CHAPTER 8
CONCLUSIONS AND SCOPE FOR THE FUTURE WORK
8.1 SUMMARY AND CONCLUSIONS

The present thesis is centered on the synthesis and characterization of pure SnSe synthesized at different temperature and copper doped SnSe nanoparticles at different copper concentration. This work is based on the analysis of properties of nanoparticles or behaviour which includes structural, surface morphological, elemental confirmation, electrical, dielectric, optical and thermal characterization.

Chapter 1 constitutes the basis for the literature survey and the choice of the present problem. Doped semiconductor nanoparticles chalcogenide has been discussed in which metal ion is doped in semiconductor nanoparticles. How different properties of the material changes when material is in nanoform.

Pure SnSe nanoparticles synthesized at different synthesis temperature (i.e. 200, 300 and 400 °C) and copper doped SnSe nanoparticles (i.e. 0.001, 0.01 and 0.1 % copper concentration) have been synthesized by using aqueous solution technique. The synthesis condition or parameters used for synthesis experiment has been discussed in chapter 2. Further nucleation and growth mechanism has been discussed in detail with required mathematical relations.

Chapter 3 includes X-ray diffraction (XRD), Scanning electron Microscopy (SEM), Energy dispersive analysis of X-rays (EDAX), Transmission electron microscopy (TEM), and electron diffraction photography of all the pure and copper doped SnSe nanoparticles. EDAX report obtained for all the pure and copper doped SnSe nanoparticles sample under investigation. Polycrystalline nature of few as synthesized nanoparticles samples has been confirmed from electron diffraction photographs. The structural characterizations of pure SnSe
nanoparticles synthesized at different synthesis temperature (i.e. 200, 300 and 400 °C) and copper doped SnSe nanoparticles (i.e. 0.001, 0.01 and 0.1 % copper concentration) were carried out using the XRD technique which is briefly described in chapter 3. From the evaluated lattice parameters of all these pure and copper doped SnSe nanoparticles, it was observed that they possess orthorhombic crystal structure. The effect of synthesis temperature of pure SnSe nanoparticle (at different synthesis temperature) as well as the effect of copper doping (at copper doped SnSe nanoparticles at different copper concentration) on lattice parameters, unit cell volume and X-ray density has been investigated. Surface morphological features of all these pure and copper doped SnSe nanoparticles had presented using SEM and TEM has been used for particle size estimation.

The high temperature electrical resistivity and dielectric measurement on these nanoparticles has been reported in chapter 4. It was observed that for pure SnSe nanoparticles and all copper doped SnSe nanoparticles, resistivity decreases with the temperature which indicate that the semiconducting behavior of all these nanoparticles. The activation energy for all the nanoparticles has been calculated in different temperature range. The effect of synthesis temperature of pure SnSe nanoparticles (at different synthesis temperature) as well as the effect of copper doping (at copper doped SnSe nanoparticles at different copper concentration) on energy of activation has been investigated and this type of effect or behaviour has been supported by appropriate discussed many reported work.

In this chapter, variation of capacitance (C), dielectric constant, loss tangent (tan δ), a. c. conductivity (σac) and the real (εr) and imaginary part of dielectric constant (εi) of pure SnSe nanoparticles synthesized at
different temperatures and copper doped SnSe nanoparticles at different copper concentration level with a frequency range of 1 Hz to 1 MHz. The a. c. conductivity value obtained for copper doped SnSe nanoparticles is compared with that of pure SnSe nanoparticles synthesized at different temperatures. It is found from this chapter 4 that the conductivity of all copper doped SnSe nanoparticles samples is higher than that of the as prepared undoped or pure samples/ pellet of SnSe nanoparticles synthesized at different temperatures. Further, by increasing doping level of concentration/ content, or copper, in SnSe nanoparticles as well as by increasing synthesis temperature of pure SnSe nanoparticles, a. c. conductivity is increased and hence, energy of activation ($E_a$) is decreased.

Chapter 5 contains detail information of size quantization in the semiconducting nanoparticles. Quantum confinement effect of 1D, 2D and 3D nanostructure as well as effective mass approximation has been discussed with required mathematical formulae.

