PREFACE

The study of nanoparticle systems is a subject of great interest in physics. Nanophase or nanostructured materials composed of microstructures with a characteristic size range of 1-100 nanometres is a new branch of materials research. They are attracting a great deal of attention because of their potential applications in areas such as electronics, optics, catalysis, ceramics, magnetic data storage and nanocomposites. Nanoparticles are a bridge that links single elements with single crystalline bulk structures and provide an improved performance of the existing materials due to their peculiar microstructures and unique compositions. It has been realised that they exhibit new useful properties since they are intermediate between atomic phase and bulk solid phase.

Nowadays abundant scientific data is available to make useful comparison between nanosized materials and their bulk counterpart. For example, the hardness of nanocrystalline copper is found to be grain size dependant and 6nm particle shows hardness five times greater than the conventional copper. CdSe can yield any colour in the spectrum simply by controlling the grain size of the material. Thus physical properties have been remarkably improved through nanostructure maneuvering. Nanotechnology is the science and engineering of making materials, functional structures and devices of the order of a nanometer scale. Nanostructured materials and their base technologies have opened up exciting new possibilities for future applications in all areas of science, technology and commerce. It is expected that twenty first century could see technological breakthrough in creating materials atom by atom where new inventions will have widespread impact in all fields of science and engineering.

At present products like tennis ball, khaki cloth, medicine, etc. made and enhanced through nanotechnology are available in industrial sector.
Besides, many commercial applications are in advanced stages of development. The basis for the interest and commercialisation of nanoparticles is the unique properties and the improved performances they exhibit. These properties are determined by the particles sizes, surface structures and interparticle interaction. The transition in energy levels from discrete for single atoms to continuous bands for bulk crystalline solid is the basis of many electronic properties. A specific parameter introduced by nanomaterials is the high surface to volume ratio of atoms. A high percentage of surface atoms and their unfilled electronic bonding are required for stimulating and promoting chemical reactions. The finite size of the particle leads to quantum size effect. For magnetic materials the surface atoms experience a different local environment in their magnetic coupling with neighbouring atoms. Nanomaterials are microstructurally heterogeneous with the presence of grains, grain boundaries and large volume of interface between grains which play an important role in determining the electrical properties. However, other structural features like pores and other crystal lattice defects that can depend upon the manner in which these materials are synthesised and processed also play significant roles. A major portion of porosity appears to be capable of being removed, when desired, by means of cluster consolidation at elevated temperatures and pressures without the occurrence of significant grain growth.

The most important matter in nanoparticle physics is the production of particles of desired materials in the desired size range and to characterise its structure and properties. Many methods have been developed for the synthesis of nanoparticles, which includes physical and chemical. In chemical methods, the particle size and particle size distribution, the crystallinity and crystal structure can be affected by reaction kinetics. In addition, the concentration of reactants, the reaction temperature, the pH and the order of addition of reactants to the solution are also important. Currently scientists are interested to study the effect of grain size on the properties of materials.
This thesis consists of a systematic study of the synthesis and properties of nanoparticles of Ag₃PO₄, FePO₄ and ZnFe₂O₄. Each compound was prepared for three different reactant concentrations in order to study its effect on grain size and hence on properties. The ease of preparation of nanoparticles of these materials was one of the main considerations in choosing them for the present study. Moreover chemical method has the advantage of improved compositional homogeneity since the reactant constituents are mixed at molecular level. Ag₃PO₄ was prepared by chemical precipitation, FePO₄ by thermolysis of precursor solution and ZnFe₂O₄ by coprecipitation method. In the present study the effects of finite size of the grains on the vibrational, electrical and magnetic properties were investigated. The crystal structure and size of the particles were determined using X-ray diffraction analysis. Morphology and size of the particles were determined using SEM and TEM. IR transmission spectra of nanoparticles of these compounds were studied in comparison to bulk IR spectra. Thermal analysis was carried out using TG/DTA. The dielectric constant, dielectric loss and a.c. conductivity of pellets of these particles were measured. Impedance spectroscopy was used to separate out grain and grain boundary contribution to electrical conductivity. Magnetic measurements were carried out using VSM, SQUID magnetometer and ESR techniques.

The thesis entitled "A Study of the Properties of Certain Nanophase Materials" is divided into 9 chapters.

Chapter 1 gives a general introduction to nanoparticles and nanophase materials. This chapter begins with the historical development of nanoparticle research. Then the various preparation methods generally employed for the synthesis of nanoparticles and their characterization techniques currently in use are discussed. Unique properties of nanoparticles and consolidated nanophase materials are given in brief. Technological and commercial
applications and latest developments in this field are also discussed. This chapter ends with the description of the present work.

