

A STUDY OF OXIDE MATERIALS NANOPARTICLES : SYNTHESIS, OPTICAL, ELECTRICAL AND MAGNETIC PROPERTIES

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Abstract

Nano is a Greek word, which means dwarf, and is one billionth of a meter. A nanometer is approximately the size of a claw that grows in one second. The nanoparticles cannot be seen through the naked eyes but can be seen with help of electron microscope (Dupas *et al.* 2004). These days nanoparticles are of attraction due to the remarkable optical, magnetic and electrical properties (Eric 2015). Certain nanoparticles exist in nature, at the same time some designed nanoparticles are presently applied in numerous commercially developed products and methods. The nanoparticles are found to be in goods like cosmetics, sports product, electronic goods, strain-resisting garments, wheels and in the medicinal field (Brechignac & Lahmani 2017).

Keyword:- Approximately, Microscope, Properties, Developed.

Introduction

The designed nanoparticles are engineered at nano grade due to the enhanced quality that is not present in the bulk equivalent (Stefanita 2008). The enhanced quality such as greater surface area, the optical, electrical and magnetic property of the nanoparticles is the principle foundation for its use in the various field that includes electronics, environmental and medicine. The nanoparticles are designed in different shapes depending on the mode of application. More recently, the nanoscience and technology are a wide and multidisciplinary area of investigation, and the progress is developing globally with a notable economic impression. One of the major reasons behind the development of nanoscience and technology is nanomaterials that are the fundamental particles for research (Filipponi & Sutherland 2013).

Objectives of the Study

The aims of the present study 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. Synthesis of Sr^{2+} and Ni^{3+} doped La and Fe of LaFeO_3 respectively, as $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$, ($x = 0.0, 0.1$ and 0.2) by sol-gel combustion method to develop the physical properties such as structural, optical, electrical and magnetic properties.
4. Synthesis of Ni^{3+} doped $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$, ($x = 0.00, 0.01$ and 0.04) by a reverse micelle technique to develop the various physical properties such as structural, optical, electrical and magnetic properties.
5. Synthesis of Fe^{3+} doped $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$, ($x = 0.00, 0.10, 0.15$ and 0.20) by a reverse micelle technique to develop the various physical properties such as structural, optical, electrical and magnetic properties.

Literature Review

Bismuth Ferrite (BiFeO_3) is an attractive material exhibiting multiferroism at room temperature, which is ferroelectric ($\text{TC} = 820\text{--}850^\circ\text{C}$) and anti-ferromagnetic ($\text{TN} = 370\text{--}380^\circ\text{C}$). BiFeO_3 is an inorganic chemical compound with a perovskite structure. It is one of the most promising lead-free piezoelectric materials by exhibiting multiferroic properties at room temperature. Multiferroic materials exhibit ferroelectric or anti-ferroelectric properties in combination with ferromagnetic and antiferromagnetic properties in the same phase. The multiferroics with a coupling of at least two of the possible three orders (or degrees) of freedom viz., ferromagnetic (or antiferromagnetic), ferroelectric (or antiferroelectric), and ferroelastic are rare in nature as transition metal ions with active d electrons tend to reduce the off-center distortion necessary for ferroelectricity. BiFeO_3 is the most interesting in the family of a very few single-phase multiferroics because of its high phase transition temperatures (Curie temp 1083K and Neel temperature 675K). Several techniques have been employed in synthesizing BiFeO_3 . In the solid state route Bi_2O_3 and Fe_2O_3 are reacted at a temperature in the range of $800\text{--}830^\circ\text{C}$ and unreacted $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{Fe}_4\text{O}_9$ phases are removed by washing in HNO_3 . Another technique is simultaneously precipitation, where a solution of bismuth nitrate and iron nitrate is treated with ammonium hydroxide to get a hydroxide precipitate. The precipitate needs calcination at a temperature in the range of $550\text{--}750^\circ\text{C}$ to get phase pure BiFeO_3 . In another approach nanosized BiFeO_3 particles have been prepared by a solution evaporation (tartaric acid template) technique at a temperature as low as 450°C . It can also be prepared through co-precipitation (700°C), sonochemical (450°C) and autocombustion (400°C) routes. Incidentally, there are only a few reports of making densified and highly resistive BiFeO_3 ceramics.

Mahesh Kumar et al. reported the dielectric and ferroelectric properties of BiFeO_3 ceramics where BiFeO_3 was prepared by solid state route and there was no report about the bulk densities of the samples. The spontaneous polarization of the sample was very low.

Wang et al. showed that a rapid liquid-phase sintering of BiFeO_3 can result in 92% relative density and gave rise to spontaneous and remanent polarization of $8.9, 4.0\text{C}/\text{cm}^2$, respectively.

