A STUDY OF STRUCTURED, ELECTRICAL AND MAGNETIC PROPERTIES OF OXIDE MATERIALS

ABSTRACT

THESIS

SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy in Applied Physics

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Under the Supervision of

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Metal oxides make a very important role in various fields of chemistry, physics and materials science. The metal elements have a capability to form an enormous diversity of oxide compounds. These can adopt an enormous number of structural geometries with an electronic structure that can reveal metallic, semiconductor or insulator character. Metal oxides are used in the fabrication of microelectronic circuits, sensors, fuel cells, coatings for the passivation of surfaces of rust, catalysts, and optoelectronic devices. In the emerging field of nanotechnology, an objective is to construct nanostructures or nanoarrays with particular properties with respect to those of bulk or single particle species. The unique physical and chemical properties can be exhibited by metal oxide nanoparticles, because of their limited size and a high density of the corner or edge surface sites. Three important groups of basic properties in any material have been influenced by the size of particle is expected. The structural characteristics belong to the first one, namely the lattice symmetry and cell parameters. Generally, perovskite is the name of a more universal group of crystals that take the same structure and is now used to refer to any member of a very big family of compounds that has the basic chemical formula ABO₃ where A and B show two different cations in size and for which the B ion is surrounded by an octahedron of O ions. The Perovskite materials can present insulating, semiconducting, ionic conducting and superconducting behavior being valuable for technological applications in sensor devices, refractories, electronic components, solid oxide fuel cells (SOFC), catalytic membrane reactors for hydrogen production, and so on. Their physical properties such as structural, optical, thermal, dielectric, electrical and magnetic properties have been extensively studied. Such versatility in the family of transition metal perovskite leads to be one of the most important in material science. These properties occur primarily in the compounds whose structure deviate from an ideal cubic due to unstable types of distortions, such as polar or antipolar moves of A and/or B ions from their exact position in the center of the octahedral tilts, Jahn-Teller distortions, or magnetic ordering. The replacement and doping of various cations at the A or B sites modifies the distortion of the perovskite structure and therefore tailors the physical properties of this type of materials. ABO₃ perovskite materials have proven to be the best materials for cathodes due to their tunability. Their properties such as phase stability, thermal expansion coefficient, electronic and ionic
conductivity could be adjusted with the selection of A and B site metal cations. The perovskite oxides are very interesting and extensively studied due to the vast variety of solid-state phenomena they display. Perovskite oxides exhibit a large variety of properties, due to the variety of structures and chemical compositions.

In the present thesis, we were motivated to explore various properties of pure bismuth ferrite (BiFeO$_3$), pure and doped lanthanum ferrite (LaFeO$_3$) and a series of doped lanthanum manganite (LaMnO$_3$) nanoparticles due to their technological importance as given below:

1. **Bismuth Ferrite (BiFeO$_3$):**

Pure bismuth ferrite could be tailored in various ways. An important method to modify its properties is to replacement bismuth with another cation, such as a rare-earth metal. Samarium is a rare-earth metal which differs from bismuth with its much smaller ionic radius and the fact that samarium does not have single pairs like bismuth. Bismuth ferrite, BiFeO$_3$, is a multiferroic material with the perovskite ABO$_3$ structure. Since both the iron and bismuth cations are trivalent, Fe$^{3+}$ and Bi$^{3+}$, respectively, BiFeO$_3$ is called a III-III perovskite. The structure contains a Fe$^{3+}$ cation inside an O$_6$ oxygen anion octahedron. The vacancies between the octahedra are filled with Bi$^{3+}$ anions. In bulk BiFeO$_3$, the structure is rhombohedrally distorted due to octahedra tilting around the [001]$_{hex}$ axis. The hexagonal unit cell parameters on bulk size BiFeO$_3$ are $a_{hex} = b_{hex} = 5.5787\text{Å}$ and $c_{hex} = 13.8688\text{Å}$. The proportional sizes of the ions in the BiFeO$_3$ structure are essential for the stability of the structure. BiFeO$_3$ was supposed as the only possible candidate, which exhibits instantaneous enormous ferroelectricity and antiferromagnetism at room temperature. This discovery had led to a series of investigations in this area from around the world and a lot of extra novel properties of BiFeO$_3$ were discovered involving photovoltaic effect, light induced photostrictive effect, and controllable ferroelastic switching. Meanwhile, the majority of scientist of physics concentrates on bulk and thin film samples of BiFeO$_3$ to show its physical properties, inspired by its potential in information storage in spintronic devices and sensors, other scientist of material and chemist are working on BiFeO$_3$ through its nanostructures, a valuable way to fully understand the chemical properties and application of the material.
2. **Lanthanum Ferrite (LaFeO$_3$):**

The researcher conducted a careful study of the electronic conductivity and defect structure of LaFeO$_3$. LaFeO$_3$ is oxygen deficient and was shown a behavior of p-type semiconductor. Iron can be stable in valence states 2$^+$, 3$^+$, and 4$^+$. LaFeO$_3$ has a low lanthanum vacancy concentration, which is balanced by a low concentration of oxygen vacancies and Fe$^{3+}$/Fe$^{4+}$ oxidation couples. Holes conduct by small Polaron jumping from B-site to B-site by altering valence state. Conductivity is very low for LaFeO$_3$. **Lanthanum ferrite (LaFeO$_3$) based oxides are an important due to its unique properties.** LaFeO$_3$ has both high ionic and electronic conductivity at high temperatures, and they are potential candidates for use in high temperature electrochemical devices, such as gas sensors, oxygen permeable membranes, and electrodes in solid oxide fuel cells. Lanthanum ferrite (LaFeO$_3$) has orthorhombic symmetry perovskite Structure and an antiferromagnetic insulator with Néel temperature $T_N = 750$ K. It has a various properties such as the exchange bias, multiferroic and magnetic optics, which are very important for development so many applications, as new magnetic memory devices, low power consumption spintronic devices and magneto optical sensors.

3. **Lanthanum Manganite (LaMnO$_3$)**

Manganites frame is an important place in the material science research due to its extensive applications owing to the vast properties shown by these materials in various conditions. Manganites are richly varied and fascinating systems due to dramatic properties shown by them in diverse surroundings. These are strongly correlated electrons family wherein the correlations among electrons assign different interesting properties to this class of materials. The colossal magnetoresistive manganites always been studied by a sizable fraction of the condensed matter community and their popularity had reached the levels comparable to that of the high-temperature superconducting cuprates. A vast interest in the investigated of manganites is due to their interrelated properties and possibilities of device applications. The versatile electrical properties of perovskites are easily tunable by changing the oxygen stoichiometry, by doping or by applying an electric field. The undistorted ideal cubic SrTiO$_3$ at room temperature is an insulator, but the SrTiO$_3$-$x$
oxygen deficient derivative is conducting or superconducting. The parent manganese compound LaMnO$_3$ is anti-ferromagnetic and insulating in its ground state. LaMnO$_3$ undergoes a structural transformation at $T\sim 523 K$ from the Jahn-Teller distorted orthorhombic phase to a high temperature cubic semiconducting phase. Sr and Ca doped LaMnO$_3$ derivatives become metallic/ferromagnetic and also exhibit effects like colossal magnetoresistance in metallic multilayers. Lanthanum Manganites (LaMnO$_3$) are members of strongly correlated electrons family wherein the correlation among electrons assign various interesting properties to this class of materials and have the ABO$_3$ perovskite structure. It is important due to the following reasons:

1. The unexpectedly large magneto transport properties of these compounds.
2. When we study the manganites is, their rich phase diagram exhibiting a variety of phases with unusual spin, charge, lattice and orbital order.
3. The states formed in these compounds are dominated by coexisting clusters of competing.

A great interest in the study of manganites is due to their interrelated properties and possibilities of device applications. Mixed valence manganites with the perovskite structure have been investigated. Early research was motivated by a need to develop insulating ferromagnets with a wide magnetization for high-frequency applications. More recent work has been determined by a wish to understand and develop the large negative magnetoresistance effects which occur close and below the Curie temperature also to understand the low field magnetoresistance effect at low temperature. Research on the manganites has exhibited new phenomena such as colossal magnetoresistance (CMR) and dense granular magnetoresistance which led to the understanding of several physical concepts such as Zener double exchange and the Jahn-Teller effect. They can modify dramatically stoichiometrically in time and/or space as a result of small changes in condition.

Chapter 1 is dealing with a brief introduction about nanotechnology, nanomaterial and literature review of metal oxide nanomaterials. Perovskite oxides have been discussed in brief. Highlighting and important properties have been
illustrated to bismuth ferrite (BiFeO$_3$) and lanthanum ferrite (LaFeO$_3$) and lanthanum manganite (LaMnO$_3$) perovskite compounds.

Chapter 2 covers the necessary theoretical background and experimental details about the sol-gel combustion and reverse micelle techniques employed while the material characterization related to the structural, optical, thermal, electrical and magnetic properties of the as studied systems. The working principles of characterization equipments such as XRD, AFM, SEM, FESEM, EDS, FTIR, TGA, DSC, UV-visible, LCR meter, Set up of four prop and VSM are considered.

Chapter 3 is exploring the structural, optical, electrical and magnetic properties of AFeO$_3$ (A = Bi & La) nanoparticles. In the first section, BiFeO$_3$ (BFO) has been synthesized by sol-gel combustion. The XRD pattern obtained from the BFO confirmed the high crystalline and single phase of perovskite structure. BFO revealed a rhombohedral structure with space group R3c and lattice parameters a = b = 5.75 Å and c = 13.82 Å. It has an optical band gap energy $E_g \sim 2.1$ eV. The dielectric properties (Dielectric constant, dielectric loss, ac conductivity and impedance analysis) of BFO have been discussed in details. The magnetic behavior revealed the antiferromagnetic of BFO nanoparticles. In the second section, LaFeO$_3$ (LFO) has been a synthesis by reverse Mitchell with different ratio of water to surfactant [R = water/surfactant]. The XRD patterns showed the pure single phase for both samples (R1 and R2). LFO thermal properties have been studied. R1 and R2 optical band gap have been found at (2.62 and 2.60 eV) respectively. The dielectric properties (Dielectric constant, dielectric loss, ac conductivity and impedance analysis) of LFO have been discussed in details. The magnetic behavior revealed the ferromagnetic of R1 and R2 samples.

Chapter 4 presents all the experimental results of nanoparticles of series La$_{1-x}$Sr$_x$Fe$_{1-x}$Ni$_x$O$_3$, (x = 0.0, 0.1 & 0.42) synthesis via reverse micelle method. The X-ray diffraction patterns of the samples indicate that all the samples exhibit single phase orthorhombic perovskite structure without the presence of any secondary phase. The optical band gap energy increases with increasing x. The dielectric constant (both real and imaginary parts), loss tangent (tanδ) have been found to decrease with increasing
frequency, but the ac conductivity ($\sigma_{ac}$) is increasing with increased frequency. Also the impedance analysis has been considered in details. The magnetic behavior exhibits the ferromagnetic for all samples.

**Chapter 5** presents the experimental results of results of nanoparticles of series $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$, ($x = 0.00, 0.01 \& 0.04$) synthesis via reverse micelle method. The X-ray diffraction patterns of the samples indicate that all the samples exhibit single phase orthorhombic perovskite structure without the presence of any secondary phase. The optical band gap energy is decreased with increasing $x$. The dielectric properties as a function of temperature such as (dielectric constant, loss tangent (\tan$\delta$) and ac conductivity) have been studied in details. The magnetic behavior exhibits the ferromagnetic for all samples.

**Chapter 6** presents the experimental results of results of nanoparticles of series $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$, ($x = 0.00, 0.10, 0.15 \& 0.20$) synthesis via reverse micelle method. The X-ray diffraction patterns of the samples indicate that all the samples exhibit single phase orthorhombic perovskite structure without the presence of any secondary phase. The electrical properties confirmed semiconductors of these materials as well as they exhibited the insulator to material transition. The magnetic behavior exhibits an antiferromagnetic for all samples.

**Chapter 7** presents an overview of the results concluded from all the previous chapters and scope of future work on the studied materials.
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ALIGARH MUSLIM UNIVERSITY
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2013
I dedicate this work to my wife,

Dr. Mrs. Sabah Almekhlaifi

She always believed in me and encouraged me
to keep working and try my best.

THESIS
CERTIFICATE

This is to certify that the thesis entitled "A Study of Structured, Electrical and Magnetic Properties of Oxide Materials" being submitted by Mr. Abdullah Ameen Saad Hassan bearing En. No.: GD-7915 for the award of the degree of Doctor of Philosophy in Applied Physics is a record of the bonafide research work carried out by him. He has worked under my guidance and supervision, and has fulfilled the requirements for the submission of the thesis.

The results presented in this thesis have not been submitted in part or in full, to any other University or Institution for the award of any degree or diploma.

(Dr. M. Wasi Khan)
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I, Abdullah Ameen Saad Hassan, Department of Applied Physics certify that the work embodied in this Ph.D thesis is my own bonafide work carried out by me under the supervision of Dr. M. Wasi Khan at Aligarh Muslim University, Aligarh. The matter embodied in this Ph.D thesis has not been submitted for the award of any other degree.

I declare that I have faithfully acknowledged, given credit to and referred to the research workers wherever their works have been cited in the text and the body of the thesis. I further certify that I have not willfully lifted up some other’s work, para, text, data, result, etc. reported in the journals, book, magazines, reports, dissertations, theses, etc. are available at websites and included them in this Ph.D. thesis and cited as my own work.

Date: 25-10-2013

(Signature of the candidate)

Abdullah Ameen Saad Hassan

Certificate from the Supervisor

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the supervisor:  

Name & Designation: Dr. M. Wasi Khan (Assistant Professor)


(Signature of the Chairman of the Department with seal)

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CHAPTER I

Introduction and literature review
1.1. Introduction

Nowadays, nanotechnology and nanoscience is the most reliable branch of science and technology which is widely used due to its great applications in the life days. Nanotechnology is defined in previous as the design and fabrication of materials, devices, and systems to control at the nanometer scale up to 100 nanometers while is defined in later as the focus towards the observations, study of the phenomenon at the nanometer scale and ways of manipulating matter at these scales, at which many properties of matter vary from those of bulk counterpart [1]. On the nanoscale, there is an enormous rise in the ratio of surface area to volume. Due to this, materials at the nanoscale display very various properties contrasted to what they show on a micro scale, enabling unique applications [2]. Occasionally, this technology is referred to as ‘converging technology’ as it explains the formation/integration and utilization of materials, devices, and systems through the control of nanometer-sized materials and their new applications to physics, chemistry, biology, engineering, materials science, medicine, and other endeavors. Sometimes it is called as ‘enabling technology’, due to it permits new scientific and technological developments in an extensive range of disciplines and fields of application [2]. It contains three to zero dimension structures. Nanoparticles and nanostructured materials synthesizing and characterizing in a specific area of application has always been an interesting field of investigate for the scientists around the world. Nowadays, there are many nanomaterials research focused towards device applications, system integration, film fabrication and biomedical applications. The particle size is decreasing to the nanoscale leads to the emergence of new phenomena that are not observed at bulk scale, opening a wide world of applications of nanoparticles into various physical and chemical areas. The new preparation combination techniques that allow us to find nanoparticles with narrow and well defined size distribution profiles, with great characterization techniques, give a deep approaching into the microscopic mechanisms responsible for that new phenomenology. The size combination and surface effects deeply adjust the electronic structure of the nonentities promoting a magnetic behavior completely unexpected in bulk state. The possibility of fabrication of modified nanoparticles for a particular purpose, such as biomedical applications, opens a new era for material science [3]. The formation of transition metal oxides is one of the most
fascinating classes of inorganic solids revealing inspiring physical properties such as structural, electrical transport, magnetic and optical occurring due to the strong correlation effect of electron in the systems. In the past few decades, studies of these oxides have seen interest resurgence. In recent years, there are various reasons for great interest of the scientific community toward nanotechnology, but the primary motivation is because nanomaterials typically display unique electronic, optical, magnetic and mechanical properties contrasted to their bulk counterpart and even molecular complements. The phenomenon of variation of materials electronic properties as it reduces in size is referred to as the quantum size effect. In metallic nanoparticles the quantum size effect is well documented in literature [3]. In bulk metals, the valence and conduction bands overlap, whereas is a gap between these bands in metal nanoparticles. The gap has been seen in metal nanoparticles may be similar in size to that seen in semiconductors (< 2 eV) or even insulators (> 2 eV) [3]. Fig. 1.1 shows a diagram of the electronic bands in metals, semiconductors, and insulator. The materials tailoring on the near atomic level (nanoscale) has verified to be an important tool in the achievement of preferred properties of bulk materials. For example, little changes at the atomic level in bulk materials are known to modify mechanical properties, and in particular such changes often achieved to create stronger materials. In single-phase materials, strengthening and solid-solution strengthening or alloying can be achieved by grain size reduction. Grain size reduction making strengthen materials is difficult for defects in crystals such as slip planes or dislocations to continue propagation due to the slip plane or dislocation will change direction once crossing the grain boundary, as shown in Fig. 1.2 [4]. This will be more difficult if the crystal rises in disorientation. The existence of smaller grains results in a large grain boundary area to block dislocation motion. Nanomaterials have really become a very active research field in the area of materials science including organic, inorganic and composite materials. Nanostructured materials prepared in nanosized grains or nanoparticles such as building blocks contain a significant fraction of grain boundaries with a high degree of disorder of atoms along the grain boundaries, and a large ratio of interface area to volume. The phase’s Chemical composition and the interfaces, between nano-grains, should be controlled to getting required properties in the material.
Nanostructured materials have the significant dependence of certain properties upon the size in the nanoscale region. For instance, electronic property, with quantum size effects is attributed to spatial confinement of delocalized valence electrons, depends directly on the particle size. Small particle size allows conservative restrictions of phase equilibrium and kinetics to be overcome through the synthesis and processing by the mixture of short dispersion distances and high driving forces of existing large surfaces and interfaces. An extensive range of materials, including metals, ceramics and metal oxides in crystalline, quasi-crystalline, or amorphous phases have been prepared as nanosized or nanostructured materials. The greater surface area gives higher reactivity and diffusivity. Therefore novel properties could result from surface "defects" [5,6].

Fig. 1.1. Electronic band structure of metals, semiconductors and insulators
1.2. Types of nanostructures

According to deduce the typical behavior of nanostructures we must cover a certain limit of possible systems. There are three types of nanostructured materials are given as:

- Zero dimensional (nanoparticles).
- One dimensional (nanowires and nanotubes).
- Two dimensional (thin films).

Fig. 1.3 illustrates the different types of nanostructured materials [7,8]. All of them contain different properties. Zero dimensional nanostructures or nanoparticles contain single crystal, polycrystalline and amorphous particles with all possible morphologies such as spheres, cubes and platelets. Generally, the characteristic dimension of nanoparticles ranges from 1-100 nm. If the nanoparticles are single crystalline, they are often referred to as nanocrystals. When the characteristic dimension of the nanoparticles
is sufficiently small and quantum effects are observed, they are described as quantum
dots. One dimensional nanostructure includes whiskers, fibers, nanowires and nanorods.
Although the whiskers and nanorods are in general considered to be shorter than fibers
and nanowires, the definition is less arbitrary.

Fig. 1.3. Images of different types of nanostructured materials a) nanoparticles, b) nanowires and c) thin
films.

In addition, one-dimensional structures with diameters ranging from several nanometers
to several hundred microns were referred to as whiskers and fibers in the early literature,
whereas nanowires and nanorods with diameters not exceeding a few hundred
nanometers are used predominantly in the recent literature. Nanowires in general have a
higher aspect ratio than that of nanorods. Two dimensional nanostructures include thin
films which have the thickness of the order of few nanometers.

1.3. Various applications of nanotechnology
The last century was the period of macro-science. But, the 21st century will be dominated
by nano-science, featured by microscopic. Nanotechnology helps us to fabricate a large
set of materials with unusual properties such as optical, electrical and magnetic
properties. Materials perform in different and frequently useful ways at the nanoscale.
These unusual properties applications are emerging in aerospace, agriculture,
biotechnology, medicine, energy, improvement of environmental, information
technology, transportation, impact homeland security and national defense.
Nanotechnology is used in every manufactured from electronic devices to sunscreens. Therefore, the some applications of nanotechnology in various fields are given as:

- The unusual physical properties of nanosized materials, e.g. gold nanoparticles used as inorganic dye to introduce color into glass and as a low temperature catalyst.
- The vast surface area, such as mesoporous titania for photoelectrochemical cells, and nanoparticles for different sensors.
- The small size that offers additional possibilities for manipulation and room for accommodating multiple functionalities.
- Airborne chemicals Sensors or other toxins.
- Solar cells, fuel cells and portable power give inexpensive, clean energy.
- New high-performance materials; and much more.
- Advanced drug delivery systems, including implantable devices that automatically administering drugs and capable of sensing drug level.
- The diagnostic tools of medicine, such as cancer-tagging mechanisms.
- Cooling chips to change compressors in cars, refrigerators, air conditioners and multiple other devices.

1.4. Metal oxide

Metal oxides make a very important role in different areas of chemistry, physics and materials science [9-11]. The metal elements have an ability to form a huge diversity of oxide compounds [12]. These can adopt an enormous number of structural geometries with an electronic structure that can reveal metallic, semiconductor or insulator character. Metal oxides are used in the fabrication of microelectronic circuits [13], sensors [14], fuel cells [15], coatings for the passivation of surfaces of rust [16], catalysts [17], and optoelectronic devices [18]. In the emerging field of nanotechnology, an objective is to construct nanostructures or nanoarrays with particular properties with respect to those of bulk or single particle species [19-21]. The unique physical and chemical properties can be exhibited by metal oxide nanoparticles, because of their limited size and a high density of the corner or edge surface sites. Three important groups of basic properties in any material have been influenced by the size of Particle is expected. The structural
characteristics belong to the first one, namely the lattice symmetry and cell parameters [22]. In usual, bulk oxides are strong and stable systems with well-defined crystallographic structures. Nanoparticles should have a low surface free energy to show stability of mechanical or structural. As a result of this necessity, a low stability in bulk material phases can become very stable in nanostructures. Such structural phenomenon has been detected in various oxides such as TiO$_2$, Al$_2$O$_3$, and MoO$_3$. [23-25]. Decreasing in particle size generates stress/strain and concomitant structural perturbations due to the increasing number of surface and interface atoms [26]. The electronic properties of the oxide caused the second important effect of nanoparticles size. The nanostructure generates quantum size or confinement effects which basically create from the presence of discrete, atom-like electronic states. Experiment, The general electronic effects of quantum confinement explored on oxides are correlated with the energy shift of exciton levels and the optical band gap [27,28]. The electronic properties consideration is an important on the bulk oxide surface due to the long-range effects of the modeling field, which are not present or limited in a nanostructured oxide [29-31]. Clearly, structural and electronic properties make the properties of solid (physical and chemical properties), the third group of properties influenced by size in a simple classification.

1.5. Perovskite oxide

The typical chemical formula of transition metal perovskite structure is ABO$_3$ (A and B show tow different cations) for both research and industry of great interest because of their various physical properties and technology application. The simple structure of perovskite oxide materials is cubic corresponding to the high temperature phase. Fig. 1.4 illustrates the general structure of ABO$_3$ perovskite materials, where the A atom has 12 oxygen first neighbors, while B atoms sites in the center of the octahedron composed of six oxygen atoms. Furthermore, the family member variation of ionic radius of A and B atoms will easily distort the cubic symmetry with simultaneous tilting of the oxygen octahedral. Goldschmidt developed the tolerance factor (t) to accurately describe the stability of perovskite structure. The factor t which associated with the ionic radius is given as [32]:
\[ t = \frac{r_A + r_0}{\sqrt{2(r_B + r_0)}} \] \hspace{1cm} (1.1)

where, \( r_A \), \( r_B \) and \( r_0 \) represent the ionic radius of A, B and O atoms, respectively. When \( t = 1 \), the cubic phase and the most closed packed pattern of the perovskite is conserved. Under the change of A and B atomic species and a following change of \( t \) value, the crystallographic symmetry will be lowered and can be tuned to orthorhombic, tetragonal or trigonal in many perovskites. Therefore, a broad range of extraordinary properties will be brought by the changes in molecular formula and symmetric structure which are of absolutely essentiality in either fundamental or practical.

Fig. 1.4. General Perovskite Structure.

