# PREPARATION AND PROPERTIES OF CHALCOGENIDE GLASSES IN As-Ge-S AND As-Ge-Se SYSTEMS

#### A THESIS

### Presented to

The Faculty of the Division of Graduate

Studies and Research

By

Yogesh Mehrotra

### In Partial Fulfillment

of the Requirements for the Degree Master of Science in Ceramic Engineering

Georgia Institute of Technology

June 1976

# PREPARATION AND PROPERTIES OF CHALCOGENIDE

GLASSES IN As-Ge-S AND As-Ge-Se SYSTEMS

Approved:

Joseph I. Pentecost; Chain	rman
Will; ~	
Aian 1. Chapman	
Date approved by Chairman	Jame 4. 147

#### ACKNOWLEDGMENTS

I wish to express my profound gratitude to Dr. J. L. Pentecost for his encouragement, guidance, advice, and patience during this investigation. I also wish to thank Drs. W. E. Moody and A. T. Chapman for their suggestions while serving on the reading committee and Dr. J. K. Cochran for his interest and assistance in this project.

A special word of thanks is also due to Mr. Thomas Macrovitch for his assistance in the experimental work.

My appreciation is also expressed to Mr. Donald E. Lillie of the Glass Blowing Laboratory and to Dr. Earl Meeks and Messrs. Gerald Hill, James J. Gallagher, and Barry McManus of the Engineering Experiment Station for their valuable assistance in conducting various experiments.

My profound thanks are due to Ms. Kathy D. Browning whose inspiration helped me overcome many difficult moments in this investigation and to Ms. Betty Yarborough for her excellent typing.

### TABLE OF CONTENTS

	Pag	ge
ACKNOWI	LEDGMENTS	ii
LIST OI	F TABLES	v
LIST OI	F ILLUSTRATIONS	ii
SUMMARY	Υ	ix
Chapter	r	
I.	INTRODUCTION	1
II.	REVIEW OF THE LITERATURE	2
TTT	Composition and Glass Formation Structure Physical Properties Phase Separation Optical Properties Electrical Properties	
	Compositions Selected Batch Preparation Glass Melting Ampoule Melting Furnace Glass Melting Property Measurements	30
IV.	RESULTS AND DISCUSSION	55
ν.	CONCLUSIONS	02
VI.	RECOMMENDATIONS 1	05

# TABLE OF CONTENTS (Concluded)

Chapter	r) g		Page
APPEND	ICES		
I.	CHARACTERISTICS OF THE RAW MATH	ERIALS	· 106
11.	TEMPERATURE-VAPOR PRESSURE RELA FOR S, SE, AS, AND GE	ATIONSHIPS	. 107
III.	REPORTED IMPURITY ANALYSIS OF F	AW MATERIALS	. 113
BIBLIO	GRAPHY	**********	• 114

iv

....

### LIST OF TABLES

Table		Page
1.	Compositions of the Eight Chalcogenides	31
2.	Melting Schedule of the Eight Chalcogenide Compositions	37
3.	Remelting Schedule of Compositions VII and VIII	42
4.	Diffraction Peaks in the Experimental Chalcogenide Compositions	56
5.	Indices of Refraction of Five Chalcogenide Compositions	69
6.	Absorption Peaks for Composition I (AS $_2$ S $_3$ )	73
7.	Absorption Peaks for Composition II (As $_2$ Se $_3$ )	75
8.	Absorption Peaks for Composition V (Ge $_{15}^{As} _{15}^{Se} _{70}$ )	77
9.	Absorption Peaks for Composition VII (Ge $_{15}^{As}$ $_{15}^{S}$ $_{70}$ )	79
10.	Reflectivity and Absorption Coefficient of Chalcogenide Glasses	85
11.	Correlation of Index of Refraction, Reflectivity, and Absorption Coefficients	87
12.	D.C. Electrical Conductivity of Composition III vs. Temperature (Using Plexiglas Specimen Holder)	91
13.	D.C. Electrical Conductivity of Composition V vs. Temperature (Using Plexiglas Specimen Holder)	92
14.	D.C. Electrical Conductivity of Composition V vs. Temperature (Using Teflon Specimen Holder)	94
15.	Calculation of Activation Energy (E <sub>cond</sub> )(ev) in the Low-, Medium-, and High-Temperature Range for	0.9
	compositions III and V	90
16.	Characteristics of the Raw Materials	106
17.	Vapor Pressure-Temperature Relationship for Selenium	110
18.	Vapor Pressure-Temperature Relationship for Arsenic	111

v

# LIST OF TABLES (Concluded)

Cable	3	Page
19.	Vapor Pressure-Temperature Relationship for Sulphur	111
20.	Reported Impurity Analysis of As-Recieved Raw Materials by Standard Spectrographic Methods	113

### LIST OF ILLUSTRATIONS

Figur	e	Page
1.	Areas of Glass Formation in Chalcogenide Systems	3
2.	Structural Model of $As_3s_3$	9
3.	Schematic Representation of the Density-of-States N(E) as a Function of Energy	14
4.	Change in Refractive Index of 15 Ge, 15 As, 70 Te Glass When Se is Substituted for Te	20
5.	Refractive Index as a Function of Wavelength	20
6.	Diagramatic Representation of Laser Set up for the Measurement of (A) Angle of Minimum Deviation and (B) Apex Angle of the Wedge	22
7.	Pictorial Representation of Melting Vessels and Their Accessories	33
8.	Diagramatic Representation of Melting Vessels	34
9.	Schematic Representation of Furnace Set Up for Rotational and Non-Rotational Melting	36
10.	Pictorial Representation of the Measurement of	45
11.	Pictorial Representation of the Measurement of Angle of the Wedge	46
12.	Infrared Spectra of Composition I (As $_2$ S $_3$ )	49
13.	Infrared Spectra of Composition II $(As_2Se_3)$	50
14.	Infrared Spectra of Composition V ( $Ge_{15}As_{15}Se_{70}$ )	51
15.	Infrared Spectra of Composition VII ( $Ge_{15}^{As} f_{15}^{S} f_{70}$ )	52
16.	Pictorial Representation of D.C. Conductivity Measurement	53
17.	X-Ray Diffraction Pattern of Composition I (As <sub>2</sub> S <sub>3</sub> )	57

### viii

# LIST OF ILLUSTRATIONS (Concluded)

.

Figur	e		Р	age
18.	X-Ray Diffraction Pattern of Composition II (As <sub>2</sub> Se <sub>3</sub> )	•	•	59
19.	X-Ray Diffraction Pattern of Composition III (Ge <sub>15</sub> S <sub>85</sub> )			61
20.	X-Ray Diffraction Pattern of Composition IV (GeSe)		•	62
21.	X-Ray Diffraction Pattern of Composition V (Ge <sub>15</sub> As <sub>15</sub> Se <sub>70</sub> )			63
22.	X-Ray Diffraction Pattern of Composition VI (Ge <sub>30</sub> As <sub>15</sub> Se <sub>55</sub> )			65
23.	X-Ray Diffraction Pattern of Composition VII (Ge <sub>15</sub> As <sub>15</sub> S <sub>70</sub> )			66
24.	X-Ray Diffraction Pattern of Composition VIII (Ge <sub>30</sub> As <sub>15</sub> S <sub>55</sub> )		•	68
25.	D.C. Conductivity of Composition III (Plexiglas Holder) as a Function of Temperature			88
26.	Conductivity of Composition V (Plexiglas Holder) as a Function of Temperature			89
27.	D.C. Conductivity of Composition V (Teflon Holder) as a Function of Temperature	•	•	90
28.	Temperature-Vapor Pressure Relationship for Arsenic and Germanium		•	108
29.	Temperature-Vapor Pressure Relationship for Selenium and Sulphur		•	109

#### SUMMARY

Eight chalcogenide compositions in the Ge-As-S and As-Ge-Se systems were prepared from high purity starting elements by prolonged heating in fused quartz or pyrex ampoules. In each case, the vapor pressure over the composition was not allowed to exceed three atmospheres. The fused compositions were examined by x-ray diffraction techniques for their crystalline phases.  $As_2Se_3$ ,  $As_2S_3$ ,  $As_{15}Ge_{15}Se_{70}$ , and  $As_{15}Ge_{30}Se_{55}$  were found to form good glasses while  $Ge_{15}Se_{85}$ , Ge Se,  $As_{15}Ge_{15}S_{70}$ , and  $As_{15}Ge_{30}S_{55}$  were crystalline.

Index of refraction of the glasses was measured by the angle of minimum deviation method using a CO<sub>2</sub> laser (10.6 µm). Both in the binary as well as ternary compositions, the index of refraction (n) was found to increase when the heavier chalcogen Se was substituted for S, e.g.,  $n_{As_2Se_3} = 2.77$ ,  $n_{As_2S_3} = 2.38$ .

Infrared transmission spectra of the glasses (except  $Ge_{30}As_{15}Se_{55}$ ), obtained over 2.5 µm - 40.0 µm range, revealed primarily As-O absorption bands. Contribution of Ge-O absorption bands was relatively minor. Oxide impurities were, thus, the primary cause of infrared absorption in all the compositions. The intensity of the absorption bands was found to depend on the particular composition, e.g., at 680-690 cm<sup>-1</sup>, the band was strong in  $As_2S_3$  and weak or very weak in  $As_2Se_3$ . Similarly, the location of the absorption bands varied with the composition, e.g., the strong band in  $Ge_{15}As_{15}S_{70}$  was located at 835 cm<sup>-1</sup> and not at 680-690 cm<sup>-1</sup> as in  $As_2S_3$ . Contrary to the expected behavior, the absorption coefficient (a) showed variation with thickness (t), e.g. for  $As_2Se_3$ , for t = 0.0683 cm,  $\alpha$  = 6.33 cm<sup>-1</sup>, and for t = 0.0891 cm,  $\alpha$  = 5.68 cm<sup>-1</sup>. The cause of this variation could not be ascertained. Also, the absorptivity of the glass was considerably increased when Se replaced S in binary as well as ternary compounds;  $\alpha_{As_2Se_3} = 6.01 \text{ cm}^{-1}$ ,  $\alpha_{As_2S_3} = 0.386 \text{ cm}^{-1}$ ,  $\alpha_{Ge_{15}As_{15}Se_{70}} = 11.47 \text{ cm}^{-1}$ ,  $\alpha_{Ge_{15}As_{15}S_{70}} = 1.63 \text{ cm}^{-1}$ . Besides, reflectivity and absorption coefficient increased with the index of refraction.

D.C. conductivity vs 1/T plot for the chalcogenides Ge15 Se85 and Ge15As15Se70 showed three linear regions, each having a different slope, i.e., the activation energy E cond. For Ge 15 As 15 For 70 in the heating cycle,  $E_{cond}$  (low temperature) = 0.597 ev,  $E_{cond}$  (medium temperature) = 0.228 ev, and E (high temperature) = 0.121 ev. The dc conductivity in the heating cycle was found to be lower than the conductivity in the cooling cycle at the same temperature. This was perhaps due to the non-equilibrium conditions prevailing due to the temperature gradients set up in the specimen or due to the slow polarization mechanisms effected in the glass in the heating and the cooling cycles. The exact mechanism was not ascertained. For Ge15As15Se70 at 373°K, the conductivity (heating cycle) =  $1.18 \times 10^{-12}$  mho and the conductivity (cooling cycle) =  $1.64 \times 10^{-12}$  $10^{-11}$  mho. A hysteresis was observed in the conductivity-temperature measurements. The nature of the heating and cooling curves of conductivity was affected by the specimen holder, especially at the elevated temperatures. The mechanism of this effect is not certain.

х

### CHAPTER I

### INTRODUCTION

The transmission of useful thicknesses of oxide glasses is limited by metal-oxide structural vibrations which result in a cut-off somewhere between 3 and 6  $\mu$ m.<sup>1,2</sup> To obtain glasses capable of transmitting to longer wavelengths such as 3 to 13  $\mu$ m, it is, therefore, necessary to consider Se, S, and Te chalcogen containing systems. The present state of development of chalcogenide glasses is marked by insufficient characterization of materials and properties, the main problems arising from a lack of information about impurities, defects, and the history of the glass.<sup>3</sup> Information about the inherent limits of absorption in infrared transmitting materials is scarce even in simple binaries like As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>Se<sub>3</sub>.<sup>2,4</sup>

The first attempts to extend the wavelength range of chalcogenide glasses as infrared optical materials began in 1950 when R. Frerichs<sup>5,6</sup> rediscovered  $As_2S_3$  glass. Since then, an extensive research into the properties of these chalcogenides has resulted in the glasses of improved infrared transmission and other optical characteristics.

The objectives of the present work were to obtain a familiarity with selected chalcogenide amorphous systems and to investigate their optical and electrical properties with a view to correlating the electrical conductivity and the infrared transmissivity.

### CHAPTER II

### REVIEW OF THE LITERATURE

In this review, a discussion of the glass-forming ability and the physical, optical, and electrical properties of chalcogenides is presented.

### Composition and Glass Formation

Chalcogenide glasses, primarily composed of sulphides, selenides, and tellurides of group V a, are mostly opaque to visible and UV radiation and transmit only in the infrared. For the glass-forming sulphides, the network formers are found among the small ions of the fourth and the fifth columns of the periodic table. Since 1960, a steadily increasing range of compositions has been reported in the literature. A glassforming region of a specific system or a combination of systems is mapped out systematically, Fig. 1.9 The extent of the glass-forming regions is dependent upon quench rate or the amount of material used in the sample preparation. In general, the tendency for crystallization, at room temperature, is higher in chalcogenide glasses than in oxide glasses. Within a glass-forming system, the ratios between the constituent elements may vary greatly and the associated physical properties of the resultant glasses may be expected to vary as well.<sup>7</sup> It is reasonable to assume that if all the pertinent physical parameters are considered, the glassforming systems can be re-evaluated and a new glass composition selected with better properties. The interdependence of the pertinent physical parameters and how they change with composition must serve as a guide in the selection of a new composition. According to Hilton et al.,<sup>2</sup> different applications have their individual compositional requirements;



Fig. 1. Areas of Glass Formation in Chalcogenide Systems (Savage and Nielsen<sup>1</sup>).

e.g., for a good optical glass the resistance to devitrification is relatively more important than the quench rate or the amount of material. A composition possessing this property must, by necessity, lie deep in the glass-forming region, well away from the border.

The principal disadvantages of  $As_2S_3$  and other chalcogenide glasses made earlier were their low softening temperatures, no higher than 200°C. Constant investigations have resulted in compositions with softening temperatures as high as 500°C. Since the late sixties, considerable attention has been given to the problem of finding infrared optical materials having properties suitable for use with high-energy  $CO_2$  lasers emitting at 10.6 µm. Each material considered was found to have its own set of advantages and disadvantages. However, if the absorption at 10.6 µm reflects a quality state of the glass, considerable improvement may be realized by increasing the purity of the glasses. Moynihan et al.<sup>4</sup> have quantitatively studied impurities and bulk absorption in  $As_2Se_3$  glass, with particular attention to absorption at the wavelengths of the  $CO_2$ laser (9.2-10.8 µm, 1090-920 cm<sup>-1</sup>) and of the CO laser (5-6 µm, 2000-1700 cm<sup>-1</sup>) in order to seek more information about the inherent limits of absorption.

Qualitatively, one can state that the glass-forming tendency decreases with increasing atomic mass. For elements that have been important in optical materials, the glass-forming tendency changes in the following orders,<sup>2</sup>

> Si > Ge > Sn S > Se > Te P > As > Sb

There is some question about the ability of P and As to form glasses.<sup>8</sup> The location of glass-forming regions and the factors important in glass formation have been discussed in the literature.<sup>8,9</sup> Glasses with high softening temperatures have been made from combinations of the elements Si, Ge, P, As, and Sb with S, Se, or Te. Glasses with low softening temperatures have been melted from combinations of the elements As, Sb, Bi, Tl, Br, and I with S, Se, or Te.<sup>1</sup>

Glass formation in the system As-S is not limited to the stoichiometric composition  $As_2S_3$ . Formation of glass is possible between about 35 to 90 weight percent sulphur, Fig. 1, (as the sulphur content is increased, the color of the glass changes from the deep red of  $As_2S_3$  glass to pale yellow at the highest sulphur concentration). A large area of glass formation is noted in the As-S-Se ternary system (these glasses have the remarkable ability to wet and bond to ceramics, plastics, and silicate glasses and also allow a wider variation of the physical properties). In the As-S-Ge ternary system, ternary sulphide glasses can be made containing as little as 30% S while the binary sulphide glasses can be made containing 60% to 90% S.

The arsenic in  $As_2S_3$  glass can be partially replaced by other elements of group V. Sulphur can also be replaced by the chemically similar elements such as Se and Te.<sup>9</sup> In addition, other elements can be added to these glasses, giving rise to a large number of compositions, having as basic constituent the network former  $As_2S_3$ . Depending on the sulphur content in excess of  $As_2S_3$ , the softening temperature decreases from 200°C to below room temperature.

The starting point in understanding how individual elements affect

the properties of glasses is the glass-forming tendency of each element. Hilton et al.<sup>8</sup> have discussed the mixed molecule approach wherein compositions along the boundaries of the glass-forming region of a ternary system produce crystalline materials. Small crystallites of stoichiometric binary compounds precipitate from the glass, suggesting that in the molten state glasses are composed of a mixture of different stoichiometric molecules. If the concentration of one specific composition becomes great enough, nucleation occurs rapidly during the quench and a crystalline phase results. The molecules from the three binaries act as a diluent for each other, preventing crystallization and promoting the formation of amorphous materials. Therefore, the larger the number of molecules that can form between three specific elements, the larger the glass-forming region.

