Abstract

Material Science encompasses various disciplines, namely, physics, chemistry and engineering and is truly interdisciplinary in nature. The evolution of material science is always an indicator to man’s progress and his urge to improve upon the existing and replace the obsolete with newer and novel materials often results in newer materials and innovations. The emergence of nanoscience and nanotechnology as a leading technology of the 21st century has only accelerated the growth of material science. Today nanoscience and nanotechnology has become synonymous with material technology. Magnetism and magnetic materials has been playing a seminal role in ones life. The magnetic industry is all set to surpass the semiconductor industry with the proliferation of new gadgets based on magnetic materials and new innovations in the area of nanomagnetism. The realm of modern day magnetism and magnetic materials is always a subject of intense research. Newer devices based on magnetism are hitting the markets. For example, we have spintronic devices, GMR sensors, magnetic random access memories and other novel gadgets based on nanomagnetism. So it is only natural that magnetism and magnetic materials at the nanoscale attracts the attention of researchers worldwide.

The shape and size distribution of the nanoparticles is one of the key parameters that determine the physical and chemical properties and phenomena of nano material, and to the realization of their potential applications. The variation of physical properties with the method of synthesis has made ferrite the most demanding and technologically important material. All the ferrite nanoparticles have room temperature-specific magnetization values less than that of the corresponding bulk state.

The interest in nano sized spinel ferrites has greatly increased due to their importance in understanding fundamentals in nano magnetism and their wide range of applications such as high density data storage, Ferro-fluid technology, sensor technology, spintronics, magneto caloric refrigeration, heterogeneous catalysis, fuel cells cathodes, high temperature oxygen permeation membranes, waste water cleaning, magnetically guided drug delivery and magnetic resonance imaging.

A significant motivation of current research into nanometer sized materials is the need to develop an understanding of the various properties sensitive to synthesis methods. It is well known that methods of preparation play a very important role in determining the chemical, structural, elastic, optical, electrical, magnetic and biological properties of spinel ferrites. Ferrites are commonly produced by ceramic technique that involves high temperature solid state reaction between the constituent’s oxides, carbonates or oxalates. The particles obtain by ceramic techniques are large and of non-uniform size. It is believed that ferrites product obtained from ceramic method are in most cases not reproducible in terms of their magnetic properties. The high frequency ferrite-cores used in switch mode power supplies must have low power loss at high frequencies. This is a challenging problem of synthesis of Co-Mn ferrites having suitable microstructure. Other ferrites for high frequency applications will also be prepared by different techniques.

Since the study of the present researcher is based on nano particle synthesis by various methods, it requires crossing the traditional boundary of the physics subject. The work carried out by the author is not only limited to synthesis and characterization of certain ferrites, but it also covers the comparative studies of the materials to check the effect of synthesis method selected. Therefore, this interdisciplinary research work requires integrating data, theories, methodologies, perspectives, and concepts from multiple disciplines like physics, chemistry and material science.

The aim of the present thesis is to establish various synthesis routes of wet-chemical techniques alternative to well-established ceramic routes such as Auto Combustion Method, Citrate Precursor Method, Co-precipitation Method, Flash Combustion Method, Hydrothermal Method and Polymeric Precursor Method are to be designed and employed. This is relevant because it is known that the ceramic technique produces coarse-grained materials which are required to be ball-milled for long duration if one wants to produce nano-sized powders. The wet-chemical routes render inherently nano-sized powders of materials with desired stoichiometry and mono-phase structure. The wet chemical methods of preparation of ferrites satisfy essential requirement of obtaining well controlled uniformity and high purity materials which makes these chemical route the most preferred choice. The main purpose of this work is to study ferrites nano particles prepared by different methods, comparison of some selected samples and its special applications.

The mixed ferrites Co-Mn and Co-Ni with generic formulae Co$_{Mn_{x}}$Fe$_{3-x}$O$_{4}$ (x = 0.0 to 1.0, in step x = 0.2) and Co$_{Ni_{x}}$Fe$_{3-x}$O$_{4}$ (x = 0.0 to 1.0, in step x = 0.2), respectively have been synthesized by six different synthesis methods: Auto
Combustion Method (ACM), Co-precipitation Method (COPM), Citrate Precursor Method (CPM), Flash Combustion Method (FCM), Hydrothermal Method (HTM) and Polymeric Precursor Method (PPM). All the nano-structured ferrite powders were characterized by powder X-ray diffraction, EDAX, SEM, TEM, FTIR, Raman spectroscopy and magnetic measurements.

