

# Glass-formation region of ternary Sn-Sb-Se-based chalcogenide glasses

A. B. ADAM, S. SAKRANI\*, Y. WAHAB\*

*Electrical and Electronics Engineering Department, Universiti Teknologi PETRONAS, 31750, Tronoh, Perak, Malaysia*

*E-mail: abdallahbelal@petronas.com.my; abdallabelal@hotmail.com*

Tin-antimony-selenium (TAS)-based system belongs to the ternary chalcogenide compounds of IV-V-VI group owing to their heavy elemental masses, their glass formation region was assumed to be small comparing to their counterpart elements in the same group. However, there were rare published reports on their glass structure, while their glass boundary formation region was not yet reported. It was the aim of this paper to map their glass-forming region experimentally using XRD and validate it theoretically using the average co-ordination number,  $\mu$ , and the fraction of the bond distributions,  $f$ , from chemical order model. Theoretically, it was validated that the glass formation was arrested between  $\mu \leq 2.4$  and the fraction of Sn-Se bonds,  $f_{\text{Sn-Se}} < 44.5\%$ . XRD analyses of 66-as-prepared samples revealed that the glass formation region was located within the predicted area that mapped in structural triangle.

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## 1. Introduction

Glass formation region will be larger if groups III, VI and V elements, which have light atomic masses [1], short atomic radii [2], low ionicity high covalently bonds, large numbers of lone-pairs [3, 4] and average co-ordination numbers in the range of 2 to 3 [5], were added to chalcogenide elements [6]. On the other hand, the region of the glass formed by addition of heavy masses elements is small but it is good in IR transmission and reduces the optical energy gap of the chalcogen [7]. However, Sn and Sb are lacking the first properties, except for Sb has the two-lone pairs, and owing the later one, reduction of the optical energy gap, which is good for optical applications. These lacks of properties are strong evidences imply the difficulty of glass formation region of their ternary systems with chalcogen, particularly Se. In contrast, Ge and As are good glass former with chalcogen (Se). However, their disadvantage in wide optical 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 [8]. Researches were performed in order to overcome their disadvantages by adding heavy elements such as Sb, Bi, Pb and Sn. Such examples of those researches are Ge-Sb-Se system [9, 10], Ge-Sn-Se system [11, 12], Sn-As-Se system [13] and Ge-Sn-Sb-Se system [14]. Since, there was no or rare published report that specified the TAS-glass forming region, it was the aim of this paper to report their glass-forming region. Accordingly, the boundary of the glass-forming region of TAS

was mapped and plotted using XRD analyses of 66-as-prepared samples [15]. In order to standardise the boundary theoretical models were used such as an average co-ordination number,  $\mu$ , and fraction,  $f$  (in%), of the bond from chemical order model, COM.

## 2. Experimental procedures

Granular of Sn and Sb having 99.999% purity while that of Se having 99.99% purity were used. The containers that these materials were stored in were only opened under a controlled way to minimise contamination. These samples were batched in a closed scale balance on which Sn, Sb and Se were weighted in accurate 0.01 grams using sample percentage procedures as mentioned in [15]. The batch elements were placed in the pre-cleaned quartz tube. The ampoule was evacuated, filled with argon and sealed using an oxygen-natural gas flame melt [15]. It was recognised that selenium has high vapour pressure and high tendency to react with oxygen. Thus, care and precaution were taken to avoid any explosion during the sealing of the ampoule.

The sealed ampoule was placed into orbital-shaking furnace. The heating cycle was applied at increasing rate of 5°C per minute, up to 700°C followed by holding at this temperature for 6 h. It seems that, this melting temperature insures a complete melting of Sb and a minimum evaporation of Se. The melting and boiling temperatures of granular Sn, Sb, and Se were reported in [16, 17]. In order to prepare homogenous samples,

\*Physics Dept. Faculty of Science, University of Technology, Malaysia, 81310-Skudai, Johor, Malaysia.

agitation of 100.0 rpm was applied using the attached orbital shaker. After that, the ampoule was dropped suddenly in liquid nitrogen for fast cooling requirement. XRD analyses were performed on fine powder of 66-as-prepared samples using Diffractometer Siemens D-5000, with energy of 40 KV, current 30 mA, CuK-alpha, Lambda,  $\lambda = 1.5418 \text{ \AA}$  and resolution of  $0.04^\circ/\text{m}$  in the range of 2 to  $60^\circ$ .