Dembovskii<sup>10</sup> found the crystallization ability of selenides to be higher than that of sulphides and suggested that the process of crystallization depends on several frequently difficult to control factors which he did not specify. He concluded that it is impossible to present the whole picture of glass formation.

Several authors<sup>1,2,4,11-15</sup> have discussed the various methods of forming chalcogenide glass in the bulk and thin film forms. Generally, speaking, the higher the temperature and/or pressure over the reactants, the lower the reaction time. Baker and Webb<sup>12</sup> have reported forming their bulk glass by reacting pure elements in a pressure vessel under argon at 70 atmospheres for 1 hour, while Hilton and others have used longer reaction times and lower temperatures and pressures, thus eliminating the need of the sophisticated pressure vessel. Besides reaction

time and pressure, the various authors<sup>1,4,11</sup> mainly differ in respect of (a) the raw material purification aimed at eliminating oxygen and other impurities, (b) annealing treatments, and (c) distillation of the final product. Some authors have described elaborate distillation procedures for purification of their chalcogenide glasses. But for these variations, there is a general agreement on the experimental preparation of the bulk samples.

### Structure

A study of the structure of chalcogenide glasses is essential in order to fundamentally and completely understand the nature and the properties of these non-oxide glasses. Lucovsky's model<sup>16</sup> relates the characteristic phonon frequencies to the atomic structure for developing an understanding of the infrared absorption spectrum of amorphous chalcogenides. In this model, amorphous Se is considered to be a mixture of polymeric helical chains of trigonal Se and eight-membered ring molecules of a-monoclinic Se. The bonding within these structural units is covalent, whereas the inter-structural forces between the chains and rings are of the weak Van der Waal type. Infrared optical properties are, thus, a composite spectrum with contribution from both the ring and chain components. Such a model is applicable to systems in which the structure of the glass is describable in terms of covalently bonded monomer or polymeric units which are bound by Van der Waal type forces. For binary chalcogenide glasses the molecular and polymeric species that exist in an arbitrary mixture are limited by the constraints imposed by local valence and subject to the condition that compound formation is favored.

However, these two criteria are not sufficient to determine the possible structural species in ternary systems. This is a serious limitation of Lucovsky's model.

Frerichs<sup>6</sup> described the structure of  $As_2S_3$  glass as composed of  $AsS_{3/2}$  polyhedra units linked together with the S atom which is common to two polyhedra. Tsuchihashi and Kawamoto<sup>17</sup> have reported  $S_8$  ring formation from a solution of  $As_2S_3$  glass in  $CS_2$ . These authors have proposed a modification of Frerichs' concept so that in the glass  $AsS_{3/2}$  is represented as a tetrahedron model and rings are formed consisting of five or seven  $AsS_{3/2}$  tetrahedra, whereas in the crystalline form six such tetrahedra are present, Fig. 2. By assuming the structure of crystalline orpiment,  $As_2S_3$ , the density was experimentally found to be lower in the glass than in the crystal. Also, the distance between layers became wider in glass.

In the band model proposed by Cohen, Fritzsche, and Ovshinsky (CFO)<sup>18</sup> it is agrued that the large configurational entropy available in the liquid state of alloy glasses makes it energetically favorable, while cooling from the melt, to exchange positional and compositional ordering for the minimization of electrostatic-bonding energies, i.e., for the local satisfaction of all valence requirements regardless of the coordination number. As a consequence, the degree of positional disorder in the multi-component amorphous solid is enhanced over that in the elemental amorphous semiconductors, but the valence band of the bonding states is full and compensation is automatically assured. Moreover, a unique activation energy for band conduction still exists despite a density-of-states function, which is everywhere continuous because of



Fig. 2. Structural Model of  $As_2S_3$ . (a)  $As_2S_3$  Crystal (b)  $As_2S_3$  Glass. (Tsuchihashi and Kawamoto.<sup>17</sup>)

an abrupt change in the character of the eigen states, from extended to the localized, at a certain energy in either band. 19,20 The gap in the density-of-states function occuring in crystalline semiconductors is considered functionally replaced in amorphous semiconductors by a gap in the mobility function. Implicit in the CFO model are numerous predictions regarding the transport properties of chalcogenide glasses. Fagen and Fritzsche<sup>19</sup> did not observe extrinsic conduction in the bulk samples of chalcogenide glasses ("extrinsic" implies a regime of conduction exhibiting a thermal activation energy smaller than that of interband excitation). Knowing the least change in the electrical conductivity, one can deduce the least density-of-states necessary to pin the Fermi level.<sup>18</sup> This density cannot be less than  $5 \times 10^{19} \text{ cm}^{-3} \text{ ev}^{-1}$ . On the other hand, the absence of a regime of hopping conduction at room temperature indicates that the density-of-states can scarcely exceed  $10^{21}$  cm  $^{-3}$ ev<sup>-1</sup>. Taken together, these two observations provide the lower and the upper limits respectively on the density-of-states at the Fermi level and suggest that thermally activated hopping conduction should be observed not too far below room temperature.

Owen and Robertson<sup>21</sup> have considered the band structure of glassy semiconductors to be not very different from that of similar crystalline materials except for a splitting-off of a tail of localized states below the conduction band and above the valence band. It does not follow, however, that electron transport necessarily occurs in the conduction or valence bands; a hopping mechanism between localized states is also possible. Counter parts of (a) ordinary broad-band semiconductors in which, although trap-limited to a greater or lesser degree, transport may in

principle occur in nonlocalized states, i.e. in a band, and (b) narrowband materials in which the carriers are always strongly localized-because of a large effective mass---and transport occurs by hopping, or possibly in a polaron band, may be expected.

The strongly increasing electrical conductivity with frequency is good, but not unambiguous, evidence for hopping conduction. Even accepting this, however, it does not follow that in the dc limit conduction is also by hopping. If hopping does occur, the trap limited mobility would be given by

$$\mu = \frac{veb^2}{kT} \exp\left(-\frac{u}{kT}\right)$$
(1)

where v is a phonon frequency, b the jump distance, and U the mobility activation energy. The CFO model<sup>18</sup> involves a "mobility gap" at the boundary between the localized and nonlocalized states somewhere in the vicinity of the original band-edge. Another feature of it is an exponential tail of localized states in the forbidden-gap and probably extending right across it.

Rockstad<sup>22</sup> has taken a somewhat similar, though carefully skeptic, view on the mechanism of electronic conduction in chalcogenides. Because of the disordered lattice structure, the energy band structure cannot be as readily derived for these materials as it has been for periodic lattices. Although valence and conduction bands do exist for the amorphous structure, a true band gap of forbidden energies between the two bands probably does not exist. Instead, energy states at the band edges may smear or tail into a pseudo-gap. Within this pseudo-gap the states are

localized and outside the pseudo-gap, in the valence and conduction bands, the hole and electron states are nonlocalized as in the valence and conduction bands of crystalline semiconductors. Low-field electronic conductivity could take place by intrinsic band conduction, due to a small number of carriers in the valence and conduction bands as a result of thermal excitation, or by hopping of carriers in the localized states. Rockstad<sup>22</sup> and Owen and Robertson<sup>21</sup> are in agreement regarding the increase of hopping conductivity with frequency, whereas intrinsic band conductivity is essentially frequency-independent. This difference would perhaps serve to distinguish hopping conduction from band conduction.

Kitao<sup>14</sup> has reported the frequency dependence of conductivity to be as  $\sigma \, \varpropto \, \omega^{\mathbf{S}}$  where s is a constant whose value changes from s  $\thickapprox$  1 at low frequencies to  $s \approx 2$  at higher frequencies.<sup>14,21</sup> There is, however, considerable discrepancy in the literature on the value of s; Lakatos and Abkowitz<sup>23</sup> and Crevecoeur and de Wit<sup>24</sup> observed s  $\leq 1$ . The latter also discussed the effect of electrical contacts on the dependency. The CFO model can be applied to chalcogenide amorphous semiconductors owing to the maintenance of the well-defined, short-range order. The shortrange order greatly influences the electrical conductivity. Because of the destruction of the long-range order, the band edges smear out, the tails of the density-of-states appear in the forbidden gap, and localized states arise near the band edge as discussed earlier. Also, there may be abrupt changes in mobility with energy and the presence of well-defined mobility edges introduces the concept of a mobility gap. The extent of this tailing (referred to as  $\Delta E_c$  and  $\Delta E_v$ ) has not been calculated rigorously.

Seager and Quinn<sup>26</sup> have argued that the mobility, deduced from the Seebeck and conductivity experiments, is not exponential with 1/T and the apparent activation energy at any temperature is not entirely made up of the difference between the single carrier occupation energies of two localized sites but is considerably enhanced by the variable range tunneling. Structural defects, that is, changes in the local coordination number, can contribute to the tail states. Similarly, compositional disorder can also contribute and may result in an enhanced overlap of tail states close to the center of the gap. If this happens, the Davis and Mott<sup>25</sup> model assumes that a narrow band of localized states will pin the fermi level,  $E_f$ , between the two tails, Fig. 3 (c), due to the band of localized states near the center of the gap. At the critical energies, referred to as E and E, the mobilities of electrons and holes decreases by a factor of  $10^2 - 10^3$  so that  $E_c - E_v$  denotes a mobility gap, Fig. 3 (d), within which carriers can move only by phonon-assisted hopping between the localized states. The most often quoted evidence for the existence of localized tail states in the gap is that the drift mobility appears to be trap controlled, Equation 1, in Se, As2Se3, and As2S3.

Chemical bonding in chalcogenide melts is also an important parameter in explaining the structural properties like viscosity. Although the valence electron pair is strongly localized between an atom and its bonding partner, some flexibility in the two-fold coordinated atoms permits free rotation of the chain atoms about the bonds and some variation in the bond angles, thus enabling the atoms to have a higher mobility. An increasing amount of four-fold coordinated germanium and three-fold



Fig. 3.

Schematic Representation of the Density-of-States N(E) as a Function of Energy: (a) Of Crystalline Materials, (b) Of Amorphous Materials With Well-Defined Short-Range Order, (c) Of Amorphous Materials With Compositional and Translational Short-Range Order, and (d) Of the Mobility as a Function of Energy of Amorphous Materials. (Lakatos and Abkowitz.<sup>23</sup>)

coordinated arsenic suppresses individual molecule formation and thus lowers the mobility of atoms because a more highly developed 3-dimensional network is formed. At high concentrations of tri- and/or tetra-valent elements, this network collapses at high temperature with the formation of a new bonding system containing po bonds. The short-range order then changes to an approximately octahedral configuration and a metallic-like electrical conductivity is expected.

According to Dembovskii,<sup>10</sup> the structure of  $As_2S_3$  is heterodesmic, having two or more type bonds, in the vitreous state. Heterodesmic substances such as  $As_3S_3$  are known to have a low crystallization ability.

### Physical Properties

Substantial research has been conducted into the various physical properties of chalcognide glasses.<sup>1,2,7-10,17,27,28</sup> Softening temperature measurements for any given chalcogenide composition may vary up to 10 percent among various investigators. The softening temperatures range from below room temperature to over 500°C. A relative measure of softening temperature is obtained when the sample in a heated chamber softens enough to move the quartz rod resting on the sample which in turn produces a movement of an indicator.<sup>27</sup> Qualitative conclusions concerning the softening points may be drawn based on the comparison of the softening points of different glasses. Generally, softening points decrease with increasing atomic weight of the constituent element. In the Ge-Se system, the highest softening temperature is possessed by glasses whose structures are based on tetrahedral structural units namely GeSe<sub>2</sub>;<sup>10</sup> In general, Ge-As-S glasses have softening temperatures up to 500°C and Ge-As-Se glasses up to 450°C. Ge is much more effective than As in increasing the softening temperature. An empirical rule Tg/Tm = 2/3, where Tg is the glass transition temperature of a glass composition and Tm is the melting point of its crystalline form, has been reported for inorganic systems.

Softening point is closely interrelated with hardness and thermal expansion coefficient. The higher the softening point, the higher the hardness and the lower the thermal expansion coefficient. 1,2,7,8 There is considerable variation among glasses of widely different compositions. The high melting chalcogenide glasses have thermal expansions approaching that of oxide window glass. Therefore, these glasses should have as good thermal shock properties if the mechanical strengths are sufficiently high.<sup>8</sup> Hardness is important in the production of good optical surfaces and is generally low for materials transparent at 10.6 µm, with a few exceptions. All these three properties reflect the relative strength of the average chemical bond in the respective glass compositions. For the Se- and S-based glasses a straight line relationship between the measured hardness and Young's modulus has been reported." The slopes for the two families of glasses are different reflecting, to some extent, the realtive strengths of the primary bonds formed between the metallic elements and the S or Se atoms. A decrease in Poisson's ratio, calculated from the modulii, is indicative of a change of structure in the glass. Another factor affecting Young's modulus is the density which varies linearly with the calculated average molecular weight of the glass. However, variations up to 3 percent from this linear relationship have been reported.<sup>8</sup>

Low thermal conductivity is an inherent limitation of chalcogenide

glasses when illuminated by the high energy densities of  $CO_2$  lasers. Removal of the absorbed heat is extremely slow leading to thermal lensing. In the Ge-Se system glasses, the increase in thermal conductivity, K, with increasing Ge content is related to an increase in the average phonon velocity, V, in the material, as:  $K = \frac{1}{3} C_v V \bar{\lambda}$ , where  $C_v$  is the heat capacity per unit volume and  $\bar{\lambda}$  is the mean free path for phonons.<sup>7</sup> For chalcogenide glasses with low Debye temperatures, only the phonon velocity and hence the thermal conductivity change with composition, since  $\bar{\lambda}$  (a measure of the disorder for the melt formed glass) and  $C_v$  change very little with composition.<sup>7</sup>

Some work has been done on the viscosity of chalcogenide glasses, mainly by Russian workers.<sup>10</sup> Absolute viscosity has been obtained by calibration method using standard  $B_2 O_3$  glass of a known viscosity, e.g., viscosity of  $Ge_{20}As_{15}Se_{65}$  at 335°C is  $10^8$  poise. Dembovskii<sup>10</sup> has also discussed the problems often encountered in the viscosity measurements in chalcogenides near the melting point.

Chalcogenide glasses in the As-I-S, As-Tl-S, Ge-As-S, Ge-As-Se, and As-Se are chemically durable in that they are neither attacked by tap water nor by dilute acids (HCl,  $H_2SO_4$ ,  $HNO_3$ , and HF) at low temperatures.<sup>1</sup> However, appreciable solution occurs in weak alkali solutions in the temperature range 15-65°C. In general, sulphide or selenide glasses containing much Si or P appear to be rather unstable under laboratory conditions giving off  $H_2S$  or  $H_2Se$ .

### Phase Separation

Metastable immiscibility and phase separation can strongly influence the ability to quench and maintain homogeneous amorphous nature of chalcogenides. Evidence of this phenomenon is provided by the stable immiscibility or incipient immiscibility as indicated by an abnormally flat or S-shaped liquidus in the phase diagram.<sup>47</sup> The quenched materials are unstable with respect to subliquidus phase separation. Although phase separation in multi-component chalcogenides may be a complicated phenomenon, nevertheless it can be understood and often predicted. According to Roy and Caslavska,<sup>29</sup> in principle, every "glass" has the potential of becoming diphasic; this applies to chalcogenides also, even the monovalent glasses such as Se and S based glasses. Considering the different liquid and crystal structures of the components of chalcogenide systems, tendency for immiscibility in their solutions could be expected, e.g., energy and steric bond considerations for amorphous Ge (3-dimensional), Se (rings and chains) and  $As_2Se_3$  (2-dimensional) are quite different and their mixtures would be expected to favor rather large regions of molecular associations.

Materials near the border of the glass forming regions in a multicomponent system or near compound or eutectic compositions show strong tendency towards microphase separation with and without the crystallization of one of the phases. In the GeSe-Se system, two glass forming regions are found, with not very sharp limits.<sup>29</sup> Since the two phases, GeSe and GeSe<sub>2</sub>, crystallize successively on annealing above the glass transition temperature, their recrystallization follows the process of phase separation.

#### Optical Properties

Much of the development of chalcogenide glasses occurred because

of their applications in the infrared region (1-15  $\mu$ m) where the use of oxide glasses is ruled out due to their poor optical properties. Index of refraction of chalcogenide glasses has been investigated by several researchers<sup>1,2,4,8,11,27,30</sup> with a view to improving their transmission characteristics. Refractive index increases as the atomic mass of the constituent atoms increases. According to Hilton et al.,<sup>8</sup> Fig. 4, the refractive index of chalcogenide glasses can be lowered by the substitution of an element of lower atomic mass. Variation in the index of refraction is possible depending on the particular process involved, including the annealing procedure if any. Rodney et al.<sup>30</sup> have extensively investigated the variation of the index of refraction of As<sub>2</sub>S<sub>3</sub> with wavelength, Fig. 5, and have presented the difference between the experimentally observed values and those calculated from Sellmeier-type dispersion formula.

$$n^{2} - 1 = \sum_{i=1}^{i=5} \frac{K_{i} \lambda^{2}}{\lambda^{2} - \lambda_{i}^{2}}$$
 (2)

where  $\lambda_{i}$  is the wavelength of interest and K<sub>i</sub> and  $\lambda$  are constants over wavelength range of 0.5-12.0 µm. They have also shown that the thermal coefficients of refractive index rapidly approach zero with increasing wavelength. This indicates a preponderance of the effect of shifting the absorption wavelength at short wavelengths but increasing the importance of the effect of changing the density at long wavelengths--the two effects reaching equality at wavelengths beyond about four microns. Hilton<sup>2</sup> has found that the major factor in the thermal change in the index of refraction for infrared optical materials is the thermal



Fig. 4. Change in Refractive Index of 15 Ge, 15 As, 70 Te Glass When Se is Subsituted for Te. (Hilton et al.<sup>8</sup>)



Fig. 5. Refractive Index as a Function of Wavelength. Rodney et al.<sup>30</sup>

coefficient of expansion. The larger the value of the expansion coefficient, the larger is the negative value of  $\frac{\Delta n}{\Delta T}$ .