Characteristics

The co-existence of ferroelectricity and ferromagnetism and their coupling with elasticity provide an extra degree of freedom in the design of new functional sensors and multistate devices. Due to its multiferroism, an electric field can induce change in magnetization and an external magnetic field can induce electric polarization. This phenomenon is known as the magnetoelectric effect (ME) effect and materials exhibiting this effect are called magnetoelectrics or *seignette magnets*. Further proof of it being ferromagnetic is that it produces a hysteresis loop during ferroelectric characterization. The ability to couple to either the electric or the magnetic polarization allows an additional degree of freedom in device designs. One of the major drawbacks of BiFeO₃ material is the leakage current arising out of its nonstoichiometry. This is mostly because of the difficulty in obtaining stoichiometric singlephase BiFeO₃ materials. Therefore it allows current to pass through when a high voltage is applied. Attempts to improve the electrical properties have been made by doping it with rare earth elements such as lanthanum (La), samarium (Sm), gadolinium (Gd), terbium (Tb) and dysprosium (Dy) etc. The dopant can be at the A site or the B site. A site being the edges of the perovskite cell and the B site being the centre of the perovskite cell.

1. Jiang *et al.*, J Electroceramics.21, 690 (2008):

- ✓ The BiFeO₃ ceramic sample shows low dielectric constant and low loss tangent between 100 Hz and 10 MHz. pH value has an effect on the purity of BiFeO₃.
- ✓ The sample via conventional sintering process has higher conductivity and cannot be polarized but has a low loss tangent.
- ✓ BiFeO₃ from spark plasma sintering has $\epsilon_r = 45$ and loss of 0.1-1% at $T = 600^{\circ}\text{C}$ and ϵ_r increases to 80-100 and the loss tangent up to 1-10% for $T = 700^{\circ}\text{C}$.

2. Lebeugle *et al.*, Physical Review B.76, 024116 (2007):

- ✓ Highly pure single crystal of BiFeO₃ can be grown by flux method.
- ✓ Ferroelectric hysteresis loop is observed at room temperature.
- ✓ A way to obtain higher dielectric constant and lower loss factor is to make solid solution of BiFeO₃ with another ABO₃ that is BFO-Pb(Ti,Zr)O₃.
- ✓ In epitaxial thin film polarization increases to tenfold due to structural change.

3. Donna C. Arnold *et al.*, Physical Review Letters.102, 027602 (2009):

- ✓ BiFeO₃ undergoes a first order ferroelectric to paraelectric transition at T_C (820– 830⁰C) from a phase of R3c symmetry to an orthorhombic phase with Pbnm space group.
- ✓ The nature of the transition is markedly different to the rhombohedral to orthorhombic transition in ferroelectric BaTiO₃, and to the rhombohedral-

orthorhombic (ferroelectric to antiferroelectric) transition in NaNbO_3 .

Lanthanum Orthoferrite, LaFeO_3

AFeO_3 oxides (the so-called orthoferrites) belong to a relevant class of weak ferromagnetic materials with interesting magnetic and magneto-optical properties. The magnetic structure in orthoferrites can be conventionally described by two interpenetrating pseudo-cubic face centred sub-lattices in which each Fe^{3+} ion is surrounded by six O^{2-} ions. This results in a collinear arrangement of the two sub-lattices, giving an antiferromagnetic ordering. However, the FeO_6 octahedra can be tilted to different degrees depending on the size of the rare-earth cation, leading to a net magnetic moment.

Lanthanum orthoferrite, LaFeO_3 , is one of the most common perovskite-type oxides and has an orthorhombic perovskite structure with space group Pbnm . LaFeO_3 consists of FeO_6 octahedra units with La^{3+} ions inserted between these units. Bulk LaFeO_3 is known to be antiferromagnet with a Neel temperature T_N of 740 °C. It has much practical interest for electroceramic applications due to their attractive mixed conductivity displaying ionic and electronic defects. The mixed ionic-electronic conductivity of LaFeO_3 exhibits a linear response to oxygen pressure and provides oxygen sensor applications. The excellent sensitivity and selectivity towards various toxic gases such as CO and NOx are observed as well. Moreover, LaFeO_3 nanoparticles exhibited good photocatalytic properties under visible light irradiation. These properties are enhanced by the homogeneity and high surface area of the fabricated LaFeO_3 particles. Fine particles with diameter of less than 100 nm are potentially required for these purposes. its spontaneous magnetization is considerably small, 0.044 $\mu\text{B}/\text{Fe}$. However, antiferromagnetic nanoparticles often exhibit increasing net magnetization due to the presence of uncompensated surface spins. If the ferromagnetic behaviour is promoted in LaFeO_3 , it should provide facile handling of their applications by using magnetic field.

