

**STUDIES OF TERNARY TIN-ANTIMONY-SELENIUM-BASED  
CHALCOGENIDE GLASSES**

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A thesis submitted in fulfilment of the requirement for the award of the Degree of  
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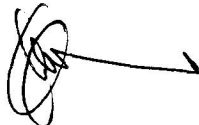
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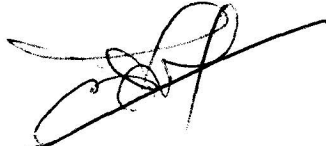
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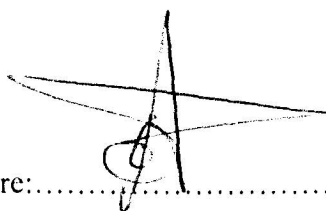
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## DECLARATION

I declare that this thesis entitled “Studies of Ternary Tin-Antimony-Selenium-Based Chalcogenide Glasses ” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.



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Date: ...05/03/2002.....

**DEDICATION**

TO MY LATE PARENTS PURE SPRITS  
AND  
MY WIFE HAYAT AND MY CHILDREN  
MOHAMED, YUSRA, YAQIN AND ZAINAB  
AND  
MY BROTHERS AND SISTERS

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## ABSTRACT

Tin-antimony-selenium (TAS)-based alloys belong to the ternary chalcogenide compounds of IV-V-VI group, which have been studied for their crystalline structure, however, their amorphous boundary region has not well reported. It is the purpose of this thesis to determine experimentally and theoretically the properties and the boundary of the glass formation region of ternary Sn-Sb-Se systems. Alloy percentages over a wide range of compositions were prepared, in specially designed shaking-furnace and melt-sealing evacuated quartz ampoule using the melt-quenching technique from 700 °C into liquid nitrogen. The characterisation properties including structural, chemical compositions, glass transition, melting and crystallisation temperatures, surface morphology, density and molar-volume, infrared transmission, Raman shift of Sn-Sb-Se systems, were measured. XRD measurements were carried out to identify whether the as-prepared samples were amorphous or crystalline structure and to determine the boundary between the two states. It showed that Sn was incorporated in the ternary systems and formed glass-state up to 12.5-mole percentage. However, crystalline phases such as  $\text{Sn}_2\text{Sb}_4\text{Se}_8$  and  $\text{Sb}_2\text{Se}_3$ , were mostly counted and dominant in crystalline structure samples with Sn-mole percentage more than 12.5. XGT and EDX proved that the samples preserve their theoretical compositions and there was no excessive loss of either chalcogen or the additives. Glass formation region was theoretically validated and mapped when the fraction of Sn-Se bonds is less than 44.5 % or the average co-ordination number is less than or equal 2.4. However, it was experimentally obtained within this region except at excluded areas in the triangle structure. DTA revealed that the glass transition temperature decreased by increasing Sn-mole percentages and increased by increasing the Sb-mole percentages. As shown in SEM micrographs, addition of a small quantity of Sn and Sb to the glassy Se-based alloy influenced little on the morphology with the kind of the crystallised phases, while markedly observed when a large amount of them was added. The density increased gradually by increasing Sn-mole percentages, while the molar volume decreased more with Sn than Sb. However, addition of Sn-mole percentage to the systems, showed a new IR-transmission band around 125-145  $\text{cm}^{-1}$ , which was assigned to asymmetrical of tetrahedral  $\text{SnSe}_4$  mode. Raman spectra for pyramidal  $\text{SbSe}_3$  occurred at 190  $\text{cm}^{-1}$ , which was reduced and shifted towards 183  $\text{cm}^{-1}$  when Sn was added to the systems. IR and Raman results confirmed the validity of assuming in amorphous state that 4, 3 and 2 are co-ordination numbers of Sn, Sb and Se, respectively. They were used for proposing the unit structure of the ternary Sn-Sb-Se systems, which was described as a solid solution of  $\text{Se}_8$  rings with the network structure formed by Se-Sn-Se<sub>3</sub>-Se-Se-Sb-Se<sub>2</sub>. Suggestions were made for alternative investigations in future.