Their physical properties such as structural, optical, thermal, dielectric, electrical and magnetic properties have been extensively studied [33-40]. Such versatility in the family of transition metal perovskite leads to be one of the most important in material science. These properties occur primarily in the compounds whose structure deviate from an ideal cubic due to unstable types of distortions, such as polar or antipolar moves of A and/or B
ions from their exact position in the center of the octahedral tilts, Jahn-Teller distortions, or magnetic ordering [41,42]. The replacement and doping of various cations at the A or B sites modifies the distortion of the perovskite structure and therefore tailors the physical properties of this type of materials [43-45]. ABO$_3$ perovskite materials have proven to be the best materials for cathodes due to their tunability. Their properties such as phase stability, thermal expansion coefficient, electronic and ionic conductivity could be adjusted with the selection of A and B site metal cations. The perovskite oxides are very interesting and extensively studied due to the vast variety of solid-state phenomena they display. These perovskites are extensively studied due to the exciting and fascinating physical properties such as insulating, semiconducting, ferromagnetism, antiferromagnetism, spin glass, charge/spin density wave transitions, superconductivity, ferroelectricity and colossal magnetoresistance in diverse states and phases. Most of these phenomena appear in materials that are lattice matched within a few percent of one another; giving rise to the opportunity of heteroepitaxial structures using perovskite oxides, accessing these multiple degrees of freedom. In general, the electrical and magnetic properties of these perovskites depend on the selection of element A, B and doping element either of A or B site [46] or by leaving from ideal stoichiometry. The electronic energy bands of the perovskites are very unusual in that they reveal two-dimensional behavior that leads to the unique structure on properties such as the density of states, Fermi surface, dielectric function, phonon spectra and the photoemission spectra. Some perovskites have delocalized energy-band states, some have localized electrons, and others display transitions between these two types of behavior. A lot of the perovskites are magnetically ordered and a large diversity of magnetic structures could be found. Furthermore, the structure of perovskite has the nosy property that the central atom does not touch its coordination neighbors in violation of Pauling's rules. This structure provides the piezoelectricity property and sometimes ferroelectricity. Many oxides such as LaMnO$_3$, LaNiO$_3$, LaFeO$_3$, BiFeO$_3$ etc. are known as representative compounds. These materials also offer an extensive variety of phase transitions (ferroelectric, antiferroelectric) or purely structural transitions. The majority of the transitions encountered in the perovskite crystal contain only a small alteration in the atomic position parameters, changes that leave the essential topology of the structure
unaltered. The perovskite oxides are also important in many technological areas. They are used in photochromic, electrochromic, and image storage devices. Their properties such as ferroelectric and piezoelectric are utilized in other device applications such as switching, filtering, and surface acoustic wave signal processing. Research on these interesting perovskites has been investigated since decades. However, it is only in recent years that experimental and theoretical information on the electronic structure has begun to become available [47-51]. The calculation of the energy band gap, neutron diffraction and inelastic scattering data, photoemission spectra, optical spectra, and transport data are now existing for materials such as LaAlO$_3$, LaMnO$_3$, BiFeO$_3$, LaFeO$_3$, SrTiO$_3$, BaTiO$_3$, LaCoO$_3$, and a variety of other perovskites [52-58]. Fig. 1.5 illustrates chemical elements that could be accommodated within the structure of perovskite [59]. It is clear that most of the elements can fill either A or B lattice places in the lattice of perovskite, involving dopants except for noble gases. The stables and the crystal group are mainly determined by the ratio of the ionic radii of the A and B cations. Certainly, the structure is dependent on the size as well as on the nature of the A and B atoms.

Fig. 1.5. Chemical elements that can occupy sites in the perovskite structure.
Perovskite oxides exhibit a large variety of properties, due to the variety of structures and chemical compositions. Table 1.1 gives some examples of the typical properties of perovskite oxides [59].

Table 1.1. Typical properties of perovskite oxides.

<table>
<thead>
<tr>
<th>Property</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetic property</td>
<td>BaTiO$_3$, PdTiO$_3$</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>Pb(Zr, Ti)$_3$O$_3$, (Bi, Na)TiO$_3$</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>ReO$_3$, SrFeO$_3$, LaCoO$_3$, LaNiO$_3$, LaCrO$_3$</td>
</tr>
<tr>
<td>Superconductivity</td>
<td>La$<em>{0.6}$Sr$</em>{0.4}$CuO$_3$, YBa$_2$Cu$_3$O$_7$, HgBa$_2$Ca$_2$Cu$_2$O$_8$</td>
</tr>
<tr>
<td>Ion conductivity</td>
<td>La(Ca)AlO$_3$, CaTiO$_3$, La(Sr)Ga(Mg)O$_3$, BaZrO$_3$, BaCeO$_3$</td>
</tr>
<tr>
<td>Magnetic property</td>
<td>LaMnO$_3$, LaFeO$_3$, BiFeO$_3$, La$_2$NiMnO$_6$</td>
</tr>
<tr>
<td>Catalytic property</td>
<td>LaCoO$_3$, LaMnO$_3$, BaCuO$_3$</td>
</tr>
<tr>
<td>Electrode</td>
<td>La$<em>{0.6}$Sr$</em>{0.4}$CoO$<em>3$, La$</em>{0.8}$Ca$_{0.2}$MnO$_3$</td>
</tr>
</tbody>
</table>

1.6. Bismuth Ferrite (BiFeO$_3$)

Pure bismuth ferrite could be tailored in various ways. An important method to modify its properties is to replacement bismuth with another cation, such as a rare-earth metal. Samarium is a rare-earth metal which differs from bismuth with its much smaller ionic radius and the fact that samarium does not have single pairs like bismuth. Bismuth ferrite, BiFeO$_3$, is a multiferroic material with the perovskite ABO$_3$ structure. Since both the iron and bismuth cations are trivalent, Fe$^{3+}$ and Bi$^{3+}$, respectively, BiFeO$_3$ is called a III-III perovskite. The structure contains a Fe$^{3+}$ cation inside an O$_6$ oxygen anion octahedron. The vacancies between the octahedra are filled with Bi$^{3+}$ anions. In bulk BiFeO$_3$, the structure is rhombohedrally distorted due to octahedra tilting around the [001]$_{\text{hex}}$ axis [60-62]. The hexagonal unit cell parameters on bulk size BiFeO$_3$ are $a_{\text{hex}} = 5.5787\AA$ and $c_{\text{hex}} = 13.8688\AA$ [62]. The proportional sizes of the ions in the BiFeO$_3$ structure are essential for the stability of the structure. BiFeO$_3$ was supposed as the only possible candidate, which exhibits instantaneous enormous ferroelectricity and antiferromagnetism at room temperature. This discovery had led to a series of investigations in this area from around the world and a lot of extra novel properties of BiFeO$_3$ were discovered involving
photovoltaic effect [63], light induced photostrictive effect [64], and controllable ferroelastic switching [65]. Meanwhile, the majority of scientist of physics concentrates on bulk and thin film samples of BiFeO$_3$ to show its physical properties, inspired by its potential in information storage in spintronic devices and sensors [66], another scientist of material and chemist are working on BiFeO$_3$ through its nanostructures, a valuable way to fully understand the chemical properties and application of the material. Fig. 1.6 shows Structure and properties of BiFeO$_3$.

![Diagram of BiFeO$_3$ structure](image)

**Fig. 1.6.** (a) Schematic of the crystal structure of BiFeO$_3$ and the ferroelectric polarization (arrow) and antiferromagnetic plane (shaded planes) and (b) Ferroelectric polarization loops measured on epitaxial BiFeO$_3$ films with different crystallographic orientations.

### 1.7. Lanthanum Ferrite (LaFeO$_3$)

The researcher conducted a careful study of the electronic conductivity and defect structure of LaFeO$_3$ [67]. LaFeO$_3$ is oxygen deficient and was shown a behavior of p-type semiconductor. Iron can be stable in valence states $2^+$, $3^+$, and $4^+$. LaFeO$_3$ has a low
lanthanum vacancy concentration, which is balanced by a low concentration of oxygen vacancies and Fe^{3+}/Fe^{4+} oxidation couples. Holes conduct by small Polaron jumping from B-site to B-site by altering valence state. Conductivity is very low for LaFeO_3. The electrical conductivity has been measured of 0.6 S/cm at 1000 °C [67]. By replacement Sr^{2+} on the La^{3+} site, electrical and ionic conductivity is substantially increased. The electrical conductivity as high as 350 S/cm at 550 °C has been reported [68], for La_0.5Sr_0.5FeO_3.6 with a transition from semi-conductive to metallic conductivity at about the same temperature, meanwhile, the ionic conductivities between 0.10-0.35 S/cm at 750 - 950 °C for La_0.3Sr_0.7FeO_3.5 also reported [69]. The ionic conductivity increases, it is thought to be of particular aide in reducing polarization losses associated with Redox reduction-oxidation at lower temperatures. The well-matched electrolyte, due to similar thermal expansion coefficients (~12 ×10^{-6} K^{-1}) [70,71], is (Ce_{0.9}Gd_{0.1})O_{2-δ}, which is a rapid ionic conductor at intermediate temperature operation. Fig. 1.7 illustrates the LaFeO_3 structure.

![Schematic diagram of the crystal structure of LaFeO_3.](image-url)
1.8. Lanthanum Manganite (LaMnO$_3$)
In the family of ABO$_3$ perovskites with B as Mn ion forms a special class of perovskites known as manganites. A typical orthorhombic distorted perovskite lattice of manganite with A = La/Sr, B = Mn is shown in Fig. 1.8 (a,b). Manganites frame is an important place in the material science research due to its extensive applications owing to the vast properties shown by these materials in various conditions. Manganites are richly varied and fascinating systems due to dramatic properties shown by them in diverse surroundings. These are strongly correlated electrons family wherein the correlations among electrons assign different interesting properties to this class of materials. The colossal magnetoresistive manganites always been studied by a sizable fraction of the condensed matter community and their popularity had reached the levels comparable to that of the high-temperature superconducting cuprates. A vast interest in the investigated of manganites is due to their interrelated properties and possibilities of device applications. Mixed valence manganites with the perovskite structure have been studied for almost 50 years.

![Schematic of perovskite oxide unit cells for, (a) LaMnO$_3$ and (b) La$_{1-x}$Sr$_x$MnO$_3$.](image)

Fig. 1.8. Schematic of perovskite oxide unit cells for, (a) LaMnO$_3$ and (b) La$_{1-x}$Sr$_x$MnO$_3$. 
The versatile electrical properties of perovskites are easily tunable by changing the oxygen stoichiometry [72], by doping or by applying an electric field as shown in Fig. 1.9 [73-75]. The undistorted ideal cubic SrTiO₃ at room temperature is an insulator, but the SrTiO₃₋ₓ oxygen deficient derivative is conducting or superconducting [76,77]. The parent manganese compound LaMnO₃ is anti-ferromagnetic and insulating in its ground state. LaMnO₃ undergoes a structural transformation at T~523K from the Jahn-Teller distorted orthorhombic phase to a high temperature cubic semiconducting phase [78]. Sr and Ca doped LaMnO₃ derivatives become metallic/ferromagnetic and also exhibit effects like colossal magnetoresistance in metallic multilayers [79].

![Diagram of SrTiO₃, LaMnO₃, La₁₋ₓSrₓMnO₃, and Ni](image)

**Fig. 1.9.** Electronic band structure of SrTiO₃, LaMnO₃, La₁₋ₓSrₓMnO₃ and Ni. The filled bands are shown in dark and arrow denotes electron spins. The SrTiO₃ is a band insulator, LaMnO₃ is a p-type semiconductor, La₁₋ₓSrₓMnO₃ is halfmetallic (up electron spin denotes metallic and down insulating), and Ni is a conventional ferromagnetic metal with both up and down spin occupied.

**1.9. Motivation to present work and thesis outlines**

Perovskite oxide materials are complex functional materials which have produced wide ranging interest because of the variety of their electrical properties. The aim of this work was to study physical properties (structural, optical, Electrical and magnetic properties) for different type of perovskite materials of general formula ABO₃ with different synthesis methods (sol-gel combustion and reverse micelle methods) and various characterization techniques. The ABO₃ perovskite understanding remnants among the
majority challenging topics at the interface between solid state chemistry and solid state physics, both from academic and application viewpoint. Presently, the coupling phenomena between multiferroics and new properties at interfaces in heterostructures of perovskite attract a particular interest. Many of the most interesting physical phenomena such as ferromagnetism, ferroelectricity, multiferroicity magnetoresistance are directly related to solid state phase transitions. As well as the most functional materials used in electronics and spintronics exhibit specific properties that can optimize, which is attributed to the presence of phase transitions. Through the studied materials, ABO₃ perovskites are particularly important since they exhibit an extraordinary range of structures, chemical bonding and physical properties. Although perovskites have been known for a long time, new intriguing physical effects are periodically discovered and their understanding remains an internationally highly-competitive area. A considerable amount of research presently focuses on multifunctional materials in which have various physical properties can potentially be used at the same time in an application. One of the key questions for the future progress and multifunctional materials understanding concerns the mutual coupling between the properties, its fundamental mechanism and whether it could be used in applications. Perovskites are at the topic heart, as demonstrated by multiferroic perovskites which are multifunctional material par excellence.

The aim of the present work is to synthesize the nanoparticles of different ABO₃ perovskite materials and to investigate the effect of doping on their structure, optical, electrical and magnetic properties. Also, we have taken magnetic compound possessing nanostructure and were doped them and were doped with other magnetic elements Fe³⁺, Ni³⁺ (ferromagnetic) in B sites and Sr²⁺ (paramagnetic) in A sites. According to this motivation, we doped Sr²⁺ in A sites and Ni³⁺ in B sites simultaneously in LaFeO₃ and Ni³⁺ in La₀.₇Sr₀.₃FeO₃, meanwhile we doped La₀.₇Sr₀.₃MnO₃ by Fe³⁺. A lot of researchers [35,80-84] have illustrated that such substitution modifies their structural, optical, electrical and magnetic properties.

Bismuth ferrite (BiFeO₃) nanopowder is difficult to prepare in pure phases due to the narrow temperature range in which BiFeO₃ stabilized and there are a number of other phases of Bi and Fe occurred if temperature is not controlled perfectly [85]. BiFeO₃
properties (structure, optical, electrical and magnetic properties) had been widely studied [86-88], its applications were hampered by the leakage current problems increasing out of nonstoichiometry, it is typically due to the difficulty in finding stoichiometries single phase of this material. Bismuth ferrite has a rhombohedral perovskite structure based systems could be used to develop new applications in information storage of radio, television, microwave and satellite communication, bubble memory device, audio-video, and digital recording, spintronic devices and sensor technology. Recently, it has been observed that BiFeO₃ could be used in the medical treatment of cancer [89].

Lanthanum ferrite (LaFeO₃) based oxides are an important due to its unique properties. LaFeO₃ has both high ionic and electronic conductivity at high temperatures [90-92], and they are potential candidates for use in high temperature electrochemical devices, such as gas sensors, oxygen permeable membranes, and electrodes in solid oxide fuel cells [93-96]. Lanthanum ferrite (LaFeO₃) has orthorhombic symmetry perovskite structure and an antiferromagnetic insulator with Néel temperature $T_N = 750$ K. It has a various properties such as the exchange bias, multiferroic and magnetic optics, which are very important for development so many applications, as new magnetic memory devices, low power consumption spintronic devices and magneto optical sensors [97,98].

Lanthanum Manganites (LaMnO₃) are members of strongly correlated electrons family wherein the correlation among electrons assign various interesting properties to this class of materials and have the ABO₃ perovskite structure. It is important due to the following reasons:

1. The unexpectedly large magneto-transport properties of these compounds.
2. When we study the manganites is, their rich phase diagram exhibiting a variety of phases with unusual spin, charge, lattice and orbital order.
3. The states formed in these compounds are dominated by coexisting clusters of competing.

A great interest in the study of manganites is due to their interrelated properties and possibilities of device applications. Mixed valence manganites with the perovskite structure have been investigated. Early research was motivated by a need to develop insulating ferromagnets with a wide magnetization for high-frequency applications. More recent work has been determined by a wish to understand and develop the large negative
magnetoresistance effects which occur close and below the Curie temperature also to understand the low field magnetoresistance effect at low temperature. Research on the manganites has exhibited new phenomena such as colossal magnetoresistance (CMR) [79] and dense granular magnetoresistance [99] which led to the understanding of several physical concepts such as Zener double exchange [100] and the Jahn-Teller effect [101,102]. They can modify dramatically stoichiometrically in time and/or space as a result of small changes in condition.

The aims of the present thesis are given as the following:

1. Synthesization of nanoparticles of bismuth ferrite BiFeO$_3$ pure single phase of sol-gel combustion method to investigate the structural, optical, electrical and magnetic properties.

2. Synthesization of nanoparticles of lanthanum ferrite LaFeO$_3$ pure single phase of the reverse micelle technique to investigate the structural, thermal, optical, electrical and magnetic properties.

3. Synthesization of Sr$^{2+}$ and Ni$^{3+}$ doped La and Fe of LaFeO$_3$ respectively, as La$_{1-x}$Sr$_x$Fe$_{1-x}$Ni$_x$O$_3$, (x = 0.0, 0.1 and 0.2) by sol-gel combustion method to develop the physical properties such as structural, optical, electrical and magnetic properties.

4. Synthesization of Ni$^{3+}$ doped La$_{0.7}$Sr$_{0.3}$Fe$_1$-$x$Ni$_x$O$_3$, (x = 0.00, 0.01 and 0.04) by a reverse micelle technique to develop the various physical properties such as structural, optical, electrical and magnetic properties.

5. Synthesization of Fe$^{3+}$ doped La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, (x = 0.00, 0.10, 0.15 and 0.20) by a reverse micelle technique to develop the various physical properties such as structural, optical, electrical and magnetic properties.
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CHAPTER II

Experimental techniques
2.1. Introduction
This chapter is prepared to illustrate the main techniques used in the presented work. It will start with the synthesis routes and characterization techniques. It will also outline theory and physics behind the routes used, followed by experimental aspects of these techniques. Nanomaterials are created by using several methods. The creation methods are involved attrition and pyrolysis. The synthesized methods of nanomaterials, which are classified in two methods are bottoms up and top down. Top down methods include breaking the large materials into nanoparticles via solid state routes and ball milling, while wet chemical routes like sol-gel, reverse micelle, hydrothermal, co-precipitation, etc. come in the class of bottom up approach. The nanomaterials characterization is necessary to analyze their various properties. Therefore, this chapter describes the various methods of synthesis such as sol-gel combustion and reverse micelle methods as well as characterization of nanomaterials. Characterization techniques include X-ray diffraction (XRD), scanning electron microscope (SEM), field emission scanning electron microscopy (FESEM) energy-dispersive X-ray spectroscopy (EDS), Fourier transforms infrared spectroscopy (FTIR), atomic force microscopy (AFM), thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC), UV-Visible spectroscopy, LCR meter, four probes set up and vibrating sample magnetometer (VSM).

2.2. Synthesis of Nanomaterials
The nanomaterials fabrication becomes a very important for the nanotechnology applications in various fields such as catalysis, electronics and medicine due to the strict control size, shape and crystalline structure. In usual, the nanoparticles synthesis methods usually are classified into two classes: “top-down” and “bottom-up” approach. The top-down is involved the partition of a considerable solid into smaller and smaller portions, successively reaching to nanometer size. This approach could include milling or attrition. The bottom-up is involved the concentration of atoms or molecular entities in a gas phase or in the liquid phase to form the material in the nanometer range. The liquid phase approach entails a wet chemistry route as well as a popular in the nanoparticles synthesis due to the several advantages associated with it. Fig. 2.1 gives us the general idea of the two approaches. There are several bottom up methods of synthesizing metal oxide...
nanomaterials, such as hydrothermal, [1,2] combustion method [3,4], gas-phase routes [5,6], microwave technique, sol-gel method [7,8], coprecipitation route [9] and reverse micelle method [10]. Sol-gel combustion and reverse micelle processing techniques will be discussed in detail in this chapter because the materials reported in following chapters were synthesized via these methods.

Fig. 2.1. General chart of Top-down and Bottom-up fabrications.

2.2.1. Sol-gel combustion method
Combustion synthesis or self-propagating high temperature synthesis (SHS), is a facile and economic technique to prepare a large variety of advanced materials, such as ceramic, intermetallics, composites, and functionally graded materials [11-14]. Combustion synthesis processes characterized by high temperature, fast heating rates and short times of reaction [15]. The various routes have been used to synthesize the new
materials via self sustained exothermic chemical reaction in place of the long time heat treatment by the furnace. Almost all known advanced materials oxide and non-oxide in several types' nanosize, films and whiskers have been synthesized by a sol-gel combustion method [16]. Fig. 2.2 shows a flow chart for the preparation of sol-gel combustion method.

**Fig. 2.2.** Flow chart for the preparation of Sol-Gel combustion method.
The sol-gel Combustion method leads to highly crystalline particles with large surface areas [17,18]. During the dehydration process, the polycondensation reaction between citric acid and nitrates takes place [19]. The process includes a rapid heating of a solution containing redox groups [20]. During combustion, the temperature reaches approximately 300 °C for one or two minutes making the material crystalline [19,21].

2.2.2. Reverse micelle method

Reverse micelles, or water-in-oil microemulsions, Based synthesis is found to be a versatile technique to prepare a several type of nanomaterials [22]. It always allows the incorporation of substantial amounts of water in very hydrophobic solvents, such as saturated hydrocarbons. Thus, the presence of the surface active agent (surfactant), which is recognized to reduce the interfacial tension between two immiscible phases and water, allows the solubilization of a wide range of polar solutes into the organic solvent. The solute can be distributed between the organic solvent and the microaggregates due to its intrinsic inhomogeneity and large surface or volume ratio; it can engage a variety of microenvironments [23]. Fig. 2.3 shows the schematic diagram of a reverse micelle method. The medium of reverse micelles makes a large surfactant aggregate with water, meanwhile the aggregates are very small with the absence of water. Water pool contents are formed due to the solubilized of water in the polar core. The characterizations of water pool contents are distinguished by \( W = \text{water/surfactant} \) molar ratio. The aggregates including a small amount of water \((W<15)\) are usually called reverse micelles while aggregates equivalent to droplets including a large amount of water molecules \((W>15)\) are called microemulsions [24]. According to the ratio of several components and the hydrophilic-lipophilic balance value of the surfactant used, the configuration of microdroplets could be in the form of oil-swollen micelles distributed in water as oil-in-water (O/W) microemulsion or water swollen micelles distributed in oil as for water-in-oil (W/O) microemulsion, are shown in Fig. 2.4 and these nanodroplets can be used as nanoreactors to carry out the chemical reactions [25]. Water in oil microemulsion in which polar head groups of surfactant molecules are attracted by the aqueous core and directed towards inside and the hydrocarbon chain is known as a reverse micelle [25]. It involves a nanometer sized, monodispersed water droplets. The size of nanoparticles can
be controlled by the molar ratio of the aqueous phase to surfactant, $W = \frac{\text{water}}{\text{surfactant}}$ [26].

**Reverse Micelle Method**

- **Metal Nitrate Solution (0.1M)**
  - CTAB + n-buty alcohol + iso-
    - Stirring (30 min)
    - Clear Solution
    - Reverse Micelle I (RM1)
  - Mixed Solutions (RM1 + RM2)
  - Ammonium added to adjust
  - Stirring for 24 hours

- **NaOH (0.1M)**
  - CTAB + n-buty alcohol + iso-
  - Clear Solution
  - Reverse Micelle II (RM2)

---

**Fig. 2.3.** Flow chart for the preparation of reverse micelle method.
Fig. 2.4. A typical structure of reverse micelle.

Fig. 2.5. A phase diagram illustrating the effects of the water/oil/surfactant ratio of the solution phase.
Fig. 2.5 shows a hypothetical phase diagram of a reverse micelle [25,27]. The phase inversion is a peculiarity of a reverse micelle that takes place in a given water to oil concentration ratio. At a small amount of water microemulsion includes very small droplets of water dispersed in oil (W/O), while at large amount of water content the situation is reversed and the system includes oil droplets distributed in water (O/W). The situation exists between these two phases an intermediate which the system includes layers of surfactant separating vary layers of water and oil. However on the w/o side more difficult structures seem to exist. Initially, by increasing the amount of water the droplets of water originally increase their radius slightly and then their shape undergoes a change becoming an extended cylinder. In the final the status layer is achieved from which, again increasing the water content, the system passes directly to the o/w droplets situation.

2.3. Characterization Techniques

2.3.1. X-ray Diffraction

X-ray diffraction is one of the most commonly used non-destructive materials characterization techniques for analyzing the crystallographic arrangement of powder samples. This technique can be used for phase identification, particle and unit cell size determination. When an electromagnetic wave enters a crystal it will be scattered by the electrons inside. From certain angles of incidence there will be constructive interference between the different scatters, but for most of the angles destructive interference will cancel the diffracted beams. By measuring at which angles the constructive interference take place, it is possible to study about the geometrical ordering of the atoms inside the crystal [28-30]. X-ray diffraction is a valuable non destructive technique of structural analysis. The most common uses of X-ray diffraction in our type of work are:

1. To verify if the sample consists of a single phase.
2. To verify the crystallographic arrangement of the sample.
3. To see whether the sample is polycrystalline or a single crystal
4. To measure and calculate the crystalline and particle size.
5. To verify the density of the sample.
X-ray diffraction is the most widely used basic structural characterization technique for studying the samples which are in their respective powder form. In normal $\theta - 2\theta$ scan mode, a beam of monochromatic X-rays is made to an incident on the sample, making an angle $\theta$ with the sample surface. The detector motion is coupled with that of the X-ray source so that it is always kept in a position at an angle of $2\theta$ with the incident direction of the X-ray beam. The spectrum is recorded as intensity versus $2\theta$. The schematic of the X-ray diffractometer is given in Fig. 2.6.