Chapter 6 includes study of optical properties of SnSe nanoparticles at different synthesis temperatures (200, 300 and 400 °C) and copper doped SnSe (at 0.001 %, 0.01 % and 0.1 % M concentrations of copper) nanoparticles within the wavelength range 200 nm to 2000 nm. The effect of synthesis temperature of pure SnSe nanoparticles (at different synthesis temperature) as well as the effect of copper doping level (at copper doped SnSe nanoparticles at different copper concentration) on energy of the direct band gap has been investigated. This type of effect or behaviour has been supported by appropriate discussed many reported work. Optical parameters such as transmittance ($T$), reflectance ($R$), refractive index ($n$) and extinction coefficient ($k$) determined of all the said nanoparticles and represented as a function of wavelength under the investigation. Effective Mass
Approximation (EMA) is used to calculate particle size of pure SnSe and Cu doped SnSe nanoparticle form. Similar type of effect of synthesis temperature of pure SnSe nanoparticles (at different synthesis temperature) as well as the effect of copper doping level (at copper doped SnSe nanoparticles at different copper concentration) on particle size from optical absorption spectra were observed for that of crystallite size obtained from X-ray diffraction technique as well as particle size obtained from TEM photography has been investigated.

Chapter 7. Thermal characterization of all the pure and copper doped SnSe nanoparticles has been understood in detail from chapter 7. This includes past reports on size dependant melting point and other thermal properties of different metal nanoparticles. The effect of synthesis temperature and copper doping concentration on weight losses from TGA curve along with DTA peaks position of all the pure and copper doped SnSe nanoparticles has been investigated. Similarly effect of temperature and copper doping effect on thermal parameters e.g. energy of activation (E_a), Arrhenius or frequency factor (A), change in entropy (∆S), change in enthalpy (∆H) and Gibbs mean free energy (∆G) of all the pure and copper doped SnSe nanoparticles has been presented by employing Broido and Coats-Redfern (C-R) in this chapter.

8.2 SCOPE FOR THE FUTURE WORK

Semiconducting materials in nanostructures form remain an extensively investigated subject in current Physics (nanoscience, nanotechnology, materials science and solid state physics) and Chemistry. Most of the promising technological applications deals with size dependant properties. The binary IV-VI compounds form a significant group of semiconductors, besides IV group elements and III-V compounds, but the attention paid to them has not been by far so great
as in the case of latter two group of materials. Among these IV- VI compounds there are two important families of materials, especially those with cubic rock salt structure (PbS, PbSe, PbTe, SnTe) and those with distorted rock salt structure of the orthorhombic space group namely GeS, GeSe, SnS and SnSe. The nanostructures particularly PbSe, CdSe, CdS and PbS have been studied intensively, whereas little attention has previously been paid to the materials of the second group.

The ability to manipulate matter at the atomic scale bears promise to produce devices of unprecedented speed and efficiency. The emerging area called nanoscience and nanotechnology which has seen phenomenal growth in the past decade and is likely to be the frontal area of research for the next few decades. The outcome of this research is likely to revolutionize technology. Nanotechnology is based on the fact that some structures usually smaller than 100 nm have new properties and behaviour that are not exhibited by the bulk matter of the same composition. This is because particles that are smaller than the characteristic lengths associated with the specific phenomena often display new physics and new chemistry that lead to new properties that depend upon size. Perhaps one of the most intuitive effects is due to the change in the surface to volume ratio. When the size of the structure is decreased, this ratio increases considerably and the surface phenomena predominate over the chemistry and physics of the bulk. So it is important to design and to control better in the fabrication of devices, sensors, LED's, LASER's, because nanoscience deals with new phenomena and new sensor devices may being built that take advantage of these problems.

From the introductory chapter, author has shown that almost all the properties (electrical, optical, mechanical, magnetic, dielectric and thermal) of nanoparticles strongly depends on particle size or crystallite
size or grain size. It means that in order to control all of these physical properties of the nanoparticles, particle size should be tuned or changed. Further particle size can be controlled by using synthesis parameters of appropriate synthesis technique. Here author used aqueous solution technique/ sol gel technique to synthesize SnSe and Copper doped SnSe nanoparticles. In order to get range of different particle size of this compound, author has synthesize this nanoparticles at 200, 300 and 400 °C temperatures for constant duration (i.e. 2 hour). By changing this duration, one can control particle size. Few work reported that if these samples are characterized after few days or few months, particle size has been increased. In this investigation, no capping agents were used. Actually particle size also depends on nature of capping agents as well as proportion of this.