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\*Keywords: Amorphous Sn-Sb-Se, Average-Co-ordination Number, Bond Fraction, Raman, Infrared, Glass-Transition-Temperature and Density

## ABSTRAK

Timah-Antimoni-Selenium (TAS) adalah unsur aloi yang tergolong dalam sebatian kalkogenida kumpulan IV-V-VI di mana struktur hablurnya telah dikaji tetapi mempunyai kawasan sempadan amorfus yang belum dilaporkan dengan begitu jelas. Dengan itu, tujuan tesis ini ialah untuk menentukan secara eksperimen dan juga teori tentang ciri-ciri dan sempadan kawasan pembentukan sistem kaca pertigaan Sn-Sb-Se. Aloii dalam peratusan yang luas telah disediakan dalam ketuhar-gegar yang direka khas dan teknik pelindapan-cair dari suhu  $700^{\circ}\text{C}$  ke suhu cecair nitrogen. Pencirian seperti struktur, peratusan berat, peralihan kaca, suhu lebur and penghabluran, morfologi permukaan, ketumpatan dan isipadu molar, penghantaran infra-merah, anjakan Raman sistem Sn-Sb-Se juga dikaji. Dalam analisis XRD penumpuan dibuat sama ada sampel berupa amorfus atau berstruktur hablur dan untuk menentukan sempadan di antara kedua-dua keadaan tersebut. Didapati bahawa Sn wujud dalam sistem pertigaan dan membentuk kaca sehingga peratusan mol-12.5 dengan penghabluran  $\text{Sn}_2\text{Sb}_4\text{Se}_8$  dan  $\text{Sb}_2\text{Se}_3$  sering ditemui dan terserlah dalam sampel yang berbentuk hablur dengan peratus mol-Sn melebihi 12.5. Hasil XGT dan EDX membuktikan sampel-sampel mengekalkan komposisi yang diramalkan secara teori dan tiada kehilangan berlebihan unsur kalkogen mahupun campuran. Kawasan pembentukan kaca ditentukan secara teori dan dipetakan apabila ikatan fraksi ikatan Sn-Se kurang daripada 44.5% atau purata nombor koordinasi kurang atau sama dengan 2.4 dan kawasan ini diperolehi secara eksperimen kecuali kawasan yang tidak termasuk dalam struktur segi tiga. Hasil DTA menunjukkan suhu peralihan kaca susut apabila peratus mol-Sn meningkat tetapi menunjukkan peningkatan dengan bertambahnya peratus mol-Sb. Penambahan Sn dan Sb dalam kuantiti yang kecil tidak banyak merubah morfologi aloi berasaskan Se dalam fasa hablur seperti ditunjukkan dalam mikrograf SEM. Ketumpatan bertambah apabila peratus mol-Sn bertambah sementara isipadu molar berkurangan dengan bertambahnya Sn berbanding dengan Sb. Pertambahan peratus mol-Sn dalam sistem tersebut menunjukkan jalur penghantaran infra-merah yang baru sekitar  $125\text{-}145\text{ cm}^{-1}$  yang ditumpukan kepada asimetri mod tetrahedra  $\text{SnSe}_4$ . Spektra Raman bagi  $\text{SbSe}_3$  piramid terdapat pada  $190\text{ cm}^{-1}$  yang dikurangkan dan dianjak ke  $183\text{ cm}^{-1}$  apabila Sn ditambah ke dalam sistem. Keputusan daripada Infra-Merah dan Raman mengesahkan andaian keadaan fasa amorfus 4, 3 dan 2 masing-masing bagi nombor koordinasi Sn, Sb dan Se. Ia digunakan untuk mencadangkan struktur unit bagi sistem Sn-Sb-Se pertigaan yang dikatakan penyelesaian jati bagi gelung  $\text{Se}_8$  dengan struktur rangkaian pembentukan oleh Se-Sn- $\text{Se}_3$ -Se-Se-Sb- $\text{Se}_2$ . Cadangan-cadangan telah dibuat untuk kajian pada masa depan.

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## LIST OF SYMBOLS

$\lambda$	Wavelength
$\mu$	Average co-ordination number
$\pi$	Bond strength over and above $\sigma$ ,
$\rho$	Density
$\nu$	Frequency
$\alpha$	Absorption coefficient
$\theta$	Bragg angle
$\beta$	Apex angle
$\sigma$	Bond strength
$\Delta$	Energy
$\Delta\varepsilon$	Energy difference
$\alpha_{1,2}$	Wavelengths in the plane
$\Delta S_l$	The change in configuration entropy,
$\alpha_{uv}$	Ultraviolet absorption
$a$	Cation radius,
$a_{1,2}$	Constant depend on structure unit type
ASTM	American Standard Testing Materials
$C$	Constant
COM, COCN or CON	Chemical order, chemical order chain network or chemical order covalent network model
$D$	Bond energy
$d$	The bond length
$D_E$	Entropy distribution
DTA	Differential thermal analysis
$E$	Energy
$e$	Electron charge

