The deformation of the ideal cubic symmetry is caused by the fact that the ionic radii of the La^{3+} and Fe^{3+} ions do not match and the octahedra structures of FeO_6 are cooperatively tilted. LaFeO_3 has a relatively low structural distortion than other orthoferrites of the rare earths since the larger ionic radius of La^{3+} leads to a relatively larger angle of the Fe-O-Fe bond and to a larger orbital overlap.

Magnetic Properties:

LaFeO_3 has a high Neel temperature ($T_N=740\text{K}$) which is the result of the intense superexchange between the adjacent Fe^{3+} ions with the help of oxygen (Fe^{3+} high O^{2-} low Fe^{3+}). The predominantly antiferromagnetic nature of a material is often accompanied by a small ferromagnetic component, caused by some slight spin canting caused by the Dzyaloshinskii Moriya interaction. This renders LaFeO_3 especially attractive in applications in which it is necessary to have a stable magnetic behavior at high temperatures [11, 19].

Electrical and Dielectric Behavior:

LaFeO₃ is electrically a p-type semiconductor, and the conduction of charge carriers is mainly characterized by thermally activated hopping of charge carriers between Fe³⁺ and Fe²⁺ states. This hopping mechanism is also promoted by the availability of oxygen vacancies and this leads to electrical conductivity. The electrical characteristics are important and are:

- ✚ Resistivity that decreases (negative temperature coefficient) with temperature.
- ✚ Frequency-dependent dielectric behavior
- ✚ Addition of grain boundaries and defects to polarization.

Synthesis conditions, grain size and defect chemistry are very sensitive to the electrical properties [20, 21].

Optical Properties:

LaFeO₃ has an optical band gap of between 2.0-2.3 eV which is active in the visible region of the electromagnetic spectrum. The optical absorption is primarily as a result of charge transfer between transitions of O-2p and Fe-3d states. Its band gap is relatively small thereby making it suitable in photocatalytic and optoelectronic applications [11].

Effect of Doping on LaFeO₃:

A lot of work has been done on the cation substitution (doping) of the properties of LaFeO₃ at B-site or the A-site. Doping causes defect states, charge imbalance and lattice distortions, causing significant structural and functional changes [19].

A-site Doping (e.g., Sr²⁺, Ca²⁺) [22-26]:

- ✚ Produces charge imbalance (La³⁺ Sr²⁺), and causes the formation of Fe⁴⁺ or oxygen vacancies.
- ✚ Enhances electrical conductivity
- ✚ Reduces band gap
- ✚ Improves catalytic efficiency

B-site Doping (e.g., Mg²⁺, Co³⁺, Mn³⁺) [27]:

- ✚ Changes the Fe-O-Fe interactions.
- ✚ Alters magnetic exchange and magnetic ordering.
- ✚ Weakly ferromagnetic, as a result of enhanced spin canting.
- ✚ Has effects on optical absorption properties.

These and similar adjustments allow tuning of properties to fine-tuning of applications.

Catalytic and Gas Sensing Applications:

LaFeO₃ has proven to be a good gas sensing gas, especially in the detection of gases like CO, NO₂ and volatile organic compounds (VOCs). The sensing mechanism of it is mainly based on [28]:

- ✚ Gas molecules adsorbed on surface.
- ✚ Transfers of charges between the adsorbed species and the material.
- ✚ Differences in the electrical resistance.

Furthermore, LaFeO_3 is a good catalyst in oxidation reactions, because it has:

- ✚ High oxygen mobility
- ✚ Oxidation states of iron that are variable.
- ✚ Surface defect sites

Energy and Environmental Applications:

LaFeO_3 is a popular material in [29]:

The methods include:

- ✚ photocatalysis (organic pollutant degradation).
- ✚ Conversion systems of solar energy.
- ✚ Supercapacitors and electrochemical.
- ✚ Solid oxide fuel cells (SOFCs) are also known as solid oxide fuel cells.

The performance of nanostructured LaFeO_3 materials is better since there is more surface area and better charge transfers.

2.4 YFeO_3 (Yttrium Orthoferrite):

Yttrium orthoferrite (YFeO_3) is an important constituent of the rare-earth orthoferrite family that has distinctive multiple characteristics in structural distortion, strong magnetic ordering, and is also technologically important with multifunctional characteristics. YFeO_3 has a better lattice distortion over LaFeO_3 since the ionic radius of Y^{3+} is smaller and thus decisively influences shaping its physical behavior [17].

YFeO_3 is crystallized in the form of orthorhombically distorted perovskite (space group: Pnma) in which the Fe^{3+} ions are enclosed by oxygen atoms which form FeO_6 octahedra. These octahedra share corners of geometry, and create a three-dimensional net-work. The reduced size of Y^{3+} results in an increased octahedral tilting and strain in the lattice thus substantially lowering the Fe-O-Fe bond angle than in LaFeO_3 . This distortion of structure has a direct impact on the overlap of Fe 3d and O 2p orbitals which impact the magnetic exchange interactions, as well as, the electronic transport characteristics [20].

Magnetic Properties and Spin Dynamics:

YFeO_3 is also G-type antiferromagnetic ordered with each Fe^{3+} spin being antiparallel with its nearest neighbors. It is however, because of the existence of the antisymmetric exchange interaction, called the Dzyaloshinskii Moriya (DM) interaction, a weak canting of the spins is produced leading to weak ferromagnetism [17].

Another peculiarity of the YFeO_3 is that spin reorientation transitions (SRT) can be observed at low temperatures. These transitions will be a slow turning of the axis of spin without annihilating the antiferromagnetic order. The spin reorientation phenomenon is very sensitive to:

- ✚ Crystal anisotropy
- ✚ Exchange interaction strength
- ✚ Temperature variation

The property of this phenomenon renders YFeO_3 especially promising in the use in magnetic switching and spintronic devices.