Doping elements as well as proportion or concentration of the dopant controls lattice parameters and particle size. Increment or decrement of particle size depends on the atomic radius/ ionic radius of host and that of the dopant element. In present work, decrement in lattice parameter by increasing copper concentration in copper doped SnSe nanoparticles or by introducing copper doping in pure SnSe nanoparticles, is because atomic radius of Cu$^{2+}$ (135 pm) is almost similar to that of Sn$^{2+}$ (140 pm). But the ionic radius of Cu$^{2+}$ (87 pm) is less than to that of Sn$^{2+}$ (140 pm), which may enable copper to substitutionally replaces Sn in the SnSe nanoparticles lattice. Similarly Iron Fe, Cobalt Co, Nickel Ni, or other types of magnetic or nonmagnetic dopant can be used based on atomic radius of the host atom and that of the dopants element as that of this present investigation.

It should be noted that here we use ferromagnetic element as a dopant i.e. copper, but magnetic properties of this as synthesized nanoparticles has not been studied like that by using VSM. So one can
conclude by doing that magnetic properties of as prepared ferromagnetic dopants depends on the particle size as well as the nature of the dopants that which dopant has been used.

Here in presented work, pure SnSe nanoparticles were subjected to 200, 300 and 400 °C temperature, so it was possible to study the effect of the particle size of these pure SnSe nanoparticles on structural, electrical, dielectrical, optical and thermal characteristics. But copper doped SnSe nanoparticles (i. e. 0.001, 0.01 and 0.1 % copper concentration doped) were prepared at only room temperature. Hence as a future scope of this, one can synthesize all these copper doped SnSe nanoparticles as 200, 300 and 400 °C temperature and find the effect of particle size on all the mentioned properties of these copper doped SnSe nanoparticles.

Actually our group has also synthesize pure SnSe single crystal by Vapor transport technique as well as Copper doped SnSe single crystal at different copper concentration level. So one can easily make a comparison of the structural, electrical, dielectric, optical and thermal properties obtained from bulk SnSe/ single crystal form prepared by Vapor transport technique and SnSe nanoparticles prepared by aqueous solution technique.

High pressure characterization of as synthesized pure SnSe and copper doped SnSe nanoparticles can be studied. Because according to author knowledge, no report or rare publications has been made which reports on high pressure studies of IV- VI compounds especially on SnSe or Copper doped SnSe or any used dopant in nanoparticle form not in bulk or single crystals form. It is clear from the bulk compounds study that all the properties of the materials can be changed by employing the material under high pressure. So particularly for these pure and copper
doped SnSe nanoparticles, high pressure study may show that all the structural, electrical, dielectrical, optical and thermal characteristics will be change.

In present thesis, UV VIS NIR absorption spectrophotoscopy had been presented and analyzed as optical characterization of as synthesized pure and copper doped SnSe nanoparticles. One can expand optical characterization of as synthesized nanoparticles by employing Photoluminiscence (PL) Spectroscopy, Raman Spectroscopy and FTIR Spectroscopy.

From PL spectra analysis, band structure related information like energy gap, excitons, band off state and band tails can be investigated. Further impurities and defects related information like their types and concentration as well as trapping efficiency can be achieved.

From the Raman Spectroscopy of these nanoparticles, impurities and defects related information like their types and concentration can be studied. Further free carrier concentration related information like, free carrier density and carrier mobility value can be obtained.

Here high temperature resistance measurements had been presented as electrical characterization of as synthesized pure and copper doped SnSe nanoparticles. It is clear that Hall effect measurement of these pure and copper doped SnSe nanoparticles has not presented in thesis hence one can expand electrical characterization by this. From this free carrier concentration related information like, free carrier density and carrier mobility value can be obtained. And these obtained values can be compared with that of the Raman Spectroscopy analysis.
Thermoelectric power (TEP) measurements can be obtained on these nanoparticles samples. From this variation of Thermo electric power with temperature can be obtained and one can confirms the semiconducting nature of all nanoparticles samples as well as from positive or negative value of Seebeck coefficient that these nanoparticles posses p- type or n- type conductivity.

In presented thesis, thermal characterization of pure and copper doped SnSe nanoparticles had been achieved by employing Thermoanalytical techniques, viz. TGA and DTA and Broido and Coats-Redfern (C- R) methods or models. One can expand this thermal characterization by including two more thermoanalytical model i. e. Horowitz- Metzger (H- M) and Piloyan- Novikova (P- N) model. And by doing this one can evaluate different thermal parameters viz. activation energy, entropy, enthalpy, Gibbs mean free energy etc, of as synthesized nanoparticles and these parameters can be compared with that of Broido and Coats- Redfern (C- R) methods or models.