EDX	Energy dispersive X-ray analysis
$E_g$	Photon energy
$E_{n,l}$	Eigen value
EXAFS	Extended X-ray absorption fine structure.
$f$	the fraction of the bond
$h$	Plank's constant
IR	Infrared
$k$	Boltzman's constant
$K_\delta$	Bond bending force constant
$K'_\delta$	Correlation bond bending force constant
$K_{AB}$	Stretching force constant between A and B
$K'_{AB}$	Correlation stretching force constant
$K_g$	Hruby paramter
$k_i$	Extinction coefficient
$L$	Lone pair electrons
$l$	Quantum number
$l'$	$l$ -dependent parameter
$l_{ih}$	Component of angular momentum
$M$	Mass
$m$	co-ordination number
$M_a$	Molar mass
$M_{A,B}$	The atomic masses
$M_h$	Harmonic mean of the masses
MRO	Medium range order
$N$	The number of outer shell electrons
$n$	Quantum number defect
$N_{1,2 \text{ or } 3}$	Number of the bonds
$n_{A,B}$	Principle quantum numbers
$N_b$	The bond order
$N_{co}$	The number of co-ordinate atoms
$N_d$	The number of the degree of freedom
$N_o$	The bond order
$N_p$	The number of cross unit in the glass
$n_r$	Refractive index



$N_T$	Total of the constituent atoms.
$N_x$	The number of polymer chain
$P_t$	A projection operator
$q$	The charge of the atom
$r$	Ionic radius
$R$	Reflectivity
$r_{\sigma}^{\alpha}$	s-p $\sigma$ -hybrids on atom $\alpha$
$r_{\pi}^{\alpha}$	s-p <sup>2</sup> $\pi$ -hybrids on atom $\alpha$
$r_{1,2}$	Covalent radii
$R_{\pi}^{AB}$	The metalicity of the bond
$R_{\sigma}^{AB}$	The ionicity of the bond
RCN	Random covalent networks model.
$r_p$	the orbital dependent ionic radius of p-orbital
$r_s$	the orbital dependent ionic radius of s-orbital
$S_0$	Configuration entropy
SEM	Scanning electron microscope
SRO	Short range order
$T$	Temperature
$T_x$	Glass transition temperature of infinitely long chain
TAS	Tin-Antimony-Selenium
$T_c$	Crystalline temperature
$T_g$	Glass transition temperature
$T_m$	Melting temperature
$T_R$	Re-crystalline temperature
$V$	Volume
$V(r)$	Ionic potential of orbital ionic radii
VVF	Valence force field
$x$	Length of the polymer chain
$X$	Length of the chain
$x_{A, B}$	Electronegativities of elements A and B
$X_{AP}$	Pauling electronegativity
$X_{AS}$	Sanderson electronegativity

XGT	X-ray guide tube
XRD	X-ray diffraction
$Z$	Valence electron
$Z_{A, B \text{ or } R}$	The neighbour atoms
$Z_n$	The net core charge

## CHAPTER I

### INTRODUCTION

#### 1.1 Overview

Chalcogenide elements, namely, sulphur, S, selenium, Se and tellurium, Te, are well known to form non-oxide glasses, which have predominately covalent bonding structures. These elements are called chalcogenide because of pronounced tendency of their atoms to link together to form long-chain homo-polymers (Ray, 1978). Ray also defined an inorganic polymer as a substance with giant molecules composed of atoms other than carbon and linked together by mainly covalent bonds. With this definition, he clearly included elements of chalcogenide glasses such as S, Se and Te and oxide-glasses such as phosphoric oxide and boric oxide. Other semimetal-elements from group IV and V of the periodic table such as Si, Ge, Pb and Sn or P, As, Sb and Bi, have also been added to modify the structure and properties of chalcogenide glasses (Seddon, 1995).

The mechanical strength and thermal stability of such chalcogenide glasses are much lower than those of oxide glasses, and the thermal expansion, temperature coefficient of refractive index, and relative photoelastic coefficient are much higher than those of oxide glasses (Hilton, *et al.* 1966a). Their transparency to infrared radiation, on the other hand, generally increases towards smaller wave numbers owing to higher atomic masses and smaller bonding force constants. The decrease in the mean bonding energy, associated with increase of atomic masses in homologous

series of the Periodic System, leads to a reduction of the band gap towards the oxides (Rawson, 1967, Zarzycki, 1991). Chalcogenide glasses, in addition to electronically conducting oxide glasses, are thus a second group of vitreous substances with semiconductor properties. Their high reflectivity leads to the fact that some of them have a highly glossy appearance (Kreidl, 1983).