In the literature, a wedge shaped specimen has been preferred over a disk-like slice for the index of refraction measurements. Hilton<sup>2</sup> has reported measuring the angles involved to six significant figures. The index of refraction 'n' of any given composition, as calculated from the "Angle of Minimum Deviation" method,<sup>31</sup> is given by

$$n_{\lambda} = \frac{\sin \frac{1}{2}(A+\delta)}{\sin \frac{1}{2}A}$$
(3)

and

$$\delta = \cos^{-1} \frac{(xy)^2 + (yz)^2 - (xz)^2}{2(xy) \cdot (yz)}$$
(4)

where

n = Index of refraction of the composition at the wavelength  $\lambda$ .

A = Apex angle of the wedge.

 $\delta$  = Angle of Minimum Deviation for which xy, yz, and xz are shown in Fig. 6.

The index of refraction as calculated from the method of perpendicular incidence is given as

$$n_{\lambda} = \frac{\sin (A + D_{\lambda})}{\sin A}$$
(5)

where  $D_{\lambda}$  = Angle between the refracted and the undeviated beams.

The advantages of the angle of minimum deviation method over the angle of perpendicular incidence method are discussed in the standard texts on measurement techniques. Also the index of refraction of chalcogenide glasses must be measured in the infrared in a nondispersive











CO<sub>2</sub> LASER Hg-Cd-Te LASER MIRROR ï

LL: M:



LL

6. Diagramatic Representation of Laser Set Up for the Measurement of (A) Angle of Minimum Deviation and (B) Apex Angle of the Wedge. Fig.

region and well on the long wavelength side of any absorption which causes an electronic transition.

The linear relationship between the density and the molecular weight suggests that the index of refraction may be additive and predictable.<sup>8</sup> Refractive index is also related to the molar refraction 'r' and the molecular volume 'V' of a substance as

$$r = \frac{n^2 - 1}{n^2 + 2}, \quad V = \frac{n^2 - 1}{n^2 + 2}, \quad \frac{\text{molecular weight}}{\text{density}}$$
(6)

This famous Lorentz-Lorenz relationship has been applied to the study of bonding in organic and inorganic compounds. Hilton et al.<sup>8</sup> have presented a detailed analysis of molar refraction as applied to chalcogenide glasses.

The reflectivity 'R' of a specimen may be calculated from the index of refraction as follows

$$R = \frac{(n-1)^2}{(n+1)^2}$$
(7)

Knowing the reflectivity, the infrared transmission 'T' may be empirically calculated from the following equation

$$T = (1 - R)^2 e^{-\alpha X}$$
 (8)

where  $\alpha$  = bulk absorption coefficient of the material, and

X = thickness of the specimen.

A more precise calculation of the absorption coefficient uses the following equation

$$T = \frac{(1 - R)^2 e^{-\alpha X}}{1 - R^2 e^{-2 \alpha X}}$$
(9)

According to Moynihan et al.,<sup>4</sup> this equation is valid for normal incidence of the beam and for  $\alpha\lambda \ll 1$  where  $\lambda$  is the wavelength. Hilton<sup>2</sup> has suggested that the material should be considered useful over the wavelength range in which  $\alpha < 1$  cm<sup>-1</sup>.

Various researchers have investigated the infrared absorption characteristics of chalcogenide glasses. Moynihan et al. 4 have suggested that the two principal sources of I R absorption in As<sub>2</sub>Se<sub>3</sub> glasses are light atom impurities (oxygen and hydrogen) and intrinsic multiphonon processes. They investigated these absorption characteristics by doping the glass with known amounts of impurities. According to Hilton et al., the three main sources of infrared absorption are the absorption edge, the impurity absorption, and the molecular vibration of the constituent elements. A possibility of I R active overtones at shorter wavelengths exists but such absorption bands must be fairly weak. There appears to be a general consensus in the literature that assigning a particular absorption band in a glass to a particular impurity is complicated by several factors. The exact form of the molecular oxide causing a specific infrared absorption is extremely difficult to identify. Absportion by metal oxides, present as trace impurities, occurs in the wavelength region of major interest and, therefore, limits the usefulness of the glass. Oxygen can contaminate the chalcogenide glasses as an impurity in the reactive elements or as a residual gas in the melting ampoule.<sup>8</sup> The former possibility has also been considered by Moynihan

et. al4 In their highly acknowledged work on the oxide impurities in chalcogenide glasses, Vasko et al.<sup>3</sup> have studied As<sub>2</sub>0<sub>3</sub>, As<sub>4</sub>0<sub>6</sub>, and other oxide bands in the infrared spectra of various glass systems and have proposed three types of arsenic oxide bands, namely, (a) As406 molecules present in isolated form dissolved in the glass or segregated as crystallites of arsenolites (the cubic form), (b) pure glassy As203, the structure of which is closely related to claudetite structure of As203, and (c) an "intermediate" glassy form of  $As_20_3$  between the cubic and pure glassy forms or possibly a superposition of the molecular  $As_4^{0}_{6}$  and chain-layer forms in different relative concentrations dependent on the oxidation conditions and the thermal history. In their study of As2Se3 glass in the wavelength region of the CO $_2$  laser (10.6  $\mu$ m) Moynihan et al.  $^4$  found the absorption coefficients to be limited by intrinsic multiphonon processes to values of the order of  $10^{-2}$  cm<sup>-1</sup>. Selenide glasses are thus markedly inferior in their I R transparency in the CO2 laser region to materials such as those semiconductor materials for which 10.6 µm absorption coefficients approaching  $10^{-4}$  cm<sup>-1</sup> have been reported.

According to Hilton,<sup>2</sup> qualitatively speaking, the useful transmission range for a chalcogenide glass lies within two values. The short wavelength limit is determined by the absorption edge, the location of which corresponds roughly to the width of the forbidden gap in the material if it were crystalline. The long wavelength cutoff is determined by the infrared absorption of constituent atoms either in a primary mode or an overtone.

As a result of the limitations on the application of chalcogenide glasses, some researchers, <sup>4</sup>,<sup>11</sup> have suggested purification procedures
such as baking of the melting ampoules, reactant purification, and vacuum distillation of the chalcogenide glass, in order to eliminate the oxide and other impurities.

#### Electrical Properties

In chalcogenide glasses the electrical conductivity is thermally activated, increasing exponentially with decreasing 1/T, where T is the absolute temperature. Rockstad<sup>22</sup> and Lakotos and Abkowitz<sup>23</sup> have shown that conductance is frequency independent at sufficiently low frequencies but increases rapidly with frequency at higher frequencies. In general, the conductivity for the glass could be expressed as the sum of a frequency independent component and a frequency dependent component, the latter varying as  $\omega^{S}$ . This variation has already been discussed above. Rockstad<sup>22</sup> has attributed the frequency dependent component to hopping and the frequency independent component to intrinsic band conduction. At dc or ac frequencies up to 10 kHz, the latter contribution dominates.

Baker and Webb<sup>12</sup> investigated the dc conductivity in some chalcogenide glasses and found that at the lower temperatures, the conductivity plots are linear, indicative of semiconductor behavior, and can, therefore, be expressed as

$$\sigma = \sigma_{o} \exp \left(-\frac{E_{cond}}{kT}\right)$$
(10)

where E is the activation energy. They, however, observed approximately linear decrease in the activation energy with temperature, given as

$$E = EO - \nu T$$
(11)

Assuming  $\sigma_0$  to be constant up to reasonably high temperatures, Equation (10) modifies to

$$\sigma = \sigma_{o} \exp(\nu/k) \exp(-\frac{E_{o}}{kT})$$
(12)

Plot of log σ vs 1/T thus yields E<sub>o</sub> directly. E<sub>o</sub> for As<sub>2</sub>Se<sub>3</sub> has been reported to be 1.07 ev. At higher temperatures, Baker and Webb<sup>12</sup> have observed flattening-off of the conductivity plots which is indicative of a departure from the linearity expressed in Equation (12). Owen and Robertson<sup>21</sup> have also reported a change of slope which they attribute to the "extrinsic" conduction. Similar breaks have been observed by Fagen and Fritzsche<sup>19</sup> in their more complex conductive systems. Owen and Robertson, however, considered the basic conductivity equation to be

$$\sigma = \sigma_{o} \exp \left(-\frac{E_{cond}}{2kT}\right)$$
(13)

and have reported  $E_{cond}$  for  $As_2S_3$  to be 2.1-2.3 ev and for  $As_2Se_3$  to be 1.8-2.0 ev. Lakatos and Abkowitz<sup>23</sup> have measured the dc and ac conductivities of Se up to 377°K and found the former to be two orders of magnitude lower than the latter at room temperature and  $10^2$  Hz. As the temperature is increased, the ac conductivity seems to approach the dc conductivity asymptotically at all frequencies. Kitao<sup>14</sup> investigated the dc conductivity of  $As_2Se_3$  using Equation (10) and found  $E_{cond}$  to be 1.05 ev and 0.9 ev at the temperature range above and below 473°K respectively. His observations are in agreement with those of Lakatos and Abkowitz<sup>23</sup> and Rockstad.<sup>22</sup> These investigators have provided an extensive theoretical analysis of the frequency dependence of conductivity. No conductivity studies seem to have been done on chalcogenide systems containing Ge-S and Ge-As-Se and Ge-As-S compositions. The bulk of investigation centers around the study of the conductivity of arsenic sulphides, selenides, and tellurides.

Several researchers have discussed the effect of electrical contacts on the conductivity measurements. 14,22-24 While Crevecoeur and de Wit<sup>24</sup> have recommended aluminum rather than gold as electrodes for As, Se, Lakatos and Abkowitz<sup>23</sup> have pointed out the blocking characteristics of aluminum electrodes in reporting that at  $10^2$  Hz, the conductivity of  $As_2Se_3$  using gold electrodes is 10 times higher than that using aluminum electrodes. Their measurement of parallel conductance was found to scale with thickness when gold electrodes is 10 times higher than that using aluminum electrodes. Their measurement of parallel conductance was found to scale with thickness when gold electrodes were deposited on As<sub>2</sub>Se<sub>3</sub>, but did not scale when aluminum electrodes were used. Kitao<sup>14</sup> has reported the variation in the conductance values with aluminum electrodes and with heat treatment at 150°C. He concurred with the views expressed by Lakatoes and Abkowitz.<sup>23</sup> According to Seager and Quinn,<sup>26</sup> In-Ga eutectic alloy provided good ohmic contacts on As<sub>2</sub>Se<sub>3</sub>; they found no difference in the electrode characteristics among In-Ga alloy, Au or Ag paint as electrode materials. ASTM standard method  $D257-66^{32}$  does not discuss the merits and the demerits of different electrodes in terms of their performance and applicability.

Lakatos and Abkowitz<sup>23</sup> investigated the dielectric characteristics of Se,  $As_2Se_3$ , and  $As_2S_3$  at different frequencies. They found less than 5% changes in the dielectric constants of Se ( $\approx 6.36$ ) and  $As_2Se_3$  ( $\approx 11.2$ )

and about 15% change in the dielectric constant of  $As_2s_3$  ( $\approx$  7.8) in the frequency range  $10^2 -10^{10}$  Hz. Some authors<sup>12,21</sup> have investigated the Hall mobility and the thermoelectric power in chalcogenide glasses. Hall coefficient of chalcogenides has always been found to be negative. The Hall mobility is low ( $\approx$  0.1 cm<sup>2</sup>/V sec); it is virtually independent of temperature and its magnitude also seems to be practically independent of the particular material. This temperature independent mobility is not necessarily an evidence against a hopping mechanism of conduction.<sup>21</sup> Thermoelectric power is positive, approximately inversely proportional to temperature and its magnitude is typical of semiconductors.

#### CHAPTER III

#### PROCEDURE

Batch preparation and the melting schedules of eight chalcogenide compositions in the Ge-As-Se and Ge-As-S systems are described below. Measurement of the index of refraction, I R spectra and dc electrical conductivity of some glassy and crystalline compositions are described together with the problems encountered therein.

#### Compositions Selected

Glass forming regions in the ternaries As-Ge-S and As-Ge-Se<sup>8,9</sup> are shown in Fig. 1. Of the eight compositions selected for the present study, Table 1, binaries  $As_2Se_3$  and  $As_2S_3$  easily form glasses, whereas the binary  $Ge_{15}S_{85}$  falls on the borderline of its glass-forming region and binary GeSe falls outside it.

#### Glass Melting Ampoule

According to the high temperature vapor pressures, Appendix II, and the melting temperatures, Table 1, fused quartz or pyrex glass ampoules were required for melting the eight compositions. The selection of pyrex or fused quartz ampoules for melting a particular chalcogenide composition was based on its melting point and the temperature vapor pressure relationship of its constituent elements.

For most of the compositions, vapor pressure less than two atmospheres was the limiting factor in determining the maximum attainable

Chalcogenides
Eight
the
of
Compositions
Ŀ.
Table

Composition Designation	Batch Formula	Constituents	Atomic %	Weight %	Melting Pt.(°C)	Source of Melting Point
I	As <sub>2</sub> s <sub>3</sub>	S As	60 40	39.096 60.904	310	Phase Diagram <sup>33</sup>
II	$As_2Se_3$	Se As	60 40	61.252 38.748	370 360	Literature <sup>10</sup> ,26 Phase Diagram <sup>34</sup>
III	Ge15 <sup>8</sup> 85	s Ge	85 15	71.452 28.548	515	Phase Diagram <sup>35</sup>
IV	Ge <sub>50</sub> <sup>Se</sup> 50 (GeSe)	Se Ge	50	52.100 47.900	687	Phase Diagram <sup>36</sup>
Δ	Ge15 <sup>AS</sup> 15 <sup>Se70</sup>	Se As Ge	70 15 15	71.412 14.520 14.068		
ΛI	Ge <sub>30</sub> As <sub>15</sub> Se <sub>55</sub>	Se As Ge	55 15 30	56.812 14.700 24.428		
ΙIΛ	Ge <sub>15</sub> As <sub>15</sub> 870	S Ge	70 15 15	50.360 25.212 24.428		
VIII	Ge30 <sup>As</sup> 15 <sup>S</sup> 55	S As Ge	55 15 30	34.816 22.188 42.996		÷

temperature. Rotation of the ampoule was considered essential for homogenizing the melt. Accordingly, 23 mm O.D. x 21 mm I.D. x 100 mm rotational melting ampoules of pyrex or fused quartz were fabricated, each having an "O" ring joint of pyrex glass (Corning #6780) connnected through an 11 mm O.D. graded seal. An extension below the graded seal allowed subsequent sealing under vacuum. A 2 mm bore high vacuum stop-cock (Corning #7544) was used with a S<sup>J</sup> #18/9 ball joint connector and an ASTM #9 "O" ring to retain the vacuum inside the ampoule prior to its sealing, Fig. 7 and 8.

#### Batch Preparation and Melting-Ampoule Loading

Eight melting ampoules were thoroughly cleaned and baked for moisture removal. The ampoules, together with their accessories, raw materials, a Mettler P 163 balance and mortar and pestle were placed in an air tight glove box. After evacuating overnight, the box was flushed with  $N_2$  gas for four hours, thus ensuring a reasonably good inert atmosphere inside the box. After crushing the coarse As and S raw materials to a suitable size in separate mortars, 25 gram batches of the eight compositions were accurately weighed and carefully loaded in the ampoules. The stop-cocks were closed thus entrapping  $N_2$  gas over the mixtures and the ampoules were quickly transferred to a diffusion pump unit where they were sealed under a high vacuum after an overnight evacuation and degassing.

A stainless steel bomb was used for safety reasons and as a means of rotating the ampoule while melting to obtain homogeneity of the composition. The bomb and the other melting accessories are shown in Fig. 8.



Pictorial Representation of Melting Vessels and Their Accessories. Figure 7.





For remelting of compositions VII and VIII, non-rotational fused quartz ampoules, 50 mm O.D. x 48 mm I.D. x 18 mm, were used, Fig. 8. An extension allowed subsequent sealing under vacuum.

#### Melting Furnace

A Harrop "electrikiln" with an indicator and a recorder was used for the initial melting of all the compositions, Fig. 9. Holes were drilled in the front and the back walls in a horizontal alignment to support the bomb inside the furnace. The bomb was coupled to a 16 2/3 r.p.m. motor. The furnace was supplied with power through an automatic Leeds and Northrup temperature-power controller. The temperature, monitored through a Chromel-Alumel thermocouple (type K), was controlled to within 1°F. For remelting compositions VII and VIII, the non-rotational ampoule, Fig. 8, was placed on an alumina refractory bridge in the center of the furnace so as to minimize thermal gradients.

#### Glass Melting

#### General

For rotational melting, the melting ampoule was placed inclined inside the stainless steel bomb so as to collect the melt at the bottom of the ampoule as a slug. Kaowool packing provided the insulation from sudden thermal shocks, shielding from the scratches due to the rough bomb surface and the incination. The bomb containing the ampoule was loaded into the furnace and firmly coupled with the motor in a horizontal alignment. Tubular sleevings in the furnace wall prevented undue torque on and the consequent overheating of the motor.

After setting the soaking temperature, Table 2, on the controller,





LEGEND

Compositions
Chalcogenide
e Eight
of th
Schedule
Melting
Table 2.