### 3. Results and discussions

#### 3.1. XRD results

Locations of the 66 samples made are shown on the ternary systems in Fig. 1. Coloured circles represent the glassy samples, while the opened circles represent the crystalline samples upon XRD analyses.

#### 3.2. Theoretical validation of Sn-Sb-Se glass formation region

The aim of this paper is to locate the glass-formation region of TAS system. Experimentally, XRD analyses showed that some areas are glass and some are in crystalline structure. In order to characterise, describe, specify and standardise the boundary and the properties of the glass-formation region, standard theoretical models are therefore be developed and applied for Sn-Sb-Se system. The used models are average co-ordination number and chemical order models as follows:

##### 3.2.1. Average co-ordination number ( $\mu$ )

Philips [5] regarded  $\mu$  as the average co-ordination number of virtual atoms; its characteristic feature is the recognition of the topological significance of non-integral co-ordination numbers and  $m_A$  and  $m_B$  are the co-ordination numbers of atoms  $A$  and  $B$ , respectively, thus  $\mu$  stated as:

$$\mu = xm_A + (1 - x)m_B \quad (1)$$

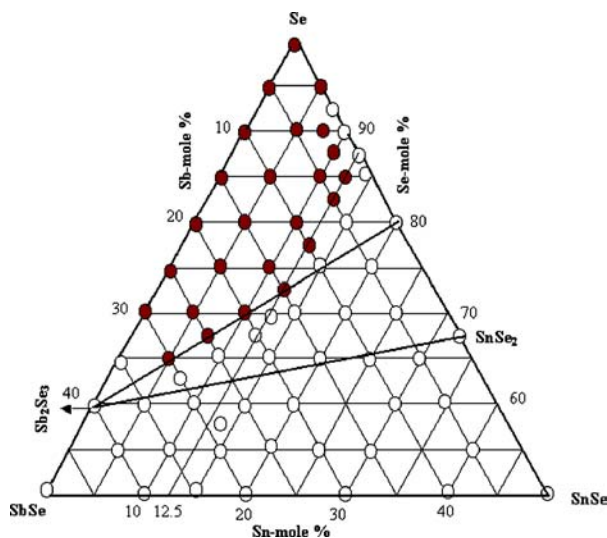


Figure 1 XRD results of Sn-Sb-Se- system coloured circles represent the glassy samples while opened circles represent crystalline samples.

His condition of glass formation of binary compositions in Equation 1 is:

$$2 \leq \mu \leq 3 \quad (2)$$

In this range the glass formation between binary alloy with  $B$  as chalcogen and  $A$  as any element from Group IVA or VA. Philips [5] noted that the best glass former have a small  $\Delta S_g$  compared to the change in entropy of melting ( $\Delta S_m$ ). In glasses, in order for the configuration entropy to reach zero, the glass structure must not be allowed any freedom movement. Regarding this to occur, the atoms in the glass must be completely constrained, that is, the number of force field constraints per atom ( $N_{co}$ ) must be equal to the number of degrees of freedom ( $N_d$ ). He calculated the number of constraints on an atom to be equal to:

$$N_{co} = \frac{(\mu)^2}{2} \quad (3)$$

The number of transitional degrees of freedom of an atom, which is not cross-linked, is 3. Upon solving these equations, the glass system becomes completely constrained at the  $\mu$  value of 2.45. Philips prediction that this composition should be the best glass former does fit in the case of Ge-Se glasses. Thorpe [18] suggested that both the rigid (over-constrained) and floppy (under-constrained) regions occur in amorphous materials. He determined that the threshold between the properties of the rigid and floppy region should be occurring at  $\mu = 2.4$ . This number was also confirmed in [19]. Philips' Equation 1 has been developed for ternary systems in [9, 20] by defined  $\mu$  as the weighted averaging that can be extended to any numbers of atoms. They described and calculated  $\mu$  for ternary  $Ge_x-As_y-Se_z$  and  $Ge_x-Se_y-Te_z$  systems as follows:

$$\mu = \frac{[4x + 3y + 2z]}{x + y + z} \quad (4)$$

where  $x$ ,  $y$  and  $z$  are the atomic percentages of Ge, As (Se) and Se (Te), while 4, 3, and 2 their co-ordination numbers in amorphous state, respectively. Referring to [5] average co-ordination number and its development for ternary system by [21], so Equations 1 and 4 are modified and applied in order to map the glass formation region of Sn-Sb-Se system.

