Non-crystalline or amorphous alloys form an important class of materials from the point of view of fundamental condensed matter research as well as technological applications. They differ from their crystalline counterparts by the absence of long-range order. Their interesting electrical, optical and magnetic properties along with the wide flexibility in preparation and composition make them unique in several applications. Like crystalline materials, non-crystalline materials can be ionic, covalent, metallic or van der Waals' bonded materials. Consequently, they can be insulating, semiconducting or metallic in nature.

Amorphous semiconductors can be generally classified into two groups as tetrahedrally coordinated semiconductors like a-Si, a-Ge etc. and chalcogenide semiconductors like Ge-Se, As-Se etc. Chalcogenide glasses contain one or more of the chalcogen elements, S, Se or Te of the sixth group of the periodic table. The four-fold coordination in Si leads to symmetrical bonding and the formation of rigid structures, while the two-fold coordination in chalcogens is highly asymmetrical and the structure gives rise to greater degree of flexibility for interatomic bonds. Like other glassy solids, these materials also possess only short-range order and because of this, the theories developed for crystalline materials cannot directly be applied to them.

Chalcogenide glasses form an important class of amorphous solids. They have very interesting physical properties and can be prepared in the bulk as well as thin film forms. One of the greatest advantages of these glasses is the composition dependent tunability of their properties, which enables one to design materials for
specific requirements. They have potential technological applications such as materials for threshold and memory switching, inorganic photoresist, xerography, IR detection and transmission etc. These materials are suitable for IR optical elements such as cell windows and prisms and as FIR beam condensers, splitters and other accessories, since they do not absorb IR radiation. Many of these glasses can be formed by the conventional melt quenching technique over a wide composition range making them suitable model systems for systematic studies on composition dependent properties.

In order to explain the features observed in the composition dependence of various properties of chalcogenide glasses, various models like random network models and topological models have been proposed. According to the chemically ordered covalent network (COCN) model, heteropolar bonding is maximized, thereby favouring chemical order. Topological models use the concept of average coordination number $Z$ and interpret the properties of chalcogenide glasses in terms of $Z$.

It has long been known that intrinsic chalcogenide glasses behave like $p$-type semiconductors and are insensitive to ‘doping’ in small amounts. This behaviour is attributed to the local valence saturation of the dopant atoms. Fermi level is considered to be pinned due to the equilibrium between positively and negatively charged defect states, known as valence alternation pairs (VAPs). The presence of a large number of defect states in the band gap makes them normally insensitive to impurity doping. However, of late, it has been found that the addition of heavy elemental metallic impurities like Pb or Bi to Ge-Se glasses or Pb to In-Se glasses can enter the network as charged species, alter the concentration of VAPs and
consequently change the conduction type from $p$ to $n$-type at a certain composition. This discovery has led to extensive research on these materials and to a reconsideration of the existing theories of electronic structure of chalcogenide glasses. The $p$ to $n$-type change over or carrier type reversal (CTR) gets reflected in electrical transport properties such as activation energy, thermoelectric power, Hall coefficient etc. We have measured the composition dependence of thermal parameters of Pb doped Ge-Se, Bi doped Ge-Se and Pb doped In-Se systems, which are reported to undergo $p$ to $n$ transition as Pb/Bi doping level is varied, using photopyroelectric (PPE) and photoacoustic (PA) techniques. Specifically, we have measured composition dependence of heat capacity and thermal conductivity across the transition composition. It is found that the thermal parameters show anomalous variations at compositions corresponding to the $p$ to $n$ transition or carrier type reversal. We have also studied the composition dependence of photoconductivity in these systems.

Electrical switching is an interesting property exhibited by certain Te based chalcogenide glasses. It is the rapid and reversible transition between a highly resistive OFF state and a conductive ON state driven by an external electric field and characterized by a threshold voltage. Depending on the material, switching can be of threshold type or memory type. In threshold type switching, the ON state persists only while the current flows, down to a certain holding voltage, whereas in memory type switching the ON state is permanent until a suitable reset pulse is applied. We have measured the variation of thermal parameters in In-Te glass system during electrical switching using PPE technique.
Ge-As-Se is a typical ternary chalcogenide glass system. It has got one of the largest glass forming regions. We have measured the thermal parameters of this system as a function of the average coordination number and studied the effect of various topological thresholds on them.

