

## INVESTIGATION ON THE PROPERTIES OF $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$ CHALCOGENIDE SEMICONDUCTOR

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### ABSTRACT

Studies on tin-antimony-selenium (TAS) systems of  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  ( $x = 0, 5, 10, 12.5, 15, 20$  and  $30$ ) have been carried out using XRD, XGT and DTA and density measurement, so as to elucidate the structural states and thermal properties. XRD analysis for  $x = 0, 5, 10$  and  $12.5$  gave an indicative of amorphous phase, while that of the samples with  $x = 15, 20$  and  $30$  maintained the crystalline structures. These were further confirmed by XGT results, which measured the weight percentages and elemental mapping of the samples. It was also observed that  $x$  plays important roles in determining the thermal quantities and density of the samples.

### INTRODUCTION

An element that has a light atomic mass, short atomic radius, low ionicity and high covalently, large 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 [1-4]. An element with a heavy mass and small energy gap is a good choice for IR transmission. However, Sn and Sb are lacking the first properties (except for Sb has the 2-lone pairs) and owing the later one, low energy gap, which is good for optical applications. These discrepancies may suggest the difficulty in glass formation and lead our attention to perform studies on the ternary glass systems of Sn and Sb elements with a chalcogen, particularly Se. The main interest is focussed on the glass forming region of  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  based on our current studies. To date, an understanding of the TAS system was not covered elsewhere except those reported by Adam [5].

In contrast, similar group elements such as Ge and As are good glass former with Se. However, their disadvantage in wide energy gap, which causes intrinsic optical loss that imposes difficulties for application in long distance fibre communication [1]. In addition to their light masses that transmitted in mid IR region. In order to overcome these disadvantages there was possibilities of adding heavy elements such as Sb, Bi, Pb and Sn. Examples of these are reported in Ge-Sb-Se systems [6,7], Ge-Sn-Se systems [8,9] Sn-As-Se systems [10] and Ge-Sn-Sb-Se systems [11]. It is the aim of this paper to clarify the glass formation composition of the system and its physical properties such as density and glass transition temperature.

### EXPERIMENTAL PROCEDURES

TAS samples were prepared from 5N-purity batch materials of Sn, Sb and Se. The mixture was subjected into an electrical furnace at a constant rate of heating  $5\text{ }^\circ\text{C}/\text{min}$  up to  $700\text{ }^\circ\text{C}$ ,

rate of shaking 100 rpm and was maintained for three hours. The melt was quenched using liquid nitrogen. Powder XRD analysis was employed to characterise the glassy samples. Elemental mapping of the samples was held in Horiba's Laboratory, Japan using X-ray guide tube, (XGT-2700). As prepared samples were polished on emery paper and mapped in air with X-ray tube voltage of 50 KV, while 1.0 mA current was applied. Diameter of X-ray guide tube is  $\phi$  100  $\mu$ m, which provides ranges of intensity as follows 6.16-6.63 KeV, 7.24-7.60 KeV, 9.01-9.35 KeV and 9.35-9.75 KeV. Glass transition temperature  $T_g$ , melting temperature  $T_m$  were obtained using Differential Thermal Analysis at a heating rate of 10  $^{\circ}$ /min. The apparent density and its corresponding molar volume were obtained using a Densitometer.

### RESULTS AND DISCUSSION

XRD analysis on  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  systems, where  $x = 0, 5, 10, 12.5$  showed an amorphous state, as indicated by a series of broad plateau and intermittent small peaks of background noise in Figure 1. The addition of Sn to the system from  $x = 0$  to 12.5 mole %, incorporated in glass formation with 4-coordination number. The system was completely crystalline where the Sn mole % increases up to 15, which is close and beyond the ternary crystalline  $\text{Sn}_2\text{Sb}_4\text{Se}_8$  phase that has molar form of  $\text{Sn}_{14.3}\text{Sb}_{28.6}\text{Se}_{57.1}$ .

