CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 SUMMARY

Literature survey on the growth, properties and applications of II-VI, I-III-VI$_2$ and CdIn$_2$S$_4$ compound semiconductors has been made. The survey showed that these crystals have relatively higher melting points and exhibit higher vapour pressure. The later is due to presence of chalcogen group elements such as S and Se. In addition, they undergo one or more number of solid state phase transitions from their melting points to room temperature. Though the growth of these materials from their melt is difficult, the CVT technique has been found to be a suitable method to grow single crystals of these compounds at temperatures lower than their melting points.

II-VI compounds such as CdS and ZnSe have been studied because of their wide range of applications especially as substrate materials in making devices. A thermodynamical model has been introduced for predicting optimum temperature for growth of CdS single crystals by CVT technique using iodine as the transporting agent. Single crystals of CdS have been grown in different experimental conditions. A good agreement has been observed between the results of our experiments and prediction of theoretical analysis. The crystals grown at predicted optimum temperature showed better optical quality and morphological perfection compared to those grown in some other temperatures. Single crystals of ZnSe have been grown by CVT technique in different experimental conditions including different undercooling values and stability of the temperature at the growth
interface. The structural and microstructural analysis were carried out for the grown crystals. The grown crystals showed cubic and hexagonal structures with various morphologies such as pyramidal, hexagonal and tetragonal. Different microstructures such as microsteps, spirals and kinks have been observed on the surface of the as-grown crystals using optical microscope and scanning electron microscope. It was observed that surface of the crystals grown with higher undercooling are rough compared to the surface of the crystals grown with lower undercooling. This roughening of crystal surfaces was discussed in correlation with the inconstancy of flow of material migrating from source zone to the growth zone and also to the different mechanisms such as diffusion and convection involved in the mass transport. Single crystals of CdIn$_2$S$_4$ have been grown by CVT technique and crystals with reasonable size and good optical quality of their natural faces have been obtained.

I-III-VI$_2$ compound semiconductors has been investigated because of their possible applications in different areas such as solar cells, nonlinear optical devices, visible and infrared light emitting diodes and optical parametric oscillators. In the present investigation single crystals of CuInS$_2$, AgGaS$_2$, AgGaSSe and new pentenary compound Cu$_{0.5}$Ag$_{0.5}$InSSe have been grown by CVT technique. The structural studies have been carried out for the grown crystals using different X-ray analysis methods such as powder diffraction and computer aided single crystals X-ray diffraction. Results have shown that all the grown crystals have tetragonal chalcopyrite structures with lattice parameters close to those of the reported values. Optical band gap and electrical properties of the CuInS$_2$ single crystals have been measured by using optical transmission, four probe and Hall measurements. The as-grown crystals were found to be p-type and they were changed to p-type by proper annealing in sulphur atmosphere. The crystals were grown in needle and platelet shapes and their more developed (112) faces. The microscopic investigation has been carried out on the surface of the as-grown crystals which showed different microstructures such as
microsteps and hillocks. This study revealed that crystals are grown by layer-by-layer growth mechanism.

The optical properties of crystals grown by CVT technique have been studied using optical transmission, Raman scattering, Infrared reflectivity and photoluminescence measurements. Raman scattering studies on ZnSe single crystals have shown that these crystals are good quality and morphologically well structured. The optical transmission measurement showed that there is an absorption edge at 2.55 eV due to a deep impurity band nearly 0.15 eV below the conduction band. The photoluminescence emission spectra of the crystal have been measured for its temperature dependence as well as for excitation energy dependence. The photoluminescence has been found to be in accordance with a donor-acceptor complex formation involving iodine activated donors and self-activated acceptors. The iodine which is used as the transporting agent incorporates effectively as a donor in lattice of the growing crystals and produces donor-activated centres and changes the optical properties of the grown crystals. The configuration coordinate model has been used to explain the temperature dependent changes in the peak position and the bandwidth of the emission band. The decrease in luminescence efficiency with increasing temperature has been explained by using a simple model for thermal quenching. The activation energy at low temperature range (T<200 K) has been found to be different from that at high temperature range (200K<T<300K). The optical properties of the CdIn₂S₄ single crystals have been determined by optical transmission, Raman scattering and Infrared reflectivity measurements. The grown crystals showed an absorption edge at 2.16 eV slightly lower than the reported direct energy gap for this material. The Raman and IR active modes observed for this crystals agreed with literature and appearance of a new peak and shift in position of one of the peaks have been discussed to be due to cation disordering in the lattice of these crystals.
Mechanical properties of the II-VI as well as I-III-VI$_2$ compounds were studied using Vickers microhardness test. The effect of hydrogen pressure on the mechanical properties of CdS single crystals grown with hydrogen transport technique has been studied. Results showed that by the increase in hydrogen pressure, the hardness and fracture toughness of these crystals decrease. The decrease in hardness has been discussed based on reduction in density of point defects which is in agreement with optical absorption measurements for these crystals. The mechanical properties of some I-III-VI$_2$ single crystals such as CuInS$_2$ and Cu$_{0.5}$Ag$_{0.5}$InSSe have been studied using Vickers microhardness test. This study showed that I-III-VI$_2$ compounds are harder than other compounds such as II-VI due to their covalent bond and Vickers microhardness test also revealed anisotropy in hardness of CuInS$_2$ single crystals.

6.2 SUGGESTIONS FOR FUTURE WORK

The optical absorption measurements on the CdS single crystals grown by hydrogen transport in different hydrogen pressure atmosphere show lower absorption in the visible and NIR regions for these crystals. Though the hydrogen can be used as a proper transporting agent for the growth of other compounds by CVT technique which has several advantages including less contamination of the grown crystals from the transporting agents.

The growth of pentenary Cu$_{0.5}$Ag$_{0.5}$InSSe by CVT technique can be extended to the other classes of multinary I-III-VI$_2$ compounds in order to grow single crystals with tuned lattice parameters and optical band gap for device applications. More understanding about the thermodynamic of the growth of multinary I-III-VI$_2$ compounds will be useful in optimizing the growth conditions to improve the quality of the grown crystals. The methods such as using seed crystals or TVTP can be adopted to improve the size of the these crystals grown by CVT technique.