Chalcogenide glasses have been studied for different applications, such as xerography (Kawamura, 1983), solar cells (Ciureanu and Middelhoek, 1992, Robert, *et. al.* 1998), infrared optics (Quiroga, *et al.* 1996, Lenz, *et. al.* 2000) and switching devices (Bicerono and Ovshinsky, 1985, Ovshinsky, 1968, 1994). For xerography, the glass needs good durability and a large number of electrons trapping states from which the electron can be freed by high intensity photons. For infrared transmission, the glasses must possess a multi-phonon cut-off in mid up to far infrared, low scattering and absorption losses and a reasonable strength. For switching between high and low electrical conductivity, the glass must be able to be repeatedly crystallised and then be quenched to an amorphous state. The compositions, which satisfy the requirements of each application, are different and often the reason of these differences is understood empirically, not theoretically. In this thesis, chalcogenide glasses of tin-antimony-selenium (TAS), Sn-Sb-Se, system will be studied. Theoretically, this system has a relatively small glass-forming region than its counterparts, Si-Sb-Se and Ge-Sb-Se (Kreidl 1976, Elliott, 1990). The glasses of TAS system should have composition and property interdependence similar to other chalcogenide glasses built from atoms with equivalent valences. This may allow us to transfer what we have learned about TAS glasses to other glass-forming systems such as Ge-Sb-Se, Ge-As-Se and Ge-Bi-Se system. Through the research performed on Sn-Sb-Se glasses, we have a quantitative understanding of how their composition influences their properties in several areas of ternary phase diagram.

Philips, (1979) used a number which he referred as an average co-ordination number ( $\mu$ ) to describe the structure of glasses formed from cross-linked chains. By linking this  $\mu$  to the number of constraints prohibiting movement of the atoms in the glass, Philips was able to predict the glass-forming tendency of Ge-Se and As-Se glasses. This study attempts to use  $\mu$  to transform the composition of a glass into a model in which the glass is considered as a system of chains and cross-links. In order

to make this conversion, bond strengths between cross-linking units and chain forming units should be similar to those in chain units. By making the assumption that the  $\mu$  is a valid parameter, one can examine the properties in terms of structure as well as composition.

This co-ordination numbers have been applied for Ge-Sb-Se, Ge-As-Se in many previous studies (Nang, *et al.* 1979, Mahadevan, *et al.* 1988, Gapochenko and Bazakutsa, 2000). In the current research work we followed the same procedure and ascribed co-ordination number of the atoms of Sn, Sb and Se to be 4, 3 and 2, respectively. The structure of Se glasses is believed to consist of long chains of selenium atoms, each having a co-ordination number of 2, to these selenium chains, cross-linking atoms such as Sn and Sb may be added. The Sn atoms are 4 co-ordinated and the Sb atoms are 3 co-ordinated when covalently bonded. When added in small concentrations into Se glass, the Sn enters the structure as a chain-ending unit for 4 chains and Sb acts as a chain-ending unit for 3 chains.

A popular model is the chemically ordered covalent network model (COCN), which states the condition that "hetero-polar bonds, Sn-Sb, Sn-Se and Sb-Se, are favoured than home-bonds in all composition (Lucovsky, *et al.* 1977). This leads to a network in which cross-linking atoms will bond to chains preferentially before they bonded to other cross-linking atoms. In this study, the boundary of glass formation region of Sn-Sb-Se glasses can be visualised by using only the average co-ordination number and the chemical order chain network COCN model. Using White, (1974) random covalent network model (RCN), we assumed here, Sn-Sn, Sb-Sb and Se-Se bonds may be formed in place of hetero-polar bonds. This occurs due to the probability of 2 Sn or Sb and Se atoms being near each other.

Fuxi, (1987) in his review article performed on non-oxide glasses showed that properties reach their maximum or minimum in the region where the selenium co-ordination number ( $m=2$ ) exists between each germanium or antimony atom ( $m=4$  and 3, respectively) and no Se-Se bonds are necessary. However, Sn atom was nominated in this study to take the location of Ge before the region of the stoichiometric compounds. The compositions where the co-ordination matches these requirements are on the tie line between  $\text{SnSe}_2$  and  $\text{Sb}_2\text{Se}_3$  (referred as

“stoichiometric compositions”) whereas  $\text{As}_2\text{Se}_3$  compositions showed similar behaviour (Arsova, *et al.* 1994).