![Diagram of X-ray diffractometer](image)

**Fig. 2.6. Schematic diagram of X-ray diffractometer.**

The interaction of X-ray radiation with crystalline sample is governed by Bragg’s law, which illustrates a relationship between the diffraction angles, X-ray wavelength, and interplanar spacing of the crystal planes. According to Bragg’s law, the X-ray diffraction can be visualized as X-rays reflecting from a series of crystallographic planes as shown in Fig. 2.7. The path differences introduced between a pair of waves travelled through the neighboring crystallographic planes are determined by the interplanar spacing. If the total path difference is equal to $n\lambda$, the constructive interference will occur and a group of diffraction peaks can be observed which give rise to X-ray patterns. The quantitative account of Bragg’s law can be expressed as:
where $d$ is the lattice spacing between the crystal planes, $\lambda$ is the wavelength of X-ray, $n$ is the integer of a reflection order and $\theta$ is the incident angle with the sample surface.

Fig. 2.7. Geometrical illustrations of crystal planes and Bragg’s law.

X-ray diffraction for this study employed Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) at room temperature is a Rigaku Miniflex-II, shown in Fig. 2.8, and operated at a voltage of 30 kV and filament current of 40 mA. The phase identification of all the samples reported in this thesis was performed by matching the peak positions and intensities in XRD patterns to those patterns in the JCPDS (Joint Committee on Powder Diffraction Standards) database. The diffraction method is based on the effect of broadening of diffraction reflections associated with the size of the particles (crystallites). All types of defects cause displacement of the atoms from the lattice sites. One equation has been derived from the intensity of the Bragg reflections from a crystal defect, which enabled all the defects to be derived conventionally into two groups [31]. The defects in the first group
only lower the intensity of the diffraction reflections but do not cause the reflection broadening.

Fig. 2.8. X-ray Diffractometer (XRD) equipment.

The broadening of the reflections is caused by the defects of the second group. These defects are micro-deformations, inhomogeneity (nonuniform composition of the substance over their volume) and smaller particle size. The size of nanomaterials can be derived from the peak broadening and can be calculated by using the Scherrer equation (2.2), provided that the nanocrystalline size is less than 100 nm.

\[ D = \frac{k\lambda}{\beta \cos\theta} \]

(2.2)

where \( D \) is the average crystalline dimension perpendicular to the reflecting phases, \( \lambda \) the X-ray wavelength, \( k \) the Scherrer’s constant which equals 0.9 for spherical particles, whose value depends on the shape of the particle (crystallite, domain) and on diffraction flection indices (hkl), and \( \beta \) is the full width at half maximum (FWHM) of the peaks. The Scherrer formula is quite satisfactory for small grains (large broadening) in the absence
of significant microstrain. A microstrain describes the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain it is reasonable to assume that there is a radial strain gradient, but from X-ray diffraction only a homogeneous, volume-averaged value is obtained.

2.3.2. Atomic Force Microscopy

Scanning probe microscopy (SPM) consists of a large group of instruments used to picture and calculate properties of nanomaterials surfaces. The pictures are achieved by scanning across the surface with a sharp probe that monitors and assembles the tip sample interactions to produce an image. There are two forms of SPM: Scanning Tunneling Microscope (STM) and Atomic Force Microscope (AFM) as shown in Fig. 2.9.

Fig. 2.9. Atomic Force Microscope (AFM) modern equipment.
Gerd Binnig and Heinrich Rohrer invented STM in the early eighties for which they received the Nobel Prize in 1986. But the greatest reduction of STM is that it can only image materials that can hold a tunneling current. Atomic Force Microscope (AFM) was invented by Binnig and Quate in 1986 to overcome the limitations of STM. AFM generate images, almost at the level of atomic resolution, by measuring the distribution scheme of the sample. The image is established by quantifying the forces between the probe (cantilever tip) and the sample surface. AFM can provide extremely high-resolution images by using an ultra-small probe tip at the end of a cantilever. AFM was originally devised to investigate material surfaces.

Fig. 2.10 shows the principle of AFM machine which, both AFM and light microscope increase the sample image but the main difference between them is that the previous does not use visible light, but it uses a cantilever fabricated from silicon or silicon nitride with a very low spring constant to image a sample. At the cantilever end, a very sharp tip is fabricated using semiconductor processing methods. The cantilever scans above the surface of the sample by gradually moving backward and forward across the sample surface. The crystal of piezoelectric moves the cantilever upper and down to preserve a constant bending of the cantilever. The force applied on the tip differs with the difference in the surface height and thus leads to the bending of the cantilever. The top of cantilever reflected a laser beam constantly towards a position-sensitive photodetector including four side by side photodiodes. This laser beam detects the bend appearing in the cantilever and evaluates the actual position of the cantilever. Thus, AFM has been recording a three dimensional image of the surface topography of the sample under a constant applied force, which gives a maximum resolution image without causing any break to the sample surface. As the tip scans the surface of the sample, the force between the tip and the sample differs. This modifies in force is sensed by the tip attached to the flexible cantilever. The quantity of force between the probe and the sample is dependent on the spring constant of the cantilever and the distance between the probe and the sample surface. This force can be described with respect to Hooke’s law as:

\[ F = -k\Delta x \]  

\( (2.3) \)
where \( F \) is the force, \( k \) is the spring constant and \( x \) is the distance between the probe and the sample surface. The tip of the cantilever and the sample surface interaction are regulated by various types of forces, such as van der Waals forces, capillary and adhesive forces, and double layer forces. Through these, the most commonly associated with AFM is van der Waals force. According to equation (2.3) the distance between the cantilever tip and the surface of the sample in the contact region is a few angstroms (Å) and therefore the probe experiences repulsive van der Waals force. But, in the non contact region, the cantilever tip is various tens or hundreds of angstroms away from the surface of samples and therefore experiences an attractive van der Waals force.

Fig. 2.10. Schematic principle of AFM equipment.
2.3.3. Scanning Electron Microscopy (SEM)

Electron microscopes are scientific instruments, which use a beam of energetic electrons to study objects on a very fine scale. Electron microscopes have been developed due to the limitations of Light Microscopes which are limited by the physics of light. In the early 1930's this theoretical limit had been reached and there was a scientific wish to see the well details of the interior structures of organic cells such as nucleus, mitochondria. This required 10,000X plus magnification which was not possible using accessible optical microscopes. The first Scanning electron microscope (SEM) appeared for the first time in 1938 by Von Ardenne with the first commercial instruments around 1965 as shown in Fig. 2.11. Its development was late due to the electronics involved in "scanning" the beam of electrons across the sample. Scanning electron microscopy (SEM) can give a highly magnified image of the surface and the composition information on near surface regions of a material [32].

---

Fig. 2.11. Schematic diagram of SEM equipment.
The SEM resolution can move toward a few nanometers and the magnifications of SEM can be easily adjusted from about 10 times to 300,000 times. In SEM, electron beam, accelerated by a relatively low voltage of 1 - 20 kV, is scanned on the sample surface. As the electron beam hits the surface, a large number of signals are produced from or through the surface in the form of electrons or photons. These signals emitted from the sample are collected by detectors to form images and the images are exhibited on a cathode ray tube screen. There are three types of images generated in SEM: secondary electron images, backscattered electron images, and elemental X-ray maps. Secondary electrons (SE) are considered to be the electrons resulted from inelastic scattering with atomic electrons and with the energy less than 50 eV. The secondary emission of electrons from the sample surface is usually restricted to an area near the beam impact zone that permits images to be obtained at high resolution. These images, as seen on a cathode ray tube, give a three dimensional appearance due to the large deepness of field of the SEM as well as the shadow release of the secondary electrons contrast. Backscattered electrons (BSE) are considered to be the electrons resulted from elastic scattering with the atomic nucleus and with the energy more than 50 eV [32]. The backscattering will likely take place in a material of higher atomic 50 numbers, so the contrast caused by elemental differences can be built up. After the primary electron beam collides with an atom in the sample and ejects a core electron from the atom, the excited atom then decomposes to its ground state and emits either a characteristic X-ray photon or an Auger electron [33].

2.3.4. Field Emission Scanning Electron Microscopy (FESEM)
Field Emission Scanning Electron microscope (FESEM) used for probing surfaces and microstructural characterization of the solid samples [34]. This technique is widely used to get information about the topographical features, morphology, phase distribution, crystal structure, crystal orientation, the presence and location of defects. In FE-SEM, as the name suggests, the electron beams are moved by the electric field to scan the sample. In this technique, a beam of electrons is produced by heating a metallic filament. The electron beams, focused with the help of electromagnetic lenses, falls on the sample with
energy typically ~ 30 keV. When the beam strikes on the sample surface the backscattered electrons, secondary electrons, Auger electrons and photons are ejected from the sample with typical energy. Detectors collect the secondary or backscattered electrons and an image is produced on a cathode ray tube screen by recording the intensity of the detected signal as a function of position. The signal magnitude varies as a result of differences in surface topography as the electron beam is scanned across the sample surface. In this way, SEM can be employed to visualize surface features with a good resolution of the order of nanometers.

2.3.5. Energy Dispersive X-ray Spectroscopy (EDX)

EDX is an analytical technique used for the elemental analysis or chemical characterization of samples. It is one of the alternatives of X-ray fluorescence (XRF). As a type of spectroscopy, it relies on the exploration of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response being struck with charged particles. Its characterization capabilities are due to in large part to the primary principle that every element has a unique atomic structure, allowing X-rays that are characteristic of an element atomic structure, to be recognized uniquely from each other.

There are four main components of the EDX set up: the beam source; the X-ray detector; the pulse processor; and the analyzer. A number of freestanding EDX systems are present. However, EDX systems are usually found on scanning electron microscopes (SEM-EDX) and electron microprobes. Scanning electron microscopes are equipped with a cathode and magnetic lenses to generate and center a beam of electrons and since the 1960’s they have been equipped with elemental analysis capabilities. A detector is used to change X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and surpasses them onto an analyzer for show and study data.

2.3.6. Fourier Transformation Inferred Spectroscopy (FTIR)

The organic or inorganic chemicals are most useful identifying by FTIR. It can be employed to constitute some components of a strange mixture. It could be applied to the analysis of solids, liquids and gases. The term Fourier Transform Inferred Spectroscopy
(FTIR) refers to a fairly new development in the manner in which the data are grouped and converted from an interference pattern to a spectrum. At the present time, FTIR instruments are computerized which builds them faster and more sensitive than the older dispersive instruments. Fig. 2.12 shows the FTIR instrument (Perkin Elmer spectrometer model Spectra Two). FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is the powerful tool for identifying various types of chemical bonds. The light wavelength absorbed is a feature of the chemical bond. By interpreting the infrared absorption spectrum can be determined the chemical bonds in a molecule.

Fig. 2.12. Fourier transformation infrared spectroscopy (FTIR) equipment.

FTIR spectra of pure compounds are commonly so unique that they are like a molecular "fingerprint", whereas organic compounds have very rich, detailed spectra; inorganic compounds are usually greatly simpler. For most common materials, the spectrum of an unknown can be identified by contrast to a library of known compounds. Molecular
bonds vibrate at different frequencies depending on the elements and the type of bonds. For any given bond, there are a number of specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to reason the molecular vibration frequency to rise is to excite the bond of having it to absorb light energy. For any given transition between two states, the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state ($E_0$) and the first excited state ($E_1$)]. The energy corresponding to these transitions (between molecular vibration states) is generally 1-10 kcal/mol which corresponds to the infrared portion of the electromagnetic spectrum [35-37]. The difference in energy states = Energy of the light absorbed:

$$E_f - E_i = \frac{hc}{\lambda} \quad \text{(2.4)}$$

where the symbols $E_f$ is the excited state energy, $E_i$ is the ground state energy, $h$ is the plank's constant, $c$ is the speed of light in free space and $\lambda$ represent the wavelength of the infrared light.

2.3.7. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) uses stoichiometry and heat ratios to find out percentage of the mass of a solute. Test and analysis are realized by raising the temperature of a sample progressively while plotting weight as a function of temperature so effectively monitors material transformation where compounds degrade or forms at different temperatures. The laboratory’s TGA can be used to raise temperatures between room temperature and 1400 °C in different gas atmospheres such as air, nitrogen or inert gases. The TGA schematic principle measurement is displayed in Fig. 2.13 [38]. The sample is heated under nitrogen with constant heat rate while the difference of the mass during this process is measured. A mass loss shows that a degradation of the measured material takes place.
2.3.8. Differential Scanning Calorimetry (DSC)
Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows coupled with transitions in materials as a function of time and temperature in a controlled environment. These measurements give quantitative and qualitative information about physical and chemical changes that include endothermic or exothermic processes, or changes in heat capacity.
The DSC can be used to find out the thermal critical points like melting point, enthalpy specific heat or glass transition temperature of materials. The schematic principle of the DSC is described in Fig. 2.14 [39]. The sample and an empty reference crucible are heated at constant heat flow. A difference in the temperature of both crucibles is caused by the thermal critical points of the sample and can be detected.

2.3.9. UV-Visible Spectroscopy
Ultraviolet-visible (UV-visible) spectroscopy is extensively utilized to quantitatively characterize organic and inorganic nano-sized molecules. A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is investigated through the resulting spectrum [40,41]. It could be employed to identify the component of a substance, determine their concentrations, and to identify functional
groups in molecules. Fig. 2.15 shows a typical UV-visible absorption experiment for a liquid and thin film samples.

![Image of UV-visible spectrophotometer equipment](image)

**Fig. 2.15.** UV-visible spectrophotometer equipment.

The organic or inorganic samples may exist in gaseous, liquid or solid form. The characterization of different sized materials ranging from transition metal ions and small molecular weight organic molecules, whose diameters can be several Ångstroms, to polymers, supramolecular assemblies, nano-particles and bulk materials. Size dependant properties can be observed in a UV-visible spectrum, especially in the nano and atomic scales. These involve peak broadening and shift in the absorption wavelength. Several electronic properties, such as the band gap of a material, can also be determined by this technique. The energies associated with UV-visible ranges are sufficient to excite molecular electrons to higher energy orbital [42,43]. Photons wavelength in the visible range is between 800-400 nm, which corresponds to energies between 36 and 72 kcal/mol. The near UV range includes wavelengths down to 200 nm, and has energies as
high as 143 kcal/mol. UV radiations of lower wavelengths are difficult to handle for safety reasons, and is rarely used in routine UV-visible spectroscopy.

Fig. 2.16. A schematic representation of UV-visible spectrophotometer.

Fig. 2.16 shows a schematic set up of UV-Visible spectrophotometer. A beam of monochromatic light is divided into two beams, one of them is passed through the sample, and the other passes a reference (in this figure, a solvent in which the sample is dissolved) [44]. After transmission during the sample and reference, the two beams are directed back to the detectors where they are compared. The difference between the signals is the basis of the measurement. Liquid samples are usually contained in a cell (called a cuvette) that has flat, fused quartz faces. Quartz is commonly used as it is transparent to both UV and visible lights. UV-visible spectroscopy suggests a relatively
straightforward and effective way for quantitatively characterizing both organic and inorganic nanomaterials. Moreover, as it works on the principle of absorption of photons that promotes the molecule to an excited state; it is an ideal technique for determining the electronic properties of nanomaterials. In the spectrum of nanoparticles, the absorption peak's width strongly depends on the chemical composition and the particle size. As a result, their spectrum is different from their bulk counterparts. For example, for semiconductor nanocrystals, the absorption spectrum is broadened owing to quantum confinement effects. [45,46] and as their size decreases, there is no longer a distinct peak, rather there is a band. Furthermore, semiconductor nanoparticle's absorption peaks shift towards smaller wavelengths (higher energies) as their crystal size decreases [46-49]. An important consequence of using the UV-visible spectroscopy is that the band gap of nanosized materials can be determined.

2.3.10. Electrical Properties

The dielectric, ac conductivity and impedance measurements carried out as a function of composition, frequency (75Hz-5MHz) and temperature from room temperature to 450 °C using (Agilent-4285A-LG) LCR meter as shown in Fig. 2.17.

2.3.10.1. Dielectric Measurement

For dielectric and ac impedance measurements, the silver pastes on the opposite sides of the pellet to make parallel plate capacitor geometry. The value of dielectric constant ($\varepsilon'$) has been calculated using the following formula [50]:

$$\varepsilon' = \frac{C_p d}{\varepsilon_o A}$$ .................................................. (2.5)

where $\varepsilon_o = 8.854 \times 10^{-12}$ F/m is the permittivity of free space, $d$ is the thickness of pellets, $A$ is the area of a cross section of the pellet and $C_p$ is capacitance of the pellet. The complex dielectric constant has been calculated from the following relation:

$$\varepsilon'' = \varepsilon' tan\delta$$ .................................................. (2.6)

where $\varepsilon''$ is the complex part of the dielectric constant and $tan\delta$ is the dielectric loss.
2.3.10.2. Dielectric Loss (\(\tan\delta\))

Generally, the energy loss is characterized by the dielectric loss factor (\(\tan\delta\)) which is expressed as the ratio of the imaginary part of the dielectric constant of the real part, i.e.

\[
\tan\delta = \frac{1}{\frac{\epsilon}{2\pi f \epsilon_0 \rho}} \tag{2.7}
\]

where \(f\) is the frequency of the applied ac field and \(\rho\) is the resistivity of the dielectric material. The dielectric loss appears due to the polarization lags behind the applied field as well as by the impurities and imperfections in the crystal lattice. The material density also plays an important role in the difference of dielectric constant. High porosity and low density results in low dielectric constant and dielectric losses [51].
2.3.10.3. a.c. Conductivity

The whole conductivity of any system is the sum of the ac conductivity and dc conductivity and is given by the following relation:

\[ \sigma_{\text{tot}} = \sigma_o(T) + \sigma(\omega, T) \] ................................. (2.8)

The first term at the right hand side (R.H.S.) of equation (2.8) is dc conductivity appeared due to the band conduction, which is a frequency independent function while the second term of the equation represents the pure ac conductivity due to electron hoping between the two ions at octahedral sites. In the present work of ABO₃ perovskite nanomaterials we have studied the ac conductivity as a function of frequency and temperature for different compositions using the following relation:

\[ \sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta \] ................................. (2.9)

where \( \omega = 2\pi f \) is the angular frequency.

2.3.10.4. Impedance Spectroscopy

The first used for this technique was in 1969 by Bauerle [52,53], to separate bulk from interfacial properties in polycrystalline ceramics. In complex diagrams of impedance (Nyquist orCole–Cole plot) the impedance imaginary part \( Z'(\omega) \) is plotted versus the impedance real part \( Z''(\omega) \). The response of an ideal parallel circuit of resistance \( R \) and capacitance \( C \) is a semicircle centered on the real axis. \( R \) is determined from the diameter of the semicircle, while \( C \) is calculated from the frequency of semicircle maximum. Impedance spectroscopy is perfect for studying the electrical response of dielectric materials as a function of frequency. It is a powerful technique for separating the complexities of materials, whose properties and applications depend on the close control of structure, composition, ceramic texture, dopants (or defects) and dopant distribution, which functions by utilizing the different frequency dependencies of constituent components for their separation. The impedance analysis of a material is based on an idealized circuit model with discrete electrical components. The analysis is mainly accomplished by fitting the impedance data to an equivalent circuit, which is representative of the material under investigation. It has been among the most useful
investigation techniques since the impedance of grains can be separated from the other sources of impedance, namely grain boundaries and electrode effects [54]. When the grain boundary resistance is larger than the resistance of bulk, two semicircles are often obtained in Cole-Cole plot. Deviations from ideal semicircles have been attributed to the distribution of relaxation times arising from the micro-structural inhomogeneity or disorder in the samples [55,56]. A sine wave signal was fed to the input terminal (T1) of the LCR meter and the sample from the signal generator (SG) terminal. The output (T0) measured the output signal from the sample, which was a voltage drop across a standard resistance of 1 kΩ. LCR, then automatically analyzed the signals from T1 and T0 to give phase difference (θ) between the input and out signals. The complex impedance plot is obtained after plotting \( Z'' \) versus \( Z' \). When an ac voltage \( V = V_0 e^{j\omega t} \) is applied across the sample, the current that flows across the sample is given by:

\[
i = j\omega CV = \frac{j\omega (\varepsilon' - j\varepsilon'') \Delta \varepsilon V}{d} \tag{2.10}
\]

The complex impedance plot can be represented in terms of any of the five possible complex formalisms, the permittivity (\( \varepsilon^* \)), the admittance (\( Y^* \)), the electric modulus (\( M^* \)), the impedance (\( Z^* \)) and the loss tangent (\( \tan \delta \)). These parameters are related to each other [57-59] by the formula:

\[
tan \delta = \frac{\varepsilon'}{\varepsilon} = \frac{M'}{M} = \frac{Y'}{Y} = \frac{Z''}{Z'}, \tag{2.11}
\]

Whereas the real and imaginary parts of the complex impedance are given by:

\[
Z' = \frac{R_g}{1 + \omega^2 C_g^2 R_g^2} + \frac{R_{gb}}{1 + \omega^2 C_{gb}^2 R_{gb}^2} \tag{2.12}
\]

and

\[
Z'' = \frac{-R_g^2 \omega C_g}{1 + \omega^2 C_g^2 R_g^2} + \frac{-R_{gb}^2 \omega C_{gb}}{1 + \omega^2 C_{gb}^2 R_{gb}^2} \tag{2.13}
\]

where the terms \( R_g \) and \( C_g \) represents the resistance and capacitance of the grain, while \( R_{gb} \) and \( C_{gb} \) represents the corresponding terms of the grain boundary volume [60]. The resistance value of the grain and grain boundary have been calculated from the intercepts on the real part of \( Z(Z') \) axis, where as the capacitance values have been calculated from
the frequency peaks of the semicircle arcs. Since the value of $Z' = -Z''$ at the maximum, we have:

$$C_y = \frac{1}{R_g \omega_g} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (2.14)$$

$$C_{gb} = \frac{1}{R_{gb} \omega_{gb}} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (2.15)$$

Also, the relaxation times and have been calculated from the frequency peaks using the equations:

$$\tau_g = \frac{1}{\omega_g} = C_y R_g \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (2.16)$$

$$\tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (2.17)$$

2.3.11. Vibrating Sample Magnetometer (VSM)

The usual route for formative the magnetic properties of the extensive variety of magnetic samples is Vibrating Sample Magnetometer (VSM). With this technique, the magnetic moment of a sample can be measured with high accuracy. An illustration of VSM is shown in Fig. 2.18. The new features of this magnetometer are: (i) sample motion perpendicular to the applied field; (ii) detection coil configurations, with effective area-turns nonsymmetrically dispersed about the axis of vibrations, which allow this oscillating dipole field to be observed [61]. The VSM is based upon Faraday's law, according to which an electromotive force (e.m.f.) is induced in a conductor by a time-varying magnetic flux. In VSM, a material is subjected to a uniform magnetic field and is made to undergo mechanical vibrations in the vicinity of pick-up coil, which causes the change in magnetic flux. This induces a voltage in the pick-up coils, which is proportional to the magnetic moment of the sample. A lot of the modifications occurred here for this vibrating sample magnetometer was directed toward the development of a high sensitivity, versatile, laboratory instrument. A production line instrument, useful for quality control measurements of ferrimagnetic or ferromagnetic materials at room temperature, can be made with the minimum elements [61].
Fig. 2.18. An illustration of vibrating sample magnetometer equipment.
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Chapter III

Structural, optical, electrical and magnetic properties of AFeO$_3$, (A = Bi & La)
This chapter describes the various physical properties of AFeO$_3$ (A = Bi, La) perovskite oxide nanomaterials, such as structural, optical, electrical and magnetic properties. First system bismuth ferrite (BiFeO$_3$) has a single phase and exhibits the antiferromagnetism and ferroelectricity at room temperature and above [1]. Second studied system orthoferrite (LaFeO$_3$) is chemically stable in both reducing and oxidizing atmospheres. The doped LaFeO$_3$ shows high electrical conductivity, high dielectric constant, low dielectric loss, ferroelectricity, piezoelectricity therefore used as separator material in solid oxide fuel cell (SOFC).

3.1. BiFeO$_3$ Nanoparticles

3.1.1. Introduction

The research on magneto-electric multiferroics and on the associated interplay of their electric, elastic and magnetic properties has been developed over recent years because of the single phase compound, in which coexistence of ferromagnetism and ferroelectricity in the same phase. Essentially, the materials display such manners, especially at room temperature and above; hold considerable promise for various applications including multi-state memory elements, spintronic devices as well as more conventional applications such as ferroelectric random access memory or piezoelectric devices [2]. So, the multiferroic materials investigation has been an interesting area under discussion not only from the viewpoint of solid state physics but also because of their achievable applications on an electrical device such as electric field induced magnetic memory effects, electro-optic transducer controlled by magnetic fields [3]. BiFeO$_3$ (BFO) is perhaps the most promising single phase, the multifarious candidate material commonly studied due to its large ferroelectric and magnetic ordering temperatures, $T_C = 1123$ K, $T_N = 643$ K [4,5]. BFO has a complicated magnetic structure, which exhibiting G-type antiferromagnetism with each Fe$^{3+}$ ion surrounded by six antiparallel spins as well as very strong ferroelectricity at room temperature and above [1].

