S.P.40. MADHUSOODANAN, K.N. – Photoacoustic Investigation of the Optical and Thermal Properties of Selected Amorphous Chalcogenide Semiconductors – 1989 – Dr. Jacob Philip.

Amorphous semiconductors form an important class of materials from the point of view of fundamental condensed matter research as well as technological applications. It has become a frontier area of research during the past two decades. Since these materials, like other glassy solids, possess only short-range order, the theory developed for crystalline materials cannot be applied to them. Eventhough several models and theoretical formulations have appeared in literature, extensive studies are still going on because a clear theoretical understanding of the physics of non-periodic or random systems is yet to be evolved. Several problems in this area still remain unsolved.

Amorphous semiconductors find several applications in electronic and optoelectronic devices such as solar cells, memory and switching elements, imaging technology etc. But the full potential of these materials for technological applications is yet to be completely explored for which a thorough understanding of their properties is essential. The preparation, characterisation and systematic study of the properties of amorphous semiconductors are very important in the light of the above facts.

Our aim has been to investigate systematically the optical and thermal properties of selected bulk chalcogenide semiconducting glasses. We have concentrated our studies on $A^{IV}B^{VI}$ and $A^{V}B^{VI}$ type binary chalcogenides where, $A^{IV}$is a group IV semiconductor atom such as Ge or Si, A^{V} is a group V atom such as As and B^{VI} is a chalcogen atom such as Se or Te. We have used a relatively new technique viz., the photoacoustic (PA) technique for these investigations. The PA technique, which is based on the detection of acoustic signals generated when a sample absorbs modulated light beam and relaxes non-radiatively has proved to be very effective in the study of optical and thermal properties of solids, liquids and gases. Photoacoustic spectroscopy (PAS) is especially powerful in the study of highly absorbing and scattering materials where other conventional spectroscopic techniques often fail. The technique is very convenient to do spectroscopy of amorphous semiconductors as these materials are highly light absorbing and are often in the powder form. We have carried out a detailed and systematic investigation of the optical absorption and thermal transport properties and their composition and temperature dependences in a few selected $A^{IV}B^{VI}$ and $A^{V}B^{VI}$ chalcogenide glasses in the glass-forming range using the PA technique.

One of the important advantages of compound amorphous semiconductors is that they can be prepared over a very wide composition range. Since the physical properties do change with composition, this provides composition dependent tunability of these properties which is helpful for the selection of desired materials for specific applications. Therefore the study of the composition dependent variation of the physical properties such as optical energy gap and thermal diffusivity are very important for these materials. A number of studies, using different techniques, for determining composition dependence of various other physical properties, appeared in literature have provided a great deal of information about the short–range order, the glass-forming tendency of the solid, network stiffening etc. A large percentage of such investigations have been on materials prepared in the thin film form. But not much work has been done on the composition dependence of the energy gap and thermal diffusivity in bulk amorphous semiconductors. Temperature dependence of such parameters have not been reported at all on these materials. The samples have been prepared by the well established melt-quenching technique for bulk samples. A detailed account of the results of the work done by us as mentioned above is presented in the thesis which we are going to submit. In the following paragraphs we give a chapterwise description of the thesis in brief.

The first chapter of the thesis, written in two parts, is an introductory one giving general introduction to the physics of amorphous semiconductors and to the principle and technique of photoacoustic spectroscopy. The first part viz., part-A is devoted to a review of the status of amorphous semi-conductor research and part-B gives a review of photoacoustics and photoacoustic spectroscopy. Here emphasis is given to topics which are relevant to the work presented in the thesis. Preparation, classification and characterisation methods of different types of amorphous semiconductors are briefly reviewed. Some of the interesting properties and theoretical models of these materials are also outlined and discussed. The principle of the photoacoustic effect, its use as an analytical tool and its various applications are presented with special reference to the absorption spectroscopy of semiconducting samples in part B. The necessary theory of the PA effect is also briefly outlined in this first chapter.

Chapter 2 is devoted to the description of instrumentation and the experimental set-up used in the work. The PA spectrometer used in our experiments consists of a 1 KW Xenon lamp, a source monochromator, light beam chopper, lock-in amplifier etc. The PA cell which forms the most important part of the PA spectrometer has been fabricated in our laboratory. A sensitive electret microphone is used to detect the generated acoustic signal. Two cells have been fabricated, one is a small volume non-reasonant cell for room temperature measurements and the other is a Helmholtz resonator type cell for measurements at higher temperatures with which measurements can be made upto 500K. The PA cells are so designed that different backing materials can be used for the sample. Organisation of th PA spectrometer, design and calibration of the cells etc., are described in detail in this chapter.

Chapter 3 deals with the optical absorption studies on $A^{IV}{}_xB^{VI}{}_{1-x}$ binary glassy systems using photoacoustic technique. The systems studied include several compositions in the glass-forming region of Ge_xTe_{1-x} (0.15 < x < 0.28), Si_xTe_{1-x} (0.10 < x < 0.28) and Ge_xSe_{1-x} (0.10 < x ≤m 0.38) glasses. The PA spectra, which is essentially the variation of PA amplitude with incident wavelength, give the optical absorption characteristics of the samples. These are reported for the above three systems. The variation of the optical energy gap, determined from the PA spectra, with the composition parameter x is presented for all the three systems. It is found that the energy gap increases with increase in the concentration of group IV element with a marked change in slope at x = 0.20. In Ge-Se system, in which measurements have been taken for compositions with x upto 0.38, the optical energy gap is found to have a peak value around the x = 0.33 composition which is the stoichiometric composition for these systems. The observed behaviour is explained on the basis of chemical bonding and the change in short range order in the network.