Table 1.1: Previous studies of Sn, Sb, and Se alloys for different applications

Compound	Method	Application	References
Sb-Sn-O	Spray pyrolysis	For $\text{CO}_2$ laser beam	Kojima, <i>et al.</i> (1996, 1997)
$\text{Sb}_2\text{Se}$	vapour deposition	For optical recording	Barton, <i>etm al.</i> (1986)
Se-Te-Sb	Quenching	Properties investigation.	Nagels, (1980)
Sn-Te-Se	Vapour deposition	optical recordings	Terao, <i>et al.</i> (1989).
Te-Se-Sb	Flash evaporation	Phase change optical recording	Van der Poel, <i>et al.</i> (1986).
$(\text{Ge}_{1-x}\text{Sb})\text{Se}_2$	Melt-quenching	Short range order	Uemura, <i>et al.</i> 1995).
Ge-Sn-Se	Melt-quenching	Raman study	McNeil, <i>et al.</i> 1987
$\text{Ge}_x\text{As}_{40-x}\text{Se}_{60}$	Thermal evaporation	Optical applications	Arsova, <i>et al.</i> (1994)
Ge-Se-Bi	Flash evaporation	Photo-emission characterisation	Matsuda, <i>et al.</i> (1996).
$\text{Te}_{87}\text{Ge}_8\text{Sn}_5$	Thermal evaporation	Optical data storage	Chen, <i>et al.</i> (1985).
Ge-Sb-Te	Magnetron sputtering	Digital audio recording	Nishiuchi, <i>et al.</i> (1992)
$\text{SnSe-Sb}_2\text{Se}_3$	Melting	Crystalline structure study	Mukherjee, <i>et al.</i> (1982)
Ge-Sb-Sn-Se	Melt-quenching	Physicochemical properties	Kislitskaya and Kokorina, (1971)
Sn-Sb-Se	Solid-state reaction	Switching application	Adam, (1998)

Table 1.1 represents previous studies of tin, antimony and selenium compounds in different alloy compositions for different applications. An important observation that can be deduced from these studies is that it shows rare published studies of Sn-Sb-Se systems, particularly in amorphous state. However, each of two of these elements Sn, Sb or Se have received a high attention in ternary systems with other elements, such as Ge, As, Si, S, Te, O<sub>2</sub>, Bi etc.

An element that has a light atomic mass, short atomic radius, low ionicity and high covalently, number of lone-pairs and average co-ordination numbers in the range (2 to 3) is considered as a good glass former with chalcogenide elements. On the other hand, an element that has a heavy mass is good in IR transmission and has small energy gap. However, Sn and Sb are lacking the first properties (except that for Sb has the two-lone pairs) and owing the later one, low energy gap, which is good for optical applications. The lack of these properties is strong evidence of the difficulty of glass formation, which pushes the researcher attention to perform studies on the ternary glass systems of Sn and Sb elements with chalcogen, particularly Se.

In contrast, Ge and As are good glass formers with chalcogen (Se). However, their disadvantage in wide energy gap causes intrinsic optical loss, which imposes difficulties for application in long distance fiber communication. In addition to their light masses that transmitted in mid IR region (Reitter, *et al.* 1992). In order to overcome this disadvantage a possibility of adding heavy elements such as Sb, Bi, Pb and Sn were performed. Examples of these were reported in Ge-Sb-Se systems (Mahadevan and Giridhar, 1991, Goyal and Mann 1995), Ge-Sn-Se systems (McNeil, *et al.* 1987, Mikrut and McNeil, 1989), Sn-As-Se systems (Jagatab and Zope, 1991) and Ge-Sn-Sb-Se systems (Kislitskaya and Kokorina, 1971).

## 1.2 Problem of the Study

Currently, there is no or rare published report that specifies the location and the boundary of the glass-formation region of ternary Sn-Sb-Se-based systems. Therefore, experimental and theoretical works are needed to map, characterise and specify the location and the boundary of the glass-formation region of ternary Sn-Sb-Se-based systems.

Theoretical arguments considered Sn and Sb as weak glass-forming elements because of their heavy atomic masses that favour crystalline structure, particularly in their stoichiometric compositions. Nevertheless, many questions may be raised; what are the actual concentrations of Sn, Sb and Se that are required to form amorphous Sn-Sb-Se systems? What is the temperature and time that are required for the preparation? What are the physical and chemical properties of these as prepared samples? For what applications can these samples be nominated? However, it is the intention of this study to determine experimentally the glass region of Sn-Sb-Se and the corresponding percentage of each element. To clarify this the glass-forming region can be described as a triangle formed in the rich Se corner (50-100%) while Sn and Sb percentages in the range 0.0 to 50.0-mole % of ternary Sn-Sb-Se systems as shown in Figure 1.1. In this Figure, the upper highlighted region represents all samples prepared in this study, while the dot line connects the stoichiometric  $\text{SnSe}_2$  and  $\text{Sb}_2\text{Se}_3$  compounds. Diagrams of different glass-forming regions of other ternary systems are compared to glass-forming region of Sn-Sb-Se. The glass-forming region of ternary TAS system excludes the stoichiometric compounds  $\text{SnSe}_2$  and  $\text{Sb}_2\text{Se}_3$ .