Structure of LaFeO_3

LaFeO_3 first in the series of rare earth orthoferrites, exhibits like all of its members, an orthorhombically distorted perovskite structure with space group Pbnm .

The atomic positions in the unit cell have been determined by X-ray diffraction on small twinned single crystals. In this structure Fe^{3+} ions are located at the centers of slightly distorted O^{2-} octahedral. The Fe^{3+} ions are coupled antiferromagnetically to six Fe^{3+} nearest neighbours via Fe-O-Fe super exchange and exhibit G-type antiferromagnetic ordering like all the other rare earth perovskites. It has been assumed that the magnetic moments point along the crystallographic a-direction because such is the case with all the other members of the series at high temperatures.

Lanthanum ferrite, LaFeO_3 , crystallises in the orthorhombic space group Pbnm at temperatures below ~ 1273 K. [27] At temperatures above 1273 K, it has a rhombohedral structure with space group $\text{R}\bar{3}\text{c}$.

Synthesis of LaFeO_3 by Different Route

LaFeO₃ is synthesized by many methods. There are various type of method to process LaFeO₃ which can classify in major four types:

- [1] Co-precipitation Method
- [2] Combustion Method
- [3] Sol–gel Method
- [4] High energy ball milling

Applications of LaFeO₃

Metal oxides and perovskites are being employed as catalysts for various applications. LaFeO₃ is one of the important perovskite widely reported for various applications including

1. Solid oxide fuel cells
2. Sensors
3. Oxygen permeation membranes.
4. As environmental catalyst

In this section the important work carried out in last few years related to synthesis of LaFeO₃ by different method and the substitution effect on the properties has been reviewed.

Lanthanum manganite (LaMnO₃)

Among the manganese oxides, lanthanum manganite (LaMnO₃) is particularly important because it is the parent compound of the family of the manganites which exhibit the CMR effect [6, 12, 13].

LaMnO₃ exhibits rich and interesting physical properties related to a strong interplay between lattice distortions, transport properties, and magnetic ordering. In stoichiometric LaMnO₃, in which all the manganese ions are formally in the Mn³⁺ oxidation state, the electronic configuration of Mn³⁺ is postulated as $t_{3g}^3 e_g^1$. This electronic configuration is susceptible to a strong JT distortion [14, 15] which breaks the local octahedral symmetry and removes the twofold degeneracy of the e_g states. The JT distortion can be looked upon as a cooperative shifting of the oxygens within the ab plane away from one of its two nearest-neighbor manganese atoms toward the others, thereby creating long and short Mn-O bond lengths. The bond lengths are modified from 1.97 Å for the cubic lattice to 1.91 Å, 1.96 Å, and 2.18 Å for the orthorhombic variant [13].

Scope of the Present Study

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 ABO_3 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. 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. Perovskite oxides exhibit a large variety of properties, due to the variety of structures and chemical compositions.

Research Methodology

The science and technology of nanomaterials has created great excitement and expectations in the last few years. By its very nature, the subject is of immense academic interest, having to do with very tiny objects in the nanometer regime. There has already been much progress in the synthesis, assembly and fabrication of nanomaterials, and, equally important, in the potential applications of these materials in a wide variety of technologies. The next decade is likely to witness major strides in the preparation, characterization and exploitation of nanoparticles, nanotubes and other nanounits, and their assemblies. In addition, there will be progress in the discovery and commercialization of nanotechnologies and devices. These new technologies are bound to have an impact on the chemical, energy, electronics and space industries.

The recent developments are mainly focused on the synthesis, characterization and applications of metal oxide based nanomaterials. Nowadays, the ability to control the particle size and morphology of nanoparticles is of vital importance both from fundamental and

industrial point of view. Future technologies based on nano materials will hinge on the production of a controlled size, shape and structure of oxide material. Indeed, further development and optimization of nanostructured materials will be reached by better fundamental understanding of unique physico-chemical properties and electronic structure as well as a better match between the materials design. The thirist areas for the continuous development includes devices like dyesensitized solar cells, displays and smart windows, chemical gas sensors and biosensors, lithium batteries and supercapacitor due to their tremendous amount of high-tech applications.

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 magnototransport 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.

Conclusion

Pure BiFeO_3 and $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$, ($x = 0.0, 0.1 \text{ \& } 0.2$) nanoparticles (NPs) were synthesized using sol-gel combustion method as well as Pure LaFeO_3 , $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$, ($x = 0.00, 0.01 \text{ \& } 0.04$) and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$, ($x = 0.00, 0.10, 0.15 \text{ \& } 0.20$).

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:

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