Also, an increase in the structural distortion in YFeO_3 increases magnetic anisotropy, which results in:

- ✚ Higher coercivity
- ✚ Improved magnetic stability
- ✚ External magnetic response which is tunable.

Structural Distortion and Its Impact:

The Y^{3+} (ionic radius, approximately 0.90 Å) is much smaller than that of La^{3+} (approximately 1.16 Å) and so the tolerance factor is reduced and the deviation is increased. Consequently:

- ✚ FeO_6 octahedra have intense tilting and rotation.
- ✚ There is a reduction in the Fe–O–Fe bond angle.
- ✚ Parameters in lattices are very anisotropic.

This further distortion results into:

- ✚ Reduced electronic bandwidth
- ✚ Increased resolution of charge carriers.
- ✚ Change in the phonon dynamics.

The raman and infrared spectroscopic experiments further attest to the fact that YFeO_3 has stronger lattice vibrations and shift in phonons which are characteristic of greater structural distortion as compared to LaFeO_3 [20].

Electrical and Dielectric Properties:

YFeO_3 is a semiconductor like other orthoferrites, with small polaron hopping between Fe^{3+} and Fe^{2+} ions being the predominant conduction mechanism. But owing to more effective lattice distortion [30]:

- ✚ Mobility of charge carriers is also low.
- ✚ It has a greater electrical resistivity than LaFeO_3 .

- Dielectric response is very frequency dependent.

The dielectric properties of YFeO_3 are affected by:

- Grain boundary effects
- Space charge polarization
- Defect states (in particular oxygen vacancies)

Intriguingly, YFeO_3 exhibits a high dielectric stability at high temperatures, and can therefore be used in high-temperature electronics [31].

Optical and Magneto-Optical Properties:

YFeO_3 is an optical absorber with an optical absorption visible range of around 2.1 -2.5 eV. Fe^{3+} electronic states and oxygen-mediated charge transfer processes are largely linked with the optical transitions.

The magneto-optical behavior of YFeO_3 is one of the most significant features of this compound as a result of high levels of interaction between the magnetic ordering and optical response. This includes:

- Faraday rotation and Kerr effects.
- Magnetic-field-dependent optical properties
- Spin-photon interaction between the spin and photon states.

These properties render YFeO_3 very promising in magneto-optical devices, optical isolators and sophisticated photonic systems [32].

Thermal Stability and Functional Advantages:

YFeO_3 has been known to have good thermal and chemical stability which is paramount in the practice of the devices. It has structural integrity and magnetic ordering even at high temperatures, which is beneficial in [33]:

- High-temperature sensors
- Magnetically powered equipment in harsh conditions.
- Ceramic-based multifunctional systems

Applications of YFeO_3 :

YFeO_3 is a versatile material that is utilized in many advanced applications in part due to its unusual combination of properties [20, 30-31]:

- Spintronics:** because of spin reorientation and weak ferromagnetism.
- Magneto-optical devices:** the light and the magnetism are strongly coupled.
- Sensors:** gas sensors, in particular, high-temperature sensors.
- Multi responses:** magnetic, dielectric, and optical multifunctional ceramics.
- Energy devices:** may find application in photocatalysis and in energy conversion.

Structure–Property Insight:

The increase in structural distortion of YFeO_3 over LaFeO_3 is a major factor that characterizes the physical properties of the former. The decreased Fe-O-Fe bond angle enhances the superexchange interactions but decreases spin canting and magnetic anisotropy. On the same note, lattice distortion and defect chemistry have a great impact on electrical and optical properties. Therefore, YFeO_3 is a good system to learn the importance of using ionic size-induced structural distortion to design multifunctional characteristics.

To conclude, YFeO_3 is an orthoferrite which has a distorted structure, is antiferromagnetically ordered, weakly ferromagnetic, and exhibits a spin reorientation mechanism. Its increased lattice distortion, thermal stability and magneto-optical response makes it a promising candidate next-generation multifunctional and spintronic applications [29-33].

2.5 BiFeO_3 -Based Multiferroic Perovskites:

Bismuth ferrite (BiFeO_3) is a single-phase multiferroic material that has been widely researched and is technologically relevant because it is a multiferroic material that is both ferroelectric and magnetic, at room temperature. This unusual multifaceted of ferroic orders in a material is what makes BiFeO_3 an excellent model system to study magnetoelectric coupling, and to develop next-generation functional devices [34].

BiFeO_3 exhibits:

- 🚦 4°C 1100 K Ferroelectric transition temperature ($T_C \approx 1100$ K)
- 🚦 Antiferromagnetic Néel temperature ($T_N \approx 640$ K)

Such large transition temperatures are needed to make both ferroelectric and magnetic properties be maintained at room temperature, which is important in practice.

Crystal Structure and Structural Distortion:

The crystal structure of BiFeO_3 is rhombohedrally distorted perovskite structure (space group $R3c$) that forms as a result of:

- 🚦 Turning of FeO_6 octahedra.
- 🚦 Removal of Bi^{3+} and Fe^{3+} ions of $[111]$ direction [35].

The distinctive aspect is that the $6s^2$ lone pair electrons exhibit $6s^2$ lone pair electrons which are stereochemically active and the cause of strong ferroelectric distortion in Bi^{3+} ions. This causes a high displacement of ions off-center which causes a high spontaneous polarization [36].

Magnetic Structure and Spin Modulation:

BiFeO_3 is magnetically G-type antiferromagnetically ordered, like other orthoferrites. BiFeO_3 , however, is not similar to LaFeO_3 and YFeO_3 in that it exhibits a long-range cycloidal spin

structure, with a modulation period of about 62 nm. This cycloidal structure overpowers the overall macroscopic magnetization, although there is a weak ferromagnetism at the microscopic level [37].