It should be mentioned here that most of the research works that were performed on the ternary systems use a combination of any two of Sn, Sb and Se elements, were focused on stoichiometric area of  $\text{SnSe}_2$  or  $\text{Sb}_2\text{Se}_3$ . Thus, one of the contributions of this study is to investigate a wide range of composition of non-stoichiometric area. Furthermore, some theoretical arguments will be discussed and used for comparing the findings with counterpart compounds, such as average coordination number, chemical order model and atomic radii.



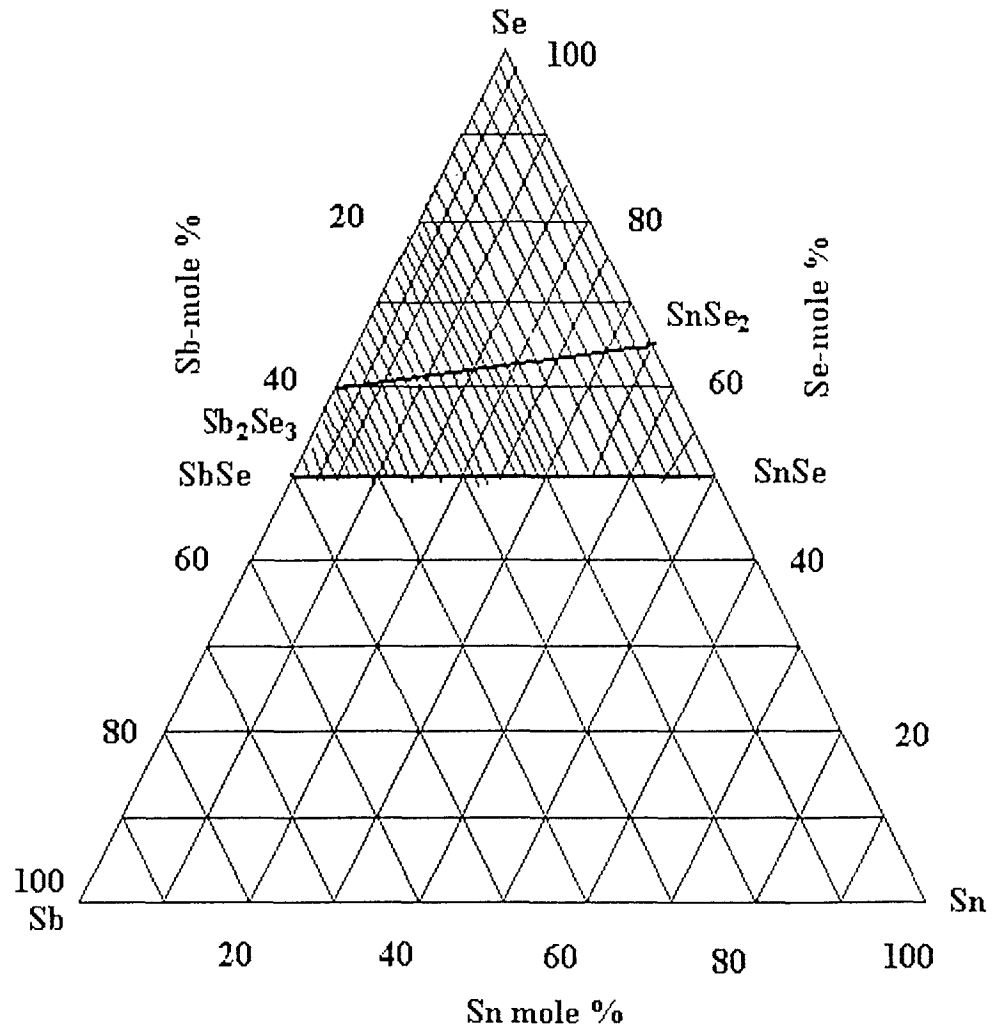


Figure 1.1: Triangle structure of ternary Sn-Sb-Se system, the shadowed portion represents the region that covered in this study.

### 1.3 Objectives of the Study

- i. To prepare amorphous Sn-Sb-Se-based alloys in bulk forms (where  $50 \leq \text{Se} \leq 100$  and  $0 \leq \text{Sn} + \text{Sb} \leq 50$  mole %) using melt-quenching technique in a specially designed and constructed shaking furnace and quartz ampoule-attached valves.
- ii. To establish a triangle structure of Sn-Sb-Se systems. X-ray diffraction (XRD), X-ray guide-tube (XGT) and Energy dispersive X-ray analysis (EDX) are used for the analyses.
- iii. To validate the boundary of the glass-formation region using average coordination number and chemical order models.
- iv. To characterise the physical and microstructure properties of the samples (thermal, density surface morphology and local structure) using Differential Thermal Analysis, Densitometer, Scanning electron microscope (SEM), IR and Raman spectroscopes.

