Optoelectronic behavior of some spinel oxides for sustainable engineering

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Abstract. Spinel oxides have a pivotal role in material science due to their structural, electrical, magnetic and optical properties, rendering them essential for wide range of applications. Spinel oxides, characterized by their spinel crystal structure, belong to a group of inorganic compounds with a general chemical formula of AB2O4, where A and B represent distinct metal ions. These compounds are frequently encountered in minerals, rocks, and soils, and their versatility makes them invaluable in numerous domains, including catalysis, energy storage, electronics, and ceramics. This paper briefly reports existing fascinating structural, opto-electronic properties of some spinel oxides, to understand electronic band structure, density of states and optical properties such as dielectric function, refractive index, absorption and optical conductivity for their applications in engineering devices. Basically, spinel compounds have physical properties such as high reflectivity, high melting point, high strength and chemical resistivity at elevated temperatures as well as low electrical loss. Therefore, we have made an attempt to showcase considered properties of these materials at one place.

1 Introduction

Spinel oxides have a pivotal role in material science due to their physical properties such as high reflectivity, high melting point, high strength, and chemical resistivity at elevated temperatures and low electrical loss,[1,2] rendering them essential for a wide range of applications. So, what is the group? In a simple sense, we can say those spinel oxides are characterized by their spinel crystal structure, and belong to a group of inorganic compounds having a general formula AB2O4, A and B are any metal ions[3]. In 1915, Sir William Henry Bragg penned a seminal paper delving into the intricate structural properties of the spinel oxide family. Here astutely observed that the atomic arrangement within this group bore a striking resemblance to the crystal structure of a diamond, which is celebrated for its exceptional symmetry and remarkable cohesion at the atomic level. Bragg’s keen insight shed light on the extraordinary structural congruence between spinel oxides and diamond, these profound observations underscore the enduring significance of the spinel oxide family in the realm of crystallography and materials research. The spinel crystal structure consists of oxygen ions arranged in a cubic close-packed pattern, while the metal ions A and B are located in octahedral and tetrahedral sites within the structure, respectively. This precise arrangement creates a remarkably organized and symmetrical crystal lattice[4,5], leading to distinctive electronic and magnetic properties. Spinal oxides have different electronic behaviors because of their unique structures and elements[6]. In addition to their magnetic and electrical properties, spinel ferrites also exhibit interesting optical properties. These properties have been investigated in recent years for their potential applications in fields such as optoelectronics, photonics, and optical sensing[7,8]. This chapter primarily focuses on spinel ferrite as an illustrative example. Spinel ferrites, belonging to a class of magnetic insulators, have been a subject of intense study due to their exceptionally unique magnetic and electrical properties[9]. They present intriguing possibilities for numerous applications. Spinel ferrites are anticipated to play a substantial role in catalyzing the degradation of pollutants and the production of clean energy, encompassing methods like water splitting.
Moreover, they are regarded as adaptable materials with broad applications in large-scale settings, notably in energy storage devices like supercapacitors and electrodes. These materials hold significance in the realm of commercial electroceramics[10,11]. Spinel ferrites also offer versatile nanostructures and enhanced magnetism, promising applications in diverse fields like recording media, sensors, drug delivery, and intracellular imaging, bridging magnetic and biological realms [12].