The fact that this spin structure is spiral:

- ✚ Dilutes out macroscopic magnetization.
- ✚ Constrains a direct view of magnetoelectric coupling.
- ✚ Decreases its usefulness in magnetic devices.

Ferroelectric Properties:

BiFeO₃ is also famous because of its very high level of spontaneous polarization (>100 $\mu\text{C}/\text{cm}^2$) that is much higher than most traditional materials of ferroelectric. This arises from:

- ✚ Good hybridization Bi 6s-O 2p orbital.
- ✚ Huge ionic movement in the direction of polarization [38].

Key ferroelectric features include:

- ✚ Strong polarization in the room temperature.
- ✚ Switchable electric domains
- ✚ Close interaction between lattice and electronic structure.

Magnetoelectric Coupling

The magnetoelectric (ME) coupling of BiFeO₃ is one of the most significant details in this material as the magnetic and electric orders are coupled with each other. This enables:

- ✚ Magnetization control with an electric field.
- ✚ Control of polarization with a magnetic field.

Applications of such coupling are very desirable in:

- ✚ Spintronics
- ✚ Memory devices (ME RAM)
- ✚ Sensors and actuators

The cycloidal spin structure tends to suppress the observable magnetoelectric effect, though, and thus requires alterations, either by doping or structural design [39].

Electrical and Optical Properties:

BiFeO₃ is a semiconductor that has optical band gap usually in the range of 2.1- 2.7 eV and is thus active in the visible light spectrum [40]. Its optical behaviour is controlled by:

- ✚ Transfers of charge (O 2p $\rightarrow$ Fe 3d)
- ✚ Good absorption of light in the visible range.

Such characteristics render BiFeO₃ to be applicable in:

- ✚ Photocatalysis

- ✚ Solar energy harvesting
- ✚ Optoelectronic devices

Limitations of BiFeO₃

Although BiFeO₃ has good multifunctional characteristics, the material is hampered by a number of limitations:

High leakage current

- ✚ Might be because of oxygen vacancies and impurity phases.
- ✚ Results in low ferroelectric capabilities.

Low remanent magnetization

- ✚ Due to spin structure that is cycloidal.
- ✚ Limits magnetic applications

Secondary phase formation

- During synthesis (e.g., Bi₂Fe₄O₉, Bi₂O₃)

These concerns limit its direct use in devices and need optimization measures.

Strategies for Property Enhancement:

To eliminate the limitations mentioned above, much effort has been invested in research to alter BiFeO₃ in a number of ways [41]:

1. Rare-Earth Substitution (A-site Doping) [42-44]:

Substitution of Bi³⁺ with rare-earth ions such as La³⁺, Nd³⁺, Sm³⁺ leads to:

- ✚ Suppressing cycloidal spin structure.
- ✚ Decrease in leakage current.
- ✚ Increase in magnetic properties.
- ✚ Structural change (R3c to Pnma or mixed phases)

2. B-site Doping (Transition Metals) [45, 46]:

Ion doping with ions like Mn, Co or Ti:

- ✚ Changes magnetic exchange interactions.
- ✚ Enhances magnetization
- ✚ Improves electrical resistivity

3. Structural Engineering [40]:

- ✚ Fabrication on thin films increases effects caused by strain.
- ✚ Nanostructuring enhances surface area and defects.
- ✚ The size of grain affects electrical and magnetic properties.

Effect of Structural Modification [39]:

These changes result in great enhancements in the performance of materials:

- ✚ Improved polarization of ferroelectric and leakage.
- ✚ More magnetization under an inhibition of spin cycloid.
- ✚ Improved magnetoelectric coupling
- ✚ Transformation of rhombohedral (R3c) to orthorhombic (Pnma).
- ✚ More efficient optical absorption and photocatalytic activity.

Applications of BiFeO₃

Because of being multiferroic, BiFeO₃ has been extensively investigated in [38]:

- ✚ Multiferroic devices
- ✚ Spintronic applications
- ✚ Non-volatile memory devices
- ✚ Photocatalysis and solar cells.
- ✚ Sensors and actuators

This is because of its capability of being able to couple both electric and magnetic properties in a single phase and thus it is a promising material in terms of being used in future smart materials.

Structure–Property Insight:

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- Non-volatile memory devices

Photocatalysis and solar cells.

- Sensors and actuators

This is because of its capability of being able to couple both electric and magnetic properties in a single phase and thus it is a promising material in terms of being used in future smart materials.

Structure–Property Insight:

BiFeO₃ is a special situation in which:

- ✚ Structural distortion (because of the lone pair electrons) → causes ferroelectricity.
- ✚ Magnetic ordering - controlled by Fe-O-Fe superexchange.
- ✚ Coupling the two to each other → results to multifunctionality.

Therefore, the manipulation of structure by means of doping and synthesis is the main to optimize its performance.

To conclude, there is a high potential of BiFeO₃ as a multiferroic perovskite which has a simultaneous ordering of ferroelectric and magnetic at room temperature. Despite inherent

drawbacks like leakage current and low magnetization, there have been numerous modification strategies with great success to increase its multifunctional characteristics in making it a good candidate in advanced electronic and energy applications [41-45].

2.6 Synthesis Techniques for RFeO_3 Compounds :

The formation of the RFeO_3 ($\text{R} = \text{La}, \text{Y}, \text{Bi}$) perovskites compounds is a determinant factor that dictates their structural, microstructural and functional qualities. Contrary to the simple oxide systems, orthoferrites are very sensitive to processing conditions and even slight changes in temperature or precursor chemistry, or even the route of synthesis can result in a significant change in the number of phases, grain growth, or defect concentration. This has resulted in the development of a number of synthesis methods that are used to design the material properties to suit particular multifunctional applications [20, 41, 46].