Thus, the Iso- $\mu$  of ternary Sn-Sb-Se system were calculated and presented [15]. It should be mentioned that binary stoichiometric  $Sb_2Se_3$  and  $SnSe_2$  were co-ordinated at their stoichiometric compositions with 5 and 6, resulting in Se co-ordination changed from 2 to 3, where their corresponding average co-ordination numbers,  $\mu = 3.8$  and 4, respectively, which are more than  $\mu = 3$  [3, 5]. In order to apply Equations 1 and 4 to Sn-Sb-Se system the following assumptions have been used:

1. Equation 4 is applied for calculating  $\mu$  with 4, 3 and 2 co-ordination numbers of Sn, Sb and Se, respectively, even beyond the stoichiometric compositions of

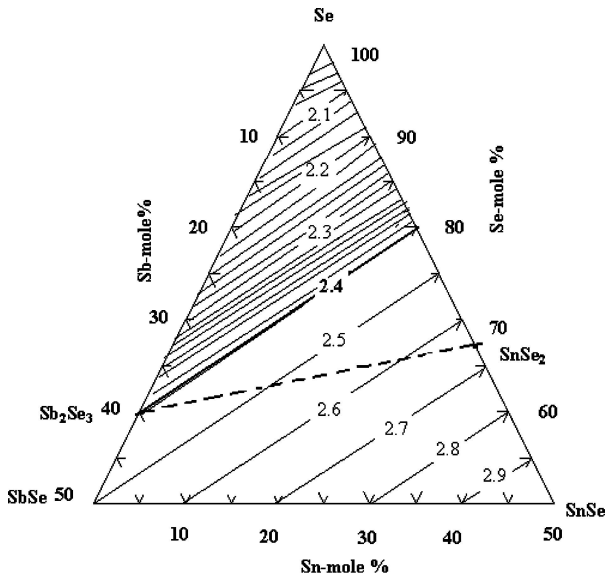


Figure 2 Iso- $\mu$ -lines that drawn on the ternary Sn-Sb-Se system, using 4, 3 and 2 co-ordination numbers of Sn, Sb and Se, respectively.

SnSe<sub>2</sub> and Sb<sub>2</sub>Se<sub>3</sub>. Thus, calculation of  $\mu$  of ternary Sn-Sb-Se systems is shown graphically in Fig. 2.

2. The co-ordination numbers of Sn, Sb and Se are 4, 3 and 2, respectively, in the experimental triangle before the stoichiometric binary composition Sb<sub>2</sub>Se<sub>3</sub>. Then after reached Sb-mole percentage = 40, the co-ordination number of Sb is changed from 3 to 5 resulting in Se co-ordination number of 3 instead of 2, while Sn co-ordination number remains as 4. In this case Equation 4 is modified in the following form:

$$\mu = \frac{[4x + 5y + 3z]}{x + y + z} \quad (5)$$

3. The co-ordination number of Sn, Sb and Se are 4, 3 and 2, respectively, in the experimental triangle before the stoichiometric binary compositions Sb<sub>2</sub>Se<sub>3</sub>. After reaching Sb-mole% = 40, the co-ordination number of Sb is changed from 3 to 5 resulting in Se co-ordination number 3 instead of 2, while Sn co-ordination number remains as 4 up to the stoichiometric SnSe<sub>2</sub> at which Sn-mole% = 33. Then, Sn co-ordination number is changed from 4 to 6, while Se co-ordination number remains 3 and Sb co-ordination number is reduced from 5 to 3. Equation 4 is modified in third form as follows:

$$\mu = \frac{[6x + 3y + 3z]}{x + y + z} \quad (6)$$

Iso- $\mu$ -lines that drawn on the ternary Sn-Sb-Se systems, using Equations 5 and 6 are shown in Fig. 3. The results obtained from the three calculation modes indicate that using 4, 3 and 2 co-ordination numbers of Sn, Sb and Se are required conditions for validating the glass-forming region. In contrast, increasing the co-ordination numbers from 4, 3 and 2 to 6, 5 and 3 for each or all three elements, respectively, increase the crystallinity of the samples. The approaches of