2 STRUCTURE OF SPINEL OXIDES

Spinel oxides have a fascinating crystal structure, these crystal structures AB2O4 has a normal spinel structure which is cubic and holds the topmost symmetries, this structure is similar to that of a diamond[4], it comprises two face-centered cubic crystals that possess a certain type of symmetry structure which means the FCC cubic lattice is modified by introducing additional symmetry elements that are also invading each other[5]. In the spinel structure, metal cations are arranged in two distinct crystallographic sites: tetrahedral and octahedral. The A cation occupies tetrahedral sites in the crystallographic lattice. These cations have a coordination number of 4 and are mainly divalent for example Mg2+, Cu2+, Zn2+Ni2+. The B cations occupy octahedral sites in the crystal lattice. These cations usually have a coordination number of six and are trivalent or tetravalent for example Fe3+, Al3+, Ti4+, etc. Oxygen ions(O2-) fill the space between the cations in the crystal structure forming a cubic close-packed array. So, in the arrangement of cations in the spinel structure one-eighth of the tetrahedral sites and half of the octahedral sites are occupied[13,14]. The inverse spinel structure is just a variation of the regular spinel structure in which the arrangement of cations in the crystal lattice is different. Here inverse distribution indicates B [AB2] O4. AB in the parenthesis fills octahedral sites. This normal and inverse structure can be depicted (A1-y by) -(Ay B2-y) the parameter y is termed as the degree of inversion, when y=1 the structure is inverse[15]. Ferrites like NiFe2O4 and CoFe2O4 can make an inverse structure where half of Fe3+ occupy tetrahedral sites and a mixture of the remaining fe3+ and other cations occupy the octahedral site16. The term that describes the symmetrical arrangement of atoms in a 3D crystalline solid is called space group, in the case of spinel oxide it is fd-3m(no.227). in this structure, more importance is given to two parameters which are the lattice parameter and anion position parameter u. The cation A which is in the tetrahedral position occupies 8a lattice sites and B in the octahedral position occupies 16d lattice sites[15,16,17]. The separation between each cation relies on unit cell dimension a. The distance between B-B is shorter than between A-B and A-A. All the A ions within the crystal lattice are equidistant from B ions[18,19]. The anions in the spinel structure occupy 32 e lattice sites, and a single parameter u resolves their displacement. The bond length depends on u and a[20]. The single parameter u value for a perfect cubic close-packed structure is 3/8(0.375) and 1/4(0.250) based on established selection on the origin of the unit cell it will be either 43m (tetrahedral cation) and 3m (octahedral vacancy). The unit cell dimension depends on the cationic radius in a given compound and as for the anionic partial parameter it has a strong dependence on the inversion parameter[21,22].

Figure 1 Representation of the cubic AB2O4 spinel structure, with light grey A atoms in tetrahedral positions and light blue B atoms in octahedral positions within a red face-centered cubic oxygen sublattice.[23]
3 ELECTRONIC PROPERTIES

Electronic properties play a crucial role in understanding a material like how the electron is going to behave and interact in a given material which will lead to various applications and Technologies the electronic properties of spinal oxide depend on its chemical composition, structure, and arrangement of cation. different spinal oxides have different electronic behaviors[6]. 6 oxide ions surround transition metal ions in the octahedral region, in this situation d orbitals split into triplet t2g and doublet eg like for the tetrahedral field the d orbitals split into doublet e and triplet t2. in case of tetrahedral crystal field this is due to the direct electrostatic repulsion between orbitals dx, dy and dzx, and surrounding anions as for octahedral dz2 and this dx2-y2 are repelled directly. The density of states which tells us about available electronic States at different energy level and electronic band gaps of materials are more concentrated on these electronic properties[22,25]. We will discuss this through ferrite spinal oxide examples.

CoFe2O4
The total density of States explains the distribution of electronics States in this case of co-fe2o4 the study of the total density of state considering at the Fermi level gives a non-zero value, and the missing gap at Fermi level also indicates the metallic behaviour of CoFe2O4. This spinal can behave as a conductor[26]. Here tetrahedral site will be occupied by Fe, the majority of electrons are in low energy and they occupy both tetrahedral and octahedral sites. There is a single electron with an unpaired spin in the tetrahedral site this unpaired electron proposes that this site is closer to having a d6 electronic configuration splitting of Co and Fe in the octahedral position suggesting that there is an interaction between these States this interaction can affect the electrical conductivity magnetic behaviour and electronic properties[23]. The total density of the state represents the total density over a given energy range where the partial density of the state allows to breaking down of the overall density of the state into contributions from individual atoms and orbital within the material. The non-spin polarized density of state considers available energy States without any distinction between two possible electron spin states. when we consider this distinguishing, it is called spin-polarized density of state[27].