In general, the synthesis approaches to RFeO_3 can be categorized as high-temperature solid-state and low-temperature chemical synthesis, with their own advantages and drawbacks.

2.6.1 Solid-State Reaction: Diffusion-Controlled Approach:

The solid-state reaction approach is essentially a diffusion-based reaction wherein the creation of RFeO_3 is by interdiffusion of ions at high temperatures. Oxide precursors are normally combined and subjected to high temperatures (over 1000°C) to form the phase.

Kinetically, it seems to me:

- ✚ The rate of reaction depends on ionic diffusion, across grain boundaries.
- ✚ Activation energy barriers have to be overcome by high temperature.

Grain growth: Phase formation goes hand in hand with grain growth.

Although this is a good approach to guarantee thermodynamic stability and high crystallinity, it is limited by:

- ✚ Little control over microstructure
- ✚ Lack of homogeneous distribution of elements.
- ✚ Creation of coarse grains.

Therefore, it is not as useful in the applications that need control on a nanoscale, although it is appropriate in large-scale ceramics [47].

2.6.2 Sol–Gel Method: Molecular-Level Engineering:

Sol -gel is a bottom-up chemical strategy, in which the precursor ions are combined on the molecular level, which guarantees a high level of homogeneity. The sol to gel transformation enables even distribution of cations followed by thermal decomposition.

In terms of materials engineering:

- ✚ Removes diffusion constraints of solid-state processes.

- ✚ Allows one to form RFeO_3 phase at much lower temperatures.
- ✚ Eases the regulation of nucleation and growth process.

This results in:

- ✚ Fine-grained nanostructures
- ✚ Reduced agglomeration
- ✚ Enhanced surface-to-volume ratio

The process however demands a strict control of parameters of synthesis, including pH, chelating agents and drying conditions to prevent undesired phases or impurities left over [9,10].

2.6.3 Co-precipitation Method: Controlled Nucleation Strategy:

The co-precipitation method is based on the principle of co-precipitation of a variety of cations, which guarantees their distribution on an atomic level. This technique can be used to a significant effect to regulate stoichiometry and obtain uniform compositions.

Mechanistic aspects key include:

- ✚ Quick nucleation and followed by regulated growth.
- ✚ Dependence on solution chemistry (pH, temperature, concentration)
- ✚ Formation of intermediate stages of hydroxide or carbonate.

This method offers:

- ✚ Fine particle size
- ✚ Better compositional accuracy
- ✚ Reduced synthesis temperature with solid-state routes.

Nonetheless, the issues of particle agglomeration and sensitivity to conditions of processing should be properly addressed [8].

2.6.4 Hydrothermal and Combustion Methods: Advanced Chemical Routes:

(a) Pressure-Assisted Growth.

Hydrothermal method entails the crystallization process in the presence of high pressure and temperature conditions in water where the crystals are allowed to grow in a controlled fashion.

Structurally:

- ✚ Increases the crystallinity but does not need the very high temperatures.
- ✚ Enables a fine control of the morphology of particles (nanorods, nanospheres, etc.)
- ✚ Lowers the number of defects relative to other low-temperature processes.

This technique is especially beneficial in the synthesis of high-quality orthoferrites in the form of nanostructures [48].

(b) Combustion Method – Energy-Driven Synthesis

The exothermic reaction is self-sustained, and the combustion process of the fuels is founded on the reaction between the metal nitrates and organic fuels that rapidly react to create oxide powders [49].

Key characteristics:

- ✚ Very rapid kinetics of reaction.
- ✚ Production of high temperature, which enhances the formation of phases.
- ✚ Creation of porous and nanosized powder.

Although it is simple and fast, it has the following limitations:

- ✚ Lack of control over uniformity [48].

Comparative Insight: Method vs Material Outcome:

The different synthesis techniques have varying impacts on RFeO_3 properties because of the differences in thermal history and reaction path [11]:

- ✚ High temperature process → increased crystallinity but increased grains.
- ✚ Chemical paths → smaller size but more defects.
- ✚ Rapid synthesis techniques → high surface area and may be disordered.

Scientific Interpretation:

The synthesis technique defines [5, 9]:

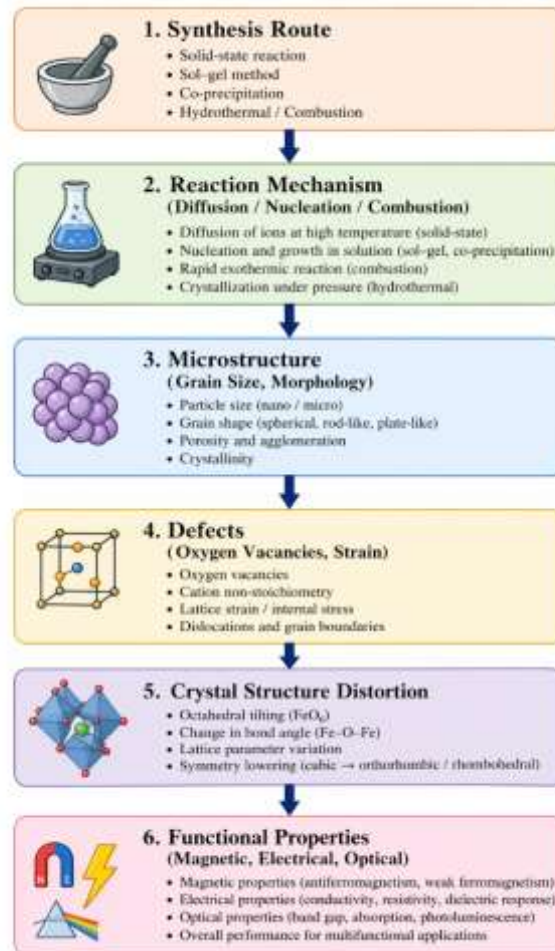
- ✚ Octahedral tilting (by lattice strain) extent.
- ✚ Defect chemistry (oxygen vacancies to conductivity)
- ✚ Grain boundary properties (affecting dielectric and magnetic properties)

Therefore, the customization of the synthesis environment is an excellent avenue to design structure-property relationships in the RFeO_3 systems.