BFO based systems could be used to develop new applications in information storage of radio, television, microwave and satellite communication, bubble memory device, audio/video, and digital recording, spintronic devices and sensor technology [6,7]. Recently, it has been observed that BFO could be used in the medical treatment of cancer [8]. The responsibility of ions for the production of ferroelectricity and
antiferromagnetism in BFO multiferroic are Bi\(^{3+}\) and Fe\(^{3+}\) ions respectively [9]. Phase purity of BFO is the very importance of high quality of the functional properties to obtain the pure phase of these materials there are a problem as it much difficult because the temperature stability range of single phase BFO is very narrow [10]. The main obstacle for BFO applications is large leakage current because of the second phase is exist. However, due to the complex phase diagram of Bi\(_2\)O\(_3\)-Fe\(_2\)O\(_3\), with Bi\(_2\)Fe\(_4\)O\(_9\) and Bi\(_{22}\)FeO\(_{40}\) being the stable compounds surrounding BFO [11], and to Bi\(_2\)O\(_3\) loss during high temperature treatments for long periods. Although, the BFO is a non-centrosymmetric rhombohedral distorted perovskite that crystallizes in space group \(R\bar{3}c\) symmetry [12]. In the single phase multifeorric materials the small magnetolectric coupling hampered initial developments in this field, that development of the explore proximity and interfacial effects between magnetic and ferroelectric materials to form composite structures with enhanced coupling between electric and magnetic properties due to alternative approaches. In this respect, BFO is the most suitable magnetolectric materials because of their simple structure and high temperatures of magnetic and electric orderings [13]. So far, BFO have the several alternative chemical synthesis routes proposed to synthesize single phase BiFeO\(_3\), including the solid-methods [14,15], sol-gel techniques [16,17], auto-combustion [18], solution chemistry (precipitation/co-precipitation) method [19], sono-chemical [20], mechanochemical [21], hydrothermal processes [22] and polyvinyl alcohol (PVA) route [7].

In the present work, single phase NPs of BFO were prepared using the sol-gel combustion route. The structural, optical, electrical and magnetic properties were investigated to confirm the formation of BFO NPs and their utility in practical application.

3.1.2. Experimental details

3.1.2.1. Synthesis

The equimolar amounts (0.2M) of Bi(NO\(_3\))\(_3\).5H\(_2\)O and Fe(NO\(_3\))\(_3\).9H\(_2\)O were dissolved in dilute nitric acid and citric acid with molar ratio 1:1 was added. Then ammonia solution (NH\(_3\)) was slowly mixed to adjust the pH \(\sim\) 7.5. This solution was heated under constant stirring on a hot plate to its boiling temperature until all the liquids evaporated. Afterwards, the homogeneous sol was heated slowly at 120 °C for 40 min.
This fluffy brown powder was collected and calcined at 600 °C in the air for 5h. The preparation procedure by sol-gel combustion method is schematically shown in Fig. 3.1.

3.1.2.2. Characterization

The crystal structure was investigated by XRD (Rigaku, Miniflex-II) in the 2θ range from 20° to 80°. SEM (JSM-6510LV) equipped with an EDS was used to check the morphology and elemental test of the NPs. The infrared absorption spectra of the samples were recorded in the wave number range 400 - 2000 cm\(^{-1}\) by using a Perkin Elmer spectrometer (model Spectra Two) using KBr as a reference. UV-visible absorbance was carried out in the 200 - 800 nm range, and the atomic force microscope (Veeco-contact mode) was used to examine the morphology and the surface roughness. The dielectric constant was studied as a function of temperature (35°C–400°C) using an Agilent LCR meter (4285 A). Room temperature magnetic properties (M–H) were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

Fig. 3.1. Schematic representation of BiFeO\(_3\) preparation.
3.1.3. Results and discussion

3.1.3.1. Structural studies

XRD pattern obtained from the BFO NPs is shown in Fig. 3.2. The position of the main sharp peaks (012), (104), (101), and (024), confirmed the high crystallinity and perovskite structure of the NPs. Moreover, no other impurity peaks were detected in the XRD pattern, which revealed the high phase purity of the BFO NPs. Furthermore, BFO NPs show rhombohedral structure with space group R3c, which is well consistent with the standard data (JCPDS card no.: 86-1518) and lattice parameters were found $a = 5.75 \text{ Å} = b$ and $c = 13.82 \text{ Å}$.

![XRD pattern of BiFeO3 nanoparticles with crystallite size ~ 28 nm](image)

Fig. 3.2. XRD pattern of the BiFeO$_3$ nanopowder.

The average crystallite size ($D_{hkl}$) of the most intense peak (101) was observed ~ 28 nm as estimated using Debye–Scherrer’s formula [23].

$$D_{hkl} = \frac{\beta \cos \theta}{\lambda} \quad \text{.................................................. (3.1)}$$
where λ is the X-ray wavelength (λ = 1.5418 Å), β is full width at half maximum (FWHM) in radians, B is the shape factor (usually taken 0.89) and θ is the Bragg’s angle.

Atomic force microscope (AFM) is using to study the surface morphology at an extremely high resolution. It considers the roughness as an important parameter and gives an idea about the surface quality under investigation in addition to providing some insight on the growth morphology. Fig. 3.3(a,b) shows typical images in two and three dimensions of BiFeO₃. Actually, a homogeneous surface was formed and the grains were observed in different area. The surface roughness of BiFeO₃ nanoparticles as given in Fig. 3.2a for different lines (I, II & III) are 0.105 nm, 0.170 nm and 0.149 nm respectively. The average surface roughness of the sample is observed ~ 0.141nm.

![AFM images](image_url)

**Fig. 3.3.** AFM images (a) two dimensions image for BiFeO₃ NPs at 0.2µm x 0.2 µm, (b) three dimensions image for the same and (I, II and III) are the standard roughness area of BiFeO₃ NPs.

SEM image of BFO NPs is displayed in Fig. 3.4. The surface morphology of BFO NPs reveals the uniform grains, which indicates that the complete incorporation of BFO as supported by XRD analysis. Furthermore no morphological alterations
were observed in the SEM image. In addition the EDS analysis also confirms the presence of Bi, Fe and O elements in good stoichiometric as displayed in the Fig. 3.5.

![SEM image of the BiFeO₃ nanopowder](image)

**Fig. 3.4.** SEM image of the BiFeO₃ nanopowder.

![EDS spectrum for the BiFeO₃ nanopowder](image)

**Fig. 3.5.** EDS spectrum for the BiFeO₃ nanopowder

Fig. 3.6 shows the FTIR result of BiFeO₃ NPs recorded in the wave number range 400-2000 cm⁻¹. The strong absorption peak at 444 was attributed to the Fe-O and O-F-O bond vibrations of FeO₆ groups in BiFeO₃ perovskite, respectively [24]. The absorption peak 557cm⁻¹ was attributed to the vibration of metal-oxygen bond,
indicating that BiFeO$_3$ was formed. The bands located around 1100 to 1399 cm$^{-1}$ indicated by nitrate ions and the last band appeared at 1655 cm$^{-1}$ was assigned to the asymmetric COO$^-$ stretching vibrations [25].

Fig. 3.6. FTIR spectrum of the BiFeO$_3$ NPs.

3.1.3.2. Optical properties

The UV-visible absorption spectroscopy is a powerful technique to explore the optical properties of semiconductor nanoparticles. In order to obtain the fundamental band gap energy ($E_g$) of BiFeO$_3$ NPs, we have measured the optical absorption spectra as a function of wavelength as shown in Fig. 3.7. The $E_g$ of the nanopowders was determined using following Tauc’s relation:

$$ a(h\nu) = K(h\nu - E_g)^n $$

(3.2)
where $K$ is a constant, $h\nu$ is the photon energy, the value of $n = 1/2$, $3/2$, $2$ and $3$ is an index depending on the nature of the electronic transition responsible for the absorption, and $\alpha$ is the absorption coefficient was calculated as follows [26]:

$$\alpha = 2.303(A_{k}\lambda)$$

where $A_{k}$ is absorbance and $t$ is the thickness of cuvette.

![BiFeO₃ Nanoparticles](image)

**Fig. 3.7.** UV-visible absorbance of the BiFeO₃ NPs.

The Fig. 3.8 displayed the plot of $(\alpha h\nu)^2$ versus $h\nu$ for direct transitions to determine the band gap of the BiFeO₃ NPs. The absorption edge depicts that the sample has a direct band gap. The strong absorption could be ascribed to the electronic transition from the valence band to the conduction band ($O_{2p}$ - $Fe_{3d}$). The value of $E_g \sim 2.1$ eV was found for the BiFeO₃ nanopowders, which is well consistent with earlier reported...
result [26]. This is indicating that the BiFeO$_3$ nanopowder prepared by this method may be useful as photocatalytic material.

\[ E_g = 2.1 \text{ eV} \]

\[ (\alpha h \nu)^2 \times 10^4 \]

\[ h \nu \text{ (eV)} \]

Fig. 3.8. Band gap energy of the BiFeO$_3$ NPs.

3.1.3.3. Dielectric properties

Basically, to investigate an effect of temperature on dielectric properties, its variation plotted as a function of temperature with different frequencies.

The electrical properties are illustrated through which interactions as the following:

\[ \epsilon^* = \epsilon' - j \epsilon'' \]

(3.4)

where, \( \epsilon^* \) is a complex relative permittivity of the material, \( \epsilon' \) is a real part of dielectric constant and \( \epsilon'' \) is an imaginary part of dielectric constant.

The real and imaginary parts have been described the stored energy and dissipated energy respectively and the values of \( \epsilon' \) and \( \epsilon'' \) were calculated by relations:

\[ \epsilon' = \frac{Cpd}{\varepsilon_{o}A} \]

(3.5)
where \( C_p \) is the capacitance of the sample in Farad (F), \( d \) (cm) is the thickness of pellet, \( \varepsilon_r \) is the permittivity of free space \( \approx 8.854 \times 10^{12} \, \text{F/m} \) and \( A \) (cm\(^2\)) is the cross sectional area of the surface of the pellet.

\[
\varepsilon'' = \varepsilon' \times \tan \delta \tag{3.6}
\]

where \( \tan \delta \) is the dielectric loss or dielectric factor which represents the energy dissipation in the dielectric medium.

\[
\tan \delta = \frac{1}{2\pi f \varepsilon_0 \varepsilon_r \rho} \tag{3.7}
\]

where \( f \) is the frequency of the applied ac field and \( \rho \) the resistivity of the dielectric material.

The a.c. conductivity was calculated as the following:

\[
\sigma_{ac} = \varepsilon'\varepsilon_0 \omega \tan \delta \tag{3.8}
\]

where \( \omega \) is the angular frequency of the applied a.c. field.

3.1.3.3.1. Dielectric constant

Fig. 3.9 shows the dielectric constant \( \langle \varepsilon' \rangle \) as a function of temperature. A sharp dielectric anomaly occurs at the 100 °C because of BiFeO\(_3\) is a piezoelectric at all temperatures below 827 °C, in fact, every magnetoelastic phenomena at its magnetic phase transactions is appropriate to produce responses in the dielectric response [27]. It is found that the dielectric constant value at room temperature was around 85 at 175 kHz. The dielectric constant of BiFeO\(_3\) NPs increases gradually with increased temperature for all frequencies. The values of dielectric constant increase with decreasing frequency, it may be due to the presence of various dispersion mechanisms for BiFeO\(_3\) NPs.

3.1.3.3.2. Dielectric loss

In general, the dielectric system energy dissipation is represented by the dielectric loss \( \langle \tan \delta \rangle \) as well as the losses observed from the Fig. 3.10 to be lower at higher frequencies, due to the inhibited of domain wall motion and force of magnetization, which is changed rotation. The behavior peaks appearing when the hopping of localized electric charge carrier frequency equals to the applied ac field frequency. The relaxation behavior appears in the system due to the slight shift in the position of peaks to increase in frequency.
Fig. 3.9. The variation of dielectric constant with temperature for BiFeO$_3$ NPs at different frequencies.

Fig. 3.10. The variation in dielectric loss (tanδ) for BiFeO$_3$ NPs at different frequencies.
3.1.3.3. a.c. Conductivity and activation energy

The variation in ac conductivity ($\sigma_{ac}$) with temperature for various fixed frequencies has shown in Fig. 3.11. In general, the total conductivity has written as the following relation:

$$\sigma_{tot} = \sigma_0(T) + \sigma(\omega, T) \tag{3.9}$$

where $\sigma_0(T)$ at R.H.S. is dc conductivity due to the band conduction, which is a frequency independent function and the $\sigma(\omega, T)$ is represented the pure ac conductivity due to electron migration between the metal ions. The values of the activation energy ($E_a$) evaluated from the Fig. 3.12.

![Graph showing the variation of ac conductivity ($\sigma_{ac}$) with temperature for BiFeO$_3$ NPs at different frequencies](image)

Fig. 3.11. The variation in ac conductivity ($\sigma_{ac}$) with temperature for BiFeO$_3$ NPs at different frequencies

It observed that at low frequency $E_a$ is large and $\sigma_{ac}$ is small as well as at high frequency $E_a$ exhibits small and $\sigma_{ac}$ appears large. This behavior occurs due to the ionic conduction, which is characterized by low conductivity and high activation energy conduction, while the association of relatively higher conductivity and lower
activation energy with electronic conduction. The values of $\sigma_{ac}$ and $E_a$ have been tabulated in table 3.1.

**Table 3.1.** ac conductivity and Activation energy for BiFeO$_3$ NPs at different frequencies.

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>a.c. Conductivity ($\sigma_{ac}$) ($\Omega$.m)$^{-1}$</th>
<th>Activation Energy ($E_a$) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>$3.93 \times 10^{-4}$</td>
<td>0.35</td>
</tr>
<tr>
<td>575</td>
<td>$7.98 \times 10^{-4}$</td>
<td>0.25</td>
</tr>
<tr>
<td>1300</td>
<td>$1.41 \times 10^{-3}$</td>
<td>0.21</td>
</tr>
<tr>
<td>2500</td>
<td>$2.46 \times 10^{-3}$</td>
<td>0.20</td>
</tr>
</tbody>
</table>

**Fig. 3.12.** The variation of $\ln(\sigma_{ac})$ with inverse of temperature for BiFeO$_3$ NPs at different frequencies.
3.1.3.3.4. Impedance analysis

The complex impedance plots (Nyquist plots) of BiFeO$_3$ NPs at different temperature are shown in Fig. 3.13. The single semicircular behavior has been observed in Cole-Cole plots, due to the dominant of grain boundaries contribution and grain contribution is not resolved. The various electrical parameters can be calculated for the grain and grain boundary from the Cole-Cole plots by the following relations:

\[ C_g = \frac{1}{R_g\omega_g} \]  \hspace{1cm} \text{(3.10)}

\[ C_{gb} = \frac{1}{R_{gb}\omega_{gb}} \]  \hspace{1cm} \text{(3.11)}

\[ \tau_g = R_g C_g \]  \hspace{1cm} \text{(3.12)}

\[ \tau_{gb} = R_{gb} C_{gb} \]  \hspace{1cm} \text{(3.13)}

Fig. 3.13. Nyquist plots of BiFeO$_3$ NPs at different temperature.
These electrical parameters are listed in the table 3.2. It is clear that the grain boundary resistance increases with increasing temperature while capacitance values of grain boundaries decrease with increasing temperature.

Table 3.2. Variation of different impedance parameters as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$R_{gb}$ (MΩ)</th>
<th>$C_{gb}$ (µF)</th>
<th>$T_{gb}$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 (RT)</td>
<td>0.21</td>
<td>$1.0 \times 10^{-4}$</td>
<td>21.0</td>
</tr>
<tr>
<td>350</td>
<td>0.25</td>
<td>$8.6 \times 10^{-5}$</td>
<td>21.5</td>
</tr>
<tr>
<td>400</td>
<td>0.63</td>
<td>$3.4 \times 10^{-5}$</td>
<td>21.4</td>
</tr>
<tr>
<td>450</td>
<td>1.10</td>
<td>$1.9 \times 10^{-5}$</td>
<td>20.9</td>
</tr>
<tr>
<td>500</td>
<td>2.10</td>
<td>$10 \times 10^{-6}$</td>
<td>21.0</td>
</tr>
</tbody>
</table>

3.1.4. Magnetoelectric effect

The variation of magnetoelectric (ME) in output with AC magnetic field has shown in Fig. 3.14. The ME Output linearly increases with increase in AC magnetic field for BFO NPs. The slope of the plot $\Delta E/\Delta H$ is found to be 0.064 mV/Cm.Oe.

Fig. 3.14. AC magnetic Field versus magnetoelectric output.
3.1.5. Magnetic measurements

Magnetic measurements were performed in order to study the magnetization hysteresis (M–H) loop at room temperature to a maximum applied field of 20 kOe as displayed in Fig. 3.15. This clearly shows the linear curve of the magnetization and the plot of magnetization indicating the antiferromagnetic behavior. This may be due to ferromagnetic is not universal and perhaps explained even a very small concentration of impurities at low temperature [27]. The inset shows the magnified image up to 1.5 kOe for the BFO nanoparticles. For our knowledge we note that only 1 mol% of paramagnetic Fe$^{3+}$ (maybe due to the presence of Bi$_{25}$Fe$_{30}$) could be occurred all the magnetic enhancement in their single crystal at low temperature, and the removing like that impurities with HNO$_3$ removes almost all remains of ferromagnetism in their samples [27].

![Magnetization versus magnetic field for BiFeO$_3$ NPs.](image.png)
3.2. LaFeO₃ Nanoparticles

3.2.1. Introduction
Reverse micelles, or water-in-oil microemulsions, have as a feature a variety of solutes. The distribution of the solute between the surrounding solvent and the micelles can be described in terms of a partition constant based on a two pseudophases model that can be expanded to three pseudophases in micelles with high water to surfactant mole ratios. In these systems, two partition constants can be defined, one between the external solvent and the micellar interface, and another between the external solvent and the inner water pool [28]. The molecular structure of the surfactant affects the size of micelle water pools and it is common in some surfactant systems to use a co-surfactant to produce a larger range of micelle sizes, such as cetyltrimethylammonium bromide, hexadecyltrimethylammonium bromide (CTAB), Nonylphenol Ethoxylate-4 (NP-4) and Nonylphenol Ethoxylate-7 (NP-7). It has been shown that using this combination also improves solubilization and overall micelle stability when compared to the corresponding single surfactants [29]. The perovskite structures with general formula ABO₃ have been formed by mixed oxides of rare earth elements at A site and transition metals at B site. These materials are interesting for catalytic applications due to the extensive range of elemental compositions that can be prepared as crystalline structures [30]. The orthoferrrites, LaFeO₃ has been crystallized in the perovskite structure with Fe³⁺ ion surrounded by six oxygen ions giving octahedral coordination. It is chemically stable in both reducing and oxidizing atmosphere and has an orthorhombic symmetry perovskite structure (a = 8.250 Å, b = 6.020 Å, and c = 8.740 Å) with the space group Pbnm [31]. At room temperature is exhibiting a ferromagnetic nature [31] as well as forms a family of Dzyaloshinsky interaction which displays an unusual variety of the magnetic properties and changed in its structural [32-34]. The perovskite structure of LaFeO₃ widely uses in catalytic oxidation, gas sensitivity characters surface electronic states [35-38], magnetic materials [39] and electrode material in solid oxide fuel cell (SOFCs) [40]. LaFeO₃ is a suitable solid oxide fuel cell (SOFC) cathode due to its react more slowly with the yttria stabilized Zirconia (YSZ) electrolyte than LaMnO₃ at high temperature [41]. So far, LaFeO₃ has been synthesized via the several alternative chemical synthesis routes proposed to single phase LaFeO₃, including the
emulsion method [39], glycine combustion method [42], polymerizable complex method [43] sol–gel method using citric acid as complex agent [44,45], thermal decomposition of $\text{LaFe(\text{CN})}_6\cdot5\text{H}_2\text{O}$ compounds [46], hydrothermal method [47], sonochemical [48], and co-precipitation method [49].

The objective of the present work is to investigate the effect of water to surfactant structure, thermal, optical, dielectric and magnetic properties of $\text{LaFeO}_3$ NPs synthesis by reverse micelle technique.

### 3.2.2. Experimental

#### 3.2.2.1. Synthesis

$\text{LaFeO}_3$ NPs were prepared using reverse micelle (RM) technique. A quaternary system of iso-octane/CTAB/n-buty alcohol/water was selected in this RM process. The size of nanoparticles was controlled by the molar ratio of the aqueous phase to surfactant, $R = \text{[water/surfactant]}$ [50]. We have synthesized $\text{LaFeO}_3$ NPs by different value of $R$. In the first process when $R_1 = 0.67$ we used two kinds of RM solutions namely RM1 and RM2. For first solution RM1 contained (5 wt%) an aqueous solution of an equimolar mixture (0.1M) of lanthanum nitrate hexahydrate $[\text{La(NO}_3)_3\cdot6\text{H}_2\text{O}]$ and ferric nitrate nonahydrate $[\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}]$, CTAB as a surfactant (7.5 wt%), n-buty alcohol as a co-surfactant (7.5 wt%) and iso-octane as oil (30 wt%). The stirring was continued for 30 min resulting in a stable reverse micelle (RM1). While RM2 contained the same constituent as RM1 except that the aqueous solution was NaOH (0.1 M) instead of $[\text{La(NO}_3)_3\cdot6\text{H}_2\text{O}]$ and $[\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}]$ was prepared under similar conditions. These two reverse micelles were mixed under constant stirring and a brown color solution was obtained. In addition ammonium NH$_3$ was slowly added to adjust the pH and stirred 24 h on a magnetic stirrer. In second process when $R_2 = 2$ we used the same RM system as above except the (10 wt%) an aqueous solution of an equimolar mixture (0.1M) of lanthanum nitrate hexahydrate $[\text{La(NO}_3)_3\cdot6\text{H}_2\text{O}]$ and ferric nitrate nonahydrate $[\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}]$, CTAB as a surfactant (5 wt%), n-buty alcohol as a co-surfactant (5 wt%). The resulting precipitate was separated from the surfactant and a polar solvent by centrifugation and washing it one time by ethanol and three times with distilled water. The precipitate was dried in an oven at 80 °C for 6 h to obtain R1 and R2 samples and heated at 750 °C for 6 h in air.
3.2.2.2. Characterization

The crystal structure was investigated by X-ray diffraction (Rigaku, Japan, Miniflex-II) using Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) in the 2$\theta$ range from 20° to 80°. The atomic force microscopy (Veeco-contact mode) was used to examine the morphology and the surface roughness and the scanning electron microscope (JEOL JSM-6510LV) equipped with an energy dispersive spectrometer (EDS) was used to check the morphology and particle size. The infrared absorption spectra of the samples were recorded in the wave number range 400 - 2000 cm$^{-1}$ by using a Perkin Elmer spectrometer (model Spectra Two) using KBr as a reference. Thermal properties carried out using thermogravimetric analysis (Pyris 1 TGA, PerkinElmer) and differential scanning calorimetry (DSC 600, PerkinElmer). UV-visible absorbance was carried out using (UV-visible, PerkinElmer spectrophotometer) in the 200-800 nm range, LCR Dielectric and impedance spectroscopy measurements were performed in the frequency range of 75 kHz to 5 MHz using meter (Model: Agilent-4285A). Room temperature magnetic measurements (M–H) were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

3.2.3. Results and discussion

3.2.3.1. Structure and morphology analysis

Structure of LaFeO$_3$ has been described to be an orthorhombic perovskite structure with Pnma space group [51]. Fig. 3.16 shows the XRD patterns of the single phase perovskite for both R1 and R2 samples calcined at 750 °C. The main diffraction peaks of the NPs confirmed the high crystalline, which is well consistent with the standard JCPDS card of perovskite LaFeO$_3$ (JCPDS88-0641) [52]. The average crystallite size of the most intense peak (120) at angle 2$\theta$ ~ 32° was estimated using Debye–Scherrer’s formula [53] and the lattice parameters for R1 and R2 samples are given in the table 3.3.

The AFM images in two and three dimensions have shown in Fig. 3.17(a,b) for R1 sample and Fig. 3.18(a,b) for R2 sample. They are showing the uniform grains of R1 and R2 sample surface morphology. Actually, homogeneous surfaces were formed and the grains were observed in different area. The images of two and three dimensions have shown the surface roughness of R1 and R2 samples. The roughness of the different lines as shown in Fig. 3.17 (I, II & III) 0.140 nm, 0.129 nm and 0.302
nm respectively as well as, the roughness of R2 sample for different lines (I, II & III) are given in Fig. 3.18 at 0.319, 0.356 and 0.137 nm respectively. The average surface roughness of R1 and R2 samples ~ 0.190 nm and 0.270 nm respectively.