The X-ray diffraction results showed that all the samples synthesized by different methods exhibit single phase cubic spinel structure with no traces of any other crystalline phase or un-reacted ingredient confirming purity of the ferrite samples. The compositional stoichiometry was confirmed by EDAX and grain morphology was also seen by SEM images. Moreover, the change in the particle size for all investigated samples is due to the change in the growth rate of ferrite particles which is also reflected in variation in X-ray density, this might be due to the use of different starting solutions like metals acetate, chloride, citrate, nitrate, perchlorate, and sulfate and fuels in combustion synthesis for preparation of the ferrite materials. The distribution of cations in the tetrahedral (A) and octahedral (B) sites of the spinel lattice deduced from X-ray diffraction for the samples of both the ferrite systems exhibit variation for different methods of preparation. This was expected and found in conformity with the general conjecture that the method of preparation plays vital role with regard to the cation distribution conducive to structural and magnetic properties of ferrites. The TEM images and SAED patterns confirmed the formation of spinel phase of the ferrites and particle size in nano-regime. The FTIR characterization showed the presence of water content and CO\textsubscript{2} in case of combustion synthesis in addition to the normal tetrahedral and octahedral cation absorption bands for spinel ferrites. The elastic parameters were calculated using the FTIR and XRD data with software developed in JAVA.

The saturation magnetization values of all the ferrite samples at room temperature are as per the expectation except for the samples prepared by polymeric precursor method. This confirms the standardization of the synthesis methods used. The low values of saturation magnetization compared to the Neel's value are due to large coercivity and non-saturating behavior even at very high applied magnetic field and thermal agitation at room temperature. In addition to this, magnetically dead layer in “core-shell” structure of nano-sized ferrite particles also contribute in reduction in magnetization. All the samples exhibit broad hump in thermal variation of low field AC susceptibility curves due to the presence of very fine superparamagnetic particles showing the characteristic of single domain to superparamagnetic transition upon tuning of magnetic energy and thermal energy. The AC susceptibility versus temperature plot for NiFe\textsubscript{2}O\textsubscript{4} exhibit normal ferromagnetic behavior with absence of hump and sharp magnetic phase transition. The addition of Co\textsuperscript{2+} cations induces the development of hump in the \(\chi\sim T\) plots.

Room temperature (300K) Raman spectra of nano sized Co-Mn and Co-Ni ferrite samples synthesized by various wet chemical techniques were recorded with two different powers (2.5 and 10mW) show the characteristic absorption bands of tetrahedral and octahedral site cations in spinel ferrites confirming consistency of ferrite products prepared by different methods. Broadening of Raman band indicates disorder and presence of nano-sized particles. The variation of dielectric constant and loss tangent with frequency exhibits standard behavior for all the ferrite samples prepared by different methods.

In the last part of this work, three different spinel ferrite nanoparticles MnFe\textsubscript{2}O\textsubscript{4} (M = Co, Mn, Ni) were prepared by four different methods viz., ACM, FCM, CPM, COPM with various different coating materials like silica, silica - DEG, PEG etc. It is very interesting to note that all nanoparticles are found to be strong antimicrobial agents. Thus, the nanoparticles prepared in this study are very potent antimicrobial agents and it is possible to design experiments on these particles for biomedical applications. The concentration of Fe - ions from PEG coated MnFe\textsubscript{2}O\textsubscript{4} nano particles prepared by Co-precipitation method (COPM) is reduced using biological process using specified bacteria. This type of material is very useful due to its magnetic properties for targeted drug delivery and magnetic hyperthermia for cancer treatments.

Thermography or thermal imaging using thermal camera enables one to see and measure the heat which cannot be detected by human eye or any other type of temperature probe due to rapid change of reaction temperature within very small time interval. The results showed that the lowest reaction temperature at which combustion process starts is nearly 200°C and the highest reaction temperature at which combustion process ends is about 700°C with total time of reaction approximately 5 to 20 minutes which depends on the proportion of starting materials and fuel materials used for the combustion process. Thus, these two preparation methods ACM and FCM are very useful and cost effective processes preparation of nano-structured ferrites in bulk for industrial production. Cobalt ferrite as an alternative adsorbent
surface for ability of removal of various dyes in this study was investigated. The removal percentage of dyes confirmed the various dyes adsorption onto Cobalt ferrite. It can be concluded that the Cobalt ferrite being as a magnetic adsorbent with high dye adsorption capacity might be a suitable alternative to remove dyes from colored aqueous solutions. Thus, the problem of waste product of dye of various dyeing industry can be easily solved. The ESR spectra of spinel ferrite prepared by combustion routes show characteristic signature of nano-structured spinel ferrites.

In order to study the gas sensing application of nano-structured ferrites, a gas-sensor experimental set-up was designed and fabricated and measurements were recorded for CoFe$_2$O$_4$ nano-particles using LPG for different temperature. Finally, computer programme for speedy and accurate calculation of structural and elastic parameters of spinel oxides written in JAVA is presented with calculation of elastic and structural parameters for CoFe$_2$O$_4$.

In a nut shell, the research work presented is focused primarily on understanding the reaction mechanisms of various wet-chemical preparation techniques for synthesizing nanoscale ferrite materials which ultimately leads to the standardizing of the techniques used and after optimizing the processing conditions for nano-structured ferrites, different ferrite compounds in bulk can be synthesized for special applications.