To sum up, the synthesis of RFeO_3 perovskites is not just a preparative process but a determinant of structure and functional performance of perovskites. Although solid-state

techniques are more stable and crystalline, recent chemical techniques allow fine tuning of the nanoscale characteristics and defect engineering. Thus, it is important to choose a suitable synthesis method, which will allow maximizing the use of such materials in multifunctional applications [23].

Process–Structure–Property Correlation

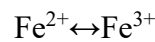


2.7 Electrical Properties of RFeO₃:

Electrical behavior of rare-earth orthoferrites (RFeO₃) is complicated and heavily depends on the crystal structure, defect chemistry and microstructural aspects. These materials are generally semiconducting in nature with the transport of charges being dominated by localized hopping processes as opposed to band-like processes. It is the interactions between Fe valence states (Fe²⁺/Fe³⁺) and oxygen vacancies as well as their grain boundaries that determine their electrical response [22,29, 45].

2.7.1 Conduction Mechanism: Small Polaron Hopping:

In the RFeO_3 compounds, the electric conduction mainly takes place as a result of the small polaron hopping mechanism, within which charge carriers (electrons or holes) jump between neighboring Fe ions of varying valence states:



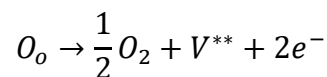
This aspect of hopping is thermally activated and relies on:

- ✚ Activation energy
- ✚ Spacing between FeFe ions.
- ✚ The overlap of Fe 3d and O 2p thus occurs.

Hopping is promoted by large temperature, and results in high electrical conductivity. This is why such a negative temperature coefficient of resistance (NTCR) is normally witnessed in RFeO_3 systems [50].

2.7.2 Role of Oxygen Vacancies:

One of the most important defects that affect the electrical behavior is oxygen vacancies. These vacancies are created either in high temperature synthesis or as a result of non-stoichiometry:



The main consequences of oxygen deficiencies:

- ✚ Donate a free charge carrier (electrons).
- ✚ Enhance hopping conduction
- ✚ Increase leakage current
- ✚ Dielectric behavior Influence dielectric relaxation behaviour.

Nevertheless, too many oxygen vacancies can cause increasing dielectric loss and decreased insulating behaviour and this is not desirable as far as device applications are concerned [20].

2.7.3 Grain Boundary Effects

RFeO_3 materials are normally poly-crystalline and therefore are highly influenced by the boundaries of the grains in their electrical properties. The MaxwellWagner model of interfacial polarization states that [21]:

- ✚ Grains (bulk) are not very conductive.
- ✚ Grain boundaries are the most resistant.

At low frequencies:

- ✚ Grain boundaries accrue charge carriers.
- ✚ Huge dielectric constant is experienced.

At high frequencies:

- ✚ Charge carriers are not able to follow alternating field.

- Dielectric constant decreases

Therefore, grain boundaries are a possible barrier that has a huge impact on:

- Resistivity
- Dielectric dispersion
- Relaxation phenomena

2.7.4 Dielectric Properties

Dielectric properties of RFeO_3 compounds have large frequency and temperature dependence.

Key features include [20, 21]:

(a) Frequency Dependence:

- Polarization by space charge to give high dielectric constant at low frequencies.
- Slowly decreasing with frequency.
- Inability of dipole to respond to high frequencies, saturation.

(b) Temperature Dependence:

- Dielectric constant rises up with temperature.
- Increased mobility of charge carriers results in increased polarization.

(c) Dielectric Loss:

- Is caused by the conduction losses and dipolar relaxation.
- Increases with low frequency, as a result of space charge.

2.7.5 AC Conductivity

The AC conductivity (σ_{ac}) in RFeO_3 compounds follows Jonscher's universal power law [30,31]:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

where:

- σ_{dc} = DC conductivity
- ω = angular frequency
- A = constant
- n = frequency exponent ($0 < n < 1$)

Key observations:

- There is an increase in the conduction of AC with frequency.
- Suggests hopping conduction mechanism.
- Increased frequencies raise mobility of the charge carriers.

2.7.6 Effect of Doping and Structural Distortion

Doping plays a vital role in modifying the electrical properties of RFeO_3 :

(a) A-site Doping (e.g., Sr^{2+} , Ca^{2+}) [42-44]:

- ✚ Introduces charge imbalance
- ✚ Increases Fe^{4+} concentration or oxygen vacancies
- ✚ Enhances electrical conductivity
- ✚ Reduces resistivity

(b) B-site Doping (e.g., Mg^{2+} , Co^{3+}) [45, 46]:

- ✚ Alters Fe–O–Fe interaction
- ✚ Modifies hopping pathways
- ✚ Influences activation energy

(c) Structural Distortion [49]:

- ✚ Influences the angle of Fe-O-Fe.
- ✚ Hopping probability of controls electron.
- ✚ Has effects on carrier mobility and band structure.

So, not only doping, but also lattice distortion, is a useful method to engineer electrical properties.

2.7.7 Implications for Energy Storage Applications:

RFeO_3 is electrically and dielectrically active and thus can be used in energy related applications [20, 31]:

- ✚ Large dielectric constant - capacitors are appropriate.
- ✚ Controlled conductivity → find use in resistive switching gadgets.
- ✚ Minimized leakage (optimized systems) → greater energy storage efficiency.