Table 3.3. Optical band gap (E_g), Urbach energy (E_u), Threshold wavelength (\(\lambda_s\)), crystallite size, Lattice parameters and unit cell volume for R1 and R2 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E_g (eV)</th>
<th>E_u (eV)</th>
<th>(\lambda_s) (nm)</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameters (Å)</th>
<th>Unit cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>R1</td>
<td>2.63</td>
<td>0.73</td>
<td>224</td>
<td>22</td>
<td>8.135</td>
<td>6.040</td>
</tr>
<tr>
<td>R2</td>
<td>2.60</td>
<td>0.56</td>
<td>215</td>
<td>23</td>
<td>8.156</td>
<td>6.050</td>
</tr>
</tbody>
</table>

Fig. 3.16. X-ray diffraction patterns of R1 and R2 samples.
Fig. 3.17. AFM images (a) two dimensions image of the R1 sample at $0.1\mu m \times 0.1\mu m$, (b) three dimensions image for the same and (I, II and III) are the standard roughness area of R1 sample.

Fig. 3.18. AFM images (a) two dimensions image of R2 sample at $0.1\mu m \times 0.1\mu m$, (b) three dimensions image for the same and (I, II and III) are the standard roughness area of R2 sample.
The SEM images with the different molar ratio of water to surfactant of LaFeO₃ NPs (R1 and R2 samples) are shown in the Fig. 3.19. The Porous structures are seen in the nearly clear form of SEM image. The particle size is narrow of distribution of these nanoparticles, because of the morphology surface is nearly in a uniform agglomeration of R1 and R2 samples.

Fig. 3.19. SEM micrograph images for (a) R1 sample and (b) R2 sample.

Fig. 3.20. EDS spectra of (a) R1 sample and (b) R2 sample.
The FTIR spectra of R1 and R2 samples correspond to the hydroxy group.

The FTIR spectra of R1 and R2 samples are shown in Fig. 3.21. The energy dispersed X-ray spectra (EDS) of R1 and R2 samples confirm the presence of Cu and O, without any impurities, while the Cu signals originate from the coated Cu film with carbon homon.
3.2.3.2. Thermal properties

Thermal properties of R1 and R2 were carried out by thermogravimetric analysis (TGA) in nitrogen up to 800 °C with an increment of 10 °C / min in the air. Fig. 3.22 shows the R1 and R2 curves of TGA, which the weight loss processes appearing in two steps, the first step in the temperature range 44-360 °C with a weight loss 5% of R1 sample and 9% of R2 sample and the second step in the temperature range 360 – 480 °C with a weight loss 1% of R1 sample and 2% of R2 sample. Finally, the weight loss is 0.3% of R1 sample and 1% of the R2 sample on the TGA curves were observed in the range of temperature 500-800 °C is due to the removal of residual organic [56].

![TGA curves of R1 and R2 samples](image)

**Fig. 3.22.** TGA curves of R1 and R2 samples

Furthermore, the thermal weight loss behavior companied with endothermic and exothermic effect in the DSC curves in a range of temperature up to 400 °C. Fig. 3.23 shows the R1 and R2 curves of DSC, the two endothermic peaks are found at 50 °C for both samples and 85 °C of R1 sample and 82 °C of R2 sample, these peaks characterize the phase transition of LaFeO₃ NPs [57] and the four exothermic peaks are found at 62 °C, 95 °C, 143 °C and 347 °C for R1 sample and 65 °C, 98 °C, 228 °C...
and 361 °C for R2 sample respectively. The displacement of the exothermic peaks in R2 curve may be attributed to the particle size and the peaks of R1 and R2 are occurred due to the evaporation of water and organics [58].

![Graph showing DSC curves for R1 and R2 samples.]

Fig. 3.23. DSC curves for R1 and R2 samples.

3.2.3.3. Optical properties

Generally, the semiconductor optical absorption performance is related to the electronic structure feature and their band gaps. The sample's optical properties were studied by measuring their UV-visible diffuse reflectance absorption spectra. As shown in Fig. 3.24, the absorption spectra of R1 and R2 samples were measured. The absorption spectra show that R1 and R2 samples with absorption two peaks. The first peak indicates that the LaFeO$_3$ NPs may be a kind of photocatalytic materials [39] and second peak appeared due to the activity of LaFeO$_3$ NPs under the visible light. Basically, the oxide photocatalysts valance band consists of the O$_{2p}$ orbital and the electronic transition takes place from O$_{2p}$→Fe$_{3d}$ orbital [38]. The Fig. 3.25 shows the indirect band gap of R1 and R2 samples, which could be estimated by extrapolating the linear portion of $(ahv)^{1/2}$ versus $(hv)$; the band gap energy for both samples are given in table 3.1. Fig. 3.26 shows the plot of absorption coefficient ($\alpha$) as a function of photon energy, which it was evaluated from the relation (3.3).
Fig. 3.24. UV-visible absorbance of R1 and R2 samples

Fig. 3.25. The optical band gap energy for R1 and R2 samples.
Fig. 3.26. Absorption coefficient for R1 and R2 samples

The extinction coefficients ($k$) have been shown in Fig. 3.27 as a function of photon energy and it was calculated from the absorption coefficient ($\alpha$) as the following equation [59]:

$$k = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (3.14)

where $\lambda$ is the wavelength of the absorption spectrum. Due to the normal dispersion the extinction coefficient behavior decreases with increasing photon energy ($h\nu$) for both samples.

In the mediated of the last century Franz Urbach proposed the model to calculate the energy tail width ($\Delta E$) of the state density, which is presented as the following relation [60]:

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_o}\right)$$  \hspace{1cm} (3.15)
where α is the absorption coefficient, hν is the photon energy, $E_u = k_B T / \sigma(T)$ is called Urbach energy and $\sigma(T)$ is called a steepness parameter. Fig. 3.28 shows the ln(α) as a function of photon energy, $E_u$ represents an inverse slope of the absorption coefficient logarithmic. The Urbach energies of R1 and R2 samples have been calculated and tabulated in Table 3.3. In crystalline and amorphous systems $E_u$ used to characterize the degree of disorderliness. The maximum wavelength of incident radiations required to eject the electrons from a metallic surface is defined as threshold wavelength. The maximum wavelength of incident radiations required to eject the electrons from a metallic surface is defined as threshold wavelength.

To calculate the maximum wavelength or threshold wavelength ($\lambda_\alpha$) of the incident radiation, we analyzed UV. visible as the following relation [61,62]:

$$\left(\frac{\alpha}{\lambda}\right)^2 = \sigma \left(\frac{1}{\lambda} - \frac{1}{\lambda_\alpha}\right)$$

(3.16)
Fig. 3.28. Variation of the Lna with hv for R1 and R2 samples

Fig. 3.29. Typical $(A/\lambda)^2$ versus $1/\lambda$ plot for R1 and R2 samples.
where A is the absorption, \( \lambda \) is the wavelength and G is the empirical constant. Threshold wavelength values have been evaluated from the Fig. 3.29 to be 224 nm for R1 and 215 nm for R2.

3.2.3.4. Dielectric analysis

Basically, to investigate an effect of temperature on dielectric properties, its variation as a function of temperature with different frequencies (100 kHz-5 MHz) was observed. The electrical properties are illustrated through which interactions as the equation (3.4). The real and imaginary parts have been described the stored energy and dissipated energy respectively and the values of \( \varepsilon' \) and \( \varepsilon'' \) were calculated by relations (3.5) and (3.6). The a.c. conductivity was calculated as the equation (3.8).

3.2.3.4.1 Dielectric constant

Fig. 3.30(a,b) shows the variation of the real part of the dielectric constant (\( \varepsilon' \)) as a function of temperature at different frequencies (100 kHz - 5 MHz), for the both samples R1 and R2 respectively.

![Dielectric constant graphs](image)

**Fig. 3.30.** Variation of dielectric constant real part with temperature of (a) R1 sample at different fix frequencies (100 kHz-5 MHz) and (b) R2 sample for the same.

Fig. 3.31(a,b) shows the imaginary part of the dielectric constant, which are the prominent peaks at \( T \approx 330 \) K for R1 and \( T \approx 337 \) K for R2 appeared in spectra of
\( \varepsilon' \) and \( \varepsilon'' \) also observed by DSC, it is attributed to paraelectric and the ferroelectric phase transition [57]. The variation of dielectric constant for both samples increase with decreasing frequency, it may be due to the presence of various dispersion mechanisms for LaFeO_3 NPs. The dielectric constant values for both samples at (300 K) and (673 K) have been tabulated in Table 3.4 for various frequencies.

![Dielectric Constant vs Temperature](image)

**Fig. 3.31.** Variation of dielectric constant imaginary part with temperature of (a) R1 sample at different fix frequencies (100 kHz - 5 MHz) and (b) R2 sample for the same.

### 3.2.3.4.2 Dielectric loss and capacitance

Generally, the energy dissipation of the dielectric system is represented by the dielectric loss (tan\( \delta \)) as well as the losses observed from the Fig. 3.32(a,b) for R1 and R2 samples respectively to be lower at higher frequencies, it can be attributed to the inhibited of domain wall motion and force of magnetization, which is changed rotation. The behavior peaks appearing when the hopping of localized electric charge carrier frequency equals to the applied ac field frequency. The dielectric loss (tan\( \delta \)) appears as the dielectric constant (\( \varepsilon' \)) behavior having loss peaks corresponding to the transition peaks in dielectric constant as a function of temperature. The relaxation peak appears in the system due to the slight shift in the position of peaks to increase in frequency. The dielectric loss values for both samples at (300 K) and (673 K) have been tabulated in table 3.4 for various frequencies.
Fig. 3.32. Variation in dielectric loss (tanδ) for (a) R1 sample at different frequencies (100 kHz-5MHz) and (b) R2 sample for the same.

Table 3.4 Dielectric constant, dielectric loss, ac conductivity and activation energy for R1 and R2 samples at different frequencies.

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>$\varepsilon'$</th>
<th>$\tan\delta$</th>
<th>$\sigma \times 10^{-4} (\Omega.m)^{-1}$</th>
<th>Activation Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
<td>R2</td>
<td>R1</td>
<td>R2</td>
</tr>
<tr>
<td>300 (K)</td>
<td>124</td>
<td>14</td>
<td>518</td>
<td>67</td>
</tr>
<tr>
<td>300 (K)</td>
<td>673</td>
<td>673</td>
<td>673</td>
<td>300 (K)</td>
</tr>
<tr>
<td>100</td>
<td>124</td>
<td>14</td>
<td>518</td>
<td>67</td>
</tr>
<tr>
<td>500</td>
<td>64</td>
<td>12</td>
<td>174</td>
<td>41</td>
</tr>
<tr>
<td>500</td>
<td>64</td>
<td>12</td>
<td>174</td>
<td>41</td>
</tr>
<tr>
<td>1000</td>
<td>45</td>
<td>11</td>
<td>110</td>
<td>36</td>
</tr>
<tr>
<td>1000</td>
<td>45</td>
<td>11</td>
<td>110</td>
<td>36</td>
</tr>
<tr>
<td>2000</td>
<td>30</td>
<td>10</td>
<td>75</td>
<td>31</td>
</tr>
<tr>
<td>2000</td>
<td>30</td>
<td>10</td>
<td>75</td>
<td>31</td>
</tr>
<tr>
<td>5000</td>
<td>20</td>
<td>9.5</td>
<td>45</td>
<td>27</td>
</tr>
<tr>
<td>5000</td>
<td>20</td>
<td>9.5</td>
<td>45</td>
<td>27</td>
</tr>
</tbody>
</table>


Fig. 3.33(a,b) show the two regions for the behavior of the capacitance for R1 and R2 samples respectively as a function of the frequency of different temperature. In first region for all different temperatures the capacitance is decreased sharply in R2 sample more than R1 sample with increasing frequency, that is may be appropriately illustrated on the basis of decreasing in the space charge region at the electrodes [63]. At second region, the behavior of the capacitance is decreased slightly with increasing frequency; due to the some part of charge carriers close to the electrodes have been blocked.

![Graph showing variations of capacitance (C) with frequency at different fixed temperature for R1 and R2 samples.](image)

Fig. 3.33. Variations of capacitance ($C_p$) with frequency at different fixed temperature of (a) R1 sample and (b) R2 sample.

3.2.3.4.3 a.c. Conductivity and activation energy

The variation a.c conductivity ($\sigma_{ac}$) with temperature for various fixed frequencies has shown in Fig. 3.34(a,b) for the both samples R1 and R2 respectively. In general, the total conductivity has written as the equation (3.9). The values of the activation energy ($E_a$) evaluated from the Fig. 3.35(a,b) for the both samples R1 and R2 respectively. It observed that at low frequency $E_a$ is large and $\sigma_{ac}$ is small as well as at high frequency $E_a$ exhibits small and $\sigma_{ac}$ appears large. This behavior occurs due to the ionic conduction, which is characterized by low conductivity and high activation energy conduction, while the association of relatively higher conductivity and lower activation energy with electronic conduction. The values of $\sigma_{ac}$ and $E_a$ have been tabulated in table 3.4.
Fig. 3.34. Variation in ac conductivity ($\sigma_{ac}$) with temperature of (a) R1 sample at different fix frequencies (100 kHz-5MHz) and (b) R2 sample for the same.
Fig. 3.35. Variation of $\ln(\sigma_{dc})$ with inverse of temperature at different fixed frequencies for (a) R1 sample and (b) R2 sample.
3.2.3.4.4 Impedance analysis

The complex impedance plots (Nyquist plots) of LaFeO$_3$ NPs at different temperature are shown in Fig. 3.36(a,b). The single semicircular behavior has been observed in Cole-Cole plots, due to the dominant of grain boundaries contribution and grain contribution is not resolved [64]. The various electrical parameters can be calculated for the grain and grain boundary from the Cole-Cole plots as given in the relations (3.10), (3.11), (3.12) and (3.13).

These electrical parameters are listed in the Table 3.5. It is clear that the grain boundary resistance increases with increasing temperature while capacitance values of grain boundaries decrease with increasing temperature.

Table 3.5. Variation of different impedance parameters as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$R_{gb}$ (MΩ)</th>
<th>$C_{gb}$ (µF)</th>
<th>$\tau_{gb}$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_1$</td>
<td>$R_2$</td>
<td>$R_1$</td>
</tr>
<tr>
<td>300 (RT)</td>
<td>2.05</td>
<td>0.020</td>
<td>7.7 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>350</td>
<td>2.13</td>
<td>0.028</td>
<td>7.5 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>450</td>
<td>7.43</td>
<td>1.69</td>
<td>2.1 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>550</td>
<td>7.52</td>
<td>0.25</td>
<td>2.1 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>650</td>
<td>0.36</td>
<td>0.025</td>
<td>4.4 $\times$ 10$^{-6}$</td>
</tr>
</tbody>
</table>
Fig. 3.36. Nyquist plots for (a) R1 sample at different fixed temperature and (b) R2 sample for the same.
3.2.3.5. Magnetic properties

The magnetization hysteresis (M-H) loops measured at room temperature for both samples R1 and R2 with maximum available field of 20 kOe as displayed in Fig. 3.37(a,b). From the hysteresis plot, we can see that the both samples exhibit the ferromagnetic behavior. In case of R1 sample as shown in Fig. 3.37(a) the ferromagnetic behavior weak more than ferromagnetic behavior of the R2 sample as shown in Fig. 3.37(b), that is may be attributed to the particle size of R1 sample less than the particle size of R2 sample. The magnetization of R1 sample is 0.137 (emu/gm) and 0.115 for R2 sample. The magnetic parameters for both samples are given in table 3.6. It is clear that the hysteresis behaviors establish the weak ferromagnetic interaction which increases with an increase in the ratio of water to surfactant. The decrease in the remanent magnetization (M_r) and increase in coercivity (H_c) magnetic has been observed with increased values increase in the ratio of water to surfactant it may be attributed to orbital moment contributions to the actual electronic magnetic moment [65,66].

![Magnetization plots](image)

**Fig. 3.37.** Magnetization versus field of (a) R1 sample and (b) R2 sample.

**Table 3.6.** Various magnetic parameters for R1 and R2 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Remanent magnetization (M_r) (emu/gm)</th>
<th>Coercivity (H_c) (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.0047</td>
<td>18</td>
</tr>
<tr>
<td>R2</td>
<td>0.0102</td>
<td>279</td>
</tr>
</tbody>
</table>
3.3. Conclusions

BFO NPs with average crystallite size ~ 28 nm were successfully prepared by sol-gel combustion method. XRD pattern reveals the perovskite nature and having a rhombohedral crystal structure and these results were supported by SEM and EDS. The magnetization measurements suggest very weak ferromagnetic behavior at room temperature. In addition BFO NPs reveal an optical band gap ~ 2.1 eV, which may be useful as a photocatalytic material. The dielectric constant of BiFeO$_3$ NPs increases gradually with increased temperature for all frequencies and dielectric loss (tanδ) as well as the losses observed from to be lower at higher frequencies. The ac conductivity has been found to increase with increasing temperature.

In a similar way the other system LaFeO$_3$ NPs have been successfully synthesized by using a reverse micelle technique and studied their structural, thermal, optical and dielectric properties. Orthorhombic provskite structure and high crystalline of LaFeO$_3$ NPs confirmed by using XRD and these results were supported by SEM and EDS. The exothermic and endothermic peaks are occurring due to the evaporation of water and organics as well as LaFeO$_3$ NPs revealed an optical band gap (E$_g$ ~ 2.63 eV and E$_g$ ~ 2.60 eV) for R1 and R2 samples respectively, which may be useful as a photocatalytic material. Temperature dependent dielectric data exhibit higher values of dielectric constant at lower frequency, capacitance is decreased sharply with increasing frequency and dielectric loss decreased with increase the temperature. The values of the activation energy (E$_a$) evaluated and observed that at low frequency E$_a$ is large and $\sigma_{ac}$ is small as well as at high frequency E$_a$ exhibits small and $\sigma_{ac}$ appears large.
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CHAPTER IV

Structural, optical, electrical and magnetic properties of \((La_{1-x}Sr_x)(Fe_{1-x}Ni_x)O_3\),
\((x = 0.0, 0.1 & 0.2)\)
4.1. Introduction

The general formula of perovskite oxides is ABO₃, where the A sites could be filled with rare earth, alkaline earth, alkali, or other large ions, and the B sites always filled by transition metal cations. In such perovskite materials the oxygen makes a decisive role in the electronic transport properties. For instance, the oxygen mediates electron hopping between Fe and Fe, or Fe and Ni, by exchange interactions where the oxidation state and the spin state of the metal ions determine whether jumping across oxygen can take place or not [1]. Lanthanum ferrite (LaFeO₃) has an orthorhombic symmetry perovskite structure (a = 8.250 Å, b = 6.020 Å, and c = 8.740 Å) and an antiferromagnetic insulator with Néel temperature $T_N = 750K$ [2]. It has a various properties such as the exchange bias, multiferroic and magnetic optical [3-5] which are very important for development so many applications, as new magnetic memory devices, low power consumption spintronic devices and magneto optical sensors. In case of pure or doped simultaneously with Sr (an alkaline earth metal) on A site and Ni (transition metal) on B site have been suggested as a cathode material in solid oxide fuel cells (SOFCs) [6] due to their mixed ionic and electronic conductivity. Pure and doped LaFeO₃ have a various properties like high stability, non-toxicity and small band gap energy [7,8] also widely studied as SOFCs [6,9]. A thermodynamic study of La₁₋ₓSrₓFeO₃ [10] proposed that the doping of the trivalent A site (La³⁺ ions) with divalent ions that have a different valence state, such Sr²⁺ produced the oxygen vacancies and ion conductivity. However, the system structure becomes destabilized due to the oxidation of some of the Fe³⁺ to Fe⁴⁺ to form the La₁₋ₓSrₓ(Fe³⁺)₁₋ₓ(Fe⁴⁺)ₓO₃ [11].

Furthermore, the structural, electrical and magnetic properties of LaFe₁₋ₓNiₓO₃ compounds with $x ≤ 0.5$, which revealed the semiconductor ferromagnetic behavior with an orthorhombic structure [12,13]. The most reports studied the perovskite structure have examined the effect of A site doping, which is typically accompanied by strong lattice strain effects. In opposing, the B site is doping by
transition metal oxides. Such structural doping should adjust the catalytic 
behavior of the perovskite [14]. The sol-gel combustion method has a various 
advantages in the synthesis of Nanoparticles (NPs). It is a simple technique, 
formation of high purity products, stabilization of metastable phases and it is 
characterized by short reaction time, fast heating rates, high synthesis 
temperatures [15].

The aim of this chapter is to investigate the influence of Sr and Ni to the 
LaFeO$_3$ forming the (La$_{1-x}$Sr$_x$)(Fe$_{1-y}$Ni$_y$)O$_3$ structure, on the optical, dielectric and 
magnetic properties.

4.2. Experimental

4.2.1. Synthesis

(La$_{1-x}$Sr$_x$)(Fe$_{1-y}$Ni$_y$)O$_3$, (x = 0.0, 0.1 & 0.2) NPs were synthesized by sol-gel 
combustion method. The starting raw materials used in this work were analytical 
grade (AR) and used without further purification. Lanthanum nitrate hexahydrate 
[La(NO$_3$)$_3$.6H$_2$O], ferric nitrate nonahydrate [Fe(NO$_3$)$_3$.9H$_2$O], strontium nitrate 
[Sr(NO$_3$)$_2$] and nickel nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O] were used as 
oxidizing agents, whereas citric acid [C$_6$H$_8$O$_7$] was used as fuel. All chemicals 
completely dissolved in 100 ml diluted water in a beaker under the constant stirrer 
at 60 °C until the homogeneous sol as solution formed. In addition ammonia 
solution (NH$_3$) was slowly added to adjust the pH ~7. Afterwards, the 
homogeneous sol was heated slowly at 120 °C for 2.5 h. The change in color and 
viscosity was observed, which on further heating automatically gets ignited. The 
solid dry gel was calcined at 600 °C in the air for 5h.

4.2.2. Characterization

The crystal structure was investigated by X-ray diffraction (Rigaku, Japan, 
Miniflex-II) using Cu-K$_\alpha$ radiation (λ = 1.5418 Å) in the 2θ range from 20° to 80°. 
A scanning electron microscope (JEOL JSM-6510LV) equipped with an energy 
dispersive spectrometer (EDS) was used to check the morphology and particle
size. The infrared absorption spectra of the samples were recorded in the wave number range 400-2000 cm\(^{-1}\) by using a Perkin Elmer spectrometer (model Spectra Two) using KBr as a reference. UV-visible absorbance was carried out using Perkin Elmer spectrophotometer in the 200-800 nm range. LCR Dielectric and impedance spectroscopy measurements were performed in the frequency range of 75 kHz to 5 MHz using a meter (Model: Agilent-4285A). Room temperature magnetic measurements (M–H) were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

4.3. Results and discussion

4.3.1. Structural properties

The X-ray diffraction (XRD) patterns of (La\(_{1-x}\)Sr\(_x\))(Fe\(_{1-x}\)Ni\(_x\))O\(_3\), (x = 0.0, 0.1 & 0.2) nanopowders calcined at 600 °C are shown in Fig. 4.1. The position of the all peaks confirmed the high crystallinity and perovskite structure of the NPs and no other impurity peaks were detected in the XRD patterns. Furthermore, the products of the three samples were observed in the orthorhombic perovskite structure with space group Pbnm, which is well consistent with the standard JCPDS card of perovskite LaFeO\(_3\) (JCPDS88-0641) [16].

**Table 4.1.** Structure, crystallite size, optical band gap, Lattice parameters and unit cell volume of all samples.

<table>
<thead>
<tr>
<th>Sr/Ni concentrations (%)</th>
<th>Crystallite size (nm)</th>
<th>(E_g) (eV)</th>
<th>Lattice parameters (Å)</th>
<th>Unit cell volume (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.9</td>
<td>2.15</td>
<td>8.250 6.020 8.740</td>
<td>434.1</td>
</tr>
<tr>
<td>10</td>
<td>15.9</td>
<td>2.28</td>
<td>8.230 6.010 8.730</td>
<td>431.8</td>
</tr>
<tr>
<td>20</td>
<td>12.7</td>
<td>2.36</td>
<td>8.228 6.008 8.726</td>
<td>431.4</td>
</tr>
</tbody>
</table>
The lattice parameters slightly decreased when the value of Sr and Ni concentrations increased, due to the differences in ionic radii, resulted small shifting of peaks to higher 2θ values. The average of particle size using the most intense peak (021) at angle 2 (~32°) were estimated from the XRD patterns by using the Debye–Scherer’s formula [17], and the lattice parameters are given in table 4.1.

**Fig. 4.1.** XRD patterns of the \((\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)\text{O}_3\) Nanopowder.

SEM images of pure and doping NPs synthesized by the sol-gel combustion route are displayed in Fig. 4.2. The surface morphology of NPs reveals the uniform grains, which displays that the complete incorporation of \((\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)\text{O}_3\) as supported by XRD analysis. Furthermore no morphological alterations were observed in the SEM images. In addition SEM
images display the attendance of big spherical aggregates of smaller individual NPs and the attendance of Sr and Ni is confirmed by the results of XRD.

Fig. 4.2. SEM image of a) Pure LaFeO$_3$ and b) Sr/Ni doped LaFeO$_3$ NPs.

Fig. 4.3. EDS spectra for pure and doped LaFeO$_3$ NPs.