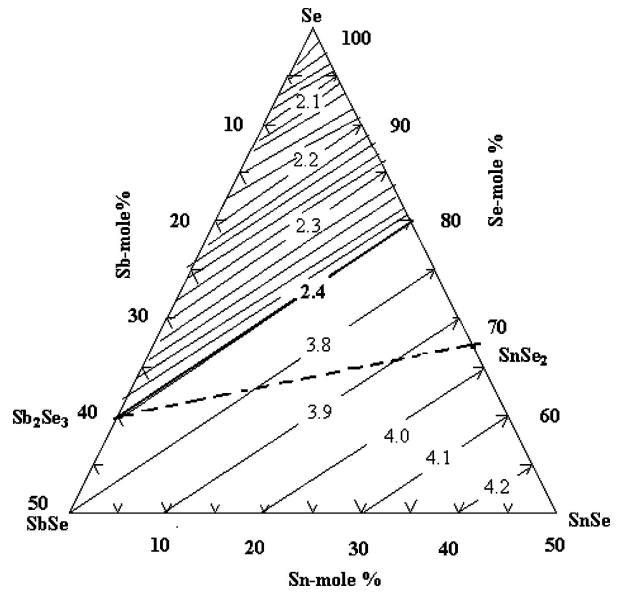


Figure 3 Iso- $\mu$ -lines that drawn on the ternary Sn-Sb-Se systems, using 4, 3 and 2 and 5, 3 and 3 co-ordination numbers before and after stoichiometric Sb<sub>2</sub>Se<sub>3</sub>, respectively and 6, 3 and 3 co-ordination numbers beyond stoichiometric SnSe<sub>2</sub>.

Equations 5 and 6 are not valid for amorphous validation and ruled out, whereas [3, 5] stated that the Sb<sub>2</sub>Se<sub>3</sub> and SnSe<sub>2</sub> stoichiometric compositions are in crystalline structure.

### 3.2.2. Fraction of the bonds from Chemical Order Model (COM)

In order to estimate the fraction of all possible chemical bonds in Sn-Sb-Se system, it is assumed that the short-range bond arrangements could be described using [21]. In chemically ordered model, the formation of Sb-Se, Sn-Se and Se-Se bonds is significantly preferred over the formation of Sn-Sn and Sb-Sb bonds [22]. Hence, for this system Sn<sub>x</sub>Sb<sub>y</sub>Se<sub>z</sub> where (x + y + z = 1) the fractions,  $f$  (in%), of the considered bonds (with respect to his condition  $2x + 3y/2 \leq z$  are also fulfilled in our system) is

$$\begin{aligned} f_{\text{Sn-Se}} &= 8x/N, \\ f_{\text{Sb-Se}} &= 6y/N \\ f_{\text{Se-Se}} &= (2z - 4x - 3y)/N \end{aligned} \quad \text{where } N = 4x + 3y + 2z. \quad (7)$$

In [23] the X-ray studies of two crystalline phases with compositions Sn<sub>2</sub>Sb<sub>4</sub>Se<sub>8</sub> and Sn<sub>4</sub>Sb<sub>4</sub>Se<sub>10</sub> in the SnSe-Sb<sub>2</sub>Se<sub>3</sub> system, were reported. They stated that SnSe has a deformed NaCl-type structure, while chains of -Sb-Se-Sb oriented along the  $c$ -axis builds up Sb<sub>2</sub>Se<sub>3</sub>. It was observed from XRD analyses of TAS samples that crystalline Sn<sub>2</sub>Sb<sub>4</sub>Se<sub>8</sub> phase was dominant when Sn-mole% is more than 12.5 or approached 15. Thus, compound Sn<sub>2</sub>Sb<sub>4</sub>Se<sub>8</sub> is transferred in molar form as Sn<sub>14.3</sub>Sb<sub>28.6</sub>Se<sub>57.1</sub> composition.

Applying [21] method for calculating the fraction of  $f_{\text{Sn-Se}}$ ,  $f_{\text{Sb-Se}}$  and  $f_{\text{Se-Se}}$  bonds of all as-prepared samples including Sn<sub>14.3</sub>Sb<sub>28.6</sub>Se<sub>57.1</sub>. In the case of