CoFe2O4 has a metallic character, however, it shows an energy gap in the electronic band structure in the range of 0.5 to 0.6eV it shows semiconducting behavior[28] this calculated minimum energy gap for the inverse cofe2o4 is 0.63eV [23]. This comparison between inverse and normal spinel structures underscores the intricate variation in electronic band structure with these spinel configurations The electronic band structure of inverse spinel will have a small bump observed around -7ev whereas normal spinel forms rather a sharp peak around -8 eV [30].

ZnFe2O4
Perfect Spinel of zinc ferrite oxide is initially characterized as a direct band semiconductor with a 1.25e band gap but its valence band maximum dispersion is described as notably flat, leading to the formation of large holes with Substantial
effective mass this makes poor p-type conductivity making it less efficient for conducting positive charge carriers. The band decreases under increasing external pressure it signifies a transition towards a more conductive state. However, the appropriate method for predicting the crystal structure in the context of normal Spinel ZnFe2O4. From the figure3, the density of states close to the Fermi level is mainly due to the presence of Fe 3d and O 2p states. Fe 3d orbitals play a major role in shaping the conduction band minimum while both Fe 3d and O 2p orbitals make significant contributions to the valence band maximum. This points to the existence of a covalent bond between Fe and O atoms[31].

Figure 3 The partial density of states data for zinc ferrite oxide vertical dashed line positioned at zero energy level marks the Fermi level[31]

The generalized gradient approximation with revised Perdew Burke Ernzerhof functional Combined with the ultrasound pseudopotential method is the most suitable approach within the framework of density functional theory. This gives a
direct band gap of 0.93eV. The partial density of states plays a significant role in shaping the atomic orbitals of various electronic energy states the highest occupied energy levels often referred to as valence bands are primarily composed of the Fe 3d states and these are located near the Fermi level[32].

NiFe2O4
The electronic band structure of a material describes the Energy levels available to electrons in a crystal lattice when considering spin-polarised materials like NiFe2O4. The energy bands are divided into two sets one electron with majority spin and another for an electron with minority spin. The majority of spins have a band gap of 2.718 eV, while minority spins have a smaller band gap of 2.550 eV [33,60].

In a semiconductor, the Fermi level falls within the energy band. The form level position within the band gap in both Spin up and spin down density of state indicates that NiFe2O4 has a fundamental energy gap making it a semiconductor[34]. Here the Octahedral site is primarily occupied by Fe3+ ions in the Neel model the spins of the Fe3+ ions at octahedral sites are aligned in a Parallel fashion which means the magnetic moments are oriented in the same direction, on the tetrahedral site magnetic moment. Oriented in the opposite direction to the moment of Fe3+ ions in the octahedral site. This Parallel and antiparallel spin Results in net magnetic moments for the entire crystal This Fermi magnetic alignment leads to a non-zero magnetization[35]. The net magnetic moment can be understood by considering the properties of the iron and nickel in the crystal lattice, the total magnetic moment is discovered to be 2 Bohr magneton[36]. The iron in the tetrahedral position has a calculated local magnetic moment of -3.6 Bohr magneton, transition metals exhibit energy level splitting due to interaction between the charge densities of their d orbitals and the surrounding charge density which disrupts their degeneracy for iron in octahedral local magnetic moment +3.81 bohr magneton and for nickel in octahedral is +1.59 Bohr magneton[34].

Figure 4  Density of States (DOS) for NiFe2O4 as determined through Density Functional Theory (DFT) calculations[37]