Fig. 4.3 illustrates EDS spectra of pure and doped LaFeO$_3$ NPs, which clearly shows the existence of Sr and Ni ions in doped sample and confirms the successful doping.
Fig. 4.4 shows the FTIR spectra of the whole series measured at room temperature in the range of 400–4000 cm\(^{-1}\) of (La\(_{1-x}\)Sr\(_x\))(Fe\(_{1-x}\)Ni\(_x\))O\(_3\), (x = 0.0, 0.1 & 0.2) nanoparticles. The FTIR spectra of all samples show a strong absorption of the vibration of metal-oxygen bond at about 618 cm\(^{-1}\) and the absorption peak around 450 cm\(^{-1}\) is indicated to the Fe-O stretching and O-F-O bending vibrations of the octahedral FeO\(_6\) groups in the perovskite type structure [18].

![FTIR spectra](image)

**Fig. 4.4.** FTIR spectra of the (La\(_{1-x}\)Sr\(_x\))(Fe\(_{1-x}\)Ni\(_x\))O\(_3\) NPs.

As well as at 868 cm\(^{-1}\) and 1119 cm\(^{-1}\) are signed to an O-H bending of hydroxide phase, 1384 cm\(^{-1}\), 1450 cm\(^{-1}\) and 1531 cm\(^{-1}\) are attributed to the stretching vibrations of C-H bond, C-N bond or C-O bond, respectively and the bands at 1634 cm\(^{-1}\) is appeared as an asymmetric deformation CH\(_2\). In this figure we can see also the absorption band ~ 2915 cm\(^{-1}\) due to the environment and last band is observed at 3445 cm\(^{-1}\) corresponds to the hydroxyl group.
4.3.2. Optical properties

The UV–visible absorption spectroscopy is a powerful technique to explore the optical properties of semiconductor NPs. It provides simple methods for explaining some features concerning the band structure and band gap energy. The optical absorption spectra as a function of wavelength of (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)O$_3$, (x=0.0, 0.1 and 0.2) NPs are shown in Fig. 4.5, we have measured the optical absorption spectra as shown in Fig. 4.5.

![Graph showing optical absorption spectra for different values of x](image)

**Fig. 4.5.** UV-visible absorbance of the (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)O$_3$ NPs.

The basic absorption, which opposites of the moving from the valence band to the conduction band, could be used to determine the optical band gap (E$_g$) of all samples by the touc’s relation giving blow:

$$a\nu = K(\nu - E_g)^n$$

(4.1)
where $\alpha$ is the absorption coefficient, $K$ is a constant, $m$ is an integer whose value depend on the nature of transition. When the value of $n = 1/2, 2/3, 1/3, 2$ for acceptable direct transition, permitted indirect transition, forbidden direct transition and forbidden indirect transition, respectively.

Fig. 4.6 displayed the plots of $(\alpha h v)^2$ versus photon energy $(h v)$ for direct transitions to determine the band gap of the $(\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)$, $(x = 0.0, 0.1 \& 0.2)$ NPs.

![Plot of $(\alpha h v)^2$ versus $h v$ for $(\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)$ NPs.](image)

Fig. 4.6. Plot of $(\alpha h v)^2$ versus $h v$ for $(\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)$O$_3$ NPs.

The optical energy band gaps have been tabulated in table 4.1 for all samples. These indicate that the band gap increases with increase in Sr and Ni concentration. The increase in the band gap could be attributed to the basis of the Burstein–Moss effect [19]. As we increase the doping of concentration, the donor states are created which pushes the Fermi level higher in energy and in the case of
the degenerate level of doping, Fermi level shift close to the conduction band above the occupied donor state. In the degenerate semiconductor only an electron can excited from the valence band into the conduction band above the Fermi level because all of the states below the Fermi level is occupied donor states. In the fact like this excitation into these occupied states prohibits on the basis of Pauli's exclusion principle. As a result we observe an increase in the optical band gap.

4.3.3. Dielectric properties

The term dielectric behavior usually refers to the variation of the dielectric properties such as constant, dielectric loss, loss factor, power factor, a.c. conductivity, d.c. conductivity, impedance and other similar properties with frequency, temperature, voltage and composition. These properties may be differing widely in solids as a function of temperature, frequency of applied electric field, crystal structure and humidity. Various dielectric parameters were calculated with the help of the following equations:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$ (4.2)

where, $\varepsilon^*$ is a complex relative permittivity of the material, $\varepsilon'$ is a dielectric constant and $\varepsilon''$ is a dielectric constant factor. The real and imaginary parts have been described the stored energy and dissipated energy respectively and the values of $\varepsilon'$ and $\varepsilon''$ were calculated by relations:

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}$$ (4.3)

In the above equation $C_p$ is the capacitance of the sample in Farad (F), d is the thickness of pellet, $\varepsilon_0$ is the permittivity of free space $\approx 8.854 \times 10^{-12}$ F/m and $A$ is the cross sectional area of the surface of the pellet.

$$\varepsilon'' = \varepsilon' \times \tan\delta$$ (4.4)

where $\tan\delta$ is the dielectric loss or dielectric factor which represents the energy dissipation in the dielectric medium.

$$\tan\delta = \frac{1}{2\pi f \varepsilon_0 \sigma}$$ (4.5)
where \( f \) is the frequency of the applied ac field and \( \rho \) the resistivity of the dielectric material. The a.c. conductivity was calculated as a function of an angular frequency \( \omega \) as the following:

\[
\sigma_{ac} = \varepsilon'\varepsilon_0\omega \tan \delta \quad \text{......................................................... (4.6)}
\]

According to the equation (4.4) the a.c. conductivity can be written as the following:

\[
\sigma_{ac} = \varepsilon''\varepsilon_0\omega \quad \text{......................................................... (4.7)}
\]

### 4.3.3.1. Dielectric constant

Fig. 4.7(a,b) shows the variation of dielectric constant \((\varepsilon' \text{ and } \varepsilon'')\) as real and imaginary parts respectively. In all compositions the values of dielectric constant \(\varepsilon'\) and \(\varepsilon''\) decrease with increase in frequency on other words it decreases systemically at lower frequencies and going to be constant at higher frequencies which refers to the dielectric dispersion. According to the basis of Koop’s theory [20] the curve of dielectric constant has been illustrated, which based on the homogeneous double structure of the Maxwell-Wagner model [21,22]. In usual at high frequencies the electronic polarizations are main contributors but dipolar and interfacial polarizations are contributors at low frequencies. In relation to the Maxwell-Wagner model, a dielectric medium suggests well conducting grains which are distributed through poorly conducting or resistive grain boundaries. The charge carriers may be migrated the grains easily, but are gathered at the grain boundaries due to the application of external electric field. The large polarization and high dielectric constant could be created in this process. The small value of grain boundary conductivity indicates to the high value of dielectric constant. With respect to inhomogeneous dielectric structure the higher value of dielectric constant may be illustrated on the basis of the interface or space polarization of charge.
Fig. 4.7. Variation of dielectric constant with frequency (a) real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$. 
4.3.3.2. Dielectric loss

The energy dissipation in a dielectric material represents by the dielectric loss or loss tangent/factor (\(\tan\delta\)). It exists can attributed to the domain wall resonance. Fig. 4.8 shows the variation of dielectric loss as a function of frequency for various concentrations. It is evident from the figure, the dielectric losses are observed to be low at higher frequency because of the domain wall motion is inhibited and magnetization is pressured to change the rotation.

![Dielectric Loss Graph](image)

**Fig. 4.8.** Variation of dielectric loss as a function of frequency of \((\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)\text{O}_3\) NPs at room temperature.
The dielectric losses exhibit the similar behavior of dielectric constant imaginary parts due to the proportional between them in an equation (4.4). The observation in the peak of dielectric losses may be attributed to the basis of Debye equation is given as:

\[
\tan \delta = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau_{\tan \delta}}{\varepsilon_s + \varepsilon_\infty(\omega \tau_{\tan \delta})^2}
\] (4.8)

In above equation \( \varepsilon_s \) represents the static d.c. and \( \varepsilon_\infty \) represents a high frequency a.c. permittivity, \( \tau_{\tan \delta} \) shows the relaxation time of dielectric loss and the angular of the applied field is presented by \( \omega \).

4.3.3.3. a.c. Conductivity
The ferrite electrical conductivity is attributed to hopping of electrons between ions of the same element available in different valence state, distributed at random throughout crystallographically equivalent lattice sites. The a.c. conductivity is studied to know the conduction mechanism of (La_{1-x}Sr_x)(Fe_{1-x}Ni_x)O_3 nanoparticles. Fig. 4.9 shows the variation of a.c. conductivity as a function of frequency for various compositions at room temperature. It is calculated dielectric date by using the relation (4.7). It is clear that the plots present the increase in a.c. conductivity for all compositions with increase in frequency refers to the appearing of conduction due to jumping of charge carriers through the localized state [23]. It has been observed that the maximum value of ac conductivity corresponding the pure sample, i.e. \( x = 0\% \). The ac conductivity systematically decreases with the increase in Sr/Ni concentration. It could be attributed to the dopants of Sr/Ni introduce the imperfection ions in LaFeO_3 system. These imperfections tend to separate at the grain boundaries due to the diffusion process produced from sintering and cooling processes.
Fig. 4.9. Variation of ac conductivity as a function of frequency of (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)$_3$O$_5$ NPs at room temperature.

4.3.3.4. Impedance analysis

The information is extracted to know the mechanism of electrical transport in Sr/Ni doped lanthanum ferrite has been studied up to 5 MHz frequency at room temperature using impedance spectroscopy method. It is widely used to investigate the electrical properties and interfaces of materials with electronically conducting electrodes. The complex impedance spectroscopy is given by the following equation:

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) \quad \cdots \quad (4.9)$$
The above equation is widely done by Bode plot, where \( Z'(\omega) \) and \( Z''(\omega) \) are the real and imaginary parts presented as the following equations:

\[
Z'(\omega) = (|Z|\cos\theta) \quad \text{.................................................. (4.10)}
\]

\[
Z''(\omega) = (|Z|\sin\theta) \quad \text{.................................................. (4.11)}
\]

where \( \omega \) is the angular frequency, \( (\omega = 2\pi f) \), \( f \) is the applied frequency, \( \theta \) is the phase angle defined as the following relation:

\[
\theta = \tan^{-1}[Z''(\omega)/Z'(\omega)] \quad \text{.................................................. (4.12)}
\]

\[
|Z| = \left[ Z''(\omega)^2 + Z'(\omega)^2 \right]^{1/2} \quad \text{.................................................. (4.13)}
\]

According to equivalent circuit including the resistance (R) and capacitance (C) in parallel connection as given in fig. 4.10 [24]:

![Fig. 4.10. The impedance spectra equivalent circuit.](image)

In relation to the equation (4.9) and as appeared in fig. 4.10 we can write \( Z' \) and \( Z'' \) as the following equations:

\[
Z' = \frac{R_g}{1+(\omega^2 c_g^2 R_g^2)} + \frac{R_{gb}}{1+(\omega^2 c_{gb}^2 R_{gb}^2)} \quad \text{.................................................. (4.14)}
\]

\[
Z'' = \frac{R_g \omega_g c_g}{1+(\omega^2 c_g^2 R_g^2)} + \frac{R_{gb} \omega_{gb} c_{gb}}{1+(\omega^2 c_{gb}^2 R_{gb}^2)} \quad \text{.................................................. (4.15)}
\]

In the above equations \( R_g, R_{gb}, C_g \) and \( C_{gb} \) represent the resistance and capacitance of the grain and grain boundary respectively, while \( \omega_g \) and \( \omega_{gb} \).
represent the frequencies at the peaks of semicircles for grain and grain boundary respectively. The values of resistance have been found out from the circular arc intercepts on $Z'$ axis, however, the values of capacitance may be derived from the maximum height of the circular arcs.

![Graph showing $Z'$ vs log(f) for different compositions](image)

Fig. 4.11 Variations of real part of impedance $Z'$ with frequency of $(La_{1-x}Sr_x)(Fe_{1-x}Ni_x)O_3$ NPs at room temperature.

Fig. 4.11 exhibits the variation of impedance (real part) with frequency at room temperature. It shows that the $Z'$ magnitude decreases with increasing frequency for all compositions, it may be attributed to the increase in ac conductivity with an increment of frequencies. Fig. 4.12 the variation of impedance (imaginary part) with frequency at room temperature. The $Z''$ magnitude also decreases with increasing frequency for all compositions, which shows the same behavior of $Z'$. It has observed that $Z'$ and $Z''$ have a higher
value at low frequencies and decrease gradually with the increment of frequency and appear as a constant at high values of frequency. It may be attributed to the reality that the region of low frequency equivalent to resistivity due to the efficiency of the resistive grain boundaries in this region and exhibits independent behavior in the region of higher frequency.

![Graph showing variation of imaginary part of impedance Z'' with frequency of (La_{1-x}Sr_x)(Fe_{1-x}Ni_x)O_3 NPs at room temperature.](image)

Fig. 4.12. Variation of imaginary part of impedance $Z''$ with frequency of $(\text{La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)\text{O}_3$ NPs at room temperature.

Fig. 4.13 shows the Nyquist plot or Cole-Cole plot which is plotted the imaginary part versus real part of impedance through a wide range frequency at room temperature for all compositions. To calculate the various electrical parameters for the grain and grain boundary from the Cole-Cole plots by the following relations:
\[ C_g = \frac{1}{R_g \omega_g} \]  \hspace{2cm} (4.16)

\[ C_{gb} = \frac{1}{R_{gb} \omega_{gb}} \]  \hspace{2cm} (4.17)

\[ \tau_g = \frac{1}{\omega_g} = C_g R_g \]  \hspace{2cm} (4.18)

\[ \tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \]  \hspace{2cm} (4.19)

The variation of impedance parameters with frequency and composition like resistance and capacitance have been defined by analyzing the impedance data using nonlinear least square fitting (NLLS) route, which are tabulated in Table 4.2.

**Table 4.2. Variation of different impedance parameters as a function of doping concentration.**

<table>
<thead>
<tr>
<th>Sr/Ni concentration (%)</th>
<th>( R_{gb} ) (Ω)</th>
<th>( C_{gb} ) (μF)</th>
<th>( \tau_{gb} ) (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 1.1 \times 10^5 )</td>
<td>( 1.8 \times 10^{-5} )</td>
<td>1.98</td>
</tr>
<tr>
<td>10</td>
<td>( 6.2 \times 10^4 )</td>
<td>( 3.0 \times 10^{-5} )</td>
<td>1.86</td>
</tr>
<tr>
<td>20</td>
<td>( 1.3 \times 10^4 )</td>
<td>( 1.2 \times 10^{-4} )</td>
<td>1.56</td>
</tr>
</tbody>
</table>

It is clear from the above table that the resistance of grain boundary \( R_{gb} \) decreases while capacitance \( C_{gb} \) decreases with increase in Sr/Ni concentration.
Fig. 4.13. Cole-Cole plots for (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)$_3$O$_3$ NPs at room temperature.

4.4. Magnetic measurements

The magnetization hysteresis (M-H) loops measured at room temperature of (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)$_3$ (x= 0.0, 0.1 & 0.2) with maximum applied field of 20 kOe as displayed in Fig. 4.14. In case of pure phase saturation the magnetization is higher than the other doped samples. The magnetic hysteresis behavior clearly established that the weak ferromagnetic interaction which decrease with an increase in Sr and Ni concentration. The magnetization for all samples decreased with increase in Sr and Ni concentrations. So, the sharp decrease in the magnetization with an increase in the dopant concentration proposes the
delocalization of d-electrons particles contributing in the conduction mechanism of exchange interaction between Fe and Ni ions. The magnetization for all samples and the clear hysteresis behavior establish the ferromagnetic interaction which decreases with increase in dopant concentration. The characterization of all samples has been tabulated in table 4.3 by a saturation magnetization ($M_s$), remanent magnetization ($M_r$) and coercivity ($H_c$) [25]. The decrease in $M_s$, $M_r$ and an increase in coercivity ($H_c$) magnetic has been observed with increased value of Sr and Ni it may be attributed to orbital moment contributions to the actual electronic magnetic moment [26-28].

![Graph](image)

Fig. 4.14. Magnetization versus field for ($La_{1-x}Sr_x$)($Fe_{1-x}Ni_x$)O$_3$ NPs.
Table 4.3. Various magnetic parameters of La$_{1-x}$Sr$_x$Fe$_{1-x}$Ni$_x$O$_3$ (x = 0.0, 0.1 & 0.2) samples.

<table>
<thead>
<tr>
<th>Sr/Ni concentration (%)</th>
<th>Saturation Magnetization (M$_s$) (emu/gm)</th>
<th>Remanent magnetization (M$_r$) (emu/gm)</th>
<th>Coercivity (H$_c$) (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.369</td>
<td>0.0790</td>
<td>525</td>
</tr>
<tr>
<td>10</td>
<td>0.163</td>
<td>0.0128</td>
<td>820</td>
</tr>
<tr>
<td>20</td>
<td>0.119</td>
<td>0.0128</td>
<td>900</td>
</tr>
</tbody>
</table>

4.5. Conclusions

In summary, the (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)O$_3$, (x = 0.0, 0.1 & 0.2) NPs were successfully prepared by sol-gel combustion method. The effect of magnetic Sr$^{2+}$ and Ni$^{3+}$ ions in (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$) was investigated by means of structural, optical, electrical and magnetic properties. The following explanation has been made on the basis of various experiments performed to prepared (La$_{1-x}$Sr$_x$) (Fe$_{1-x}$Ni$_x$) O$_3$ nanoparticles. XRD patterns reveal the single phase perovskite nature of NPs having an orthorhombic crystal structure with the pbnn space group and exclude the presence of any secondary phase, with an average crystallite size between 12.7mm-21.9nm. The decrease in the lattice constant is due to the difference ionic radii of the Sr$^{2+}$ and Ni$^{3+}$ ions with La$^{3+}$ and Fe$^{3+}$ ions respectively. The SEM measurements illustrate the nanoparticles of are (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)O$_3$ big spherical in shape. The EDX images confirm the presence of all elements in pure and doped compound. (La$_{1-x}$Sr$_x$)(Fe$_{1-x}$Ni$_x$)O$_3$, (x = 0.0, 0.1 & 0.2) NPs have a direct band gap and the optical band gap decrease with increasing in concentrations of Sr and Ni; it is attributed to the Burstein Moss effect. The dielectric constant (real and imaginary part $\varepsilon'$ and $\varepsilon''$) and loss tangent
both show normal behavior with respect to frequency at room temperature. The
dispersion in the dielectric properties has been illustrated in the light of the
electron hopping mechanism and space charge polarization discussed by
Maxwell-Wagner two layer models and Koops theory. The ac conductivity has
been found to increase with increasing frequency. The ac conductivity has been
discussed in the light of the charge hopping model. The complex impedance
spectra illustrate only one semicircle corresponding to the grain boundary
resistance up to 20% of Sr and Ni doping. The resistance of the grain boundary is
found to decrease while the capacitance of the grain boundary is found to increase
with increasing concentration. Ferromagnetic behavior was observed in all
samples and magnetization was found to decrease with increasing dopant.
References


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[11] N. Kemik, Y. Takamura, A. Navrotsky, “Thermochemistry of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ solid solutions (0 < x <1)”, *J. solid State chem.*, 184, (2011) 2118-2123.


CHAPTER V

Optical, dielectric and magnetic properties of Ni doped La_{0.7}Sr_{0.3}FeO_{3}
5.1. Introduction

The perovskite structure defined as one that has the same configuration of the same type of crystal structure of calcium titanium oxide (CaTiO$_3$) with the oxygen in the face centers. The perovskite family has a double-oxide type, mixed Ca(II)/Ti(IV) oxide with the short form ABO$_3$, where A = Ca, and B = Ti. Both research and industry have been widely studied this type material due to their diverse physical properties and technological applications. The unique properties of lanthanum ferrite based oxide materials at high temperature [1] have been strongly attractive candidates for various important applications, such as gas sensors, oxygen permeable membranes and electrodes (cathodes) in solid oxide fuel cells (SOFCs) [2]. A thermodynamic study of La$_{1-x}$Sr$_x$FeO$_3$ [3] proposed that the doping of the trivalent A site (La$^{3+}$ ions) with divalent ions that have a different valance state, such Sr$^{2+}$ produced the oxygen vacancies and ion conductivity, which are the plains hopping related to the trivalent state of the iron cations caused the LaFeO$_3$ based materials electrical conductivity [4]. However, the system structure becomes destabilized due to change in the oxidation state of some of the Fe$^{3+}$ to Fe$^{2+}$ to form the La$_{1-x}$Sr$_x$(Fe$^{3+}$)$_{1-x}$(Fe$^{4+}$)$_x$O$_3$ [5]. The structural, electrical and magnetic properties of the LaFe$_{1-x}$Ni$_x$O$_3$ compound (x ≤ 0.5) revealed the semiconductor ferromagnetic behavior with an orthorhombic perovskite structure [6,7]. In such perovskite materials the oxygen makes a decisive role in the electronic transport properties. For instance, the oxygen mediates electron jumping between Fe and Fe, or Fe and Ni, by exchange interactions where the oxidation state and the spin state of the metal ions determine whether jumping across oxygen can take place or not [8]. In addition LaFeO$_3$ has orthorhombic symmetry perovskite structure (a = 8.250 Å, b = 6.020 Å, and c = 8.740 Å) and an antiferromagnetic insulator with Neél temperature $T_N$ = 750 K [9]. It has a various properties such as the exchange bias, multiferroic and magnetic optical [10-12] which are very important for development so many applications, as new magnetic memory devices, low power consumption spintronic devices and magneto optical sensors. Pure and doped LaFeO$_3$ have at various properties like high stability, non-toxicity and small band gap energy [13,14]. The most reports studied the perovskite structure have examined the effect of A site doping, which is typically accompanied by strong lattice strain effects. In
opposing, the B site is doping by transition metal oxides. Such structural doping should adjust the catalytic behavior of the perovskite [15].

The aim of this chapter is to investigate the influence of Ni to the La$_{17}$Sr$_{0.3}$FeO$_3$ forming the La$_{0.7}$Sr$_{0.3}$Fe$_{1-x}$Ni$_x$O$_3$ structure on the optical, dielectric and magnetic properties by using a reverse micelle method.

5.2. Experimental

5.2.1. Synthesis

La$_{0.7}$Sr$_{0.3}$Fe$_{1-x}$Ni$_x$O$_3$ (LSFNO) NPs with nominal compositions $x = 0.00, 0.01$ and $0.04$ were synthesized by reverse micelle (RM) method. LSFNO solutions were prepared by using stoichiometric amounts of lanthanum nitrate hexahydrate [La(NO$_3$)$_3$.6H$_2$O], ferric nitrate nonahydrate [Fe(NO$_3$)$_3$.9H$_2$O], strontium nitrate [Sr(NO$_3$)$_2$] and nickel nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O]. A quaternary system of iso-octane/CTAB/n-butyl alcohol/water was selected in this RM process. In this process we used two kinds of RM solutions namely RM1 and RM2. The first RM1 solution contained (10 wt %) an aqueous solution of an equimolar mixture (0.1M) of metal nitrate [(La(NO$_3$)$_3$.6H$_2$O), [Sr(NO$_3$)$_2$], [Fe(NO$_3$)$_3$.9H$_2$O] and [Ni(NO$_3$)$_2$.6H$_2$O], CTAB as a surfactant (5 wt%), n-butyl alcohol as a co-surfactant (5 wt%) and iso-octane as oil (30 wt%). The stirring was continued for 30 min resulting in a stable reverse micelle RM1, while for RM2 NaOH (0.1 M) instead of metal nitrates was used and other procedure is same.

These two reverse micelles solutions were mixed under constant stirring and a black color solution was obtained. In addition ammonium solution (NH$_3$) was slowly added to adjust the pH and stirred 24 h on a magnetic stirrer. The resulting precipitate was separated from the surfactant and a polar solvent by centrifugation and washing it one time by ethanol and four times with distilled water. The precipitate was dried in an oven at 80 °C for 6 h to obtain nanopowder and heated at 750 °C for 4 h in air.

5.2.2. Characterization

The crystal structure was investigated by X-ray diffraction (Rigaku, Japan, Miniflex-II) using Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) in the 2θ range from 20° to 80°. The FTIR absorption spectra of the samples were recorded in wavenumber range 400-4000 cm$^{-1}$ by
using a Perkin Elmer spectrometer (model Spectra Two) using KBr as a reference. A field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS) was used to check the morphology and particle size. UV-visible absorbance was carried out using UV-visible, Perkin Elmer spectrophotometer (Model Lambda 35) in the 200-800 nm range. The dielectric properties were examined using LCR Dielectric and impedance spectroscopy measurement system in the frequency range of 75 kHz to 5 MHz (Model: Agilent-4285A). The Room temperature magnetic measurements (M‒H) were measured by a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

5.3. Results and discussion

5.3.1. Structural properties

The XRD patterns of undoped and Ni doped La\(_{0.7}\)Sr\(_{0.3}\)Fe\(_{3}\)O\(_{5}\) nanoparticles for different Ni concentrations are shown in Fig. 5.1.