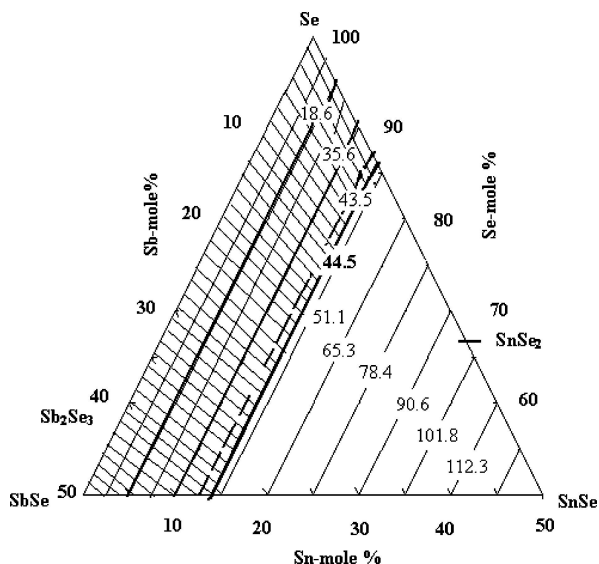


Figure 4 Iso- $f_{\text{Sn-Se}}$  bonds drawn on the ternary Sn-Sb-Se systems, using 4, 3 and 2 co-ordination numbers of Sn, Sb and Se, respectively, before and after  $\text{Sn}_{14.3}\text{Sb}_{28.6}\text{Se}_{57.1}$  compositions.

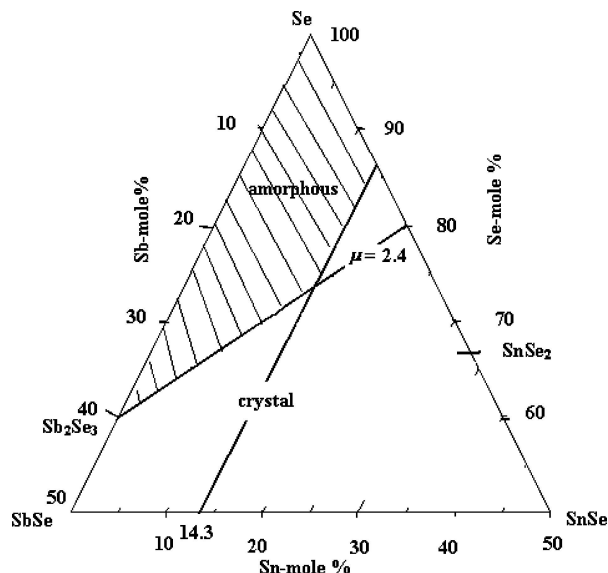


Figure 5 Theoretical mapping of glass-forming region in TAS system that deduced from emerging  $\mu$  and the  $f_{\text{Sn-Se}}$  bonds calculated from chemical order model.

$\text{Sn}_{14.3}\text{Sb}_{28.6}\text{Se}_{57.1}$ , Sn mole% was fixed at 14.3 while Sb and Se mole% were varied from 0 and 85.7 to 28.6 and 57.1, respectively. According to XRD analyses and these calculations, it is assumed that Sn-mole% = 14.3 which has  $f_{\text{Sn-Se}} = 44.5\%$  is a completely crystalline structure and beyond it there is no chance for amorphous formation. Nevertheless, the glass formation is possible if the  $f_{\text{Sn-Se}}$ -bonds in ternary system is less than 44.5%. However, it is found that the Sn-mole% equal to 12.5 is the best composition line that fits this argument.

The fractions of the bonds are calculated for 66 as-prepared samples, graphically drawn in Fig. 4. In Fig. 4, the highlighted area is a theoretical predicted glass formation region of Sn-Sb-Se obtained from COM calculations. All compositions of this region have  $f_{\text{Sn-Se}}$  bonds less than 44.5%, even in the Se deficient region at the left bottom of the triangle.

Fig. 5 represents the combination of  $f_{\text{Sn-Se}}$  bonds that calculated from the chemical order model and  $\mu$  model. In this Figure the glass formation region is obtained theoretically and located between Sn mole percentage = 14.3 and  $\mu = 2.4$ . The 4, 3 and 2 co-ordination numbers of Sn, Sb and Se support this finding. The glass formation region is theoretically governed by Sn-mole% equal to 14.3 up to the intersection point with  $\mu = 2.4$  at Sb = 12.5 and Se mole% = 73.2. However, the  $f_{\text{Sn-Se}}$ ,  $f_{\text{Sb-Se}}$  and  $f_{\text{Se-Se}}$  bonds in this intersection point are 47.5, 31.2 and 21.3%, respectively. Beyond this intersection point the glass formation is governed by  $\mu = 2.4$  line and beyond it the  $f_{\text{Sb-Se}}$  bonds is larger in glass region than  $f_{\text{Sn-Se}}$  bonds.