	2					3. 2	20
Composition	Max. Temp. Attained (°C)	Time For Max. Temp. (Minutes)	Soaking Time at Max. Temp. (Hours)	Vapor Pressure (mm)*	Type of Ampoule	Comments	10
As <sub>2</sub> S <sub>3</sub> (I)	490	40	24	873	Pyrex	Annealing at 250°C for 8 hours	
As <sub>2</sub> Se <sub>3</sub> (II)	200	65	24	2014	Fused Quartz	Annealing at 270°C for 2 hours	
Ge <sub>15</sub> 85 (III)	540	30+	24 1/2	2322	Fused Quartz	Annealing at 400°C for 2 1/2 hours	
GeSe (IV)	720 <sup>-</sup> 750	60	4 20	1365	Fused Quartz	Annealing at 370°C for about 5 hours	
Ge <sub>15</sub> As <sub>15</sub> Se <sub>70</sub> (V)	720	65	29	1859	Fused Quartz	Annealing at 370°C for 2 1/2 hours	
Ge <sub>30</sub> As <sub>15</sub> Se <sub>55</sub> (VI)	720 730	50	13 13	1978	Fused Quartz	Annealing at 370°C for 2 hours	
Ge <sub>15</sub> As <sub>15</sub> <sup>S</sup> 70 (VII)	520	35	24	1507	Fused Quartz	Annealing at 275°C for 2 hours	
Ge <sub>30</sub> As <sub>15</sub> 55 (VIII)	550	07	24	2042	Fused Quartz	Annealing at 290°C for 2 hours	
*							Υ.

\* See Appendix II

the motor and the furnace were started. The rate of increase/decrease of the temperature was accurately monitored by the recorder so as to determine the soaking temperature as well as the time of soaking for each melting, Table 2.

At the end of the soaking period, the motor was stopped and the furnace cooled. In some cases, the compositions were cooled to the annealing temperature and soaked before cooling to room temperature at various cooling rates, Table 2. In other cases, the composition was cooled straight to room temperature at a specific cooling rate, Table 2.

The cooled bomb was opened, often with considerable difficulty due to oxidation in the threads. The ampoule was carefully withdrawn from the bomb and broken open to recover the chalcogenide without including any silica glass splinters. In some cases, on opening the bomb the ampoule was found cracked or shattered.

For non-rotational melting, an identical procedure was followed except that the ampoule was kept stationary on a refractory bridge for uniform heating.

Special features of each melting are described below under "Specific Meltings."

#### Specific Meltings

<u>Composition I  $(As_2S_3)$ </u>. After soaking at 490°C in accordance with the general procedure and Table 2, the composition was cooled to 250°C, in 5 1/2 hours and soaked at this temperature for 8 hours. Following this, the motor was stopped and the composition was rapidly cooled to room temperature in less than one hour.

Composition II ( $As_2Se_3$ ). After soaking the composition at 700°C

Table 2, the motor and the furnace were stopped for readjustment of the bomb-motor coupling. Although the furnace temperature fell to 660°C, in all likelihood, the ampoule temperature was not affected significantly due to the kaowool insulation. On restarting the motor and the furnace, the temperature increased to 700°C within 5 minutes. After soaking for one hour, the motor was disconnected and the furnace tilted over to increase the ampoule inclination. The composition was cooled to 270°C in 2 hours and annealed at this temperature for 2 hours. At this stage, the furnace was stopped, cooled to 225°C in 30 minutes, followed by rapid cooling to room temperature in less than 1 hour.

Before heating further, the bomb threads were cleaned in a lubricant oil.

<u>Composition III ( $Ge_{15}S_{85}$ )</u>. While heating the composition to 540°C (soaking temperature), fumes were noticed coming out of the furnace at 425°C. The furnace, consequently, was cooled to 320°C. These fumes were perhaps emanating from the lubricant oil, used to clean the bomb threads. Furnace temperature was raised back to 540°C within 30 minutes. Four hours later, the bomb-motor coupling was readjusted. After soaking for 24 1/2 hours, Table 2, the motor and the furnace were stopped and the composition cooled to 480°C in one-half hour, followed by cooling to 160°C in 1 1/2 hours. At this stage, the composition was reheated to 400°C, annealed for 2 1/2 hours and slow-cooled to room temperature in 7 hours.

Prior to any further heating, the bomb threads were repaired and ultra-sonicly cleaned to remove the oxides due to the rusting of the threads. To reduce further oxidation of the threads, "Fel-Pro" C-100

high temperature molysulphide lubricant was applied to bomb threads before the next heating.

<u>Composition IV (GeSe)</u>. After soaking at 720°C for 4 hours and at 750°C for 20 hours, Table 2, the furnace was turned over 90° to facilitate the collection of the melt at the bottom of the ampoule; the temperature was reset at 370°C. Five hours later, the furnace was stopped and cooled to room temperature in 5 hours.

<u>Composition V  $(Ge_{15}As_{15}Se_{70})$ </u>. After soaking at 720°C for 29 hours, Table 2, the furnace was turned over 90° for the reason outlined above and soaked for 1 hour. At this stage the composition was cooled to 370°C in 4 hours, annealed for 2 1/2 hours and finally cooled to room temperature in 5 hours.

<u>Composition VI ( $Ge_{30}As_{15}Se_{55}$ )</u>. The composition was soaked at 720°C for 13 hours, Table 2. At this stage, the furnace was turned over 90° for the reason outlined above. After 1 hour's soaking, the composition was cooled to 370°C in 4 1/2 hours, annealed at this temperature for 2 hours and finally cooled to room temperature in 5 hours.

<u>Composition VII ( $Ge_{15}As_{15}S_{70}$ </u>). After soaking at 520°C for 24 hours in accordance with the general procedure and Table 2, the composition was cooled to 275°C in 2 hours, annealed at this temperature for 2 hours, and finally cooled to room temperature in 2 1/2 hours.

<u>Composition VIII ( $Ge_{30}As_{15}S_{55}$ </u>). After soaking at 550°C for 25 hours in accordance with the general procedure and Table 2, the furnace was stopped and tilted over for the reason outlined above. The composition was cooled to 290°C in 2 hours, annealed at this temperature for 2 hours, and finally cooled to room temperature in 2 1/2 hours.

#### Remelting of Compositions VII and VIII

On visually examining the eight chalcogenides described above, composition VII was found to have partially crystallized while composition VIII was completely crystallized. These crystallized compositions were, therefore, remelted in non-rotational ampoules.

The two compositions were crushed and loaded in the ampoules and placed on an alumina bridge in the center of the furnace to effect a uniform heating with reasonably good air circulation. Slightly lower temperatures, Table 3, had to be used since no bomb was employed in these remeltings. After soaking the composition at the highest temperature set, the temperature was lowered for annealing followed by cooling the mass to room temperature. Described below are the specific remelting schedules for the two compositions.

Composition VII ( $Ge_{15}As_{15}S_{70}$ ). After soaking at 510°C for 12 hours, Table 3, the composition was cooled to 260°C in 2 hours where it was held for 7 1/2 hours and finally cooled to room temperature in 5 hours.

Once again, the composition was found to have crystallized on cooling. Another melting was, therefore, attempted to form a uniform glass. After soaking at 540°C for 9 hours, Table 3, the composition was cooled to 280°C in 4 1/2 hours, followed by rapid cooling to room temperature in less than 1 hour.

Since the composition, still, did not show any glass formation, a final attempt was made by soaking the composition at 565°C for 42 hours and at 577°C for 2 hours. However, on cooling to room temperature in 9 hours, no glass formation was apparent. Table 3. Remelting Schedule of Compositions VII and VIII

Composition	Max. Temp. Attained (°C)	Soaking Time at Max. Temp. (hours)	Vapor Pressure* (mm)	Type of Ampoule	Comments
Ge <sub>15</sub> As <sub>15</sub> S <sub>70</sub> (VII)	510	12	1319	Fused Quartz	Annealing at 260°C for 7 1/2 hours
	540 565	9 42			
	577	2	2994		Annealing not attempted
Ge <sub>30</sub> As <sub>15</sub> 55 (VIII)	550	25 1/2	2042	Fused Quartz	Annealing not attempted
	565	42			
	588		2673		Annealing not attempted
* See Appendix	II				

<u>Composition VIII ( $Ge_{30}AS_{15}S_{55}$ )</u>. After soaking the composition at 550°C for 13 1/2 hours, Table 3, it was cooled to room temperature in 9 hours. No glass formation could be seen. A final attempt was, there-fore, made with improved heating arrangements by soaking the composition at successively higher temperatures of 565°, 577°, and 588°C for over 42 hours and rapidly cooling it to room temperature in 1 1/2 hours. How-ever, no glass formation was apparent.

#### Property Measurements

#### Sample Preparation

Specimens for x-ray diffraction were powdered to a fine size in pestle and mortar by hand.

Specimens for index of refraction, infrared, and electrical conductivity were sliced from the glassy ingots. As the ingots were very fragile, they were mounted on graphite blocks with a polymer resin. Slicing was attempted, first using a Micromatic precision wafering machine and then in a 0.005" wire saw; while the former was discarded because of excessively high cutting speeds, the latter was rejected being extremely slow and cumbersome process. A more convenient method of slicing employed an Isomet 11-11800 low-speed diamond saw.

Coarse polishing of some slices was done on a Majur lapping/ polishing machine using 1000  $\mu$ m SiC abrasive slurry, followed by fine polishing on lapping wheels using 400 and 600 grit SiC and 0.05  $\mu$ m Gamma micropolish powder slurries, in that order. On the other slices, hand polishing had to be carried out using the aforementioned sequence of abrasives. Wedges (less than 30°) for the index of refraction

measurements were hand polished.

Polished specimens were examined under the microscope for their finish. Following this, the specimens were removed from the graphite block and thoroughly cleaned (resin was removed with xylene or trichloroethylene) in an ultrasonic cleaner before being used for property measurements. Extreme care had to be exercised in view of the fragility and very small size of the specimens.

#### X-Ray Diffraction

X-ray diffraction analysis was carried out using a Norelco diffractometer with Copper radiation (45 KV and 20 MA) through a Ni filter. Dimensions of the angular aperture and receiving slit were 1° and 0.003 inches respectively. The detector was a sealed proportional counter. The goniometer was scanned between  $2\theta = 3^\circ$  and  $90^\circ$  at 1° per minute. Index of Refraction Measurement

Index of refraction 'n' was measured according to Equation (3), where the angle of minimum deviation, ' $\delta$ ', was measured using a CO<sub>2</sub> continuous wave laser operating at a fixed wavelength ( $\lambda$  = 10.6 µm), Fig. 6 and 10, and the apex angle of the wedge was measured using a mercurycadmium-telluride laser, Fig. 6 and 11.

Of the eight chalcogenide compositions prepared, only five were tested for the index of refraction measurements, Table 5.

The CO<sub>2</sub> laser beam, having an output power of approximately 1 watt, was collimated using two concave, double meniscus, anti-reflection coated germanium lenses with focal lengths 1" and 1 1/2" and mounted on an optical bench. The collimated beam could be detected as an 8-mm spot on the fluorescent probe illuminated by a UV lamp.



c02 Pictorial Representation of Angle of Minimum Deviation Measurement; FS: Fluorescent Screen; S: Test Specimen and Holder; CL: Collimating Lens; L: CO<sub>2</sub> Laser; LG: Laser Gas; VG: Vacuum Gauge; PM: Power Meter; PS: Power Supply. Figure 10.



Figure 11. Pictorial Representation of the Measurement of Angle of the Wedge.

A disc-shaped specimen of composition I, mounted on a turntable in horizontal alignment with and normal to the laser beam, was discarded due to the intense localized heating of the specimen. In one case the beam even melted the thin disc.

The disc was, therefore, replaced by a wedge-shaped specimen in all further measurements. For convenience, the wedge was mounted such that the normal to its inclined surface lay in a horizontal plane. On firing the laser, a spot was detected in the probe plate. The wedge was rotated until the position of minimum deviation was achieved in the spot size. Angular positions of the refracted beam and the in-line beam were measured, Fig. 6, thus yielding the angle of minimum deviation ' $\delta$ '.

For the measurement of the apex angle 'A' (=  $\theta/2$ ) of the wedge, an autocollimated Hg-Cd-Te laser beam was shone on the wedge. Angular positions of the incident and the transmitted beams yielded angle ' $\theta$ ', Fig. 6. Average thickness (t) of the wedge was also determined to make necessary adjustments in the measured dimensions.

A check on the measurements was made by comparison with the method of perpendicular incidence. The wedge of composition II was rotated until one of its faces was perpendicular to the incident beam. The refracted beam was spotted on the probe. Measurements were in accordance with Fig. 6, the angle between the refracted and the in-line beams being thus obtained.

#### Infrared Spectrum

A Perkin Elmer 457 Grating IR Spectrophotometer, operated at fast or medium scanning mode and normal slit opening, was used to scan 2.5 to 40  $\mu$ m range for percent linear transmission (100% corresponded to the uninterrupted beam). Flat polished specimens, larger than 5 mm x 3 mm size, were mounted on cardboard holders and scanned in the double beam, with an accuracy of ±1% of full scale reading, Fig. 12 to 15. Care was taken such that the beam was not blocked by the holder. Specimen thickness was measured with a micrometer, Tables 6 to 9. Of the glassy compositions, composition VI could not be tested due to its very low transmission characteristics.

#### D-C Electrical Resistivity Measurements

<u>General</u>. A Keithley 610 Electrometer was used to measure the dc resistance of compositions III and V at room temperature and as a function of temperature, Fig. 16, and Tables 12 to 14. Polished rectangular specimens were prepared from the ingot. While the specimen of composition III was prepared with a high length to area ratio, so as to minimize surface fringing effects in accordance with the ASTM standard D 257-66,<sup>32</sup> the ratio was kept low for the specimen of composition V in order to facilitate the measurement of high resistances. Dimensions of the specimens were accurately measured using a micrometer, Tables 12 to 14. Silver electrodes were painted on both the specimens. The paint was allowed to air set for 5 minutes followed by baking at 130°C for 5 minutes, thus achieving good adherence and hence good ohmic contacts.

Specimen Holder. Two different gold plated specimen holders with BNC connectors and insulated leads were tried and discarded as being too lossy. To avoid the probable leakages and such losses in the leads and the connectors, a Plexiglas specimen holder with banana plugs was used after thorough cleaning with methanol.

The specimen, held in the Plexiglas holder, was placed inside the



Fig. 12. Infrared Spectra of Composition I  $(As_2S_3)$ 



Fig. 13. Infrared Spectra of Composition III  $(As_2Se_3)$ 



Fig. 14. Infrared Spectra of Composition V  $(Ge_{15}^{As}_{15}Se_{70})$ 



Fig. 15. Infrared Spectra of Composition VII (Ge $_{15}^{AS}$  $_{15}^{S}$  $_{70}^{O}$ ).



Figure 16. Pictorial Representation of D. C. Conductivity Measurement; (A) Furnace, (B) Specimen, (C) Specimen Holder, (D) Teflon-Coated Leads, and (E) Electrometer.

oven, carefully avoiding any short-circuiting. In view of the high temperatures involved, teflon-coated leads were used to connect the specimen to the electrometer. With a thermometer placed very close to the specimen, resistance was measured both in the heating as well as the cooling cycles, Tables 12 and 13. However, with the Plexiglas holder, a temperature of 150°C could barely be reached.

For measuring resistances at still higher temperatures, a similar Teflon specimen holder, able to withstand 450°C, was used. Resistance was measured again, both in the heating as well as the cooling cycles, Table 14. However, in one case, heating to 500°C resulted in the deformation of the holder under its own weight.

#### CHAPTER IV

#### RESULTS AND DISCUSSION

Results of the x-ray diffraction, index of refraction, infrared absorption spectra, and the dc conductivity measurements on the test compositions are discussed below. A comparision with the published literature has also been presented.

#### X-Ray Diffraction

X-ray studies were intended only for qualitative, not quantitative, estimation of the glass-forming ability of the systems under consideration and the compositions therein. Each composition was studied by x-ray diffraction techniques to ascertain if any crystalline phases formed during melting or as a result of the devitrification of these glasses. Fig. 17 to 24 show the diffraction patterns of the eight compositions. In some cases, peaks due to the sample holder were observed at d = 1.30, 1.83 and 2.12 A°. These peaks are, however, not shown. Table 4 describes the observed peaks in the eight chalcogenides and their comparison with the literature, wherever possible. The results were as follows:

I As<sub>2</sub>S<sub>3</sub>

Diffraction pattern of this composition, Fig. 17, showed no crystalline phase, thus indicating a strong ability of arsenic for glass formation. However, the band at d = 2.65 A° is diffused indicating a very small likelihood of structural changes. This is possibly due to annealing at a temperature fairly close to the fusion point of the glass

Composition	E Experim	nental	Literat	ure
Composition	d (A°)	20(°)	d(A°)	2θ(°)
I	5.0922	17.4	5	17.7
	2.6496	33.8	2.65	33.8
II	8.4179	11.5	Not Observed	Not Observed
	4.9787	17.8(Broad)	4.99	17.75
	2.8030	31.9	2.84	31.50
	1.7323	52.8(Broad)	1.82	50.25
III	Crystal	lline		
IV	Crystal	lline		
V	5.2417	16.9(Shoulder)		
	3.0763-2.9568	29.0-30.2(Broad)		
	1.8023-1.7025	50.6-53.8(Shoulder)		
VI	6.2317	14.2		
	3.0867	28.9(Broad)		
VII	Crystal	lline	•	
VIII	Crystal	lline		

### Table 4. Diffraction Peaks in the Experimental Chalcogenide Compositions

Majid et al.<sup>37</sup> report a shoulder at  $2\theta = 10^{\circ}$  (d = 8.1A°)



and also to a relatively slow cooling. The two observed peaks are in very good agreement with the observations of Tsuchihashi and Kawamoto<sup>17</sup> who have proposed a ring-like structure of  $As_2s_3$  glass containing 5 to 7 tetrahedra of  $Ass_{3/2}$  per ring.