The experimental techniques used in the present study to characterize the materials are discussed in the second chapter. Experimental techniques include TEM, SEM, XRD, TG/DTA, FTIR, impedance spectroscopy, dielectric measurements and magnetic measurements.

Chapter 3 deals with the details of the preparation of nanoparticles of Ag₃PO₄, FePO₄ and ZnFe₂O₄, which are used for the present study. Along with this the determination of size, morphology and structure of the particles are described. TEM images and electron diffraction patterns of Ag₃PO₄, FePO₄ and ZnFe₂O₄ are used to determine the size and crystalline nature of the particles. SEM micrographs of Ag₃PO₄ and FePO₄ are used to give the morphological features of the particles. X-ray diffraction studies are extensively carried out to determine the size and crystal structure of the particles. Particle size was determined using Scherrer formula.

The description of FTIR spectra of nanoparticles of Ag₃PO₄, FePO₄ and ZnFe₂O₄ in comparison with its bulk spectra is explained in chapter 4. The vibrational spectra are different from the spectra of corresponding bulk material due to the size effect of small particles which causes the breakdown of vibrational selection rule k ≠ 0 forbidden. As a result the vibrational lines may be broad and frequency shifted compared to those of the bulk crystals. Another reason is the surface effect, which becomes more and more important as the particle size decreases, since the surface to volume ratio increases.

In chapter 5 thermal studies are carried out using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). High temperature phase changes, grain growth process and structural behaviour are discussed in this chapter. Also the temperature at which the formation of nanophase FePO₄ occurs from precursor powder can be studied from this analysis.
Chapter 6 deals with the qualitative analysis of impedance spectra and detailed study of the dielectric behaviour of nanophase $\text{Ag}_3\text{PO}_4$ in the pellet form. Nanoparticle materials exhibit greatly altered electrical properties compared to their bulk materials. Impedance spectroscopy probes the electrical response as a function of frequency, of components, the grains, grain boundaries and sample-electrode interface. The dielectric properties arise due to polarisation process within the grains and a major part of it in the grain boundaries. In nanophase $\text{Ag}_3\text{PO}_4$, the grain resistance is found to be very small showing only a small arc in the impedance spectrum in the high frequency side. A very large grain boundary arc is seen in the midfrequency region. A third arc in the low frequency side showing the blocking nature of electrodes, which is the case with ionic conductors. Dielectric behaviour is found to be mainly due to space charge polarisation.

The dielectric behaviour of nanophase $\text{FePO}_4$ is described in chapter 7. At low frequencies space charge polarisation effects are found to be prominent which is characteristic of nanophase materials. At high frequencies a normal dielectric behaviour is exhibited.

Chapter 8 deals with the impedance spectroscopic analysis and the study of dielectric properties of nanophase $\text{ZnFe}_2\text{O}_4$ for different particle sizes. For smaller particles a dielectric anomaly was observed, whereas larger particles exhibited a normal dielectric behaviour. Space charge polarisation effects, ion jump orientation effects and electron hopping mechanism contribute towards dielectric behaviour.

Chapter 9 discusses the magnetic studies of nanophase $\text{FePO}_4$ and $\text{ZnFe}_2\text{O}_4$. Room temperature magnetic moment measurement using VSM has shown that magnetic moment decreases with decrease in particle size, which may be due to surface spin disorder of nanoparticles. Field cooled (FC) and zero field cooled (ZFC) magnetic moment measurement with temperature using SQUID magnetometer is used to interpret the interparticle interaction
between magnetic ions and to explain superparamagnetism. ESR spectra studies of FePO₄ are found to be supporting magnetic measurements.

A major part of the work included in this thesis has been published or communicated in the following journals and some portions of the work were presented at national seminars.

**List of papers published/ communicated**


4. IR spectroscopic and magnetic study of nanophase ZnFe₂O₄, J. Magn. Magn. Mater. (communicated)

5. Dielectric and impedance spectroscopic studies on nanophase ZnFe₂O₄, Indian J. Phys. A (communicated)


**Papers presented in national/international seminars**

1. Ultrasonic investigation in suspensions of nanoparticles of AgCl and Ag₃PO₄, National seminar on “Condensed Matter and Applications to Non-conventional Energy”, March 1999, St. Berchman’s College, Changanacherry, Kerala.
2. Structural characterisation of nanostructured Ag₃PO₄. National conference on “Science and Technology of Nanomaterials and Clusters”, November 2000, Institute of Physics and electronics, Barkatullah University, Bhopal.


6. IR spectroscopic and magnetic moment variation with particle size for nanocrystalline zinc ferrite, International Conference on Nano Science and Technology, Department of Science and Technology, Government of India. December 17-20, (2003), Kolkata, India (Accepted for presentation).