From XRD analysis on 66 as-prepared samples, the glass formation region is obtained, which highlighted and located in Fig. 6. In this figure, the amorphous region is located within the theoretical predicted glass formation region. It is observed that there are three areas showing crystalline structure instead of amorphous state that was predicted theoretically. Those areas are:

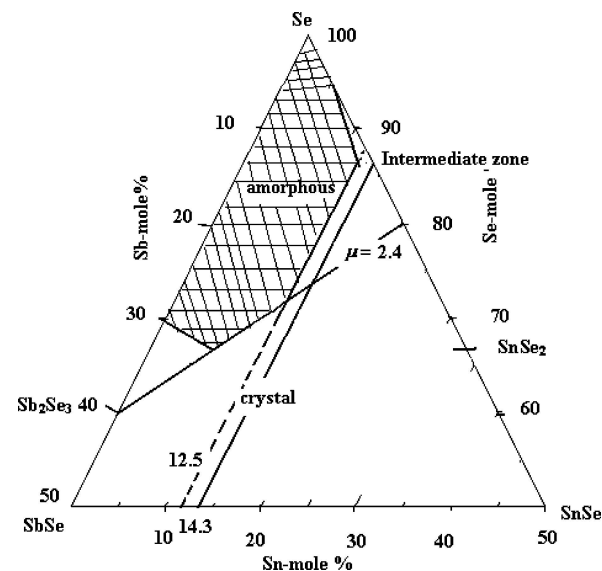


Figure 6 Experimental results of glass-forming region in Sn-Sb-Se system, which is in a shadowed region.

(a) An area started at the binary sample  $\text{Sn}_5\text{Se}_{95}$ , at this composition, the  $f_{\text{Sn-Se}}$  bond is equal to 19.0% and  $f_{\text{Se-Se}}$  bond is equal to 81.0%, which indicates the formation of the weak covalent compound  $\text{SnSe}_4$ . However, addition of little amount of Sb is sufficient to break this bond and enhances the glass formation. On the other hand, the addition of Sn mole percentage to Sn-Se binary line enhances the formation of crystalline structure and arrests the glass formation. Increasing Sn mole% in Sn-Se binary line, increases the crystalline tendency resulting in the formation of more stable crystalline compounds such as  $1/3(\text{SnSe})$  and  $1/2(\text{SnSe})$  at Sn% = 10 and 14.3, respectively. Therefore, the addition of Sb enhances the glass formation by lone-pairs property, which causes shifting in glass region far from the binary Sn-Se line until the ternary composition  $\text{Sn}_{12.5}\text{Sb}_{2.5}\text{Se}_{85}$ . At this composition the  $f_{\text{Se-Se}}$  is

49.5% and  $f_{\text{Sn-Se}}$  bond is 44.0%, which is attached to 44.5%, the  $f_{\text{Sn-Se}}$  bonds in ternary  $\text{Sn}_{14.3}\text{Sb}_{28.6}\text{Se}_{57.1}$ .

(b) An intermediate zone located between the two lines Sn mole% = 12.5 and 14.3. In this zone the difference between the two lines is 1.8-mole percentage, which is less than 2.5 mole% the regular interval of samples batch preparations. Therefore, this zone has tendency to form crystalline structure closer to Sn mole% equals to 14.3.

(c) The region located beyond Sb mole% equals to 30. It was found that after this line no glass was formed, even for composition with  $f_{\text{Sn-Se}}$  bonds less than 44.5% and  $\mu$  is less than 2.4. Appearance of crystalline structure in this region is considered to be due to the following reasons:

- (i) Existences of large numbers of cations that imply insufficient amount of Se mole% to provide the formation of Sb-Se and Se-Se bonds that enhance the glass formation.
- (ii) Formation of crystalline compound  $\text{SbSe}_2$  that is similar to the compound  $\text{As}_{33}\text{Se}_{67}$  reported by [12].
- (iii) The region is too close to crystalline  $\text{Sb}_2\text{Se}_3$  with co-ordination number of Sb and Se of 5 and 3, respectively, which is in crystalline structure [5].