## II As<sub>2</sub>Se<sub>3</sub>

Diffraction pattern of this composition, Fig. 18, showed no crystalline phase, thus confirming the strong ability of arsenic for glass formation. A comparison of the experimental values for As<sub>2</sub>Se<sub>2</sub> with the results obtained by Majid et al. 37 is given in Table 4. These authors did not observe a broad band around  $2\theta = 11.5^{\circ}$  (d = 8.4179A°) but instead have suggested the possibility of "a shoulder at about  $2\theta = 10^{\circ}$  (d = 8.1A°). However, in view of the relative intensity with respect to the band at d = 4.98A°, the band at  $d = 7.69A^\circ$  cannot be considered merely a shoulder. Instead, it is as strong a band as the one at d = 4.98A°. While the agreement for the second and third peaks is good, Bragg angles in the last case vary by as much as 0.4° (4.8%). No explanation can be offered for this discrepency in either of the two values. It may be noted that the bands at d = 1.67A° and 4.98A° are diffused or spread. According to Majid et al. 37 this indicates onset of structural changes and could be attributed to the annealing for over 2 hours. They conclude that increase in annealing time enhances these structural changes and decreases the fraction of amorphous phase and that similar effect is observed for increasing annealing temperatures.

Experimental  $As_2Se_3$  glass was annealed at 270°C for 2 hours, Table 2. In view of the slow cooling during fabrication of this glass and the sharpness of the other two peaks, namely at d = 2.80 A° and



7.69 A°, it is concluded that onset of structural changes is indicated; however, nucleation period for  $As_2Se_3$  is very large; hence no crystallization was observed in the experimental glass.

# III Ge<sub>15</sub>S<sub>85</sub>

Of the eight compositions tested, this composition has the least tendency for glass formation as revealed by numerous peaks of minor and major intensities in the diffraction pattern, Fig. 19.  $GeS_2$  shows up strongly at d = 5.64 and 3.34 A° while free S Peaks are observed at d = 3.08, 3.20, 3.34, 3.42, and 3.83 A°. Also, visual observation of a free sulphur crest on the surface of the ingot confirms the low affinity of Ge for S in solution.

#### IV GeSe

In addition to sulphur, germanium also has a low affinity for Se. The diffraction pattern of this composition, Fig. 20, reveals free Se peaks at d = 3.00 and 3.78 A°, Ge-Se peaks at d = 1.73, 1.98, 2.26, 2.71, 2.79, 3.41, and 5.40 and GeSe<sub>2</sub> peak at d = 5.90 A°. This leads to the conclusion that equimolar amounts of Ge and Se have extremely low tendency to form glass; this tendency is further diminished by extremely slow cooling from the melt during fabrication of this glass, Chapter III.  $V \ Ge_{15}As_{15}Se_{70}$ 

No crystalline phase was present in the diffraction pattern of this composition, Fig. 21, indicating a strong tendency for glass formation. The peaks at d = 1.70-1.80 and 5.24 A° could at best be considered as shoulders rather than true peaks. The peak at d = 3.03 A° is very broad. Since the fusion point of this system is not known. it is not certain if heating at 370°C was annealing or remelting of the composition.






However, the composition appears to form a very stable glass.

### VI Ge<sub>30</sub>As<sub>15</sub>Se<sub>55</sub>

No crystallinity was observed in the diffraction pattern of this composition, Fig. 22; however, the humps in the diffraction pattern of composition V were more diffused or flatter than those in composition VI. On this basis, it was concluded, though qualitatively, that the tendency of glass formation in composition VI is lower than that in composition V. This is possibly due to a higher Ge content, i.e., a lower percentage of the glass former Se than in composition V or it may be due to very slow (furnace) cooling of the composition, Chapter III. This weak tendency for crystallization is also apparent from the well defined and broad peak at d =  $3.08 \text{ A}^\circ$ .

### VII Ge<sub>15</sub>As<sub>15</sub>S 70

In addition to a broad shoulder at  $d = 1.72-1.66 \text{ A}^\circ$ , the diffraction pattern of this glass, Fig. 23, consists of broad peaks of GeS<sub>2</sub> crystals at d = 2.79 and 5.64 A°, the latter being a minor peak. Also, three other minor peaks of crystalline GeS<sub>2</sub> were observed at d = 3.30, 3.53, and 4.55 A°. A visual examination revealed regions of different colors and possibly different densities, thus confirming non-homogeneity and suggesting the possibility of phase separation or crystallization in this glass. Crystallization could be expected due to the very slow cooling of this composition, Chapter III. This conclusion is strongly supported by a high degree of crystallization subsequent to the non-rotational remelting of this composition, discussed earlier, Chapter III. Due to these peaks, the overall tendency of glass formation in this glass is low, leading to the conclusion that Se is a better glass former than S,





in contrast to the results obtained by Hilton.<sup>8</sup>

## VIII Ge<sub>30</sub>As<sub>15</sub>S<sub>55</sub>

As shown in the diffraction pattern of this composition, Fig. 24, peaks of GeS were observed at d = 2.62, 2.68, and 3.30 A°, those of  $GeS_2$  at d = 3.31 and 5.71 A° and of  $As_2S_2$  at d = 3.00, 5.47, and 5.71 A°. This implies a very weak tendency of glass formation in this composition, as compared to compositions VI and VII. Crystallization is further enhanced by a very slow cooling from the melt during fabrication of this glass, Chapter III.

In effect, compositions I, II, V, and VI, involving As as one of the constituents, have very strong tendency to form glass, although it is likely that GeS<sub>2</sub> crystallization could be avoided by a faster quenching of this composition. However, binaries involving Ge (compositions III and IV) and the ternary (composition VIII), having lower percentage of the glass forming component, sulphur, and a higher Ge content than composition VII, show extremely poor ability for glass formation. On the other hand, As appears to have a strong tendency to form glass with S and Se in the binary (I and II) compositions and with Se in the ternary (V and VI) compositions.

#### Index of Refraction

Table 5 gives the results of the index of refraction measurements on compositions I, II, V, VI, and VII. The dimensions given in the table are corrected for the thickness of the wedge in each case and measured to within + 0.05 cm.

In selecting the method of measuring the index of refraction,



Table 5. Indices of Refraction of Five Chalcogenides $^{*}$ 

		Apex	Angle o	f the Wedge	(A)	Ang	rle of Mi	nimum De	viation			
siti		PQ (cm)	PR (cm)	$\theta = \tan^{-1} \frac{PQ}{PR}$ (°)	A=θ/2 (°)	XY (cm)	XZ (cm)	YZ (cm)	\$ (°)	ц	n avg	nlitera- ture
н	to	28.90	44.48	33.01	16.51	27.20	23.50	10.60	22.66	2.33	2.38	2.3770 <sup>30</sup>
	p,	99.50	82.25	50.42	25.26	20.16	60.50	46.50	38.67	2.42		
Ц	đ	10.53	17.56	30.95	15.48	59.25	59.30	29.00	28.32	2.77	2.77	2.7760 <sup>1</sup>
	<b>.</b>	10.53	17.56	30.95	15.48	67.31	63.02	35.56	31.45	2.74 <sup>(a)</sup>		
Δ	g	22.80	82.20	15.50	7.75	35.60	33.10	7.00	10.93	2.40	2.51	2.5875 <sup>(b)</sup>
	p,	22.80	82.20	15.50	7.75	38.25	36.80	7.20	12.59	2.61		
ΙΛ	ರ	24.70	82.35	16.70	8.35	56.50	56.30	11.95	12.16	2.45	2.45	N.A.
	Ą	24.70	82.35	16.70	8.35	56.45	55.35	11.90	12.17	2.45		
IIV		53.30	82.30	32.93	16.46	40.96	5.56	35.88	22.35	2.32	2.32	N.A.
*	:											

All distances are measured within ± 0.05 cm. (a) Computed by using the method of perpendicular incidence (Equation (5)). (b) Extrapolated from Fig. 5<sup>8</sup> results. N.A.: Not Available

the availability of the equipment, namely, CO<sub>2</sub> laser operating at 10.6 µm, and the convenience of the measurement procedure<sup>\*</sup> were the primary considerations. Since the distances involved in the calculation of the apex angle of the wedge and the angle of minimum deviation could only be measured within one-half of a millimeter, accuracy of the measurements was accordingly limited.

For composition II, the index of refraction value was also calculated using Equation (5) (method of perpendicular incidence). This value is consistent with the one calculated by the method of minimum deviation, the variation being only 1.08%. The relation:  $n_1 \sin \theta_1 = n_2 \sin \theta_2$  also reduces to the method of perpendicular incidence for  $n_2 = 1$  (air).

Precise measurement of the index of refraction is possible only when the material is highly transparent. This is evident from composition V where no transmission could be observed through a wedge of 2.4 mm thickness. Instead, a 1 cm diameter strong reflection spot was observed. Reduction of thickness to 1.2 mm made it possible to observe the transmitted spot at a distance of over 35 cm.

Index of refraction varies significantly with wavelength, e.g., Rodney et al.<sup>30</sup> reported a decrease in the index from 2.636 at 0.6  $\mu$ m to 2.364 at 12.0  $\mu$ m for As<sub>2</sub>S<sub>3</sub>. Most data available in the literature concerns the refractive index measured at 5  $\mu$ m. In the present work, however, all the measurements were made at a fixed wavelength of 10.6  $\mu$ m. For As<sub>2</sub>S<sub>3</sub> (Composition I), the experimental value of 2.39 at 10.6  $\mu$ m

Angle of minimum deviation method does not require the condition of normal incidence to be met and hence was preferred over the method of perpendicular incidence.

compares very well with the value of 2.37698 computed by Rodney et al.,<sup>30</sup> based on Sellmeier type dispersion formula:

$$n^{2} - 1 = \sum_{i=1}^{i=5} \frac{K_{i} \star \lambda^{2}}{\lambda^{2} - \lambda_{i}^{2}}$$
(2)

Variation is within 0.544% of the computed value. Experimental value for  $As_2Se_3$ , n = 2.77, is in good agreement with the value of 2.78 observed by Savage and Nielsen,<sup>1</sup> the variation being only 0.725% of the literature value while the value for  $Ge_{15}As_{15}Se_{70}$ , n = 2.51, is within 3.19% of the values obtained by extrapolation in Hilton's Curve.<sup>8</sup> Comparison for other compositions could not be made due to the lack of published literature at 10.6 µm. Although the actual composition of  $As_2S_3$  and other glasses was not ascertain subsequent to the batch formation, the stoichiometry of the composition was maintained in the glass since no residual sulphur or arsenic was recovered in the ampoule subsequent to the glass formation. Seager and Quinn<sup>26</sup> have reported the possibility of forming diphasic or inhomogeneous glass samples and consequently having density variations. Possibility of such variations is, however, limited due to the very small size of the wedge.

As expected, refractive index increases as the atomic mass of the constituent atoms increases (Se > As > Ge > S), e.g.  $As_2Se_3$  glass has a higher index of refraction (2.77) than  $As_2S_3(2.38)$  and  $As_{15}Ge_{15}Se_{70}$  has a higher index value (2.51) than  $As_{15}Ge_{30}Se_{55}(2.45)$ . Similarly,  $As_{15}Ge_{15}Se_{70}$  has a higher index of refraction (2.51) than  $As_{15}Ge_{15}S_{70}$  (2.32).

#### Infrared Absorption

General

Figures 12 to 15 and Tables 6 to 9 present the infrared absorption data on four compositions, namely, I, II, V, and VII over an effective range of  $2.5 \,\mu$ m to 40  $\mu$ m. Due to the instrument limitations, results beyond 40  $\mu$ m were considered unreliable. Compositions III, IV, and VIII were crystalline and hence not examined whereas composition VI could not be analyzed due to its extremely poor transmission characteristics.

The intensity of a peak relative to the intensity of the strongest peak in the spectrum was used as the criterion to classify the peak as being strong, medium, weak, or very weak. For a strong or a medium peak, the intensity is given as a percentage of the base line maximum intensity observed over the entire spectrum. The location of each peak is given in both wave number as well as wavelength. However, for strong or medium peaks, the location is given as the wave number range at 2 percent of its minimum transmission intensity, Tables 6 to 9. This was done for consistency and convenience in the analysis. Peak assignments were based on the published literature on various systems. Since the compositions were glassy phases, most peaks were "diffused."

Principal sources contributing to the absorption peaks were found to be the impurities, oxygen and hydrogen, and the intrinsic multiphonon processes<sup>4</sup> due to the interaction of the impinging infrared radiation. Assigning a particular absorption band in a glass to a particular oxide is complicated and often questionable. As Hilton et al.<sup>8</sup> pointed out, two possible factors complicating the assignment are: (a) high dielectric field of the glass ( $\varepsilon \approx n^2$ ) shifts the molecular vibration to a lower

# Table 6-A. Absorption Peaks (cm<sup>-1</sup>) For Composition I (As<sub>2</sub>S<sub>3</sub>)

Sample	#1	Thickness	=	0.037	cm
--------	----	-----------	---	-------	----

Wave No.	λ	Peak	Relative	Maximum	% of	Assignment
$(cm^{-1})$	(µm)	Location	Intensity	Inten-	Maximum	and
(on )		$(cm^{-1})$		sity	Inten-	Comments
					sity	
				72		
1575	6.3		W			H <sub>2</sub> 0 Dis- solved in Glass <sup>4</sup>
1005	10.0	9501050	М		90.29	Molecular As <sub>4</sub> 06 or As-S <sup>4</sup> ,17 or S-S <sup>4</sup> ,17
680	14.7	660-710	S		4.17	S-S or As-S or As-O or Intrinsic 2- and 3-
2 2						Phonon 4,17 Processes
490	20.4		S		14.00	As <sub>2</sub> 0 <sub>3</sub> or or Intrinsic 2-Phonon Process4,17
310	32.3		VW			As-S <sup>8</sup>

# Table 6-B. Absorption Peaks (cm<sup>-1</sup>) For Composition I (As<sub>2</sub>S<sub>3</sub>)

Sample #2 Thickness = 0.036 cm

Wave No. (cm <sup>-1</sup> )	λ (μm).	Peak Location (cm <sup>-1</sup> )	Relative Intensity	Maximum Inten- sity	% of Maximum Inten- sity	Assignment and Comments
				77		
1575	6.3		W			H <sub>2</sub> 0 Dis- solved in Glass <sup>4</sup>
1010	9.9	950-1045	М		92.21	Molecular As <sub>4</sub> 0 <sub>6</sub> or As-S or S-S <sup>4</sup> ,17
680	14.7	665-710	S		6.49	S-S or As-S or Intrinsic 2- and 3- Phonon Pro-
490	20.4		S		17.50	As <sub>2</sub> 0 <sub>3</sub> or Intrinsic 2-Phonon Process <sup>4</sup> ,17
310	32.3		VW		, 4 21 1 2 2	As-S <sup>8</sup>

## Table 7-A. Absorption Peaks (cm<sup>-1</sup>) For Composition II (As<sub>2</sub>Se<sub>3</sub>)

Samp1	e #	1
-------	-----	---

Thickness = 0.0683 cm

Wave No. (cm <sup>-1</sup> )	(μm)	Peak Location (cm <sup>-1</sup> )	Relative Intensity	Maximum Inten- sity	% of Maximum Inten- sity	Assignment and Comments
				25		
870	11.5	825-890	М		75.5	Intrinsic 3- and 4- Phonon 4 Processes
680	14.7		VW			Intrinsic 2- and 3-
						Phonon 4 Processes
640	15.6	600-685	М		88.0	Molecular As406 or
			ia in			As-0-As Network <sup>4</sup> ,17
490	20.4	460-505	S		20.0	As-Se or
						As <sub>2</sub> 0 <sub>3</sub> or Intrinsic 2-Phonon Process <sup>4</sup>
335	29.9		VW	5) 4 104 14481 5 152 8		Fundamental As-Se-As Stretch <sup>4</sup>

# Table 7-B. Absorption Peaks (cm<sup>-1</sup>) For Composition II (As<sub>2</sub>Se<sub>3</sub>)

Sample #	₽2	Thickness =	0.089	cm
----------	----	-------------	-------	----

Wave No. (cm <sup>-1</sup> )	(μm)_	Peak Location (cm <sup>-1</sup> )	Relative Intensity	Maximum Inten- sity	% of Maximum Inten- sity	Assignment and Comments
				21		
865	11.6	825-885	М		71.4	Intrinsic 3- and 4- Phonon 4 Processes
670	14.9		W			Intrinsic 2- and 3- Phonon 4 Processes
640	15.6		W			Molecular As <sub>4</sub> 0 <sub>6</sub> or As-O-As Network <sup>4</sup> ,17
490	20.4	450-510	S		21.5	As-Se or As <sub>2</sub> 0 <sub>3</sub> or Intrinsic 2-Phonon Process <sup>4</sup>
340	29.4	1	VW			Fundamental As-Se-As Stretch <sup>4</sup>

## Table 8-A. Absorption Peaks (cm<sup>-1</sup>) For Composition V (Ge<sub>15</sub>As<sub>15</sub>Se<sub>70</sub>)

Sample #1 Thickness = 0.0572 cm

Wave No. (cm <sup>-1</sup> )	(μm)	Peak Location (cm <sup>-1</sup> )	Relative Intensity	Maximum Inten- sity	% of Maximum Inten- sity	Assignment and Comments
				19		
840	11.9	770-910	S		11.46	As203
490	20.4	465–520	S		50.00	As-Se, Ge-Se or As <sub>2</sub> 0 <sub>3</sub> or Intrinsic 2-Phonon Process17,4
370	27.0	360-390	М		65.10	Not Identi- fied
345	29.0		VW		٦	
335	29.9		W		-	Fundamental As-Se-As Stretch <sup>4</sup>