### 1.4 Scope of the Study

A large range of composition, particularly in ternary Sn-Sb-Se system, shall be prepared and tested to examine the structural, thermal, local structural properties and compositions. The concepts which, the study would like to examine are as follows:

Since very little is known about the glass formation of Sn-Sb-Se system, some of the basic properties such as density, molar volume and glass transition temperature are measured and discussed in terms of the structural variation induced by the Sn addition. The method of preparation shall be selected and tested for wide range of compositions to insure the glass formation. Most of the experimental works will be applied to determine the suitable concentrations and temperatures that enhance the preparation of good quality and homogenous amorphous Sn-Sb-Se samples. Specially designed shaking furnace has been used for preparation of TAS system. XRD was used for identification of the sample whether it is amorphous or

crystalline. SEM was used for the surface morphological observations of the samples and determined the grain size. XGT and EDX have been used for elemental mapping and weight percentages of each element that involves in the composition of each as-prepared sample.

The average co-ordination number,  $\mu$ , and the atomic radius are valuable factors in glass-formation in the selenium excess portion of Sn-Sb-Se ternary system. These factors are used as a guide in comparing this system with other systems from the same group of the Periodic Table. In this portion the co-ordination number of Sn, Sb and Se are 4, 3 and 2, respectively. The structure of glasses in the selenium excess portion of Sn-Sb-Se ternary system is believed to approximate the linked chain model (Figure 1.2). Qualitatively, this fits with our perception of all glasses where the glass transition temperature,  $T_g$ , increases with an increase of Sb, which increase the covalent bonding. While it decreases with Sn, which has an opposite effect, whether it is due to stronger bonds or a larger number of bonds. In the present work, an attempt is made to determine if the glass transition temperature conforms to this behaviour over a wider range of compositions. The study performs more systematic testing in the region of Sn-Sb-Se ternary system.

In selenium deficient region,  $\mu$  can be applied with the high values of Sn and Sb co-ordination numbers, which are 6 and 5, respectively, resulting in Se co-ordination number 3. Nonetheless, with increased numbers of higher-co-ordinate atoms, the system has high crystalline tendency and the glass transition would be accepted to disappear while the melting temperatures increased.

Mainly stretching force constants of the corresponding chemical bonds influence the position of the intrinsic infrared features, in this Sn-Sb-Se ternary system, and also by the atomic weight of the atoms forming these bonds. However, the molecular model can be accepted in the first approximation, consequently, molecular units that form the glass significantly influence the infrared activity. Therefore, the intensity of the given intrinsic infrared feature can be related to the fraction of corresponding bonds of the constituent elements.