![X-ray diffraction patterns of La\(_{0.7}\)Sr\(_{0.3}\)Fe\(_{3}\)Ni\(_{x}\)O\(_{3}\) (x = 0.00, 0.01 & 0.04) samples.](image-url)
The PowderX software has been used to index the peaks, which are well matched with orthorhombic structure, having space group Pbnn. The XRD confirmed the single phase nature of the samples and no other diffraction peaks from impurities, and the materials indicate a perovskite structure. The crystallite size of all samples has been evaluated from the full width at half maximum (FWHM) of (021) the diffraction peak using the Scherrer’s formula:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where \( \lambda \) is the X-ray wavelength (\( \lambda = 1.5418 \ \text{Å} \)), \( \beta \) is the FWHM in radians, \( K \) is the shape factor (usually taken 0.89) and \( \theta \) is the Bragg angle. All the structural parameters have been calculated and tabulated in table 5.1.

Fig. 5.2 shows the variation in lattice parameters (a, b and c) and unit cell volume (V_{cell}) as a function of Ni concentration (x) of La_{0.7}Sr_{0.3}FeO_3 compound. The lattice parameters a, b and c are increased systematically with Ni concentration, as well as V_{cell} shows similar behavior to that of the lattice parameters. The increase in lattice parameters as well as of V_{cell} may depend on lower level of Ni concentration (0 ≤ x ≤ 0.04) [16,17].

Table 5.1. Crystallite size, Lattice parameters and unit cell volume, optical band gap (E_g) and activation energy of La_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_3 (x = 0.00, 0.01 & 0.04) samples.

<table>
<thead>
<tr>
<th>Ni concentration (%)</th>
<th>D (nm)</th>
<th>Lattice parameters (Å)</th>
<th>Unit cell volume (Å^3)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>0</td>
<td>25.2</td>
<td>5.5830</td>
<td>5.9900</td>
<td>8.3950</td>
</tr>
<tr>
<td>1</td>
<td>26.3</td>
<td>5.5850</td>
<td>5.9950</td>
<td>8.3955</td>
</tr>
<tr>
<td>4</td>
<td>30.0</td>
<td>5.5855</td>
<td>6.0000</td>
<td>8.4000</td>
</tr>
</tbody>
</table>
Fig. 5.2. Variations of lattice parameters and unit cell volume with the composition of La0.7Sr0.3Fe1-xNi_xO3 (x = 0.00, 0.01 & 0.04) samples at room temperature.

The surface morphology of the nanoparticles was analyzed by using the field emission scanning electron microscope (FESEM) as displayed in Fig. 5.3(a) for pure sample and Fig. 5.3(b) for 4% Ni doped of La0.7Sr0.3FeO3 sample. The FESEM image of doped sample shows the increased in grain size with Ni doping.

The EDS pattern in Fig. 5.4(a) confirms the presence of La, Sr, Fe and O elements as well as in Fig. 5.4(b) confirms the presence of La, Sr, Fe, Ni and O elements in good stoichiometry, while C signal originates from the carbon tape used to stick to the material.
Fig. 5.3. FESEM micrograph images (a) Pure La$_{0.7}$Sr$_{0.3}$FeO$_3$ and (b) Ni doped La$_{0.7}$Sr$_{0.3}$FeO$_3$ NPs.

Fig. 5.4 EDS spectra for a) pure La$_{0.7}$Sr$_{0.3}$FeO$_3$ and b) Ni doped La$_{0.7}$Sr$_{0.3}$Fe$_{1+x}$,Ni$_x$O$_3$ NPs.
5.3.1.1. Fourier transforms infrared spectroscopy (FTIR)

Fig. 5.5 shows the FTIR spectra of the complete series measured at room temperature in the range of 2000–400 cm\(^{-1}\). The FTIR spectra of all samples show a strong absorption of the vibration of metal-oxygen bond at about 611 cm\(^{-1}\) and the absorption peak around 444 cm\(^{-1}\) is indicated to the Fe-O stretching and O-F-O bending vibrations of the octahedral FeO\(_6\) groups in the perovskite type structure [18]. As well as at 870 cm\(^{-1}\) and 1114 cm\(^{-1}\) are assigned to an O-H bending of hydroxide phase. 1484 cm\(^{-1}\), 1443 cm\(^{-1}\) and 1530 cm\(^{-1}\) are attributed to the stretching vibrations of C-H bond, C-N bond or C-O bond, respectively and the bands at 1620 cm\(^{-1}\) and 1642 cm\(^{-1}\) are appearing as an asymmetric deformation CH\(_2\).

![FTIR spectra of La\(_{0.7}\)Sr\(_{0.3}\)Fe\(_{1-x}\)Ni\(_{x}\)O\(_3\) (x = 0.00, 0.01 & 0.04) samples.](image-url)
5.3.2. Optical properties

UV-visible absorption spectroscopy technique has been widely used to explore the optical properties of various kinds of inorganic and organic NPs. The absorbance characteristics of the hybrid nanomaterials generally depend on several factors such as band gap, impurity centers, oxygen deficiency and surface roughness and impurity centers [19]. The optical absorbance versus the wavelength is observed for La_{0.7}Sr_{0.3}Fe_{1-x}Ni_{x}O_3, (x = 0.00, 0.01 and 0.04) NPs in the wavelength range 200-800 nm with distilled water as the reference and spectra are shown in Fig. 5.6.

![Absorption spectra](image)

**Fig. 5.6.** UV-visible absorbance of La_{0.7}Sr_{0.3}Fe_{1-x}Ni_{x}O_3 (x = 0.00, 0.01 & 0.04) samples.

UV-visible spectra show two peaks, the first peak indicates that the LSFNO NPs may be a kind of photocatalytic materials [20] and second peak appeared due to the activity of LSFNO NPs under the visible light. Basically, the oxide photocatalysts
valance band consists of the $O_{2p}$ orbital and the electronic transition takes place from $O_{2p}$→$Fe_{3d}$ orbital [21]. The optical band gap was evaluated using the Tauc's relation:

$$a \nu = C(\nu - E_g)^n$$

where $a$ is the absorption coefficient ($a = 2.303 \text{ A/t}$, where $A$ is the absorbance and $t$ is the thickness of the cuvette), $C$ is a constant, $\nu$ is the photon energy, and $E_g$ is the optical energy band gap and the value of $n = 1/2, 1, 3/2$ and 2 is depends on the nature of the transition and $n = 1/2$ for direct band gap semiconductor. The absorption coefficient was a function of photon energy for pure $La_{0.7}Sr_{0.3}FeO_3$ and Ni-doped $La_{0.7}Sr_{0.3}FeO_3$ nanoparticles. Fig. 5.7 shows the optical energy band gap which is calculated and tabulated in Table 5.1 for all samples. These indicate that the band gap decreases with increase in Ni concentration. The decrease in the band gap could be attributed to the basis of the Burstein-Moss effect [8,22,23].

![Graph showing optical band gap energy for $La_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_3$ (x = 0.00, 0.01 & 0.04) samples.]

**Fig. 5.7.** Optical band gap energy for $La_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_3$ (x = 0.00, 0.01 & 0.04) samples.
When the doping concentration of Ni increases, the donor states are created which Fermi level pushed to higher in energy and in the case of the degenerate level of doping, Fermi level shift close to the conduction band above the occupied donor state. In fact, the electron may only exit from the valence band into the conduction band above the Fermi level in the degenerate semiconductor because all of the states below the Fermi level is occupied donor states. But, like this excitation into these occupied states prohibits on the basis of Pauli’s exclusion principle. Then the result has been captured an increase in the optical band gap is right.

5.3.3. Dielectric properties

The dielectric behavior usually refers to the variation of the properties (dielectric constant, dielectric loss, loss factor, a.c. conductivity, d.c. conductivity and other similar properties) with frequency of applied electric field, temperature, voltage and composition.

According to Debye relaxation model the classical picture has been given the polarization relaxation with a single relaxation time [24,25]. The equation for complex permittivity is given as the following:

\[ \varepsilon^\prime = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 - i\omega \tau} \] ................................. (5.3)

where, \( \varepsilon_0 \) = Dielectric constant at low frequency

\( \varepsilon_{\infty} \) = Dielectric constant at high frequency

\( \omega \) = Angular frequency

\( \tau \) = Relaxation time

The real and imaginary parts of the dielectric constant are given by:

\[ \varepsilon^\prime = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 - i\omega \tau} \] ................................. (5.4)

\[ \varepsilon^\prime\prime = \left( \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 - i\omega \tau} \right) \omega \tau \] ................................. (5.5)

The maximum value of \( \varepsilon^\prime \) and \( \varepsilon^\prime\prime \) is given as the following:

\[ \varepsilon^\prime = \frac{\varepsilon_0 + \varepsilon_{\infty}}{2} \quad \text{and} \quad \varepsilon^\prime\prime = \frac{\varepsilon_0 - \varepsilon_{\infty}}{2} \] ................................. (5.6)

\[ \varepsilon_0 - \varepsilon_{\infty} = \left( \frac{3\varepsilon_0}{2} \right) \left( \frac{\varepsilon_0 + 2\varepsilon_{\infty}}{3} \right) \frac{4\pi n_{\mu}^2}{3kT} \] ................................. (5.7)

where, \( n \) = Dipole Moment
\[ g = \text{Parameter related to dipole interaction} \]
\[ T = \text{Temperature} \]

The Debye theory rarely adjusts with polymers due to the much broader dispersion has showed and low loss as compared to the single relaxation process. The equation of the circle of radius \( \frac{\varepsilon_0 - \varepsilon_{\infty}}{2} \) has given as is follows:

\[
\left[ \varepsilon' - \frac{\varepsilon_0 - \varepsilon_{\infty}}{2} \right]^2 + \varepsilon''^2 = \left[ \frac{\varepsilon_0 - \varepsilon_{\infty}}{2} \right]^2 \tag{5.8}
\]

But, the above equation the semicircle has physical significance when \( \varepsilon'' \) is positive. Debye semicircle applicable for materials with single relaxation time in \( \varepsilon' \) and \( \varepsilon'' \) plane has been yield but do not yield in the \( \varepsilon' - \varepsilon'' \) plane in polymers. The complex permittivity equation has been given by Cole-Cole model [26] to modify the Debye equation to be empirical for the nonidial dielectric system.

\[
\varepsilon'' - \varepsilon' = \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + (i\omega\tau)^{1-a}} \tag{5.9}
\]

Where \( a \) is the empirical parameter \((0 \leq a \leq 1)\) and it is the angle of tilt of circular arc from the real axis. Cole-Cole model expression measures the smallest deviation from the ideal Debye behavior, but some material deviates very much the Debye behavior. The new expiration form has been given as the following [27]:

\[
\varepsilon'' - \varepsilon' = \frac{\varepsilon_0 - \varepsilon_{\infty}}{[1 + (i\omega\tau)^{1-a}]^{1-\beta}} \tag{5.10}
\]

### 5.3.3.1. Dielectric constant

The dielectric constant is given by:

\[
\varepsilon' = \varepsilon' - j\varepsilon'' \tag{5.11}
\]

where \( \varepsilon' \) is the real part of the dielectric constant and described the stored energy meanwhile \( \varepsilon'' \) is the imaginary part of the dielectric constant, which describes the dissipated energy.

The dielectric constant \( \varepsilon' \) and \( \varepsilon'' \) of the materials have been calculated by the equation valid for a parallel plate capacitor:

\[
\varepsilon' = \frac{\varepsilon_{pd}}{\varepsilon_0 A} \text{ and } \varepsilon'' = \varepsilon'tan\delta \tag{5.12}
\]
where $C_p$ is the sample capacitance in Farad, $A$ is the area of the sample, $d$ is the thickness of the sample and $\varepsilon_0$ is a constant representing permittivity of free space.

**Fig. 5.8.** Variation of dielectric constant real part as a function of temperature for $La_{0.3}Sr_{0.7}Fe_{1-x}Ni_{x}O_3$ ($x = 0.00, 0.01 \& 0.04$) samples at different frequencies (75 kHz-5 MHz).

Fig. 5.8 and Fig. 5.9 show the effect of temperature on the real part $\varepsilon'$ and an imaginary part of dielectric constant $\varepsilon''$ at various fixed frequencies (75 kHz – 5 MHz) respectively. All samples are established similar behavior of dielectric constant $\varepsilon'$ and $\varepsilon''$, which are decreased with increasing frequency. Generally, the dielectric constant increases as the temperature increases, which show the semiconductor behavior of the samples. It is clearly observed that $\varepsilon'$ increases with increasing Ni concentration in LSFNO samples at all fixed frequencies and temperature. The values of $\varepsilon'$ at 75 kHz and 723 K for all
samples are tabulated in table 5.2. The undoped sample shows the constant variation of dielectric with temperature from 400 K - 631 K and the doped sample by Ni 1% and 4% exhibit the constant variation from 360 K - 640 K and 460 K to 620 K respectively. The constant variations of dielectric constant with temperature of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3 \) \( (x = 0.00, 0.01 \& 0.04) \) have been observed. This could be suggested that these materials may be used in the purpose of gas sensor.

![Graph showing dielectric constant vs temperature for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3 \) samples.]

**Fig. 5.9.** Variation of dielectric constant imaginary part as a function of temperature for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3 \) \( (x = 0.00, 0.01 \& 0.04) \) samples at different frequencies (75 kHz-5 MHz).

### 5.3.3.2. Dielectric loss

The energy dispersion in dielectric materials has been represented by loss tangent or loss factor \( \tan\delta \). It exists due to the domain wall resonance. In general, the losses for all
samples are observed low at all fixed higher frequencies and temperature; since, domain wall motion is blocked and magnetization may be forced to change the rotation. Fig. 5.10 shows the variation of loss tangent tanδ versus temperature at various fix frequencies (75 kHz – 5 MHz). It has been observed that the behavior of loss tangent tanδ has a similar behavior of dielectric constant, it increases when the temperature increase.

![Dielectric Loss vs Temperature](image)

Fig. 5.10. Variation of dielectric loss (tanδ) with temperature for La_{0.7}Sr_{0.3}Fe_{1-x}Ni_{x}O_{3} (x = 0.00, 0.01 & 0.04) samples.

It has loss peaks corresponding to the transition of dielectric loss versus temperature. The value of loss tangent tanδ is found to decrease with increasing Ni concentration and the values of tanδ at 75 kHz and 723 K for all samples are displayed in table 5.2.
The values of loss tangent $\tan \delta$ have been decreased with an increase in the Ni concentration for any particular temperature and frequencies, which may be attributed to the decrease in dc conductivity of materials with the Ni concentration.

<table>
<thead>
<tr>
<th>Ni concentration (%)</th>
<th>$\varepsilon'$</th>
<th>$\tan \delta$</th>
<th>$\sigma \times 10^{-3}$ (Ω.cm)$^{-1}$</th>
<th>Activation Energy ($E_a$) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>75 (kHz)</td>
</tr>
<tr>
<td>0</td>
<td>1012</td>
<td>34</td>
<td>115</td>
<td>1.14</td>
</tr>
<tr>
<td>1</td>
<td>1316</td>
<td>30</td>
<td>107</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>1682</td>
<td>5</td>
<td>90</td>
<td>0.23</td>
</tr>
</tbody>
</table>

5.3.3.3. a.c. Conductivity

Basically, the existent of the electrical conductivity in materials is mainly attributed to hopping of electrons between ions of the same element present in more than one valence state, distributed randomly through crystallographic equivalent lattice sites. The variation of electrical conductivity with temperature at various fixed frequencies has been shown in Fig. 5.11. Generally, the total conductivity has written as the following relation:

$$\sigma_{tot} = \sigma_0(T) + \sigma(\omega,T)$$  \hspace{1cm} (5.13)

where $\sigma_0(T)$ at R.H.S. is dc conductivity due to the band conduction, which is a frequency independent function and then $\sigma(\omega,T)$ represents the pure ac conductivity due to electron migration between the metal ions.

According to Arrhenius law, the a.c. conductivity as a function of temperature given by the following equation:
\[ \sigma_{ac} = \sigma_\infty \exp \left( - \frac{E_a}{k_B T} \right) \]  

(5.14)

where \( E_a \) is the activation energy of the electrical conduction, \( \sigma_\infty \) is a conductivity at infinitely high temperature, sometimes called the "pre-exponential constant", \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature (Kelvin).

Fig. 5.11. Variation in ac conductivity (\( \sigma_{ac} \)) with temperature for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3 \) (\( x = 0.00, 0.01 \& 0.04 \)) samples.

Fig. 5.12 exhibits the \( \ln \sigma \) as a function of \( 1000/T \) which refers to the linear trend. The values of the activation energy for all samples with higher and lower frequencies as shown in Fig 5.12 have been calculated and tabulated in table 5.2. It observed that at low frequency \( E_a \) is large and \( \sigma_{ac} \) is small as well as at high frequency \( E_a \) exhibits small and \( \sigma_{ac} \) appears large. This behavior occurs due to the ionic conduction, which is characterized by low conductivity and high activation energy conduction, while the
association of relatively higher conductivity and lower activation energy with electronic conduction.

Fig. 5.12. Variation of ln(σ∞) with inverse of temperature for La₀.₇Sr₀.₃Fe₁₋ₓNiₓO₃ (x = 0.00, 0.01 & 0.04) samples.
5.4. Magnetic properties

The magnetization hysteresis (M-H) loops measured at room temperature of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.00, 0.01 \& 0.04$) nanoparticles with maximum applied field of 20 kOe has been shown in Fig. 5.13. We can see that, the magnetic hysteresis behaviors of all samples exhibited that the weak ferromagnetic interactions which are increasing with increase in Ni concentration as shown in inset figure. It can be clearly seen that the saturation magnetization ($M_s$) increases with the increase of the Ni concentrations in the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.00, 0.01 \& 0.04$) nanoparticles.

![Graph showing magnetization versus magnetic field for different Ni concentrations](image)

**Fig. 5.13.** Magnetization versus field for $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.00, 0.01 \& 0.04$) samples.

The increase in the remanent magnetization ($M_r$) and coercivity ($H_c$) has been observed with increased value of Ni as tabulated in table 5.3 [27], it may be attributed to orbital moment contributions to the actual electron magnetic moment [29-30]. This could be proposed that these materials may be used in the purpose of recording media [31].
Table 5.3. Various magnetic parameters of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.00, 0.01 & 0.04$) samples.

<table>
<thead>
<tr>
<th>Ni concentration (%)</th>
<th>Saturation magnetization ($M_s$) (emu/gm)</th>
<th>Remanent magnetization ($M_r$) (emu/gm)</th>
<th>Coercivity ($H_c$) (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.444</td>
<td>0.011</td>
<td>224</td>
</tr>
<tr>
<td>1</td>
<td>0.659</td>
<td>0.025</td>
<td>310</td>
</tr>
<tr>
<td>4</td>
<td>1.123</td>
<td>0.077</td>
<td>348</td>
</tr>
</tbody>
</table>

5.5. Conclusions
The $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0.00, 0.01 & 0.04$) nanoparticles have been successfully synthesized by using a reverse micelle technique and studied their structural, optical, dielectric and magnetic properties. The orthorhombic perovskite structure and high crystalline nature LSFNO NPs confirmed by XRD and these results were supported by SEM and EDS. The LSFNO NPs revealed the decreasing in optical band gap with increased Ni concentrations, which could be useful as photocatalytic materials. Temperature dependent dielectric data exhibit the decreasing in dielectric constant with increased Ni concentrations. The values of the activation energy ($E_a$) evaluated and observed that at low frequency $E_a$ is large and $\sigma_{ac}$ is small as well as at high frequency $E_a$ exhibits small and $\sigma_{ac}$ appears large. All samples showed strong ferromagnetic properties. The values of the saturation magnetization ($M_s$), remanent magnetization ($M_r$) and a coercivity ($H_c$) magnetic has been observed with increased value of Ni it may be attributed to orbital moment contributions to the actual electron magnetic moment, which displayed that these materials could be used in high density recording media applications.
References


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[8] A.A. Saad, W. Khan, P. Dhiman, A.H. Naqvi, M. Singh, “Structural, optical and magnetic properties of perovskite \( \text{(La}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Ni}_x)\text{O}_3 \), (x = 0.0, 0.1 & 0.2) nanoparticles”, *Electronic Materials Letters*, 9 (2013), 77-81.


CHAPTER VI

Investigation of structural, optical, electrical and magnetic properties of Fe doped La$_{0.7}$Sr$_{0.3}$MnO$_3$
6.1. Introduction

The various methods have been discussed the synthesis of nanoparticles (NPs) but the one of the most important methods to prepared NPs is reverse micelle (RM), due to the transparent isotropic and stable dispersion of two non-miscible liquids, which are stabilized by surfactant [1]. The general formula of perovskite manganites is R\textsubscript{x}A\textsubscript{y}MnO\textsubscript{3}, where R is a trivalent rare earth ion (La, Pr, Y, Nd, etc.) and A is a divalent alkaline earth ion (Sr, Ca, Ba, etc.), have been a refreshed subject of various investigations in recent years. In the middle of last century the discovery of colossal magnetoresistance (CMR) [2] effect in hole doped manganites has attracted the significant interest due to their potential applications such as magnetic random access memory, disk drive read heads, bolometers and magnetic field sensor [3]. (La,Sr)MnO\textsubscript{3} and (La,Sr)FeO\textsubscript{3} perovskites have been proposed as a cathode material in solid oxide fuel cells (SOFCs) due to their mixed ionic and electronic conductivity [4].

In the parent compound LaMnO\textsubscript{3}, doping of the trivalent A site (La\textsuperscript{3+} ion) with the divalent cations (Sr\textsuperscript{2+}) causes the valence state of Mn (Mn\textsuperscript{3+} to Mn\textsuperscript{4+}) with the configuration (t\textsubscript{2g})\textsuperscript{3}(e\textsubscript{g})\textsuperscript{1} for Mn\textsuperscript{3+} and (t\textsubscript{2g})\textsuperscript{3} for Mn\textsuperscript{4+}. Therefore, the jumping of electron between mixed valance Mn\textsuperscript{3+} and Mn\textsuperscript{4+} during a bridging O\textsuperscript{2-} ion is explained using the double exchange (DE) mechanism [5-7] as proposed by Zener, [8] which controls the magnetic and electronic transport properties of these materials. Also, the other effects resulting suggested from the Jahn-Tellor distortions of Mn\textsuperscript{3+}ion such as strong electron phonon interaction and polaron effects might also contribute in the conduction [9,10]. In the most studies of perovskites structures concentrated on the effects of A site doping, which is exemplary attended by strong lattice strain effects. In other side, doping on the B site which other transition metal ions are an attractive substitute way of adjusting the B site valence state. The electronic and magnetic properties are strongly depending on the interaction between Mn and Fe ions with diverse valence states, which reported elsewhere [11] the doping Mn by Fe encourages an antiferromagnetic insulator behavior which is against the DE effect.

The aim of this chapter is to investigate the influence of Fe ions on the structural, optical, electrical and magnetic properties of La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3} nanoparticles synthesized by reverse micelle method.
6.2. Experimental

6.2.1. Synthesis

Polycrystalline NPs of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ (LSMFO) with nominal compositions $x = 0.00$, $0.10$, $0.15$ and $0.20$ were prepared by reverse micelle (RM) method. The preparation procedure by RM method is schematically shown in Fig. 6.1. LSMFO solutions were prepared by using stoichiometric amounts of lanthanum nitrate $\text{[La(NO}_3\text{)_3\cdot6H}_2\text{O]}$, strontium nitrate $\text{[Sr(NO}_3\text{)_2]}$, manganese nitrate $\text{[Mn(NO}_3\text{)_2]}$ and iron nitrate $\text{[Fe(NO}_3\text{)_3\cdot9H}_2\text{O]}. A quaternary system of iso-octane/CTAB/n-butyl alcohol/water was selected in this RM process. In this process we used two kinds of RM solutions namely RM1 and RM2. For the first solution RM1 contained (10 wt %) an aqueous solution of an equimolar mixture (0.1M) of $\text{[(La(NO}_3\text{)_3\cdot6H}_2\text{O}\cdotSr(NO}_3\text{)_2]}$, $\text{[Mn(NO}_3\text{)_2]}$ and $\text{[Fe(NO}_3\text{)_3\cdot9H}_2\text{O}]$, CTAB as a surfactant (5 wt%), n-butyl alcohol as a co-surfactant (5 wt%) and iso-octane as oil (30 wt%). The stirring was continued for 30 min resulting in a stable reverse micelle RM1, while in RM2 NaOH (0.1 M) instead of metal nitrates was used and other procedure same. These two reverse micelle solutions were mixed under constant stirring and a black color solution was obtained. In addition ammonium solution ($\text{NH}_3$) was slowly added to adjust the pH and stirred 24 h on a magnetic stirrer. The resulting precipitate was separated from the surfactant and a polar solvent by centrifugation and washing it one time by ethanol and four times with distilled water. The precipitate was dried in an oven at 80 °C for 6 h to obtain nanopowder and heated at 750 °C for 5 h in air.