Table	8-B.	Absorption	Pea	aks	(cm	1)	For	
		Composition	V	(Ge	a sAs	15	Sezo?	)

Sample	#2	Thickness	=	0.1240	cm
--------	----	-----------	---	--------	----

Wave No. (cm <sup>-1</sup> )	λ (μm)	Peak Location (cm <sup>-1</sup> )	Relative Intensity	Maximum Inten- sity	% of Maximum Inten- sity	Assignment and Comments
	20		8	18		
840	11.9	755-930	S		8.33	As203 <sup>17</sup>
500	20.0	465–515	S		30.56	As-Se, Ge-Se or As <sub>2</sub> 0 <sub>3</sub> or Intrinsic 2-Phonon <sup>17</sup> ,4 Process
375	26.7	365-380	М		50.00	Not Identi- fied
345	29.0		VW		1	Fundamental
330	30.3		W		ŀ	As-Se-As Stretch

Table	9-A.	Absorption	Peaks	(cm	<sup>-1</sup> )	For	
101512120	5 (553)A	Composition	n VII	(Ge	5 <sup>As</sup>	1587	0)

Sample #1 Thickness = 0.2231 cm

Wave (cm <sup>-1</sup> )	(μm)	Peak Location (cm <sup>-1</sup> )	Relative Intensity	Maximum Inten- sity	% of Maximum Inten- sity	Assignment and Comments
				33.5		
1580	6.3		W			H_O Dis- solved in Glass <sup>4</sup>
1310	7.6	1280-1340	Μ		86.6	Molecular As <sub>4</sub> 0 <sub>6</sub> or S0 <sub>2</sub> or S-S4,8,17
830	12.0	770-870	S		17.9	S-S or As20 17
335	23.9		W			Not Identi- fied
320	31.3		VW			Not Identi- fied
÷.			V & //			

Table	9-B.	Absorption	Peaks	(cm	·1)	For
		Composition	n VII	(Ge15	As,	5S70)

Sample #2 Thi

Thickness = 0.0368 cm

Wave No. (cm <sup>-1</sup> )	('tɯ)	Peak Location (cm <sup>-1</sup> )	Relative Intensit	Maximum y Inten- sity	% of Maximum Inten- sity	Assignment and Comments
				42.5		
1580	6.3	1570-1610	W		88.2	H <sub>2</sub> 0 Dis- solved in Glass <sup>4</sup>
1310	7.6	1295-1325	S		45.9	Molecular As4 <sup>0</sup> 6 or S0 <sub>2</sub> or S-S <sup>4</sup> ,8,17
835	12.0	670-915	S		17.6	S-S or As20317
340	29.4		W			Not Identi- fied
310	32.3	305-320	М		23.5	Not Identi- fied

frequency, and (b) frequency may be shifted because of chemical bonding with the surroundings by the molecular group. The latter was considered to be of importance in the assignment of these peaks, in view of the absence of any applied electric field.

#### Oxide Absorption Bands

In spite of the best possible precautions taken to eliminate any contamination by oxygen, absorption peaks were mostly located around oxygen network formation. Oxygen could have intruded as an impurity in the reacting elements or could have stayed in the ampoule as a residual gas. No attempt was made to further purify the as-received raw materials. Another possible source of oxygen could be the quartz ampoule itself  $(Si0, \rightarrow Si0)$ . Once in the system, oxygen forms very stable oxides with both arsenic and germanium. 8 Vasko<sup>3</sup> and others have observed that As Se spectrum in the 300-1000  $\text{cm}^{-1}$  region depends only on the total amount of the oxygen present. A 780 cm<sup>-1</sup> peak in As-Se and Ge-As-Se, reported by Savage and Nielsen<sup>1</sup> and others to be due to As-O absorption was, however, not observed in compositions II and V. Also, Ge-O absorption peaks could be expected at 870  $\text{cm}^{-1}$  and 543  $\text{cm}^{-1}$  or at 780  $\text{cm}^{-1}$ . However, no significant contribution to the absorption due to Ge-O was observed in both composition V as well as composition VII involving Ge. This leads to the conclusion that Ge-O was successfully prevented from forming. Often times, use of oxide getters like boron and aluminum is suggested in the literature to be an effective means of removing some oxide bands from Ge containing chalcogenides.<sup>8</sup> However, use of such elements is obviated by the observed results in the germanium systems.

An important feature of the absorption spectra of compositions I,

II, and V is the peak at 490-500 cm<sup>-1</sup>. The intensity of this peak appears to be strong in  $As_2S_3$  (composition I),  $As_2Se_3$  (composition II), and  $Ge_{15}As_{15}Se_{70}$  (composition V). The best possibility seems to be  $As_2O_3$ or intrinsic "2-phonon process." According to Moynihan et al.,<sup>4</sup> the intensity of this peak is independent of the oxide content and hence this must be a 2-phonon process intrinsic absorption band, whereas Hilton,<sup>8</sup> and Savage and Nielsen<sup>1</sup> characterize it as a Ge-Se overtone. This, however, could not be the primary reason in view of the absence of Se in the composition of  $As_2S_3$ , composition I, although it may have contributed to the peak sharpness and intensity in composition V where Se was present. Hilton concedes that although the possibility of I R overtones of As-S, Ge-S, etc., may exist, these absorption bands are fairly weak and could only be identified by comparing absorptions of different systems.

On the basis of the published literature, oxide impurity bands observed in composition I at 1005-1070 cm<sup>-1</sup> were characterized as molecular  $As_40_6$  or network >As-0-As<. An outside possibility of  $S0_2$ , as considered by Nakamoto<sup>38</sup> may exist, but this may at best have only minor contributions in view of the relative intensities of As-0 absorption peaks. Other absorption bands due to oxides were observed in compositions II, V, and VII at 825-870 cm<sup>-1</sup> and in compositions I and II at 640-680 cm<sup>-1</sup>. Burley<sup>39</sup> has also reported a broad band at 630 cm which he attributed to the dissolved monomeric form of  $Se0_2$ , whereas Moynihan et al.<sup>4</sup> have reported observing oxide bands in their  $As_2Se_3$  glass at 650 and 785 cm<sup>-1</sup>, the latter being observed at a minimum  $As_20_3$  level of 270 ppm. In the absence of this band in the experimental glass, it may be concluded that oxygen impurity level was fairly low such that  $As_20_3$ 

content was below 270 ppm. Vasko et al.<sup>3</sup> conclude that 650 cm<sup>-1</sup> band is due to the oxygen present in a network structure similar to that of vitreous  $As_20_3$  or of the  $As_20_3$  monoclinic crystal while the 785 cm<sup>-1</sup> band was due to the oxygen present as  $As_40_6$  molecules. The peak at 640 cm<sup>-1</sup> in composition II may be related to the vibrations of the oxygen incorporated substitutionally for Se in the  $As_2Se_3$  network in the form of >As-0-As< local groups. This band is, however, not characteristic of  $As_2Se_3$  composition, but is also present in composition VII.

Some authors have reported observing a number of weaker oxide absorption bands in the 900-1400 cm<sup>-1</sup> region. Due to the limited instrument accuracy and the very low intensities, these bands were not reported here. Some of these bands were questionable on account of their nonrepeatability and hence were attributed to the instrument noise. Here also, S-S absorption in compositions I and VII and As-S absorption in composition I may have made only secondary contributions. Oxide absorption is also observed in composition VII at 1310 cm<sup>-1</sup> along with the possible contributions of S-S and SO<sub>2</sub>.

Absorption bands of weak intensities were observed in compositions I and VII at 1535-1580 cm<sup>-1</sup>, Fig. 12 and 15, Tables 6 and 9. These have been attributed to  $H_20$  dissolved in the glasses resulting in -0 -H network. Savage and Nielsen<sup>1</sup> and Moynihan<sup>4</sup> have also observed hydrogen impurity band at 1585 cm<sup>-1</sup> in a variety of selenide and sulphide glasses. This band is attributed to 0-H vibrations due to the  $H_20$  dissolved in glass rather than 0-H groups bonded in turn to the network, e. g., >As-0-H<. Indeed, allowing for a slight shift to lower frequencies due to hydrogen bonding to the network, the frequency of this band agrees fairly closely with a fundamental vibrational frequency of isolated  $H_20$  molecules (1595  $\text{cm}^{-1}$ ). The H<sub>2</sub>0 must be absorbed initially on the silica melt tube or on the surface of the components.

#### Non-Oxide Absorption Bands

Several As-Se-As fundamental stretch absorption bands were observed in the higher wavelength regions: at 330-335 cm<sup>-1</sup> in compositions II and V, at 350 cm<sup>-1</sup> in composition II and at 345 cm<sup>-1</sup> in composition V. Moynihan et al.<sup>4</sup> have reported observing a shoulder at 340 cm<sup>-1</sup> and have attributed this to the fundamental As-Se-As group stretching vibrations. Lucovsky and Martin<sup>40</sup> have suggested that in As<sub>2</sub>Se<sub>3</sub> glass, the AsSe<sub>3</sub> pyramidal groups are only weakly coupled vibrationally by the bridging As-Se-As groups and that I R spectra in the fundamental region correspond to those AsSe<sub>3</sub> molecules superimposed on much less intense As-Se-As spectra. A weak absorption band at 310 cm<sup>-1</sup> in composition I was identified as As-S bond.

An absorption peak of medium intensity at 375  $\text{cm}^{-1}$  in composition V and some weak bands at 310-320 and 330-335  $\text{cm}^{-1}$  in composition VII could not be identified and assigned. It is not certain if these weak bands were due to the material characteristics or to the noise level of the instrument itself.

#### Reflectivity and Absorption Coefficient

Reflectivity and absorption coefficients of the experimental glasses are given in Table 10 as calculated from Equations (7) and (8). Reflectivity of these four compositions were computed using the corresponding index of refraction values from Table 5 at 10.6  $\mu$ m. Absorption coefficients of these glasses were calculated from the reflectivity and transmission data at 10.6  $\mu$ m. Absorption coefficients for different specimen thicknesses of the same composition showed some variation. This may be due to experimental errors although Rockstad<sup>22</sup> has also Table 10. Reflectivity and Absorption Coefficient of Chalcogenide Test Compositions

Composition	Refrac- tive Index 'n'	Reflec- tivity 'R'	Thick- ness t <sub>1</sub> (cm)	Trans- mission T_1	Absorp- tion Coeff. a(cm <sup>-1</sup> ) (At 10.6 µm)	Thickness t2(cm)	Trans- mission T2	Absorp- tion Coeff. a(cm-1) (At 10.6 µm)	Average Absorp. Coeff a(cm <sup>-</sup> 1)
As2 <sup>S</sup> 3 (I)	2.39	0.17	0.0370	0.675	0.239	0.0360	0.72	0.533	0.386
As <sub>2</sub> <sup>Se</sup> 3 (II)	2.77	0.22	0.0683	0.225	6.33	0.0891	0.190	5.68	6.01
Ge <sub>15</sub> As <sub>15</sub> Se <sub>70</sub> (V)	2.51	0.19	0.0572	0.095	14.67	0.1240	0.060	8.38	11.52
Ge <sub>15</sub> As <sub>15</sub> S70 (VII)	2.32	0.16	0.2231	0.29	1.73	0.3680	0.200	1.49	1.63

reported observing similar variations in his study of As<sub>2</sub>Se<sub>3</sub> glass.

A correlation among reflectivity, index of refraction, and the absorption coefficients is presented in Table 11. A direct relationship could be observed in the three characteristics of these glasses. There is, however, no definite correlation factor governing these characteristics.

#### D.C. Electrical Conductivity

#### **General**

Figures 25 to 27 and Tables 12 to 14 present dc conductivity of compositions III and V measured as a function of temperature in both heating and cooling. Also shown are the effects of sample holder on the conductivity.

#### Conductivity of Compositions III and V

Various authors have discussed the dc conductivity characteristics of chalcogenide glasses--mainly those involving chalcogens with arsenic. No data, however, could be found on the binary  $\text{Ge}_{15}\text{S}_{85}$  (composition III, crystalline) and the ternary  $\text{Ge}_{15}\text{As}_{15}\text{Se}_{70}$  (composition V, amorphous). Comparison with the literature is, therefore, limited and only qualitative. Dembovskii and Loitsker<sup>41</sup> have reported the conductivity of crystalline  $\text{Ges}_2$  ( $\text{Ge}_{15}\text{S}_{30}$ ) at 20°C to be  $10^{-15}$  ohm<sup>-1</sup> cm<sup>-1</sup>. In the present work, an extrapolated value of 5 x  $10^{-14}$  ohm<sup>-1</sup> cm<sup>-1</sup> was obtained for  $\text{Ge}_{15}\text{S}_{85}$  at 20°C. As the difference between the two values was very small, no valid comparison can be made except in the order of magnitude values, because (a) stoichiometry of the test composition (III) is considerably different from  $\text{Ges}_2$ ; final stoichoimetry could be  $\text{Ge}_{15}\text{S}_{85-x}$  (x>0), as

System	Composition	Formula Wt.	Refractive Index n	Reflec- tivity R	Absorption Coefficient α(cm <sup>-1</sup> ) (At 10.6 μm)
Binary	As2S3	246.04	2.39	0.17	0.386
	As2 <sup>Se</sup> 3	386.61	2.77	0.22	6.01
Ternary	<sup>Ge</sup> 15 <sup>As</sup> 15 <sup>S</sup> 70	445.75	2.32	0.16	1.63
e L	<sup>Ge</sup> 15 <sup>As</sup> 15 <sup>Se</sup> 70	773.99	2.51	0.19	11.47

Table 11.	Correlation of	Index of Refraction,	Reflectivity,
	and Absorption	Coefficients	



Fig. 25. D. C. Conductivity of Composition III as a Function of Temperature.

88









### Table 12. D.C. Electrical Conductivity of Composition III Vs. Temperature (Using Plexiglas Specimen Holder)

Electrodes: Silver Paint

Dimensions:  $A = 0.8950 \text{ cm}^2$ 1 = 0.2400 cm

Te	mperature	'T'	$\frac{10^4}{2}$ (/°K)	Resistance 'R'	Conductivity	$\log_{10^{\circ}}$
	(°K)		Τ,	(ohm)	$(\sigma = \frac{1}{AR}) (mho cm^{-1})$	)
ala tet ba	306	-	32.68	9.9 x $10^{13}$	$1.00 \times 10^{-13}$	-13.000
	311	52	32.15	$8.3 \times 10^{13}$	$1.19 \times 10^{-13}$	-12.924
	315		31.75	$6.8 \times 10^{13}$	$1.47 \times 10^{-13}$	-12.833
	321	Н	31.15	4.8 x $10^{13}$	$2.06 \times 10^{-13}$	-12.686
	338	E A	29.59	7.5 x $10^{12}$	$1.32 \times 10^{-12}$	-11.879
	355	T I	28.17	4.5 $\times 10^{11}$	$2.20 \times 10^{-11}$	-10.658
	369	N G	27.10	$1.3 \times 10^{10}$	$7.62 \times 10^{-10}$	- 9.118
	385		25.97	$3.5 \times 10^9$	$2.83 \times 10^{-9}$	- 8.548
*	387		25.84	$1.1 \times 10^9$	9.01 x $10^{-10}$	- 9.045
	390		25.64	$3.9 \times 10^9$	$2.54 \times 10^{-9}$	- 8,595
	409		24.45	$2.4 \times 10^9$	$4.13 \times 10^{-9}$	- 8.384
	412		24.27	$2.3 \times 10^9$	$4.31 \times 10^{-9}$	- 8.366
	417		23.98	$1.8 \times 10^9$	$5.50 \times 10^{-9}$	- 8.260
	423		23.64	$1.6 \times 10^9$	$6.19 \times 10^{-9}$	- 8.208
	367	С	27.25	$4.8 \times 10^9$	$2.06 \times 10^{-9}$	- 8.685
	350	0	28.57	$1.7 \times 10^{10}$	5.83 x $10^{-10}$	- 9.235
	336	I	29.76	$3.0 \times 10^{10}$	$3.30 \times 10^{-10}$	- 9.481
	325	G	30.77	6.0 x $10^{12}$	$1.65 \times 10^{-12}$	-11.782
	318		31.45	$2.3 \times 10^{13}$	$4.31 \times 10^{-13}$	-12.366

