This chapter presents the summary and conclusions drawn from the present work. The influence of different additives such as Lead, Tin, Bismuth and Selenium on the phase transformation, structure, optical and electrical properties in the Ge$_{22}$Sb$_{22}$Te$_{56}$ system have been studied.

5.1 Summary and conclusion

Conventional melt quenching technique was used to prepare the bulk samples of four different systems Pb$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$ ($x = 0, 1, 2, 3$), Sn$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$ ($x = 0, 2, 4, 6$), Ge$_{22}$Sb$_{22-x}$Bi$_x$Te$_{56}$ ($x = 0, 2, 4, 6$) and Ge$_{22}$Sb$_{22}$Te$_{56-x}$Se$_x$ ($x = 0, 2, 4, 6$) kept at 1000°C for 48 hours and then cooled using two different methods; (i) The ampoule was rapidly quenched in ice cold water (for Pb$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$), (ii) Furnace Cooling was done by switching off the furnace keeping ampoule inside (for Sn$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$, Ge$_{22}$Sb$_{22-x}$Bi$_x$Te$_{56}$ and Ge$_{22}$Sb$_{22}$Te$_{56-x}$Se$_x$ ). The bulk alloy thus obtained was used to grow the thinfilms. The structure, electrical properties and spectroscopic analysis have been performed in view of their applications in the phase change memories and various conclusions drawn from the work are summarized below:

1. The effect of preparation of initial bulk samples by two different techniques such as melt quenching and furnace cooling, the XRD patterns show the amorphous nature of the as-prepared films and the composition of the thin film was verified using EDAX. These results for the as grown films have been compared and later technique for the bulk sample synthesis was found to exhibit similarity in composition with that of the bulk sample.

2. Differential Scanning Calorimetry (DSC) studies have been performed on the Pb$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$($x = 0, 1, 2, 3$) system at a heating rate of 12°C min$^{-1}$. The effect of Lead addition on the crystallization temperature and melting temperature in the GeSbTe alloy has been investigated. The crystallization temperature was found to remain constant but the melting temperature corresponding to Ge$_2$Sb$_2$Te$_5$ phase decreases with the increase in Pb content. This decrease in the melting temperature may lead to decrease in the energy required to transfer crystalline state to amorphous state. Thus, addition of Pb must effectively decrease the energy required during writing an amorphous mark. A constant crystallization temperature with Pb addition indicates that the energy required during erasure may remain constant.
3. Only one phase transformation temperature is observed in temperature dependent sheet resistance measurements on the thermally evaporated Pb$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$($x = 0, 1, 2, 3$) thin films. The phase transformation temperature obtained for these thin films was found to increase slightly with Pb addition.

4. Microstructural analysis based on XRD measurements reveals that substitution of Ge by Pb leads to decrease in the Ge$_2$Sb$_2$Te$_5$ phase. Pb enters the Ge$_2$Sb$_2$Te$_5$ lattice and Ge/Sb ratio is observed to decrease with Pb addition. Formation of the PbTe phase in Pb rich compositions indicate that it might be filling the empty Ge positions by making less strong bonds with Te and thus responsible for decrease in melting temperature.

5. The marginal decrease in optical contrast with Pb addition is observed which is still close to 20% as earlier reported for Ge$_2$Sb$_2$Te$_5$ thin films.

6. The value of lattice parameter determined from the X-ray diffraction data for NaCl type fcc structure of Pb$_0$Ge$_{20}$Sb$_{22}$Te$_{56}$ is 6.002 ± 0.004 Å which is in good agreement with the reported value for undoped Ge$_2$Sb$_2$Te$_5$. For Pb$_{1.6}$Ge$_{19}$Sb$_{26}$Te$_{54}$, Pb$_3$Ge$_{17}$Sb$_{28}$Te$_{53}$ and Pb$_5$Ge$_{12}$Sb$_{28}$Te$_{55}$ films the value of the lattice parameter is determined to be 6.066 ± 0.001, 6.112 ± 0.005 and 6.185 ± 0.009 Å respectively, which is marginally higher than that for the undoped GST.

7. The values of optical band gap obtained for Pb$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$($x = 0, 1, 2, 3$) thin films decreases with Pb addition. However, the changes are only marginal.

8. Phase transformation temperature was found to increase with Sn addition for Sn 2 and 4 at% and decreases slightly for higher concentration of Sn.

9. Samples with Sn dopant compensate the disorder at lower Sn concentrations. Since reduction in disorder always lead to more stable state, thus resulting composition would be more stable, which is reflected in the higher value of phase transformation temperature in case of Sn 2 & 4 at% as compare to pure GST. Although for Sn 6 at% the phase transformation temperature is towards somewhat lower side.