6.2.2. Characterization

The crystal structure was investigated by X-ray diffraction (Rigaku, Japan, Miniflex-II) using Cu-$K_\alpha$ radiation ($\lambda = 1.5418$ Å) in the 2θ range from 20° to 80°. The FTIR absorption spectra of the samples were recorded in wavenumber 400-4000 cm$^{-1}$ by using a Perkin Elmer spectrometer (model Spectra Two) using KBr as a reference. A scanning electron microscope (JEOL JSM-6510LV) equipped with an energy dispersive spectrometer (EDS) was used to check the morphology and particle size. UV-visible
absorbance was carried out using UV-visible, Perkin Elmer spectrophotometer (Model Lambda 35) in the 200-800 nm range.

Fig. 6.1. The preparation scheme of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ ($x$ = 0.00, 0.10, 0.15 and 0.20) NPs through RM method.

The electrical properties were carried out using four probe set up with keithley (model 6221 DC & AC current source and 2182A nanovoltmeter) with a maximum temperature
400 °C. The Room temperature magnetic measurements (M–H) were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

6.3. Results and discussion
6.3.1. Structural studies
The X-ray diffraction (XRD) patterns of La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3, (x = 0.00, 0.10, 0.15 and 0.20) samples at room temperature (RT) are displayed in Fig. 6.2, which are revealed that all samples under investigation are of single phase orthorhombic perovskite structure with Pbnm space group without present of any secondary or impurity phase. The crystal symmetry of these samples remains the same, their lattice parameters change systematically with Fe doping.

Fig. 6.2. XRD patterns of La_{0.7}Sr_{0.3}Mn_{1-x}Fe_xO_3 (x = 0.00, 0.10, 0.15 and 0.20) NPs.
It is clearly observed in the inset of Fig. 6.2 that the peak main diffraction (020) of all samples shifted towards lower 2θ values as the Fe concentration increase, indicating that the lattice parameters increased because of the ionic radius of Fe (0.64 Å) is larger than that of Mn (0.46 Å), so the unit cell volume increases with increase the Fe substitution as the doping level goes from 0% to 20% [12]. The average crystallite size using the most intense peak (020) at angle 2θ ~ 33° determined from the XRD pattern by using the Debye–Scherrer’s formula [13]. The average lattice parameters, crystallite size and unit cell volumes obtained by whole pattern refinement are given in Table 6.1.

**Table 6.1.** Lattice parameters, unit cell volume, crystallite size, optical band gap, and activation energy for all samples.

<table>
<thead>
<tr>
<th>Fe concentration (%)</th>
<th>Lattice parameters (Å)</th>
<th>Unit cell Volume (Å³)</th>
<th>Crystalline size (nm)</th>
<th>F_0 (eV)</th>
<th>E_a (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>417.3</td>
<td>14.6</td>
</tr>
<tr>
<td>0</td>
<td>5.518</td>
<td>5.583</td>
<td>13.546</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5.522</td>
<td>5.615</td>
<td>13.565</td>
<td>420.6</td>
<td>15.0</td>
</tr>
<tr>
<td>15</td>
<td>5.524</td>
<td>5.621</td>
<td>13.572</td>
<td>421.4</td>
<td>15.1</td>
</tr>
<tr>
<td>20</td>
<td>5.527</td>
<td>5.628</td>
<td>13.582</td>
<td>422.5</td>
<td>15.3</td>
</tr>
</tbody>
</table>

The X-ray density (D_x) or the theoretical density was estimated by using the following equation:

\[
(D_x) = \sum \frac{A}{N \times V}
\]  \hspace{1cm} (6.1)

where, A is the sum of the atomic weights of all the atoms in the unit cell, N is the Avogadro’s number and V is the volume of unit cell. The apparent density (p_a) evaluated by the following equation:

\[
p_a = \frac{m}{V}
\]  \hspace{1cm} (6.2)
where m is the mass and V is the volume of the cylindrical shape of the pellets. The above calculation shows decrease in densities with increases in Fe doping because of the atomic weight of Fe is more than atomic weight of Mn. Fig. 6.3 shows that the apparent densities match enough with the theoretical densities.

Fig. 6.3. X-ray density of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ (x = 0.00, 0.10, 0.15 and 0.20) NPs.

Fig. 6.4 shows the lattice parameters (a, b and c) and unit cell volume ($V_{\text{cell}}$) as a function of Fe concentration (x) of LSMFO compound. The lattice parameters a, b and c are increased systematically with Fe concentration, as well as $V_{\text{cell}}$ shows similar behavior to that of the lattice parameters. Actually, the increasing in lattice parameters as well as $V_{\text{cell}}$ may be depending on the lower level of Fe concentration x ≤ 0.20 [14,15].
Fig. 6.4. Variations in lattice parameters and unit cell volume of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ (x = 0.00, 0.10, 0.15 and 0.20) NPs.

SEM images of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, (x = 0.00 and 0.20) NPs synthesized by reverse micelle method have been displayed in Fig. 6.5(a) for pure and Fig. 6.5(b) for 20% Fe doped LSMFO. It is observed that particles are interconnected without uniform shape and size. It is clearly seen that the average particle size in doped sample is more than the average particle size in pure one. The EDS spectra shown in Figs. 6.6(a) & 6.6(b) confirm the presence of La, Sr, Mn and O as well as La, Sr, Mn, Fe and O elements respectively and evidence of the presence of in good stoichiometry, while C
signal originates from the carbon paste. These results are in good agreement with XRD patterns.

Fig. 6.5. SEM image of a) Pure and b) Fe doped LSMFO NPs.

Fig. 6.6. EDS spectra of a) Pure and b) Fe doped LSMFO NPs.
3.1.2. Infrared spectroscopy

Fig. 6.7 shows the FTIR spectra of the complete series measured at room temperature.

![FTIR Spectra](image)

**Fig. 6.7. FTIR spectra of the La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_x\)Fe\(_x\)O\(_3\) (x = 0.00, 0.10, 0.15 and 0.20) NPs.**

The FTIR spectra of all samples show a strong absorption of a symmetric CH\(_3\) stretching at about 1398 cm\(^{-1}\). In case of doped LSMFO, the FTIR spectra show two absorption bands as an asymmetric deformation CH\(_2\) at about 1441 cm\(^{-1}\) and 1530 cm\(^{-1}\) and one absorption band as CO\(_2\)\(^{2-}\) at 871 cm\(^{-1}\), also there is no strong absorption at 1127 cm\(^{-1}\), thus indicating the absence of C-S. LSMFO samples show one absorption band at 612 cm\(^{-1}\)is
indicating to Mn-O-Fe, due to the vibration mode of MnO₆ and FeO₆ groups [16,17], and LSMO spectrum shows one absorption bands at 473 cm⁻¹ due to MnO₆ octahedral. Actually, FTIR spectra of all samples have no contained any other additional peaks, which confirmed the purity of synthesized NPs. These results are also consistent with XRD.

6.3.2. Optical properties

Generally, the interaction between the solid and the electric field of the electromagnetic wave has been governed the optical properties of the solid. UV–visible absorption spectroscopy is a powerful technique to discover the optical properties of semiconductor NPs. There are many factors such as band gap, oxygen deficiency; surface roughness and impurity centers have expected to cause the absorbance [18].

![Absorption Spectrum](image)

**Fig. 6.8.** UV–visible absorbance for La₀.7Sr₀.3Mn₁₋ₓFeₓO₃ (x = 0.00, 0.10, 0.15 and 0.20) NPs.
The optical absorbance versus wavelength is observed for La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, (x = 0.00, 0.10, 0.15 and 0.20) NPs in the wavelength range 200-800 nm with distilled water as the reference and spectra are shown in Fig. 6.8. In the case of pure sample, (i.e. x = 0%) the absorption spectrum showed only one peak in the UV - region but for 10%, 15% and 20% Fe doped samples the absorption spectra showed two peaks.

![Graph showing the change in absorbance with concentration](image)

**Fig. 6.9.** Plot of \((ahv)^2\) versus \(hv\) for La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ (x = 0.00, 0.10, 0.15 and 0.20) NPs.

The first peak indicates that the LSMFO NPs may be a kind of photocatalytic materials [19] and second peak appeared due to the activity of LSMFO NPs under the visible light.
The optical band gap energy of the NPs was determined by applying the Tauc's relationship [20] as given below:

\[ a \hbar \nu = B (\hbar \nu - E_g)^n \] ............................... (6.3)

where \( B \) is a constant, \( \hbar \nu \) is the photon energy, the value of \( n = 1/2, 3/2, 2 \) and 3 is an index depending on the nature of the electronic transition responsible for the absorption, and \( a \) is the absorption coefficient was calculated as follows:

\[ a = 2.303 (A_b / t) \] ................................................................. (6.4)

where \( A_b \) is absorbance and \( t \) is the thickness of the cuvette. Fig. 6.9 displayed the plots of \((a \hbar \nu)^2\) versus photon energy \((\hbar \nu)\) for direct transitions to determine the band gap of the \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3\), \((x = 0.00, 0.10, 0.15 \text{ and } 0.20)\) NPs. The optical energy band gap for all samples has been tabulated in table 6.1. These values indicate that the band gap decreases with increase Fe concentration. The decrease in the band gap could be attributed to the quantum confinement effect of the NPs [20].

The energy band gap \((E^*)\) of the spherical particles depends on the average particle size \(R\), where the band gap \(E^*\) can be approximated by the following equation [21].

\[ E^* = E_g^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2e R^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) - \frac{1.8e}{4 \pi \varepsilon_0 R} \frac{0.124 e^3}{\hbar^3 \left( 4 \pi \varepsilon_0 \right)^{3/2}} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right)^{-1} \] .... (6.5)

where \(E_g^{\text{bulk}}\) is the bulk energy band gap, \(R\) is the particle radius, \(m_e\) is the electron effective mass, \(m_h\) is the hole effective mass, \(m_0\) is the free electron mass, \(h\) is the Planck's constant, \(e\) is the charge on electron, \(\varepsilon\) is the relative permittivity and \(\varepsilon_0\) is the permittivity of free space.

Fig. 6.10 shows the extinction coefficient \((k)\) as a function of photon energy. It can be determined by using the following equation [22]:

\[ k = a \nu / 4 \pi \] ........................................................................................................ (6.6)

The extinction coefficient behavior decrease with increasing photon energy \((\hbar \nu)\), which that happened due to the normal dispersion [23]. Actually, the imaginary part of the
complex refractive index is the extinction coefficient, which allows for estimation of the molar concentration of a solution from its measured absorbance and gives the measure of the part of light lost due to the scattering and absorption for unit distance in the materials.

![Graph showing extinction coefficient versus hv for \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) (x = 0.00, 0.10, 0.15 and 0.20) NPs.]

Fig. 6.10. The extinction coefficient versus hv for \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) (x = 0.00, 0.10, 0.15 and 0.20) NPs.

6.3.3. Electrical properties
The four probe method is one of the standard and most widely used methods for the measurement of resistivity of semiconductors. Basically, in materials science and engineering various phenomena are classified as thermally activated processes—they require thermal energy to take place. Some energy barrier namely as activation energy is needed for thermal activated energy to be overcome in order for the process to occur.
However, the thermal energy increase with increasing the temperature, then the more particles can go above the activation energy.

![Graph showing electrical resistivity vs. temperature for different Fe concentrations](image)

**Fig. 6.11.** Temperature dependence of resistivity for La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, ($x = 0.00, 0.10, 0.15$ and $0.20$) NPs.

The temperature dependence of resistivity for all thermally activated processes can be represented by a general Arrhenius equation:

$$\rho(T) = \rho_0 \exp\left(\frac{-E_a}{k_B T}\right)$$  \hspace{1cm} (6.7)

where $\rho(T)$ is the phenomenon that is thermally activated, $E_a$ is the activation energy of the electrical conduction, $\rho_0$ is a constant, sometimes called the "pre-exponential constant", $k_B$ is the Boltzmann constant and $T$ is the absolute temperature (Kelvin). To investigate and study the electrical behavior of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, ($x = 0.00, 0.10, 0.15$
and 0.20) NPs, resistivity as a function of temperature is plotted and shown in Fig. 6.11. It is clear that when \( x = 0\% \) and \( 10\% \) the behaviors exhibited the semiconducting nature and no insulator to metal transition was observed in the studied temperature range.

In the case of doping samples the behaviors show the insulator to metal transition at 342 K and 428 K for \( x = 15\% \) and \( 20\% \) respectively. Fig. 6.12 shows the Arrhenius plot for calculating an activation energy \( (E_a) \) for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) (\( x = 0.00, 0.10, 0.15 \) and 0.20) NPs. \( E_a \) values were calculated from the slope of graphs and given in table 6.1. The decrease in activation energy with increase Fe doping may be due to the conduction in these materials attributed to the thermal helped tunneling of the charge carriers through the grain boundary barrier and transition from donor level to the conduction band [24].

![Arrhenius plot for calculating an activation energy](image)

**Fig. 6.12.** Variations in Lnp versus 1000/T for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) (\( x = 0.00, 0.10, 0.15, \) and 0.20) NPs.
6.3.4. Magnetic properties

Magnetic measurements were carried out in order to study the effect of Fe doping in LSMO NPs. Fig. 6.13. Shows the dc magnetization as a function of applied magnetic field, for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \), \( (x = 0.00, 0.10, 0.15 \text{ and } 0.20) \) NPs. The magnetization measurement revealed the antiferromagnetic nature of all samples at RT. There is a systematically decreased in the value of the magnetization with increasing Fe concentration. Because of the doping of Fe at the Mn Site reduces the ratio of \( \text{Mn}^{3+}/\text{Mn}^{4+} \) which effects of the Zener double exchange, resulting in reduction in magnetization.

![Graph showing magnetization versus field for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) NPs.](image)

**Fig. 6.13.** Magnetization versus field for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \), \( (x = 0.00, 0.10, 0.15 \text{ and } 0.20) \) NPs.
There are so many reports in the manganites reported that the antiferromagnetic alignments of spins between the Mn and Fe ions have been induced by Fe doping [11, 25-31]. Therefore, in such case perhaps the systematically decreased in the magnetization caused by the antiferromagnetic alignments developed in the samples.

6.4. Conclusions
Polycrystalline NPs of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, (x = 0.00, 0.10, 0.15 and 0.20) have been successfully synthesized in a single phase nanostructured via reverse micelle technique. The Fe doping does not affect the crystal structure, meanwhile, the crystallite size have been increased with increasing the dopant. The surface topography of both samples pure LSMO and dopant LSMFO showed that the particle size increased in the doping samples. Furthermore, the optical band gap values decrease with increasing Fe concentration as well as the activation energy decreases with increasing dopant, due to the thermal helped tunneling of the charge carriers through the grain boundary barrier and transition from the donor level of the conduction band. All samples of the series show an antiferromagnetic nature and a systemically decreased in the value of the magnetization with increasing Fe concentration.
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CHAPTER VII

Conclusions and future work
Pure BiFeO$_3$ and La$_{1-x}$Sr$_x$Fe$_{1-x}$Ni$_x$O$_3$, ($x = 0.0$, $0.1$ & $0.2$) nanoparticles (NPs) were synthesized using sol-gel combustion method as well as pure LaFeO$_3$, La$_{0.7}$Sr$_3$Fe$_{1-x}$Ni$_x$O$_3$, ($x = 0.00$, $0.01$ & $0.04$) and La$_{0.7}$Sr$_3$Mn$_{1-x}$Fe$_x$O$_3$, ($x = 0.00$, $0.10$, $0.15$ & $0.20$) NPs were synthesized using reverse micelle method. Effect of doping on the structural, optical, thermal, electrical and magnetic properties were investigated. Structural analysis was used X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM), while thermal properties carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and optical were studied by UV-Visible spectrophotometer and FTIR. Electrical measurements were carried out by using an LCR meter and four probe set up. Magnetic measurements were carried out by vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe at room temperature. According to the results obtained during the period of this work's key conclusion for every compound are summarized as follows:

1) Bismuth ferrite (BiFeO$_3$)

Bismuth ferrite (BiFeO$_3$) nanoparticles with average particle size $\sim 28$ nm prepared via sol-gel combustion method in pure form using citric acid as a fuel. XRD pattern revealed that all the corresponding peaks of synthesized bismuth ferrite nanoparticles were coordinated with the standard pattern of bismuth ferrite. Also XRD exposed the high crystalline purity in single phase perovskite nature and having a rhombohedral crystal structure with space group R3c. The SEM results suggest that all the nanoparticles considered have a spherical in shape. AFM images exhibit that the particles are in the nanodimension. The nanopowder is showing good transparency in the visible region and the calculated band gap energy reveals a direct band gap $\sim 2.1$ eV. The dielectric constant and dielectric loss (tan$\delta$) of BiFeO$_3$ NPs increases gradually with increased temperature for all frequencies as well as the losses observed to be low at higher frequencies. The ac conductivity has been found to increase with increasing temperature. The magnetization measurements showed antiferromagnetic behavior at room temperature.
Maxwell-Wagner two layer model and Koops theory. The ac conductivity has been found to increase with increasing frequency. The ac conductivity has been discussed in the light of the charge hopping model. The complex impedance spectra illustrate only one semicircle corresponding to the grain boundary resistance up to 20% of Sr and Ni doping. The resistance of the grain boundary is found to decrease while the capacitance of the grain boundary is found to increase with increasing concentration. Ferromagnetic behavior was observed in all samples and magnetization was found to decrease with increasing dopant.

4) Ni doped La$_{0.7}$Sr$_{0.3}$FeO$_3$

The La$_{0.7}$Sr$_{0.3}$Fe$_{1-x}$Ni$_x$O$_3$ ($x = 0.00, 0.01 \& 0.04$) nanoparticles have been synthesized via a reverse micelle technique and investigated their structural, optical, dielectric and magnetic properties. The orthorhombic proksite structure and high crystalline nature LSFNO NPs confirmed by XRD and these results were supported by SEM and EDS. The LSFNO NPs showed the decreasing in optical band gap with increased Ni concentrations, which could be useful as photocatlytic materials. Temperature dependent dielectric data exhibit the decreasing in dielectric constant with increased Ni concentrations. The values of the activation energy ($E_a$) evaluated and observed that at low frequency $E_a$ is large and $\sigma_{ac}$ is small as well as at high frequency $E_a$ exhibits small and $\sigma_{ac}$ appears large. All samples showed strong ferromagnetic properties. The values of the magnetization ($M_s$), remanent magnetization ($M_r$) and a coercivity ($H_c$) magnetic has been observed with increased value of Ni it may be attributed to orbital moment contributions to the actual electron magnetic moment, which displayed that these materials could be used in high density recording media applications.

5) Fe doped La$_{0.7}$Sr$_{0.3}$MnO$_3$

Polycrystalline NPs of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$, ($x = 0.00, 0.10, 0.15 \& 0.20$) have been synthesized in a single phase nanostructured by reverse micelle technique. The orthorhombic crystal structure with the pbnnm space group does not affect with Fe doping meanwhile, the crystallite size has been increased with increasing the dopant. The surface
topography of both samples pure LSMO and dopant LSMFO exhibited that the particle size increased in the doping samples. Moreover, the values of optical band gap decrease with increasing Fe concentration as well as the activation energy decreases with increasing dopant, due to the thermal helped tunneling of the charge carriers through the grain boundary barrier and transition from the donor level of the conduction band. All samples of the series show an antiferromagnetic nature and a systemically decreased in the value of the magnetization with increasing Fe concentration.

Planned future work:
Encouraged by above and exciting results of our study, I am planning to continue my research work in this direction and special focus on hyperthermia. The perovskite type magnetic nanomaterials present excellent biocompatibility and multi-purpose biomedical potential due to their unique properties. Hyperthermia of magnetic nanoparticles is thought to be a promising cancer treatment [1]. Magnetic nanoparticles hyperthermia is a novel non-invasive approach for tumor ablation and is based on heat generation of magnetic materials, such as superparamagnetic iron oxide nanoparticles, when subjected to an alternating magnetic field [2]. The perovskite nanomaterials such as (BiFeO₃, LaFeO₃ and La₀.₇Sr₀.₃MnO₃) are thought to be a promising candidate for the magnetic hyperthermia [3] due to their various physical properties and technology application.
2) Lanthanum ferrite (LaFeO₃)

The LaFeO₃ NPs have been successfully prepared via a reverse micelle technique in pure form using cetyltrimethylammonium bromide, hexadecyltrimethylammonium bromide (CTAB) as a surfactant. Structural studies propose the orthorhombic perovskite crystal system of both samples R1 and R2 with high crystalline of LaFeO₃ NPs confirmed by using XRD and these results were supported by SEM, EDS and FTIR. The exothermic and endothermic peaks are occurring due to the evaporation of water and organics as well as LaFeO₃ NPs exposed an indirect optical band gap (E₈ ≈ 2.63 eV and E₉ ≈ 2.60 eV) for R1 and R2 samples respectively. AFM images exhibit that the particles are in the nanodimension for both samples. The dielectric analysis as a function of temperature exhibits the normal dielectric behavior of dielectric constant and dielectric loss. It exhibits higher value of dielectric constant at lower frequency and decreasing value of dielectric loss with an increase in temperature and capacitance is decreased sharply with increasing frequency. The values of the activation energy (Eₐ) evaluated and observed that at low frequency Eₐ is large and σₑₑ is small as well as at high frequency Eₐ exhibits small and σₑₑ appears large. The magnetization measurements showed a weak ferromagnetic behavior at room temperature for both samples R1 and R2.

3) La₃₋ₓSrₓFe₁₋ₓNiₓO₃, (x = 0.0, 0.1 & 0.2) (LSFNO)

LSFNO NPs were successfully prepared by sol-gel combustion method using citric acid as a fuel. Structure studies reveals the single phase perovskite nature of LSFNO NPs having an orthorhombic crystal structure with Pbnm space group without any presence of secondary phase, with an average crystalline size between 12.7 nm - 21.9 nm. The SEM measurements illustrate the nanoparticles of are (La₁₋ₓSrₓ)(Fe₁₋ₓNiₓ)O₃ big spherical in shape. The EDX images confirm the presence of all elements in pure and doped compound. (La₁₋ₓSrₓ)(Fe₁₋ₓNiₓ)O₃, (x = 0.0, 0.1 & 0.2) NPs have a direct band gap and the optical band gap decrease with increasing in concentrations of Sr and Ni, it is attributed to the Burstein Moss effect. The dielectric constant (real and imaginary part ε' and ε'') and loss tangent both show normal behavior with respect to frequency at room temperature. The dispersion in the dielectric properties have been illustrated in the light of electron hopping mechanism and space charge polarization discussed by
References


LIST OF

PUBLICATIONS
List of Papers Published:

1. "Structural, Optical and Magnetic Properties of Perovskite $(La_{1-x}Sr_x)(Fe_{1-y}Ni_y)O_y$ $(x \geq 0.0, 0.1 \leq y \leq 0.2)$ Nanoparticles", Abdullah A. Saad, Wasi Khan, Pooja Dhiman, A. H. Naqvi, M. Singh, *Electronic Materials Letters* 9, 77 (2013).


List of Papers communicated:

1. "Investigation of structural, optical, electrical and magnetic properties of Fe doped $La_{1-x}Sr_xMn_{x+}Ni_{x}$ nanoparticles", Abdullah A. Saad, Wasi Khan, Pooja Dhiman, A. H. Naqvi, M. Singh, *Journal of Powder Technology (under Review).*


3. "Optical, dielectric and magnetic properties of Ni doped $La_{1-x}Sr_xFeO_{x+y}$ nanoparticles", Abdullah A. Saad, Wasi Khan, Pooja Dhiman, A. H. Naqvi, M. Singh, *Materials Chemistry and Physics (under Review).*
List of papers presented in Conferences / Symposia/Workshops:

1. "Investigation of Dielectric and Magnetic Properties Of Ni Doped La$_{0.3}$Sr$_{0.7}$Fe$_2$O$_4$ Nanoparticles Synthesized via Reverse Micelle Technique", Wasi Khan, Abdullah A. Saad, A.H. Naqvi, Second International Conference on Advanced Complex Inorganic Nanomaterials (ACIN-2013), 15-19 July 2013, Namur, Belgium.

2. "Structural, Optical and Dielectric Properties of La$_{0.3}$Sr$_{0.7}$Fe$_{0.9}$Ni$_{0.1}$O$_4$ Nanoparticles Synthesized via Reverse Micelle Method", Abdullah A. Saad, Wasi Khan, A.H. Naqvi, International Conference on Ceramics (ICC-12), 12-13 December 2012, Bikaner, India.


5. "Investigation and characterization of LaV$_2$O$_5$ Nanoparticles", Abdullah A. Saad, Wasi Khan, A.H. Naqvi, Accepted at 58th DAE Solid State Physics Symposium, 17-21 December 2013, Patiala, India.

6. "Variation in Band Gap of Lanthanum Chromate by Transition Metals Doping LaCr$_{0.7}$A$_{0.3}$O$_3$, (A = Fe/Cu/Ni)", Swaleha Naseem, Wasi Khan, A.A. Saad, M. Shoeb, Hilal Ahmed, B.R. Singh, Shahid Husain, A. H. Naqvi, Accepted at 58th DAE Solid State Physics Symposium, 17-21 December 2013, Patiala, India.