Nanostructured and doped materials of RFeO_3 exhibit:

- ✚ Enhanced dielectric response
- ✚ Enhanced capacity to store charge.
- ✚ Reduced energy loss

To conclude, a combination of polaron hopping conduction, oxygen vacancy defects and grain boundary effects determine the electrical properties of the RFeO_3 compounds. Their frequency-dependent dielectric, semiconducting properties, and tunable conductivity properties make them very promising in electronic and energy storage systems. Doping, conditions of synthesis and structural distortion must be carefully controlled to maximize their electrical performance.

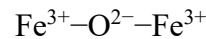
2.8 Magnetic Properties of RFeO_3 :

Rare-earth orthoferrites (RFeO_3) are rich and complexly magnetic materials that are richly interacting between Fe^{3+} ions in the perovskite structure. The interactions that dominate the magnetic properties of these compounds are interactions of superexchange, spin canting and

crystal anisotropy that are highly dependent on the structural distortion and the variation of the composition [39].

2.8.1 Superexchange Interaction Mechanism:

In $RFeO_3$ compounds the superexchange interaction between the neighboring Fe^{3+} ions with the assistance of oxygen ions is the dominant magnetic interaction:



Goodenough-Kanamori rules are that:

- ✚ The Fe-O-Fe bond angle (180 degrees) is preferred to be strong antiferromagnetically coupled.
- ✚ Incidence with 180 is not 180 and weakens the strength of the interaction.

The strength of superexchange interaction is smaller since the $RFeO_3$ compounds have distorted structures, in which the bond angles between the Fe and O and between the Fe and the Fe are less than 180° , which directly influence magnetic ordering [17, 18].

2.8.2 G-type Antiferromagnetism

$RFeO_3$ such materials have G-type antiferromagnetic ordering where:

- ✚ All the Fe^{3+} spins are anti-parallel to all the six closest neighbors.
- ✚ Ideally the net magnetic moment cancels.

This ordering remains stable more until the Néel temperature (T_N) and this depends on the rare-earth ion:

- $LaFeO_3 \rightarrow$ higher T_N (~ 740 K)
- $YFeO_3$ and others $\rightarrow$ slightly lower T_N

This Néel temperature is high to make these materials interesting in room temperature magnetic applications [19].

2.8.3 Weak Ferromagnetism and Spin Canting:

Although the $RFeO_3$ compounds are largely antiferromagnetic, weak ferromagnetism is found in these compounds, which is a result of minor canting of the spins. This effect is due to the Dzyaloshinskii-Moriya (DM) interaction, which is a type of antisymmetric exchange interaction which can be written as:

$$D \cdot (S_i \times S_j)$$

The result of this interaction is:

- ✚ Minor variation of the spins out of the antiparallel alignment.
- ✚ Production of a net magnetic moment.
- ✚ Hysteresis could be observed in MH loops [20].

The size of spin canting will vary on:

- ✚ Structural distortion
- ✚ Bond angle deviation
- ✚ Spin-orbit coupling strength

2.8.4 Spin Reorientation Transitions (SRT):

An additional interesting characteristic of the RFeO_3 compounds (Inclusively YFeO_3 and heavy rare-earth orthoferrites) is spin reorientation transitions (SRT). In this process[8,9]:

- ✚ The temperature with which the magnetic easy axis changes direction.
- ✚ The spin system rotates in the various axes of crystallography.
- ✚ The antiferromagnetic order is still preserved.

This changing is controlled by:

- ✚ Interaction between Fe-Fe exchange interaction and competition.
- ✚ Rare-earth (rare) interactions with iron (rare-earth-iron coupling).
- ✚ Magnetic anisotropy

SRT is especially significant in the applications to magnetic switching and spintronic devices.

2.8.5 Influence of Structural Parameters

The parameters of structures can affect pet transport in the same way that they do any other subject. The magnetism of RFeO_3 is extremely crystal structure sensitive [43, 44]:

(a) R-player ionic Radius:

- ✚ The bigger the ion (La^{3+}) the less distortion, the more powerful the superexchange.
- ✚ Smaller ions (Y^{3+}) is the reduction in larger ions greater distortion (spin canting).

(b) Structural Distortion:

- ✚ Reduced angle of Fe- O -Fe bonds decouples the antiferromagnetically.
- ✚ Enhances weak ferromagnetism
- ✚ Increases magnetic anisotropy

(c) Lattice Strain and Defects:

- ✚ Oxygen vacancies can disrupt exchange pathways
- ✚ Grain boundaries influence domain wall movement

2.8.6 Effect of Doping

Doping is an effective strategy to tailor magnetic properties [43, 48]:

A-site Doping (e.g., Sr^{2+} , Ca^{2+}):

- ✚ Introduces mixed valence states ($\text{Fe}^{3+}/\text{Fe}^{4+}$)
- ✚ Alters exchange interactions
- ✚ Can enhance magnetization

B-site Doping (e.g., Mn, Co, Cr):

- ✚ My altering Fe-O-Fe superexchange routes.
- ✚ Introduces the competing magnetic interactions.
- ✚ Increases spin canting and coercivity.

Nanostructuring Effects:

- ✚ Smaller particle size results in disorder of the surface spin.
- ✚ The improved weak ferromagnetism is because of finite size effects.

