

**INVESTIGATIONS OF Mn, Fe, Ni AND Pb DOPED  
ZINC SULPHIDE NANOPARTICLES**

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University of Pune*

**FOR THE DEGREE OF  
DOCTOR of PHILOSOPHY IN PHYSICS**

*by*

**PRAMOD H. BORSE**

**DEPARTMENT OF PHYSICS  
UNIVERSITY OF PUNE  
PUNE 411 007  
INDIA**

**DEC. 1999**

## **CERTIFICATE**

*Certified that the work incorporated in the thesis “Investigations of Mn, Fe, Ni and Pb doped zinc sulphide nanoparticles” submitted by Mr. Pramod H. Borse was carried out under my supervision and the work included in this thesis has not been submitted / utilized for any other degree. Such material as has been obtained from other sources has been acknowledged in this thesis.*

Prof. (Mrs.) S.K. Kulkarni  
(Guide)  
Department of Physics  
University of Pune  
Pune 411 007

Go My Parents

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## LIST OF ACRONYMS

AAS	: Atomic absorption spectroscopy
B	: Debye parameter
DFA	: Debye functional analysis
DMS	: Diluted magnetic semiconductor
DNCs	: Doped nanocrystals
DTA	: Differential thermal analysis
DTG	: Differential thermo gravimetry
EL	: Electroluminescence
EMA	: Effective mass approximation
EPM	: Empirical pseudopotential method
ESR	: Electron spin resonance
FEDs	: Field effect displays
HOMO	: Highest occupied molecular orbital
LUMO	: Lowest occupied molecular orbital
MBE	: Molecular beam epitaxy
PL	: Photoluminescence
QSE	: Quantum size effect
TBA	: Tight binding approximation
UV	: Ultra violet
W	: Wurtzite
WAXS	: Wide angle x-ray scattering
XRD	: X-ray diffraction
ZB	: Zinc blend

## LIST OF SYMBOLS

$\theta$	: Bragg angle
$\text{\AA}$	: Angstrom
$a_B$	: Bohr radius
$\mathbf{b}$	: Reciprocal scattering vector
$D$	: Fine structure constant
$d$	: Inter planer distance
$d'$	: Cluster size
$e$	: Electron charge
$E_g$	: Band gap
$g$	: $g$ - factor
$\mathbf{H}$	: Applied magnetic field
$h$	: Planck's constant
$ A $	: Hyperfine coupling constant
$L$	: Spherical cluster size
$m_e$	: Reduced mass of electron
$m_h$	: Reduced mass of hole
$\text{nm}$	: Nanometer
$\Delta H$	: ESR spectral line width
$\beta$	: Full width at half maxima
$\beta_e$	: Bohr magneton for electron
$\beta_N$	: Nuclear magneton
$\varepsilon$	: Dielectric constant

$\nu$  : Frequency of radiation

$\tau_{\text{DNC}}$  : Life time of DNC

## PREFACE

There is a growing interest in the semiconductor nanoparticles for the past few years. Semiconductor nanoparticles also known as *semiconductor clusters*, *quantum particles* or *quantum dots* form a special class of new materials for which size dependent properties are observed. Size dependent properties occur when the size of the particles is comparable or smaller than Bohr radius of exciton for that material. For most of the semiconductors the Bohr radius is few nanometers. Therefore nanoparticles of interest are in the span of a few nanometers. Synthesis and investigations of nanoparticles is therefore considered to be a difficult task as analysis methods for the bulk material often fail in case of nanoparticles. Nevertheless due to their novel optical and electronic properties observed so far many groups all over the world have undertaken research programmes on nanoparticles.

Our group in the Department of Physics, University of Pune also has been interested in the research on nanoparticles. Some work on oxide nanoparticles as well as semiconductor nanoparticles has been pursued for last few years.

In this thesis work on undoped zinc sulphide and Mn, Fe, Ni and Pb doped zinc sulphide nanoparticles will be presented.

The thesis will begin with a general introduction of the subject. It will give some ideas about nanoparticles in general and current status of the subject, specially of semiconductor nanoparticles.

The thesis is divided into four chapters.

The first chapter will cover the theory of semiconductor nanoparticles and give a review of work on zinc sulphide nanoparticles.

The second chapter will deal with the '*experimental*' part. There are large number of methods now to synthesize nanoparticles with some advantages and disadvantages. A chemical method in which the zinc sulphide nanoparticles in the size range of 1 to 5 nm are stabilized using organic molecules has been adopted in this work and described. Advantages of this method are relative simplicity, inexpensiveness, short synthesis time *etc.* whereas disadvantages are low thermal stability and need of depositing on some substrate if they are to be used in making some device. This forms then another step. However due to steric hinderance offered by the organic molecules, the particles do not coalesce to form bigger molecules. This chapter discusses the synthesis route in depth. Doping of the particles also forms a major part of work and has been described. As mentioned in the beginning characterization of nanoparticles is quite a difficult task. Therefore several techniques need to be judiciously employed in order to unambiguously understand their properties. In this chapter various techniques like UV absorption spectroscopy, X-ray diffraction, photoluminescence, atomic absorption spectroscopy, electron spin resonance and photoelectron spectroscopy used in this work are described. Principles are briefly stated and the schematics of the instrumentation is presented so that scope and limitation of the results obtained is understood well.

Chapter three forms the major part of the thesis. The experimental work carried out and interpretation of the data obtained from this work will be presented here. Initially, the results of undoped zinc sulphide nanoparticles of various sizes will be discussed. As mentioned earlier these particles are stabilized using organic molecules. The molecules used in the synthesis have a thiol group at one end which interacts with zinc sulphide perhaps through the sulphur end. Thermal stability of the

particles has been investigated and given in details.

Further the work on doped zinc sulphide nanoparticles will be described. Zinc sulphide even in the bulk form is known to be a *phosphor* material and is widely used in display screens. When some metal ions are incorporated fluorescence is known to occur in different regions of visible spectrum producing violet, green, yellow, red *etc.* light. Different colour shades and brightness also can be obtained. This makes zinc sulphide a widely used phosphor material. Here an attempt is made to see how doped nanoparticles will behave. Thus effect of dopants, their concentration, synthesis parameters *etc.* has been thoroughly investigated and their effect on luminescence properties studied. In case of manganese doped zinc sulphide an attempt is made to give a model about effect of manganese concentration on photoluminescence. Quenching effect due to iron and nickel dopants has been observed and discussed to some extent. Effect of lead doping also has been investigated to a good length. All these results are discussed in view of the current literature on the subject. This chapter ends with a conclusion of the work.

The work carried out so far has raised many new questions. Chapter four outlines some of these possibilities under the heading of 'scope for future work'.