\*Slight Change in the Set-up at this Stage

### Table 13. D.C. Electrical Conductivity of Composition V Vs. Temperature (Using Plexiglas Specimen Holder)

Electrodes: Silver Paint

Dimensions:  $A = 0.5768 \text{cm}^2$ 1 = 0.1710 cm

Temperature 'T'	$\frac{10^4}{m}$ (/°K)	Resistance 'R'	Conductivity	$\log_{10^{\sigma}}$
(°K)	т	(ohm)	$(\sigma = \frac{1}{AR}) (mho_{cm} - 1)$	)
299	33.39	$2.0 \times 10^{13}$	$1.48 \times 10^{-14}$	-13.830
351	28.49	$1.7 \times 10^{12}$	$3.70 \times 10^{-14}$	-13.432
358	27.93	$3.6 \times 10^{12}$	$8.22 \times 10^{-14}$	-13.085
363	27.55	$1.4 \times 10^{12}$	2.11 x $10^{-13}$	-12.675
368 H E	27.17	5.7 x $10^{11}$	5.19 x $10^{-13}$	-12.285
373 A T	26.81	$2.5 \times 10^{11}$	$1.18 \times 10^{-12}$	-11.927
378 I N	26.46	$1.2 \times 10^{11}$	$2.47 \times 10^{-12}$	-11.608
383 <sup>G</sup>	26.11	$5.2 \times 10^{10}$	$5.69 \times 10^{-12}$	-11.245
388	25.77	$3.0 \times 10^{10}$	9.87 x $10^{-12}$	-11.006
393	25.45	$1.8 \times 10^{10}$	$1.64 \times 10^{-11}$	-10.784
398	25.13	$1.0 \times 10^{10}$	$2.96 \times 10^{-11}$	-10.529
403	24.81	$4.7 \times 10^9$	$6.30 \times 10^{-11}$	-10.201
408	24.51	$2.8 \times 10^9$	$1.06 \times 10^{-10}$	- 9.976
413	24.21	$2.0 \times 10^9$	$1.48 \times 10^{-10}$	- 9.830
418	23.92	$1.3 \times 10^9$	$2.28 \times 10^{-10}$	- 9.643
423	23.64	$8.2 \times 10^8$	$3.61 \times 10^{-10}$	- 9.443
428	23.36	5.5 x $10^8$	5.38 x $10^{-10}$	- 9.269
431	23.20	$4.0 \times 10^8$	$7.40 \times 10^{-10}$	- 9.131

				and the second se		
Tempera	ture	'T'	$\frac{10^4}{m}$ (/°K)	Resistance 'R'	Conductivity	$\log_{10^{\circ}}$
(°K)			T	(ohm)	$(\sigma = \frac{1}{AR}) (mho_{-1})$	)
423			23.64	$5.0 \times 10^8$	$5.92 \times 10^{-10}$	- 9.228
413		14	24.21	$8.3 \times 10^8$	$3.57 \times 10^{-10}$	- 9.448
403			24.81	$1.7 \times 10^9$	$1.74 \times 10^{-10}$	- 9.759
393			25.45	$3.4 \times 10^9$	$8.70 \times 10^{-11}$	-10.060
383		C 0	26.11	7.4 x $10^9$	$4.00 \times 10^{-11}$	-10.398
373		0 L	26.81	$1.8 \times 10^{10}$	$1.64 \times 10^{-11}$	-10.784
363		I N	27.55	$4.4 \times 10^{10}$	$6.73 \times 10^{-12}$	-11.172
353		G	28.33	$1.3 \times 10^{11}$	$2.28 \times 10^{-12}$	-11.643
341			29.33	5.7 x $10^{11}$	5.19 x $10^{-13}$	-12.285
333			30.03	$1.7 \times 10^{12}$	$1,74 \times 10^{-13}$	-12.759
323	4		30.96	$4.8 \times 10^{12}$	$6.17 \times 10^{-14}$	-13.210
311			32.15	$1.8 \times 10^{13}$	$1.64 \times 10^{-14}$	-13.784
299			33.39	$4.0 \times 10^{13}$	7.40 x $10^{-15}$	-14.131

Table 13. D. C. Electrical Conductivity of Composition V Vs. Temperature (Using Plexiglas Specimen Holder) (Continued)

### Table 14. D. C. Electrical R Conductivity of Composition V Vs. Temperature (Using Teflon Specimen Holder)

Electrodes: Silver Paint

Dimensions:  $A = 0.5768 \text{ cm}^2$ 1 = 0.1710 cm

Temperatur (°K)	e 'T'	$\frac{10^4}{T}$ (/°K)	Resistance 'R' (ohm)	Conductivity $(\sigma = \frac{1}{1\pi})$ (mho	$\log_{10^{\circ}}$	
				AR cm <sup>-1</sup>	)	
363	-	27.55	$8.8 \times 10^{10}$	$3.36 \times 10^{-12}$	-11.473	
368		27.17	$4.4 \times 10^{10}$	$6.72 \times 10^{-12}$	-11.172	
383	H	26.11	$6.7 \times 10^9$	$4.40 \times 10^{-11}$	-10.355	
400	E A	25.00	$1.5 \times 10^9$	$1.97 \times 10^{-10}$	- 9.705	
616	т	16.23	$8.0 \times 10^6$	$3.70 \times 10^{-8}$	- 7.432	
623	I	16.05	$6.5 \times 10^{6}$	$4.55 \times 10^{-8}$	- 7.342	
644	N G	15.53	$3.3 \times 10^{6}$	$8.97 \times 10^{-8}$	- 7.047	
811		12.33	$2.3 \times 10^{6}$	$1.29 \times 10^{-7}$	- 6.891	
773		12.94	$1.7 \times 10^4$	$1.74 \times 10^{-5}$	- 5.759	
755	С	13.25	$1.8 \times 10^4$	$1.64 \times 10^{-5}$	- 4.784	
727	0	13.76	$2.2 \times 10^4$	$1.35 \times 10^{-5}$	- 4.871	
723	U L	13.83	$2.4 \times 10^4$	$1.23 \times 10^{-5}$	- 4.909	
700	I	14.29	$3.1 \times 10^4$	$9.55 \times 10^{-6}$	- 5.020	
673	N	14.86	$4.8 \times 10^4$	$6.17 \times 10^{-6}$	- 5.210	
644	G	15,53	9.3 x $10^4$	$3.18 \times 10^{-6}$	- 5.497	
623		16.05	$1.8 \times 10^5$	$1.64 \times 10^{-6}$	- 5.784	
616		16.23	$1.9 \times 10^5$	$1.56 \times 10^{-6}$	- 5.808	
589		16.98	$3.9 \times 10^5$	$7.59 \times 10^{-7}$	- 6.120	

Temperature (°K)	е 'Т'	$\frac{10^4}{T}$ (/°K)	Resistance 'R' (ohm)	Conductivity ( $\sigma = \frac{1}{AR}$ ) (mho cm <sup>-1</sup> )	<sup>log</sup> 10 <sup>σ</sup>
573		17.45	5.6 x 10 <sup>5</sup>	$5.28 \times 10^{-7}$	- 6.277
546		18.32	$6.3 \times 10^5$	$4.70 \times 10^{-7}$	- 6.328
533		18.76	$1.6 \times 10^{6}$	$1.85 \times 10^{-7}$	- 6.733
523		19.12	$2.5 \times 10^{6}$	$1.18 \times 10^{-7}$	- 6.927
505	C O	19.80	$4.8 \times 10^{6}$	$6.17 \times 10^{-8}$	- 7.210
477	0 L	20.96	$2.0 \times 10^{7}$	$1.48 \times 10^{-8}$	- 7.830
473	I N	21.14	$3.3 \times 10^{7}$	$8.97 \times 10^{-9}$	- 8.047
423	G	23.64	$8.3 \times 10^{7}$	$3.57 \times 10^{-9}$	- 8.448
394		25.38	$3.9 \times 10^9$	$7.59 \times 10^{-11}$	-10.120
321		31.15	4.5 x $10^{12}$	$6.58 \times 10^{-14}$	-13.182
298		33.56	7.3 x $10^{12}$	$4.05 \times 10^{-14}$	-13.392

Table 14. D. C. Electrical R Conductivity of Composition V Vs. Temperature (Using Teflon Specimen Holder) (Continued) may be expected if there is any loss of sulphur from the system. However, presumably sulphur loss from the composition could not be so much as to reduce the stoichoimetry to  $\text{Ge}_{15}\text{S}_{30}$ , (b) No annealing or other processing treatments for crystalline  $\text{Ge}_{15}\text{S}_{30}$  have been reported by Dembovskii and Loitsker,<sup>41</sup> and (c) no chemical analysis of composition III was done in these experiment. However, a crust of sulphur was found deposited over the bulk sample confirming phase separation and exclusion of sulphur from the Ge-S system. However, due to the very high resistivity of Ge-S system, in general, a difference of one order of magnitude appears to be fairly compatible with the measurements of Dembovskii and Loitsker.<sup>41</sup>

No comparison with the literature data could be made for  $Ge_{15}^{As} 15^{-5}$ Se<sub>70</sub> (composition V). As for the order of magnitude value, the observed values are in conformity with the typical resistivity values for chalcogenide compositions. Hilton et al.<sup>8</sup> have reported the resistivity of this composition to be 5 x  $10^{10}$  ohm-cm at 300°K. This, however, is too low a value to be accepted in view of the generally high resistivities of glassy chalcogenides at room temperature.

#### Resistance-Temperature Relationship

As shown in Fig. 25-27, the log  $\sigma$  vs 1/T plot gives a straight line for most of the curve. This linear nature is characteristic of the intrinsic behavior of the material. A slight departure from linearity is, however, noticed at very high temperatures attained in the experiment, Fig. 25-27, implying a variation in the activation energy with temperature. This may well be due to a change in the phases or a significant, though unknown, change in the conduction mechanism. A phase

change for composition V is unlikely due to the stability of the glass composition, whereas a phase change could have taken place in composition III. "Intrinsic" conductivity behavior signifies that a single, nearly constant, internal activation energy, Equation (10),  $E_{cond}$ , describes the conductivity throughout that temperature range. Also, the magnitude and the activation energy of conductivity are remarkably insensitive to compositional variations within the glass forming region of the equilibrium phase diagram and to other minor constituent impurities. This implies an ability for self-compensation. For compositions III and V, intrinsic behavior obtains separately over the low-, medium-, and high temperatures corresponding to regions I, II, and III. Departure from linearity may thus be contributed to the change over to some "extrinsic" mechanism of conduction such as the surface effects. Owen and Robertson<sup>21</sup> have reported similar breaks in their complex systems.

Another interesting feature of the conductivity-temperature plot was the discontinuities observed at low and high temperatures. In effect, Arrhenius relation,  $\overline{\sigma} = \sigma_0 e^{-E/kT}$  is followed over most of the temperature range, though in parts since the curves could be divided in the three regions discussed above, Fig. 25 and 27, each showing a different value of the activation energy, Table 15. Due to the lower temperatures attained, only regions I and II were observed in compositions III and V (Plexiglas). In all the three cases, for both the heating and the cooling cycles, slope of the conductivity plot (i.e., the activation energy,  $E_{cond}$ ) decreases in going from the low temperature (region I) to the medium temperature range (region II). An exception to this behavior is the tail end of the heating cycle plot of composition III which is
Calculation of Activation Energy (E  $_{\rm Cond}$ )(ev) in the Low-, Medium-, and High-Temperature Range for Compositions III and V Table 15.

ċ

		Heating	cycle				Cooling	g Cycle			4 C
Composition	Region I E <sub>I</sub> (ev)	Region II E <sub>II</sub> (ev)	Region III E <sub>III</sub> (ev)	ΔE <sub>I II</sub> (ev)	<sup>dE</sup> II III (ev)	Region I E <sub>I</sub> (ev)	Region II E <sub>II</sub> (ev)	Region III E <sub>III</sub> (ev)	ΔE <sub>I II</sub> (ev)	∆E <sub>II III</sub> (ev)	
III	1.014	0.435	١	0.669	I	1.640	0.244	I	1.396	ł	
V (PG)*	0.757	0.573	1	0.184	1	0.504	0.408	ł	0.096	I	
V(T)**	0.597	0.228	0.121	0.369	0.107	0.443	0.350	0.186	0.093	0.164	
*											

PG: With Plexiglas Specimen Holder \*\* T: With Teflon Specimen Holder

With Teflon Specimen Holder

considerably flat implying a very low activation energy ( $E_{cond} = 0.170 \text{ ev}$ ). However, the low temperature-very high resistivity measurements are likely to be uncertain, Fig. 25-27.

E cond further decreases in going from the medium to the high temperature region (region III), as observed in the case of composition V (Teflon holder), Fig. 27. No definite trend is, however, noticed in the magnitude of the decrease in activation energies, Table 15. Lowering of the activation energies is perhaps due to changes in the structure and the band gap energies of the crystalline and the glassy compositions, brought about by thermal excitation. A narrow band gap, of course, facilitates higher conduction of electrons. In view of the limited scope of the present investigations, however, a definite conclusion cannot be drawn regarding the possible mechanisms of conduction and the changes therein with temperature. In addition, due to the complexities involved in the behavior of the specimen holders at high temperatures and the high resistivities at lower temperatures, these measurements are subject to reasonable questioning and hence are uncertain. This is more so because Baker and Webb<sup>12</sup> have found that activation energies usually diminish approximately linearly with temperature, according to the relation,

$$E = E_{0} - \gamma T$$
 (11)

where E is the activation energy and  $\gamma$  is a thermoelectric parameter of activation energy, expressed in  $ev \cdot K^{-1}$ . Arrhenius type conductivity equation should, therefore, be rewritten as,

$$\sigma = \sigma' \exp(\gamma/k) * \exp - (E_kT)$$
(12)

Experimental results are consistent with Equation (11) which implies a flattening of the conductivity-temperature plot as the temperature increases.

## Hysteresis

The nature of the conductivity-temperature plot is further complicated by the observed hysteresis in the heating and the cooling cycles for all the three cases. Fagen and Fritsche<sup>10</sup> have also reported hysteresis in their measurements with chalcogenide glasses. In the cooling cycle, the furnace was cut off and the measurements were made with the falling temperatures. Since temperature recording was done in close proximity with the specimen and a reasonably sufficient time was allowed prior to each reading, this hysteresis could only be attributed to the intrinsic nature of the chalcogenide composition. At any given temperature, conductivity observed in the cooling cycle is higher than that in the heating cycle by one or two orders of magnitude or even more. This effect is more pronounced in the case of composition III and is most likely due to a thermal lag, thus implying poor thermal conductivity characteristics of both the compositions. Conductivity in the cooling cycle "leads" the conductivity in the heating cycle due to the thermal gradients set up within each material. This is also supported by the temperature-differences,  $T_1$  and  $T_2$ , between the onset of regions I and II respectively, in the heating and cooling cycles, Fig. 26 and 27. This temperature difference is greater in the case of composition III. Gradual phase or structural changes, if any, taking place with temperature variations may also cause such differences in conductivity. This is, however, unlikely, although confirmation may be obtained by investigating the reproducibility of the heating and cooling cycles.

## Specimen Holder

As for the variations in electrical parameters due to specimen holders, the high temperature nature of Teflon and Plexiglas materials was not investigated. While no definite conclusions could be drawn about the increase (at high temperatures) or decrease (at low temperatrues) in the activation energy values, the variation was found to be farily significant over the temperature range involved. No supportive information could, however, be obtained in the literature.

While hysteresis is perhaps an intrinsic characteristic of the chalcogenide compositions investigated, as discussed above, the nature of the heating and cooling curves is affected by the specimen holder, specially at higher temperatures where the conductivity of chalcogenide drops by several orders of magnitude. While the curves are converging at the ends (region II) for specimens III and V (Plexiglas holder) thus implying a closed hysteresis loop, the two curves exhibit divergence over the same temperature regions in the case of specimen V (Teflon holder). This basic discrepency cannot be explained by any intrinsic characteristic of the glassy composition V and must, therefore, be attributed to the specimen holders.

### CHAPTER V

#### CONCLUSIONS

- Binaries containing Germanium have a very strong tendency for crystallization, both with sulphur as well as selenium. The Ge-As-S ternary also have a strong tendency for crystallization while the Ge-As-Se ternary forms glass relatively easily.
- The glass forming tendency decreases as the percentage of germanium increases, both in the binary as well as ternary compositions.
- 3. The glass forming tendency decreases as  $As_2Se_3 > As_2S_3 > Ge_{15}As_{15}Se_{70}$ >  $Ge_{30}As_{15}Se_{55}$ .  $Ge_{15}As_{15}S_{70}$ ,  $Ge_{15}S_{85}$ , GeSe and  $Ge_{30}As_{15}S_{55}$  did not form glasses.
- 4. Crystallization may be expected in  $\text{Ge}_{15}\text{As}_{15}\text{S}_{70}$  and  $\text{Ge}_{30}\text{As}_{15}\text{Se}_{55}$  if the rate of cooling from the melt is very slow and the composition homogenization is not achieved by stirring the melt.
- 5. Index of refraction "n" of equimolar compositions containing Se was higher than that of compositions containing S ( $n_{As_2Se_3} = 2.77$ ,  $n_{As_2S_3} = 2.38$ ,  $n_{Ge_{15}As_{15}Se_{70}} = 2.51$ ,  $n_{Ge_{15}As_{15}S_{70}} = 2.32$ ).
- 6. Analyzing the I R spectra of Ge<sub>15</sub>As<sub>15</sub>Se<sub>70</sub> and Ge<sub>15</sub>As<sub>15</sub>S<sub>70</sub> on the basis of the reported literature, Ge-0 absorption bands were found to have only a minor contribution relative to the absorption due to arsenic oxide bands.
- Assuming a general agreement with the reported literature, oxide impurities were found to be the primary source of absorption in all

the experimental compositions.

- The most likely source of oxygen impurity were the starting elements themselves. Impurity level of oxygen was not reported in the asreceived raw materials.
- Possibility of As-S, Ge-S, etc., overtones exists. These, however, could have only secondary contribution to the oxide absorption.
- 10. Inconsistent with the expected physical behavior, the absorption coefficient,  $\alpha$ , was found to vary with thickness, t, of the glass specimen; e.g., for  $As_2Se_3$ , for t = 0.0683 cm.,  $\alpha = 6.33$  cm<sup>-1</sup> and for t = 0.0891 cm.,  $\alpha = 5.68$  cm<sup>-1</sup>. The cause of this inconsistency was not ascertained. Measurement errors could be one probable source of this discrepency.
- 11. Absorptivity of the glass is considerably increased when Se replaces S in binary as well as ternary compounds;  $\alpha_{As_2S_3} = 0.386 \text{ cm}^{-1}$ ,  $\alpha_{As_2Se_3} = 6.01 \text{ cm}^{-1}$ ;  $\alpha_{Ge_{15}As_{15}S_{70}} = 1.63 \text{ cm}^{-1}$ ,  $\alpha_{Ge_{15}As_{15}Se_{70}} = 11.47 \text{ cm}^{-1}$ .
- 12. The dc conductivity of both crystalline and glassy compositions followed Arrhenius behavior separately over low-, medium-, and hightemperature regions. The activation energy (slope of the conductivity vs. 1/T plot) varied in the three regions, e.g., for  $Ge_{15}As_{15}Se_{70}$ in the heating cycle,  $E_{cond}$  (low temperature) = 0.597 ev,  $E_{cond}$ (medium temperature) = 0.228 ev, and  $E_{cond}$  (high temperature) = 0.121 ev.
- 13. The dc conductivity in the heating cycle was lower than the conductivity in the cooling cycle at the same temperature, depending on

the thermal characteristics or the possible slow polarization behavior of the particular glass composition. For  $\text{Ge}_{15}\text{As}_{15}\text{Se}_{70}$  at 373°K, the conductivity (heating cycle) =  $1.64 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$  and the conductivity (cooling cycle) =  $1.64 \times 10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$ . A hysteresis was observed in the conductivity-temperature measurements which was consistent with the effect of a slow polarization mechanism.