In Fig. 6, the intersection of the two amorphous boundary lines, Sn mole% = 12.5 and  $\mu = 2.4$ , takes place at the point  $\text{Sn}_{12.5}\text{Sb}_{15}\text{Se}_{72.5}$ . The  $f_{\text{Sn-Se}}$ ,  $f_{\text{Sb-Se}}$  and  $f_{\text{Se-Se}}$  bonds at this composition are 41.7, 37.5 and 20.8, respectively. However, the amorphous samples located after this intersection point have  $f_{\text{Sb-Se}}$  bonds greater than  $f_{\text{Sn-Se}}$  and  $f_{\text{Se-Se}}$  bonds. Addition of Sb mole%, beyond this intersection point showed deviation in the amorphous boundary lines toward the binary Sb-Se composition line. The first deviation point is observed at  $\text{Sn}_{10}\text{Sb}_{20}\text{Se}_{70}$  composition, with corresponding  $f_{\text{Sn-Se}}$ ,  $f_{\text{Sb-Se}}$  and  $f_{\text{Se-Se}}$  bonds equal to 33.3, 50.0 and 16.7%, respectively. However, at Sb mole% = 20 on Sb-Se binary line the  $f_{\text{Sb-Se}}$  and  $f_{\text{Se-Se}}$  bonds are equal to 54.5 and 45.5%, respectively.

It is observed that, there is a similarity in  $f_{\text{Sb-Se}}$  and  $f_{\text{Sn-Se}}$  bonds, between the two binary points at Sb mole% = 18.2, which is closed to 20-mole%, and Sn mole% = 14.3. Both showed equal  $f_{\text{Se-Se}}$  bonds (50%), but amorphous state appears in Sb-Se binary line while crystalline structure is obtained on Sn-Se binary line. The appearance of amorphous state on Sb-Se side is due to the 2-lone-pair electrons of Sb, which Sn lacks.

It is clearly seen that the glass-forming region of Sn-Sb-Se system is small comparing to that reported for Ge-Sb-Se [1, 24] and Ge-Sn-Se systems [25]. However, there is a similarity in the boundary limit on Sb-Se and Sn-Se binary lines. In contrast to Ge-Sb-Se systems, there is no chance for crystalline phases to occur similar to  $\text{Sn}_2\text{Sb}_4\text{Se}_8$ . However, the glass region of Ge-Sb-Se was formed beyond the stoichiometric  $\text{GeSe}_2$  with  $\mu = 2.6$ , which is less than 3.

Regions of glass formation in the system Sb-Ge-Sn-Se with 5, 7.5 and 10 at% of Sn were reported [14]. They found that there was tendency of replacement of

Ge by Sn on glass formation and change in physico-chemical properties of glasses in the Sb-Ge-Se system. They stated that Sn does not form glasses with Se. In Ge-Se-system, which has a maximum Ge content of 25% only half (12.5%) of it can be replaced by Sn in the glass form. Their finding supports this experimental and theoretical validation of glass formation at Sn = 12.5 mole% and below. In addition, it means that Sn with 4-co-ordination number is valid in both Ge and Sb that were added to form glass with Se.

It was concluded that [11] the behaviour of the optical band gap of  $\text{Ge}_{1-x}\text{Sn}_x\text{-Se}_2$  as a function of  $x$  could be attributed to two effects. First, the decrease in  $E_g$  as  $x$  increased is due to more loosely bound valence electrons of Sn atoms. Second, the slight rise in  $E_g$  at  $x = 0.25$  (in molar form 8.0) is a result of localisation of the electrons on the smaller clusters, which causes an increase in the energy of the bands. Their result is on stoichiometric  $\text{SnSe}_2$  side while addition of Ge increases the glass formation in the ternary Ge-Sn-Se systems. However, our result is before stoichiometric  $\text{SnSe}_2$ , but the glass formation is obtained when the Sn-mole% is equal to or below 10. In this composition, most of ternary samples are completely in glass-state. Therefore, their result positively supports the glass found in this study.

## 4. Conclusions

The chemical order and Phillips average co-ordination ( $\mu$ ) models were successfully mapped and validated the boundary between glass and crystalline-forming regions of TAS systems in the structural triangle using 4, 3 and 2 co-ordination numbers of Sn, Sb and Se, respectively. Glass formation region was theoretically predicted and mapped when the  $f_{\text{Sn-Se}}$  bonds is less than 44.5% or  $\mu$  is less than or equal 2.4. Glass formation region was experimentally obtained within the theoretical region except at Sn-mole% more than 5 and Sb-mole% more than 30 on binary Sn-Se and Sb-Se lines, respectively. The glass formation region of Sn-Sb-Se systems is the smallest one to that of Ge-Sb-Se and Ge-Sn-Se systems.

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