2.8.7 Magnetic Hysteresis Behavior [9, 10]:

M-H (magnetization vs magnetic field) loops are normally used to analyse magnetic properties and typically give information about:

- Saturation magnetization (M_s)
- Remanent magnetization (M_r)
- Coercivity (H_c)

In $RFeO_3$:

- Narrow hysteresis loops indicate weak ferromagnetism
- Coercivity depends on grain size and anisotropy
- Unsaturated loops at high fields confirm antiferromagnetic nature

2.8.8 Applications of Magnetic Properties

Due to their unique magnetic characteristics, $RFeO_3$ compounds are widely used in advanced technologies [48-50]:

Spintronics:

- Utilization of spin degree of freedom
- Magnetoelectric coupling in multifunctional devices

Magnetic Sensors:

- Detection of magnetic fields
- Temperature-dependent magnetic response

Data Storage Devices:

- Magnetic memory applications
- Stable magnetic ordering at room temperature

Other Applications:

- Microwave devices
- Magnetic switching systems
- Actuators and transducers

The magnetic properties of the RFeO_3 perovskites are due to the subtle equilibrium of the superexchange interactions, structural distortion and spin canting. These materials are very versatile in recent magnetic and spintronic applications as they do exhibit weak ferromagnetism and spin reorientation transitions. The ability to multifunctionally design new materials through ionic substitution, doping and structural engineering of these properties has opened up an effective avenue to the design of materials in the next generation.

2.9 Optical Properties of RFeO_3 :

The optical characteristics of rare-earth orthoferrites (RFeO_3) is a vital factor used to decide which material is most effective in photocatalytic, optoelectronic and solar energies. These materials have high interaction with the electromagnetic radiation within the UV~visible range which is due to their electronic structures and transitional metals ionic configuration. RFeO_3 is a very sensitive optical response material in terms of crystal structure, defects and chemical composition and can be tuned using different strategies of modification [8-10].

2.9.1 Electronic Band Structure and Band Gap:

RFeO_3 compounds are typically semiconducting oxides with an optical band gap in the range of ~2.0–2.7 eV, which lies within the visible region of the electromagnetic spectrum. This makes them capable of absorbing a significant portion of solar radiation.

The band structure consists of:

- Valence band (VB): mainly formed by O 2p orbitals
- Conduction band (CB): dominated by Fe 3d orbitals

Thus, optical absorption primarily involves charge transfer transitions from O 2p to Fe 3d states, which are responsible for visible light activity [11-13].

2.9.2 Optical Absorption Behavior:

The RFeO_3 compounds demonstrate a high absorption in the UV- visible part of the spectrum and this is one of the fundamental necessities of the photocatalytic and optoelectronic functions. The absorption properties are dependent on:

- ✚ Band gap energy
- ✚ Size and shape of the particles.
- ✚ Existence of flaws and faults.

Key observations:

- ✚ Acute absorption edge that is equivalent to band gap transition.
- ✚ Increased absorption in nanostructures.
- ✚ On doping, redshift (towards the visible region) increases [21, 41].

2.9.3 Determination of Band Gap (Tauc Relation):

The optical band gap of RFeO_3 materials is commonly determined using the Tauc relation:

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

where:

- α = absorption coefficient
- $h\nu$ = photon energy
- E_g = band gap energy
- n = transition type ($n = 2$ for direct, $1/2$ for indirect transitions)

By plotting $(\alpha h\nu)^n$ vs $h\nu$, the band gap is obtained from the extrapolation of the linear region [8-10].

2.9.4 Effect of Structural Distortion:

Structural distortion, doping, and nanostructuring collectively govern the optical properties of RFeO_3 compounds. Distortion of FeO_6 octahedra alters Fe–O bond lengths and angles, thereby modifying Fe 3d–O 2p orbital overlap, which directly affects the electronic bandwidth and band gap; higher distortion (e.g., YFeO_3) leads to a wider band gap and reduced carrier mobility, whereas lower distortion (e.g., LaFeO_3) enhances orbital overlap and results in a comparatively smaller band gap [30-35]. Doping further tailors these properties, where A-site substitution (Sr^{2+} , Ca^{2+}) introduces defect states and narrows the band gap to improve visible light absorption, while B-site doping (Mn, Co, Cr) modifies Fe 3d energy levels, creates mid-gap states, and enhances photocatalytic efficiency. Additionally, nanostructuring significantly improves optical performance due to increased surface area, quantum confinement effects, and enhanced light interaction, leading to better charge separation and higher photocatalytic activity. Optical transitions in RFeO_3 are primarily governed by charge transfer from O 2p to Fe 3d states, with weaker d–d transitions, while defects such as oxygen vacancies introduce localized energy levels within the band gap, enabling sub-band-gap absorption and increased optical conductivity [20-23]. Owing to these tunable optical characteristics, RFeO_3 materials find wide applications in photocatalysis, solar energy conversion, optical sensing, and optoelectronic devices such as photodetectors.

2.10 Multifunctional Applications of RFeO_3 :

Rare-earth orthoferrites (RFeO_3) have received great interests as multifunctional material since electrical, magnetic and optical property coexist in one phase of the system. This integration of various functionalities derives out of the tight integration of charge, spin and lattice degrees of freedom such that such materials can find application in numerous technological areas. RFeO_3 compounds have been extensively studied as catalysts and photocatalysts in the energy applications domain due to variable oxidation states ($\text{Fe}^{2+}/\text{Fe}^{3+}$), high oxygen mobility and

Oxygen vacancies that are available on the surface. These add to their effectiveness in oxidation reactions, degradation of organic pollutants and visible-light-driven photocatalytic reactions. Also, the doped RFeO_3 materials are more conductive in terms of electricity and thermodynamically stable and therefore it is promising as a cathode material used in the solid oxide fuel cell (SOFCs). Their redox capability and dielectric characteristics also make it possible to utilize them in supercapacitors and other power storage networks, in which case large capacitance and periodic stability is needed [34-36].

RFeO_3 compounds have been shown to be a very good gas sensor in sensor applications because of their semiconducting properties and surface reactivity. The sensing principle is almost entirely dependent on the fact that the gas molecules adsorb on the material surface and that there are charge transfer processes, which lead to a certain change in electrical resistance. These materials are highly sensitive, responsive and well stable, especially at a high temperature. Moreover, their surface characteristics and biocompatibility have allowed their penetration in biosensing applications to detect biomolecules. RFeO_3 materials have potential in the area of spintronics, particularly because they form weakly ferromagnetic (through spin canting) and in some instances (e.g. BiFeO_3) they possess magnetoelectric coupling. These characteristics enable the manipulation of magnetic characteristics by the use of electric fields which is crucial to the fabrication of improved memory devices, spin valves and magnetic sensors [37-39].