14. The dc conductivity measurements on specimens with resistivities above 10<sup>10</sup> ohm-cm are difficult to perform over a wide temperature range.

### CHAPTER VI

### RECOMMENDATIONS

This work was primarily intended to obtain a familiarity with the chalcogenide glasses in the Ge-As-S and Ge-As-Se systems. Further work is recommended in the following areas:

1. Effect of oxygen impurity on the absorption characteristics of these glasses in the infrared region.

2. Structure of these glasses.

3. Development of an improved technique to measure the electrical conductivity over a wide temperature range, especially at low temperatures.

4. The possible slow polarization process which causes the conductivity to vary with time and temperature.

5. Applications of the glasses based on these systems.

APPENDIX I

Table 16. Characteristics of the Raw Materials

Material	Grade	Furity (%)	Size (mm)	Melting Point (°C)	Other Specifications
Selenium	ASARCO A-60	99.999+ High Purity	Dark Amorphous Pellets Approx. 5 mm Diameter	Vitrous- Indefinite; Hexagonal- 217	Density (g/cc): Vitrous: 4.28 Hexagonal: 4.79; Reported Impurity Analysis in Appendix III.
Sulphur	ASARCO A-58	99.999+ Special High Purity	Broken Lumps of Various Sizes	119.2	Rhombic; Density (20°C, g/cc): 2.07; Electrical Resistivity (20°C): 2 x 10 <sup>17</sup> ohm-cm; Dielectric Const.: 4.0; Reported Impurity Analysis in Appendix III.
Arsenic	ASARCO A-60	99.999+ Special High Purity	Random Sizes Approx. 2.5 mm Thick,25 mm or Less Square	817 (28 Atm)	Bright Gray Pieces; Density (20°C, g/cc): 5.72; Electrical Resistivity (20°C): 33.3 micro-ohm - cm; Reported Impurity Analysis in Appendix III.
Germanium	Ventron M 5 N	99.999 (Metallic Purity)	-325 Mesh	Not Reported	Very High Purity Zone Refined Mater- ial; Electrical Resistivity 47 x 10 <sup>6</sup> micro-ohm - cm; Reported Impurity Analysis in Appendix III.

ASARCO: American Smelting and Refining Company; VENTRON: Ventron Corporation

ž

### APPENDIX II

# TEMPERATURE-VAPOR PRESSURE RELATIONSHIPS

FOR Ge, Se, As, AND S

### Germanium

Total vapor pressure of germanium as determined from Fig. 28 at  $1000^{\circ}$ C was estimated to be less than  $10^{-4}$  mm Hg. Therefore, it was considered negligible for all experimental purposes.

Total vapor pressure in the binary compositions III and IV was, thus considered to be the same as that of the respective glass former, namely S or Se.

In the ternaries V to VIII, however, the total pressure was determined by the partial pressures of As plus S or Se as the case may be. Selenium

In the calculation of vapor pressure as a function of temperature, the following equation was used  $^{42}\,$ 

$$Log p = A - \frac{B}{T}$$
(14)

where A = 8.089 and B = 4989.5 and where p is the pressure in mm Hg and T is in °C.

This equation holds accurately up to 750°C, but was used only for the temperature range 675-800°C. For lower temperatures, the vapor pressure curve reported by R. E. Honig<sup>43</sup> (Radio Corporation of America) was used, Fig. 29. Various authors have reported lower vapor pressures.





Temperature-Vapor Pressure Relationship for Selenium and Sulphur.

However, for safety reasons, the reported high values were used in the calculation of partial pressures. Table 17 gives the vapor pressures used in these experiments, as calculated from the Equation (14).

Table 17. Vapor Pressure-Temperature Relationship for Selenium

Temp.(°C)	600	650	700	720	740	750	760	775	800
V.P. (mm of Hg)	260	600	914	1443	2220	2730	3342	4476	7113

Vitreous selenium, being an undercooled liquid, has no definite melting point; it becomes less viscous as the temperature rises. Melting point of metallic selenium is reported by several authors to be in the range 217-220.7°C. It is found that all forms of selenium crystallize into the metallic form in the viscinity of 250°C.<sup>44</sup>

# Arsenic

In these experiments, the following vapor pressure-temperature relationship for arsenic was used  $^{45}$ 

$$Log p = \frac{-6670}{T} + 10.47$$
(15)

where p is in mm of Hg and T in °K.

This equation was used for the temperature range 650-800°C. For lower temperatures, the vapor pressure curve reported by R. E. Honig<sup>43</sup> (Radio Corporation of America) was used, Fig. 28. Table 18 gives the vapor pressures used in these experiments as calculated from Equation (15).

Like selenium, the melting point of arsenic is not fixed and has been variously reported to be in the range 800-868°C.

Temp.(°C)	600	625	640	660	680	700	725	750
V.P. (mm of Hg)	676	1102	1460	2094	2958	4120	6118	8911

Table 18. Vapor Pressure-Temperature Relationship for Arsenic

# Su1phur

In these experiments, the following vapor pressure-temperature relationship for sulphur was used  $^{\rm 46}$ 

$$Log p = 2.6150 (2.7346 - 1000(\theta + 164)^{-1})$$
(16)

where p is in mm of Hg and T in °C

This equation was used for the temperature range 450-550°C. For lower temperatures, the vapor pressure curve reported by R. E. Honig<sup>43</sup> (Radio Corporation of America) was used, Fig. 29. Table 19 gives the vapor pressures used in these experiments as calculated from Equation (16).

Table 19. Vapor Pressure-Temperature Relationship for Sulphur

Temp.(°C)	450	470	490	500	520	530	550	570	590
V.P.(mm of Hg)	780	1062	1421	1632	2128	2415	3080	3875	4817

# Roult's Law

In the calculation of partial pressure of each element in the binary or ternary solutions, Roult's Law was used as given below

$$p_{i} = \frac{n_{i}}{\sum_{i=1,n}^{n} n_{i} p_{i}^{o}}$$
(17)

where  $p_i$  is the partial pressure of the component in the solution,  $p_i^o$  is the vapor pressure of the pure substance and  $n_i$  is the mole fraction of component i. Vapor pressures of the solutions at the maximum temperature used for the respective systems are given in Tables 2 and 3.

# APPENDIX III

Element		Imp	urities	(pa	rts	per 1	mill:	ion)	
.e.)	(In	ppm)		No	t De	tect	ed		
Selenium	Te	1	Pb,	Fe,	Ni,	Ag,	Hg,	Cđ,	
	Cu	1	Zn,	Cr,	Sn,	Mn,	Bi,	A1,	
	As	1	Ca.						
	Si	1							
Sulphur	*Na	1	Sb,	Τ1,	Mg,	Mn,	Pn,	Sn,	
	*C1	<1	Si,	Cr,	Fe,	Ni,	Bi,	A1,	
			Ca,	Cu,	In,	Cd,	Zn,	Ag,	
			Tota	al A	sh.			10000	
Arsenic	Mg	<1	Sb,	Τ1,	Mn,	Pb,	Sn,	Cr,	
	Si	<1	Ni,	Bi,	A1,	Ca,	In,	Cd,	
	Cu	1	Na,	Zn,	Ag,	Te,	Hg.		
Germanium	Si	2							
	Mg	0.2							
~3	Ca	0.2							
	A1	Few							
	Cu	0.4							

Table 20. Reported Impurity Analysis of As-Received Raw Materials by Standard Spectrographic Methods

\*Chemical Analysis

### BIBLIOGRAPHY

- Savage, J. A. and Nielsen, S., "Chalcogenide Glasses Transmitting in the Infrared Between 1 and 20 µ--A State of the Art Review," Infrared Physics, <u>5</u>, 195-204 (1965).
- Hilton, A. R., "Optical Properties of Chalcogenide Glasses," J. Non-Crystalline Solids, 2, 28-39 (1970).
- Vasko, A., Lezal, D., and Srb, I., "Oxygen Impurities and Defects in Chalcogenide Glasses," J. Non-Crystalline Solids, 4, 311-321 (1970).
- Moynihan, C. T., Macedo, P. B., Maklad, M. S., Mohr, R. K., and Howard, R. E., "Intrinsic and Impurity Infrared Absorption in As<sub>2</sub>Se<sub>2</sub> Glass," <u>J. Non-Crystalline Solids</u>, <u>17</u>, 369-385 (1975).
- Frerichs, R., "New Optical Glasses Transparent in the Infrared Up to 12 μm, Physical Review, 78, 643 (1950).
- Frerichs, R., "New Optical Glasses With Good Transparency in the Infrared," J. Optical Society of America, 43, 1153-1157 (1953).
- Hilton, A. R. and Hayes, D. J., "The Interdependence of Physical Parameters for Infrared Transmitting Glasses," <u>J. Non-Crystalline</u> Solids, 17, 339-348 (1975).
- Hilton, A. R., Jones, C. E., and Brau, M., "Non-Oxide IVA VA VIA Chalcogenide Glasses: Parts I and II," <u>Physics and Chemistry of</u> Glasses, 7(4), 105-115 (1966).
- Deeg, E. W., Habashy, G. M., and Loufti, R. O., "Preparation, Properties, and structure of As-S-Cl Glasses," <u>Sprechsaal für Keramik</u> Glas Email Silikate," 100(19), 757-759 (1967).
- Dembovskii, S. A. "Comparison of the Physico-chemical Properties of the Chalcogens and Basic Chalcogenide Compounds (Glass Formers)," <u>Inorganic Materials</u> (Trans. Akad. Nauk SSSR Izv. Neorg. Mater.), <u>5</u>(3), 385-392 (1969).
- Hilton, A. R., Hayes, D. J., and Rechtin, M. D., "Infrared Absorption of Some High Purity Chalcogenide Glasses," <u>J. Non-Crystalline</u> Solids, <u>17</u>, 319-338 (1975).
- Baker, E. H. and Webb, L. M., "Preparation and Electrical Conductivity of Some Chalcogenide Glasses at High Temperatures," J. Materials Science, 9, 1128-1132 (1974).

#### BIBLIOGRAPHY (Continued)

- Seager, C. H., "Compositional Dependence of Structural and Thermal Properties of As-Te Amorphous Alloys," <u>Materials Research Bulletin</u>, 9, 803-814 (1974).
- 14. Kitao, M., "ac Conductivity of Amorphous As<sub>2</sub>Se<sub>3</sub>," <u>Japanese J.</u> Applied Physics, 11(10), 1472-1479 (1972).
- 15. Tick, P. A., U. S. Patent 3,825,439.
- Lucovsky, G., "Comments on the Structure of Chalcogenide Glasses From Infrared Spectroscopy," 4, 505-514 (1969).
- Tsuchihashi, S. and Kawamoto, Y., "Properties and Structure of Glasses in the System As-S," <u>J. Non-Crystalline Solids</u>, <u>5</u>, 286-305 (1971).
- Cohen, M. H., Fritzsche, H., and Ovshivsky, S. R., "Simple Band Model for Amorphous Semiconductivity Alloys," <u>Physical Review</u> <u>Letters</u>, 22, 1065-1068 (1969).
- Fagen, E. A. and Fritzsche, H., "Electrical Conductivity of Amorphous Chalcogenide Alloy Films," <u>J. Non-Crystalline Solids</u>, <u>2</u>, 170-179 (1970).
- Mott, N. F. and Twose, W. D., "The Theory of Impurity Conduction," Philosophical Magazine, Supplement, 10(38), 107-110 (1961).
- Owen, A. E. and Robertson, J. M., "Electronic Properties of Some Simple Chalcogenide Glasses," <u>J. Non-Crystalline Solids</u>, <u>2</u>, 40-51 (1970).
- Rockstad, H. K., "Hopping Conduction of Amorphous Chalcogenide Films," J. Non-Crystalline Solids, 2, 192-202 (1970).
- Lakatos, A. I. and Abkowitz, M., "Electrical Properties of Amorphous Se, As<sub>2</sub>Se<sub>3</sub> and As<sub>2</sub>S<sub>3</sub>," <u>Physical Review B 3rd Series</u>, <u>3</u>(6), 1791-1800 (1971).
- 24. Crevecoeur, C. and de Wit, H. J., "Dielectric Losses in As<sub>2</sub>S<sub>3</sub> Glasses," <u>Solid State Communication</u>, <u>9</u>, 445-449 (1971).
- Davis, E. A. and Mott, N. F., "Conduction in Non-Crystalline Systems," <u>Philosophical Magazine</u>, <u>22</u>, 903-922 (1970).
- Seager, C. H. and Quinn, R. K., "D. C. Electronic Transport in Binary Arsenic Chalcogenide Glasses," J. Non-Crystalline Solids, 17, 386-400 (1975).

#### BIBLIOGRAPHY (Continued)

- Hilton, A. R., Jones, C. E., and Brau, M., "New High Temperature Infrared Transmitting Glasses-III," <u>Infrared Physics</u>, <u>6</u>, 183-194 (1966).
- Marsh, K. J. and Savage, J. A., "Infrared Optical Materials for 8-13 μm-Current Developments and Future Prospects," <u>Infrared</u> Physics, <u>14</u>, 85-97 (1974).
- Roy, R. and Caslavska, V., "Di-Phasic Structure of Switching and Memory Device Glasses," <u>Solid State Communication</u>, <u>7</u>, 1467-1473 (1958).
- Rodney, W. S., Malitson, I. R., and King, T. A., "Refractive Index of Arsenic Trisulphide," J. Optical Society of America, <u>48</u>(9), 633-636 (1958).
- 31. Wahlstorm, E. E., "Optical Crystallography," 3rd Edition, John Wiley & Sons, Inc., N. Y., 80-84 (1960)
- ASTM Standard Method of Test for D-C Resistance or Conductance of Insulating Materials, Designation D257-66 (Reapproved 1972).
- Jonker, W. P. A., "Untersuchungen uber das System: Schwefel und Arsen," Z. Anorg. Chem., 62, 89-107 (1909).
- 34. Dembovskii, S. A. and Luzhnaya, N. P., "Equilibrium Diagram of the As-Se System," <u>Russian J. of Inorganic Chemistry</u>, 9(3), 365-367 (1964).
- Liu, C. H., Pashinkin, A. S., and Novoselova, A. V., "An Investigation of the System Germanium-Sulphur," <u>Akad. Nauk SSSR, Dokl.</u> Chem., Proc. Acad. Sci., 151, 662-664 (1963).
- Liu, C. H., Pashinkin, A. S., and Novoselova, A. V., "Investigation of Germanium Selenium System," <u>Akad. Nauk SSSR, Dokl. Chem., Proc.</u> <u>Acad. Sci., 146</u>, 892-893 (1962).
- 37. Majid, C. A., Prager, P. R., Fletcher, N. H., and Brettell, J. M., "X-Ray Investigation of the Crystallization of Chalcogenide Glasses of the Type (As<sub>2</sub>Se<sub>3</sub>)<sub>1-x</sub>: (Tl<sub>2</sub>Se)<sub>x</sub>," <u>J. Non-Crystalline Solids</u>, <u>16</u>, 365-374 (1974).
- Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., N. Y., 83 (1963).
- Burley, R. A., "An Infrared Spectrophotometric Study of Vitrous Selenium Doped With Selenium Dioxide," <u>Physica Status Solidi</u>, <u>29</u>, 551-558 (1968).

### BIBLIOGRAPHY (Concluded)

- Luckovskii, G. and Martin, R. M., "A Molecular Model for the Vibrational Modes in Chalcogenide Glasses," <u>J. Non-Crystalline</u> Solids, 8-10, 185-190 (1972).
- Dembovskii, S. A. and Loitsker, E. N., "Production and Investigation of Certain Properties of Germanium Dichalcogenide Monocrystals," <u>Inorganic Materials</u> (Trans. Akad. Nauk SSSR Izv. Neorg. Mater.) <u>3</u>, 1818-1820 (1967).
- Brooks, L. S., "The Vapor Pressure of Tellurium and Selenium," J. Am. Chem. Soc., 74, 227-229 (1952).
- 43. Honig, R. E., "Vapor Pressure Curves for the More Common Elements," Radio Corporation of America, Princeton, N. J. (1957).
- Saunders, A. P., "The Allotropic Forms of Selenium," J. Phys. Chem., 4, 423-513 (1900).
- Johnston, J., "The Vapor Pressure and Volatility of Several High Boiling Metals--A Review," J. Ind. Eng. Chem., 9, 873-878 (1917).
- 46. Antoine, Ch. M., "Calcul Des Tension De Diverses Vapeurs," <u>Comptes Rendus Des Seances De L'Academie Des Sciences</u>, <u>107</u>, 778-780 and 836-837 (1888).
- Myers, M. B. and Berkes, J. S., "Phase Separation in Amorphous Chalcogenides," J. Non-Crystalline Solids, 8-10, 804-815 (1972).