Another system of glass whose optical absorption characteristics we have investigated is the Se_{1-x} system with 0.10 ≤ x ≤0.50. This system belongs to the β^{v} family of chalcogenide glasses. In chapter 4 the PA spectra of these samples are presented and the results are discussed. The variation of the optical energy gap as a function of the composition parameter x shows a minimum at x = 0.40 at which stoichiometric As_2Se_3 glass is formed. An explanation for this behaviour is again given on the basis of the chemical bonding between atoms in the network. Short-range order in the material changes with change in composition and this is explained on the basis of existing models.

The PA technique has proved to be a very effective method for determining the thermal transport properties of solid samples. We have determined the thermal diffusivity of Ge_xTe_{1-x} Si_xTe_{1-x} and Ge_xSe_{1-x} glasses belonging to the $A^{IV}B^{VI}$ system as well as As_xSe_{1-x} and As_xTe_{1-x} glasses belonging to the A^VB^{VI} system by studying the variation of the PA amplitude with chopping frequency using samples of appropriate thickness. The thermal diffusivity is Ge_xTe_{1-x} Si_xTe_{1-x} and Ge_xSe_{1-x} glasses belonging to the $A^{IV}B^{VI}$ system as well as As_xSe_{1-x} and As_xTe_{1-x} glasses belonging to the A^VB^{VI} system by studying the variation of the PA amplitude with chopping frequency using samples of appropriate thickness. The thermal diffusivity is determined from the relation $f_c l^2 = \propto$ where l is the sample thickness and f_c is the characteristic frequency above which the sample is thermally thick. In chapter 5 the results of these measurements on the systems mentioned above are reported. The variation of the thermal diffusivity as a function of the composition parameter x gives evidence for the existence of certain critical compositions in these systems. From the results obtained on the $A^{VI}B^{VI}$ systems it has been possible to establish the existence of stable structures with minimum disorder at x = 0.20 composition. At this composition the thermal diffusivity and consequently thermal conductivity is found to have a threshold maximum value in all the systems studied. Also in Ge_xSe_{1-x} system the thermal diffusivity shows a maximum value again at x = 0.33 where the stoichiometric $GeSe_2$ glass is formed. Also in A^VB^{VI} systems, in the composition range studied, ,the thermal diffusivity has got a threshold maximum value at x = 0.40 which corresponds to the stoichiometric composition for these systems.

In chapter 6 a theoretical explanation for the existence of critical ,compositions in chalcogenide glasses as evidenced by the results presented in the previous chapter is given on the basis of constraints theory and the idea of rigidity percolation in random networks. According to Phillips' theory of non-equilibrium glass formation, the glass-forming composition is optimized mechanically by equating the number of force-field constrains whcih are intact at the glass transition temperature to the number of atomic degrees of freedom. In the glass-forming region the system contains both floppy and rigid regions. The thereshould behaviour in thermal conduction exhibited by $A^{IV}B^{VI}$ and $A^{V}B^{VI}$ glasses is attributed to the mechanical stiffning of the glass network at the critical compostions as a result of the thershoold percolation of rigidity. Considering the central bond-stretching and rotationally invariant bond-bending forces for a binary alloy system A_xB_{1-x} based on the ideas of rigidity percolation and effective medium theory, the critical average coordination number works out to be 2.4 for a 3-dimensional rendom network. This agrees well with our experimental observations which give evidence for the existence of critical composition at $X = 0.4$ for $A^{V}_{x}B^{VI}_{1-x}$ glasses. The value of the average coordination number turns out to be exactly 2.4 at these critical compositons for both the systems.

In chapter 7 we present the results of the PA studies on $A^{IV}_{x}B^{VI}_{1-x}$ and $A^{V}_{x}B^{VI}_{1-x}$ glasses at high temperatures using the high temperature PA cell with which measurements can be done upto$\approx$ 500K. We have measured the variation of the PA signal amplitude and phase with temperature and their chopping frequency and wavelength dependence at various fixed temperatures. From these the temperature dependence of the optical absorption, optical energy gap and thermal diffusivity have been determined. The results obtained above, at and below the glass transition temperature are presented in detail for one representative from the $A^{IV}_{x}B^{VI}_{1-x}$ family viz., Ge_xSE_{1-x} system and for one representative from the $A^{V}_{x}B^{VI}_{1-x}$ family viz., As_xSe_{1-x} system. The absorption is found to depend on temperature and a decrease in the optical energy gap is observed with increase in temperature. A significant decrease in thermal diffusivity is found to occur at the glass transition temperature in all the samples studied. The results obtained form these high temperature studies are presented and discussed in detail in this chapter.

Chapter 8 is the concluding chapter. It incorporates the overall conclusion of the work presented in the earlier chapter. The use of the PA technique as a powerful tool for the study of some of the important physical properties of chalcogenide glasses is emphasised. The importance and relevance of the study of composition dependent variation of such properties is highlighted on the basis of the contents of the thesis. Further scope of work in this direction to investigate the optical and thermal properties of other amorphous semiconductors using PA technique is discussed.

Most of the results presented in the thesis have already been published in the form of about 10 papers in international journals recently.