4 OPTICAL PROPERTIES
Cubic Spinel is more Pliable compared to sapphire which is trigonal, making it an advantage for optical applications when optical isotropy is a necessity the benefits of cubic spinel over trigonal sapphire become evident. The spinel materials display moderate light absorption, particularly in the infrared spectrum around 3 micrometers indicating its tendency to retain and absorb light at this specific wavelength[38,39]. Here focus should be on properties such as dielectric function, refractive index, absorption, reflectivity, and optical conductivity. Dielectric function describes the response of a material to an external electric field, particularly in the context of electromagnetic waves absorption refers to the process by which a material absorbs and retains electromagnetic waves Energy loss function describes how much energy is lost as light interacts with a material. In the case of reflectivity, it is a measure of how much incident light is
CoFe2O4
In the case of cobalt ferrite, the material can interact with light in the visible and infrared regions of the electromagnetic spectrum or the direct band gap values fall within a specific range of 2.03 eV and 2.74 eV. The mean direct band gap value is 2.31 eV, while the standard deviation which measures the variation around the mean is 0.28 eV. As for the indirect band gap the range is 2.31 eV and 1.31 eV [42]. The dielectric function contains real and imaginary parts these parts provide insight into the metallic characteristics of CoFe2O4. The real part exhibits a distinctive peak at 0.82 eV which is a significant energy level, the negative value of the real part demonstrates the behaviour of the charge carrier within a single electronic band. The imaginary part of the dielectric function poses a value very close to zero in this region, indicating minimal energy loss due to absorption This tells that the material is almost transparent in the infrared region So the material's optical properties are the same in all directions. The refractive index is often represented with both real and imaginary part’s real part determines the phase velocity and the imaginary part represents absorption loss. Phase velocity sharply decreases in the low-energy region. Extinction coefficient increases linearly which describes how much incident energy is absorbed by material. CoFe2O4 exhibits nearly complete reflectivity across the entire energy spectrum spanning from 0 to 30 eV [14].

ZnFe2O4
The complex dielectric function stands as a key optical property that has real and imaginary parts so the complex dielectric function Serves as a critical optical parameter. In ZnFe2O4 after Reaching a constant value at 15 eV it reveals distinct trends in both its real and imaginary parts, in the real part, the initial optical critical point energy is approximately 0.6 eV subsequently plummeting to 1.17 eV and for the imaginary first peak appeared around 0.8 eV and gradually diminished to zero around 15 eV. The static dielectric Constant Standing at 33.5 indicates potential as a dielectric material [31]. The reflectivity of the compound exhibited distinct characteristics when subjected to varying energy levels and pressure in the visible region significant drop in reflectivity reached its minimum of approximately 3 eV this decrease suggests ZnFe2O4 absorbs a significant portion of incident light within this range . In the energy range of 10-30 eV the reflectivity displayed higher Intensity peaks across all applied pressures which means more reflective at these higher energies. The reflectivity decline in the ultraviolet region within the energy range of 31-42 eV the variation in reflectivity thus suggests that the high sensitivity towards applied pressure [43].

NiFe2O4
The complex dielectric function's real and imaginary components are initially examined when analysing the optical properties of NiFe2O4. Examining the imaginary part of the complex dielectric function within the 0-40 eV energy range provides insights into how the NiFe2O4 compound absorbs and responds to high-energy electromagnetic radiation. And as for the real part of the complex dielectric function exhibits a distinctive pattern as the photon energy increases. It undergoes steady growth, culminating in a prominent peak, and intriguingly, it reaches a point of absolute zero at about 18.73 electron volts subsequently, it undergoes another increase, culminating in a second notable peak, and then once more dips to zero, this time occurring at an energy level of 26.10 eV. The absorption peaks are identified in the ultraviolet (UV) spectral region. Within the energy span of 0 to 6 electron volts (eV), there is a discernible apex in the refractive index occurring precisely at 3.95 eV, and this peak is a result of the minority state. It’s also worth highlighting that, in the energy range of 10 to 18 eV, the refractive index follows a non-linear trend, decreasing as the frequency rises [33, 59].

NiFe2O4 possesses an indirect band gap and direct band gap characteristic. The ideal inverse spinel structure of NFO results in two direct band gaps at 2.3 eV and 2.74 eV, along with one indirect band gap at 1.526 ± 0.08 eV. Optical transmittance measurements indicate the presence of an indirect band gap at approximately 1.6 eV [37].

