5. Conclusions

In this chapter the salient features of current work on soft-solution synthesis and characterisation of silver chalcogenides will be summed up. This work serves as an initial step towards exploring the optimum experimental conditions for synthesising silver chalcogenides under soft-solution method. The known three low temperature materials of the silver chalcogenides such as acanthite, naumannite and hessite are the main phases focused in the present work.

Most of the previous studies on these phases are mainly focused on studies like

- Morphological variants in the phases with respect to the starting material and effect of chelating agents.
- Optical bandgap studies and its applications to NIR emission and absorption spectral studies.
- Besides the optical bandgap studies for powder and bulk material, thin films were also characterised for its electrical conductivity measurements coupled with optical bandgap variations.

Though there are many more reports on the above mentioned studies on silver chalcogenides, there are greater inconsistencies in $E_g$ values reported for these materials. Hence the present work is intended to make more systematic studies pertaining to synthesis at moderately low P-T conditions employing soft solution processing and an exhaustive study on experimental and theoretical determination of the band structure was undertaken. This was possible due to the availability of density functional theory packages which have highly sophisticated functional algorithms to treat even non-metallic or semiconducting structures.
The following are the salient outcome from the present work

- We could successfully synthesise all the three members of the silver chalcogenides employing soft-solution processing.

- If Water alone is used as a solvent to stabilise the silver chalcogenides, it is difficult to obtain crystalline material. However in order to obtain well crystalline phases of silver chalcogenides attempts were made to use acidic and alkaline solvents but besides stabilising the silver chalcogenide phases either excess silver of or chalcogen is found to co-exist.

- The pure phases of silver chalcogenides could be produced by using isobutanol for the synthesis of acanthite, ethyl alcohol for naumannite and hydrazine dihydrochloride for the synthesis of hessite.

- Beside synthesising low temperature forms of silver chalcogenides attempts were made to Stability high temperature forms of silver chalcogenides by employing hydrothermal Roy-Tuttle test tube type autoclaves in the P-T Range of 533-753 K and 80-130 MPa respectively.

- All the phases synthesised were characterised by x-ray diffraction studies for phase identification and structural details.

- Morphological studies revealed that the size development of homogenous phase of the acanthite is proportional to the duration and the amount of isobutanol used in the experiments while the duration played an important role in obtaining well crystalline naumannite phase which is independent of the amount of solvent used.
• The bandgap energy of polycrystalline silver chalcogenides was determined. It is significant to note that there is a direct relationship between bandgap energy and density of the material.

• The bandstructures were constructed for the entire low temperature silver chalcogenide samples and found that acanthite phase is a semiconducting material with bandgap energy of around 1.15 eV while naumannite and hessite have a very narrow bandgap which is less than 0.1 eV.

• In all the materials it was observed that p and d orbitals associated with silver and chalcogen respectively plays a very important role in determining the bandgap behaviour in such materials.

• It has been established in the present work, the inconsistency over the reported bandgap energy value could be overcome by obtaining the consistent bandgap energy value for the naumannite synthesised employing soft-solution method. Thus the soft solution synthesis method of forming naumannite is one of the best approaches in obtaining a constant bandgap energy which remained around 0.06 eV.

• It was possible to successfully overcome the inconsistencies noticed from the reports of the earlier workers in the determination of bandstructures and bandgap energy values of hessite, the choice of suitable DFT functional algorithm while simulating the energy bandgap structure of hessite.
Scope for future work

With the above said salient results of the present work there are some more aspects which have to be treated in a very detailed manner paving a way for further investigation on silver chalcogenides.

- One of the main aspects derived from the present work on the synthesis of silver chalcogenides is the use of isobutanol, hydrazine dihydrochloride as solvents to obtain well developed crystalline phases which indicates to further explore to produce single crystal materials for specific applications.

- There is ample scope for producing the silver chalcogenide variants by doping with other noble metals after careful theoretical simulation studies and establishing the possibility of tuning the bandgap for specific applications.

- Stabilisation of high temperature phases of silver chalcogenides and other associated metastable phases for characterising the ionic conductivities of these materials.