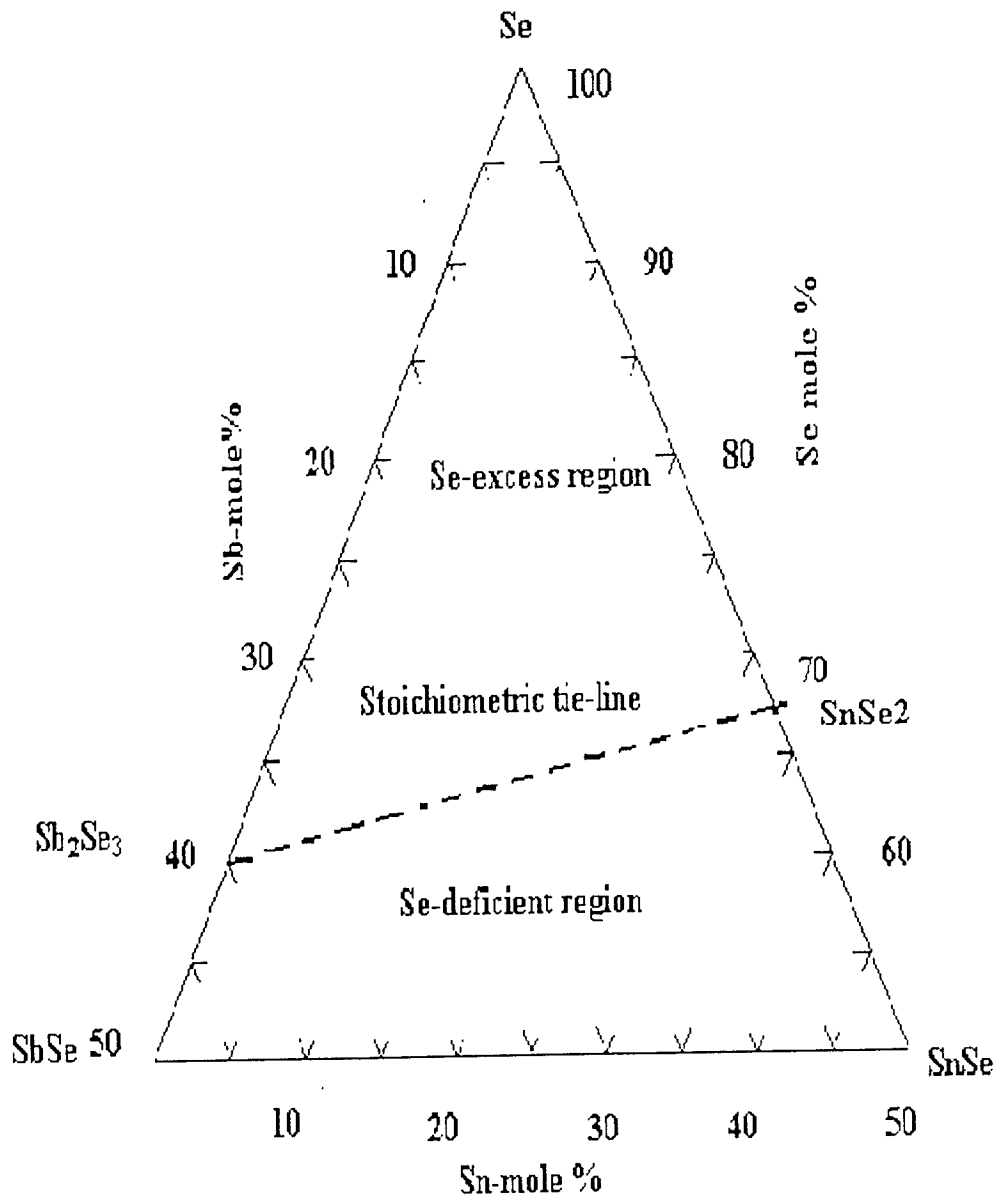


Figure 1.2: Stoichiometric tie line between  $SnSe_2$  and  $Sb_2Se_3$  in a portion of the Sn-Sb-Se ternary.

It is possible that the structures, in this Se-excess portion region, have very fine face separation, however, due to the very small differences in electronic density of Sn and Sb and their very large differences to Se density, XRD has yielded no conclusive answer to this question (Bienenstock, 1972). Observation of double glass transition-temperature using DTA and calculation of molar volumes would provide data to backup this hypothesis. The effect of microstructure units upon the properties of the glass will be examined. Bonds with less cross-linking than a 3-dimension glass would be expected to weaken the glass formation. Unsatisfied bonds may cause both  $T_g$  and chemical durability to decrease. The effect of change in co-ordination numbers will also be considered. Properties measured here as well as published will be examined and compared. Conclusions drawn from the above arguments will be used to gain a better insight into how the composition influences the structure and the properties of these glasses. This in turn may be used to suggest further studies to improve a specific application in this rare published chalcogenide glass Sn-Sb-Se system.

The major experimental work may therefore be summarised as follows: The melt quenching method which employs using a designed shaking-furnace is directly effective in forming amorphous ternary composition of Sn-Sb-Se system. TAS samples have been prepared from five-nines-purity batch materials of Sn, Sb and Se. Batch materials were weighted 5 grams and placed in quartz ampoule with inside diameter of 22 mm and length of 75 mm. In order to provide inert environment, the ampoule has evacuated, filled with argon gas and sealed using flame melt quartz glass. Rate of shaking at 100 rpm (rotate per minute) and rate of heating 5°C/min up to 700 °C are applied for the mixture elements and held for six hours. The melt is quenched using liquid nitrogen.

The sample structure is examined using X-ray diffraction (XRD), Energy Dispersive X-ray Analysis (EDX), X-ray guide tube (XGT) and Scanning Electron Microscope (SEM). The glass transition, crystallisation and melting temperatures are determined using Differential Thermal Analysis. The sample densities are measured using Archimedes balance method and accordingly the molar volumes are calculated.

The local structure is studied using IR-transmission and Raman spectra, which are obtained at room temperature in the spectral range  $4000\text{-}100\text{ cm}^{-1}$  and  $2.0\text{ cm}^{-1}$  resolution in a spectrophotometer (Shimadzu-FTIR 8000 series), while  $350\text{-}100\text{ cm}^{-1}$  for Raman spectroscopy.

A general review of ternary chalcogenide glasses, including their structural, thermal and chemical properties and the methods of preparation and analysis, is given in chapter two. The experimental procedures, including method of preparation and measurement and analysis of the as-prepared samples, are covered in chapter three. In chapter four, the results of the experimental and theoretical works together with the figures and graphs are discussed. Conclusions and suggestions drawn are found in chapter five. References and appendices are at the end of the thesis.

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