5 VERSATILE APPLICATIONS
One of the most pressing challenges facing modern society is the establishment of a sustainable energy infrastructure. A fundamental aspect of this transition is the adoption of sustainable fuels to replace our existing energy sources. Hydrogen, produced primarily from water, presents a promising solution to tackle sustainability concerns, reduce environmental emissions, and enhance energy security. Utilizing solar energy to split water and generate hydrogen, is recognized as an exceptionally efficient energy carrier for the future [44]. The use of transition metal oxides in photoelectrochemical (PEC) water splitting has become an area of significant interest, particularly following the discovery of water's photoinduced breakdown on titanium dioxide (TiO2) electrodes [45]. There is an ongoing need to explore novel materials with narrower band gaps, capable of absorbing visible light and demonstrating favorable photoelectrochemical (PEC) characteristics [23]. Here our primary emphasis is directed towards spinel ferrite materials due to their exceptional properties. Spinel ferrites are expected to have a significant role as catalysts for breaking down
pollutants and generating clean energy, including processes like water splitting. Furthermore, they are seen as versatile materials with extensive uses in large-scale applications, particularly in energy storage devices such as supercapacitors and electrodes[46]. So it has garnered recognition as a highly efficient catalyst that plays a crucial role in addressing energy and environmental challenges.

Visible light-driven hydrogen evolution can be achieved using mesoporous carbon nitride-metal ferrite nanocomposites as catalysts. These nanocomposites exhibit better catalytic performance compared to pristine mesoporous Carbon Nitride[47]. NiFe2O4 is a promising candidate for photocatalytic hydrogen production, as it can produce more hydrogen gas per unit mass and is more efficient at utilizing visible light, potentially offering economic and environmental benefits in the development of photocatalytic reactors for hydrogen production[48]. Combining NiFe2O4 with other active materials in a heterojunction leads to a cooperative effort among multiple active species, resulting in an improved Oxygen evolution Reaction performance[49].

Ferrites have become an integral part of numerous electronic circuits, including noise-minimizing amplifiers, adjustable oscillators, filters, and networks for impedance reconciliation, to name a few. Lately, their use as inductors has been driven by the consistent drive towards miniaturization and incorporation, particularly in the creation of ferrite multilayers for inert electronic devices[50]. Utilizing fully integrated inductors based on ferrite materials, including spinel ferrite, can enhance the efficiency of radio Frequency Integrated Circuit while simultaneously decreasing their footprint, presenting a compelling prospect for compact, high-performance integrated inductors[51]. Stacked arrangements of ferrite materials combined with piezoelectric oxides have the potential to usher in an innovative era of magnetic field sensors. A multi-layered specimen consisting of nickel zinc ferrite and lead zirconate titanate has been employed to assess the sensor's reaction to alternating and direct magnetic fields, field directions, frequency variations, and temperature changes[52].

spinel ferrite's magnetic properties are highly valuable and find practical applications in various fields[53,61]. These include their role in improving the quality of magnetic resonance imaging, their incorporation into electronic devices, their contribution to information storage technologies, and their significance in the precise delivery of drugs to specific locations in the body[54]. Spinel ferrite nanoparticles, also known as spinel ferrite nanoparticles (SFNPs), have significant applications in the field of biomedicine, including cancer diagnosis, cancer gene therapy, drug delivery, and controlled drug release[55]. CoFe2O4 nanoparticles hold substantial potential as efficient nanocarriers for drug delivery, as well as promising materials for both diagnostic and therapeutic applications[56,61]. NiFe2O4 nanoparticles are appreciated for MRI applications due to their affordability, outstanding electromagnetic performance, and excellent chemical stability[57,58]. Barium-based spinel ferrite doped rare earth elements have been revealed as useful in microwave applications[63]. There are other spinel materials also showing these types of applications[64]. Like spinel ferrite, the whole family of spinel oxide has incredible applications in various fields on supercapacitors[65], LPG gas sensors[66], fuel cells[67], and other optoelectronic applications.

6 SUMMARY

In conclusion, spinel ferrites, with their remarkable electrical, magnetic, and structural properties, hold immense promise across a wide spectrum of applications, from cutting-edge electronics and energy solutions to healthcare and environmental remediation. These versatile materials are poised to play a pivotal role in shaping the future of technology and science, offering innovative solutions to some of the most pressing challenges of our time. Research on spinel oxide is rapidly expanding. Scientists and medical professionals are increasingly focused on understanding its potential applications and benefits, driving a surge in studies and investigations. This growing interest in spinal oxide underscores its importance in various fields, particularly in the context of medical advancements and the treatment of spinal-related conditions.

7 References


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