Optical properties of RFeO_3 , such as excellent absorption in the visible optical spectrum and adjustable band gap also increase their scope of application in optoelectronic devices, including photodetectors, solar cells, and optical sensors. The fact they can create charge carriers when irradiated by light makes them useful in solar energy conversion devices and environmental surveillance. Notably, recent experiments have shown that R-site engineering (varying the A-site cation) is able to strongly affect the structural distortion, electronic band structure and magnetic interactions, facilitating overall multifunctional capabilities. An example of this is that La-based systems have improved electrical conductivity, Y-based compounds have greater magnetic anisotropy, and Bi-based systems are multiferroic. Due to this, RFeO_3 compounds can be successfully utilized with diverse applications by sensibly choosing the rare-earth element and controlling the synthesis environment and so are promising materials that can be used in next-generation multifunction devices [40-41].

2.11 Research Gaps:

Although there is a substantial literature source on rare-earth orthoferrites (RFeO_3), there are still some important research gaps which prevent a full picture of the materials and achieve

maximum utilization in terms of multi-functional application. A significant weakness of current research is that there is no systematic comparative research on LaFeO_3 , YFeO_3 and BiFeO_3 synthesised at the same experimental conditions. The majority of published publications are about single compositions synthesized under various synthesis paths, temperatures, and processing conditions, so it is challenging to directly correlate composition with properties. Consequently, the innate function of A-site cation (La^{3+} , Y^{3+} , Bi^{3+}) in regulating structural distortion and functional behavior is not completely comprehended.

An additional desirable gap is the partial knowledge of the structure-property correlation among the various R-site ions. Despite the fact that it has been known that the ionic radius affects the octahedral tilting and the Fe-O-Fe bond angle angles, a comprehensive and integrated model that links such structural alterations to electrical, magnetic and optical properties does not exist. Specifically, the already mentioned interaction of lattice distortion, defect chemistry (oxygen vacancies), and electronic structure is a topic that needs to be studied further to have predictive models on material performance.

Secondly, a number of calcium oxide compounds have a rising demand to establish low-temperature production methods capable of synthesizing phase-pure RFeO_3 compounds with a controlled microstructure. In the standard solid-state techniques, the temperatures are usually high, resulting in large grain size, unwanted constituents, and minimized defect control. Despite the benefits of chemical processes like sol--gel and hydrothermal processes, the issue of reproducibility, scalability, and purity of phases at the same time is not yet resolved.

Moreover, a vast majority of the literature studies usually concentrate on single properties (only magnetic, electrical, or optical behavior) instead of offering a thorough and systematized examination of all of the three properties in one material system. This piecemeal method constrains the comprehension of interactions in coupling and prevention of ideally versatile devices. Integrated study involving simultaneous measurement of electrical conductivity, magnetic ordering and optical absorption under similar experimental conditions is clearly wanted.

Lastly, despite the high potential of the RFeO_3 compounds in multifunctional functions, further optimization of the properties to address the application to real-life devices is still lagging behind. It is not easy to find a compromise between conductivity, magnetization, dielectric performance and optical efficiency in one composition. These properties need to be customized by controlled doping, nanostructuring, and synthesis engineering but need to be studied further systematically. To fill these gaps, it is thus important to develop RFeO_3 materials to include in real world applications in the energy, sensing, spintronics and optoelectronics field.

2.12 Summary:

The literature review has evidently indicated that rare-earth orthoferrites (RFeO_3) are a versatile group of perovskite compounds with diverse tunable structural, electrical, magnetic and optical characteristics. These polyfunctionalities are due to the high interplay between the distortion of the lattice, the electronic structure and magnetic interactions in the perovskite framework. The RFeO_3 compounds are very promising in advanced technological applications due to the capability of optimising such properties by compositionally modifying and defect engineering as well as controlling synthesis.

LaFeO_3 is commonly known as one of the orthoferrites, it is greatly recognized due to its high chemical stability, lower structural distortion and high catalytic and sensing functions. It is semiconducting in nature; it is a good electrical conductor and when doped, it becomes essential in gas sensors, in photocatalysis, energy related devices. Conversely, YFeO_3 has greater orthorhombic distortion owing to smaller ionic radius of Y^{3+} that promotes magnet anisotropy and stability of the dielectric medium. Its spin reorientation transition properties, as well as its robust magnetic properties are of particular interest in spintronic and magneto-optical applications. BiFeO_3 , on the other hand, is a special type of multiferroic material, and at the same time, it has ferroelectric and antiferromagnetic order at room temperature. Its high spontaneous polarization and magnetoelectric coupling provides opportunities to multifunctional devices like memory elements, sensors and optoelectronic systems.

Although these are important advances, the literature also reveals another gap, which is to carry out comparative systematic studies on LaFeO_3 with YFeO_3 and BiFeO_3 synthesized under the same conditions and under the same controlled conditions. A majority of the investigations are conducted separately on a single compound which limits a clear picture of the contribution made by A-site cation variation towards structure-property association. Moreover, there are still limited integrated studies which correlate structural, electrical, magnetic, and optical properties in one framework structure.

The direct and comparative analysis of such orthoferrite systems at the same synthesis conditions is thus necessary to have an enhanced insight into the multiradian nature of such systems. It is in this gap that the basis of the motivation of the present research work is derived where the aim of the study is to explore and correlate systematically, the structural, electrical, magnetic and optical nature of the RFeO_3 ($\text{R} = \text{La, Y, Bi}$) compounds as they can be profiled in multifunctional applications.

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