10. The lattice parameter for composition Sn$_2$Ge$_{20}$Sb$_{22}$Te$_{56}$ is determined to be 6.022±0.004 Å, which is a little larger than 6.014±0.016 Å for pure Ge$_{22}$Sb$_{22}$Te$_{56}$. Earlier studies reported the values of lattice parameter between 5.988 ± 0.008 Å and 6.027 ± 0.005 Å for pure Ge$_{22}$Sb$_{22}$Te$_{56}$. For compositions Sn$_4$Ge$_{18}$Sb$_{22}$Te$_{56}$ and Sn$_6$Ge$_{16}$Sb$_{22}$Te$_{56}$ the values of lattice parameters determined are 6.021±0.022 and 6.043±0.018 Å respectively. It is evident that the lattice parameter increases with the
increase in Sn concentration. Thus, the lattice parameters of the alloy will expand due to Sn doping.

11. The first abrupt drop close to ~115 °C in the temperature dependent sheet resistance measurement corresponds to the transition to a NaCl-type structure and the second abrupt drop close to ~150 °C corresponds to the transition to a HCP-type structure.

12. The optical band gap for Sn$_x$Ge$_{22-x}$Sb$_{22}$Te$_{56}$($x = 2, 4, 6$) thin films was found to increase marginally up to Sn 4 at% and decrease for higher concentrations.

13. Phase transformation temperature was found to increase with Se addition for Se 2 and 4 at% and decreases slightly for higher concentration of Se.

14. The lattice parameter for composition Ge$_{22}$Sb$_{22}$Te$_{54}$Se$_2$ is determined to be $6.003 \pm 0.016 \text{Å}$, which lies between $5.988 \pm 0.008$ Å and $6.027 \pm 0.005$ Å previously reported values for pure GST. For compositions Ge$_{22}$Sb$_{22}$Te$_{52}$Se$_4$ and Ge$_{22}$Sb$_{22}$Te$_{50}$Se$_6$ the values of lattice parameters determined are $6.008 \pm 0.018$ and $6.013 \pm 0.014$ Å respectively. It is evident that the lattice parameter increases slightly with the increase in Se concentration, although it remains between previously reported values for pure GST. It shows that the lattice parameter doesn’t change with Se doping, which may be due to small size of the Se atom.

15. The first abrupt drop close to ~125 °C in the sheet resistance measurement corresponds to the transition to a NaCl-type structure.

16. Large increase in the optical band gap from 0.54 to 0.75 eV as the content of Se increases from 2 to 4 at%. The increase in the band gap with increased selenium content occurs because the latter creates strong bonding with Ge in comparison to tellurium.

17. Only sample containing Bi 2 at% shows phase transformation, however for higher bismuth concentrations the phase transformation has not been observed and films showed high room temperature conductivity.

18. Two sharp peaks were observed in case of as deposited films with Bi concentration 4 and 6 at%. The peaks were identified as that of BiSb phase. This indicates that these films were crystalline in their as-deposited state.

19. The lattice parameter for composition Ge$_{22}$Sb$_{20}$Bi$_2$Te$_{56}$ is determined to be $a = 6.007 \pm 0.012$ Å. Which lies between $5.988 \pm 0.008$ Å and $6.027 \pm 0.005$ Å previously reported values for pure GST.

20. The optical band gap for composition Ge$_{22}$Sb$_{20}$Bi$_2$Te$_{56}$ is determined to be 0.53 eV. The small decrease in the optical band gap from 0.59 to 0.53 eV as the content of Bi
increases to 2 at%. The decrease in the band gap with increased bismuth content occurs because the latter creates localized states in the band gap.

5.2 Scope for future work

The present work gives a lot of preliminary information about the effect of impurity doping on the composition, structure, optical contrast, optical properties, phase transformation temperature and the comparison of the properties for the different impurity doping in GST. This information can further be utilized for the fabrication of different systems and for more detailed understanding of the selected systems, therefore, some suggested works to further enhance the quality and the knowledge of these systems for their device perspective point can be given below:

1. Local structure of the material and its atomic scale changes during phase transformation should be investigated by X-Ray absorption fine-structure spectroscopy (EXAFS). X-ray absorption near edge structure (XANES) can also be performed for much better understanding of the local structure.

2. Investigations should also be carried out using temperature modulated differential scanning calorimetry (TMDSC), $^{119}$Sn Mossbauer and Raman spectroscopy to reveal the thermal and structural interpretation for the phase transformation process having importance for designing new material properties for future technologies.

3. The a.c. conductivity measurements for some selected compositions should also be performed for having an idea about the variation or type of defects making a part in tailoring the phase transformation phenomena or leading to the improvement in the performance of these materials.

4. The ellipsometric analysis of the optical properties could be performed on Sn/Bi/Se doped GST films for accurately determining the optical constants (viz. optical band gap, refractive index, extinction coefficient) of as-prepared and annealed films could be used for identifying materials suitable for optical data storage.

5. The results of this work are for films grown by thermal evaporation technique. It is difficult control the stoichiometry of the films grown using this technique. However, to be able to fully develop phase change materials with optimal requirements one should fully exploit the stoichiometric phase. However, this can only be fruitful if an efficient criterion for evaluating and developing appropriate stoichiometric composition exists. A correlation between crystallization kinetics and stoichiometric composition could provide suitable information towards the development of new phase change media.