The thesis is divided into eight chapters. In the first chapter, an overall review of amorphous semiconductors is given. It includes an introduction to chalcogenide glasses, followed by a brief discussion on the important structural models proposed for chalcogenide glasses and their electrical and thermal properties. Photoconductivity, electrical switching and carrier type reversal in chalcogenide glasses are described in detail in this chapter.

Chapter 2 presents a description of the experimental techniques used in the present investigation. Brief description of the PA spectrometer is given. Photoacoustic measurement of thermal diffusivity is described. Simultaneous measurement of thermal conductivity and heat capacity employing photopyroelectric technique is also described. Details of photoconductivity and electrical switching experiments are also given in this chapter.

Pb-Ge-Se system forms homogeneous glass in two series (i) Pb$_{20}$Ge$_{x}$Se$_{80-x}$ ($x = 17 - 24$) and (ii) Pb$_y$Ge$_{122y}$Se$_{58y}$ ($y = 0 - 20$). Both the series exhibit carrier type reversals: series I at $x \approx 21$, and series II at $y \approx 8$. We have measured the thermal parameters as a function of composition in this system. It is found that CTR gets reflected in these measurements. The results obtained are presented in chapter 3 of the thesis. The results are explained in terms of enhancement in carrier concentration during $p$ to $n$ transition.
Bi doped Ge-Se and Pb doped In-Se are two other systems which exhibit carrier type reversal. Bi$_x$Ge$_{20}$Se$_{80-x}$ system exhibits CTR at $x \approx 7$, while Pb$_x$In$_{25-x}$Se$_{75}$ system exhibits CTR at $x \approx 5$. We have measured the variation of thermal parameters as a function of composition in these systems, the results of which are discussed in chapter 4 of the thesis. The results are discussed in terms of the mechanism of CTR already outlined in chapter 3.

Chapter 5 deals with the photoconductivity measurements in Pb-Ge-Se and Pb-In-Se systems. It is found that the $p$ to $n$ transition gets reflected in these measurements. Temperature dependence of photoconductivity is also measured. The results obtained are analyzed in terms of the existing photoconductivity models, correlating them to the mechanism of $p$ to $n$ transition in these systems.

In chapter 6 we report the results of our electrical switching studies on In$_x$Te$_{100-x}$ ($x = 20-40$) glass system that exhibit CTR. We have also measured the variation in thermal parameters of the samples during electrical switching.

Thermal parameters of Ge-As-Se system are reported in chapter 7 of thesis. We have measured the thermal parameters as a function of the average coordination number $Z$. The effects of various topological thresholds on thermal parameters are discussed in this chapter.

Chapter 8 is the concluding chapter incorporating overall conclusions of the work presented in earlier chapters. Further scopes for the work that can be done in this direction on other chalcogenide glass systems are also discussed.
Most of the results presented in this thesis have either been published or communicated for publication in the form of following papers/symposium proceedings.

1. Carrier type reversal in Pb-Ge-Se glasses: photopyroelectric measurement of thermal conductivity and heat capacity

2. Photoconduction in Pb-Ge-Se semiconducting glasses exhibiting carrier type reversal

3. Photopyroelectric determination of thermal parameters across p→n transition in Pb doped Ge-Se glasses
   Analytical Sciences 17 (2001) 599.

4. Thermal conductivity and heat capacity of certain chalcogenide glass systems exhibiting carrier type reversal (communicated).

5. Thermal properties across thresholds in Ge-As-Se glasses (communicated).

6. Thermal conductivity and heat capacity in In-Te glasses during electrical switching (communicated).

Symposium papers presented during the course of work

1. Photoconductivity properties around p→n transition in Pb-Ge-Se glasses

2. Photopyroelectric determination of thermal parameters across p→n transition in Pb doped Ge-Se glasses
3. Carrier type reversal in Pb-In-Se glasses reflected in thermal transport measurements

4. Photoconductivity across $p$ to $n$ transition in Pb-In-Se semiconducting glasses

5. Carrier type reversal in chalcogenide glasses: Some thermal facts and figures

6. Thermal properties across thresholds in Ge-As-Se glasses