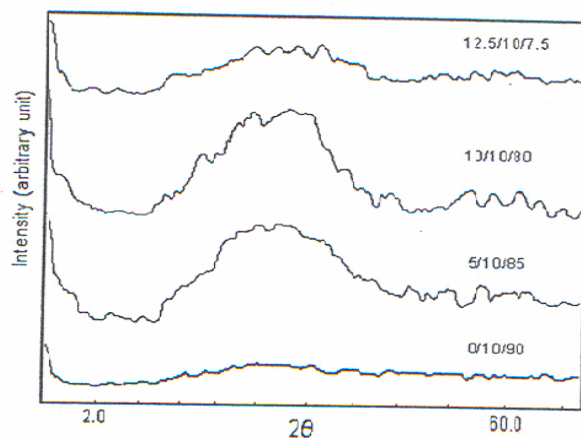


Figure 1: XRD spectrum showing amorphous state on  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  where  $x = 0, 5, 10$  and 12.5.

On the other hand, XRD analysis on  $x = 15, 20$  and 30 shows crystalline peaks that assigned for  $\text{Sn}_2\text{Sb}_4\text{Se}_8$ ,  $\text{Sb}_2\text{Se}_3$ ,  $\text{SnSe}_2$ ,  $\text{SnSe}$  and  $\text{Sn}_4\text{Sb}_4\text{Se}_{10}$  phases; their spectrum are not presented here.

XGT analysis was carried out on 6 samples and the results are presented in Table 1. The results show the measured elemental percentages of Sn, Sb and Se, which are generally in a good agreement with the predicted values. In addition, there are indication of silicon, Si (0.44–0.78%) and phosphorus, P (0.01-0.09%) present as minor impurities in the samples. Such an appearance shows the accuracy and capability of XGT as compared to EDX in which

the spectra are indistinguishable or intolerable. It was considered that Si might be originated from the quartz tube, which underwent high temperature heating up to 700 °C or during the removal of the samples by breaking the tube. In the case of P its presence is not clear but can exist along with Se granular up to 99.99 % purity. The reason is that both Se and P have same atomic radii that ease their covalent bond formation and make difficulty in their separation from each other. The amount of both Si and P is relatively small and has no significant effect on the glass formation property.

A quantitative analysis from XGT proved that glasses preserved the initial nominal composition and there was no excessive evaporation loss of either chalcogen or the additive components. This was due to a complete sealing of the tube that prohibited any evaporation during the melt. Even though the weights of the sealing quartz tube before and after melt quenching that measured for ensuring the preservation were identically similar. Small weight deviation was expected during quenching when the melting tube was not vertically adjusted so part of melt was quenched on the wall of the tube. However, the range of deviation in quantitative result, which obtained from the equipment, is 3 times of standard deviation value. An interesting result is that obtained from XGT analysis is the elemental mapping of Sn-Sb-Se alloys, which shows the distribution of Sn, Sb and Se elements at any detected area. This distribution implies homogeneously features of the samples due to agitation of the melt using orbital shaker attached to the furnace. The mapping images are not presented here.

Table 1: Theoretical (T) and measured (M) compositions of 6 representative samples of  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  analysed using XGT probe.

Sample Sn/Sb/Se	Sn (Wt %)		Sb (Wt %)		Se (Wt %)		Impurity (Wt %)	
	T	M	T	M	T	M	Si	P
0/10/90	0.00	0.00	14.63	13.1	85.37	86.12	0.78	0.00
5/10/85	6.96	7.10	14.29	14.07	78.75	78.25	0.56	0.01
10/10/80	13.61	13.44	13.96	15.13	72.43	70.76	0.64	0.03
15/10/75	19.96	21.31	13.65	15.93	66.39	62.16	0.59	0.01
20/10/70	26.03	24.95	13.35	17.57	60.62	57.01	0.44	0.02
30/10/65	37.42	37.99	12.79	13.38	49.79	47.99	0.55	0.09

The density of glass is governed both by the atomic mass of the components and the structure [12]. If chemical compositions were known, deviation from the ideal behaviour would provide information on the structural variation. Systematic determination of density as a function of chemical composition (mole percent) is therefore important. Figure 2 shows apparent density and its corresponding calculated molar volume.

It is observed that, the density increases with the addition of Sn mole % while Sb mole % was fixed at 10 for each sample. Three categories of the curve variations are observed in the Figure 2. The density increases from binary  $\text{Sb}_{10}\text{Se}_{90}$  sample, when Sn = 5 mole % was added, with composition  $\text{Sn}_5\text{Sb}_{10}\text{Se}_{85}$ . Addition of 10-mole % Sn caused a

further increasing trend up to 15 mole % of Sn, which is in crystalline structure from XRD analysis.

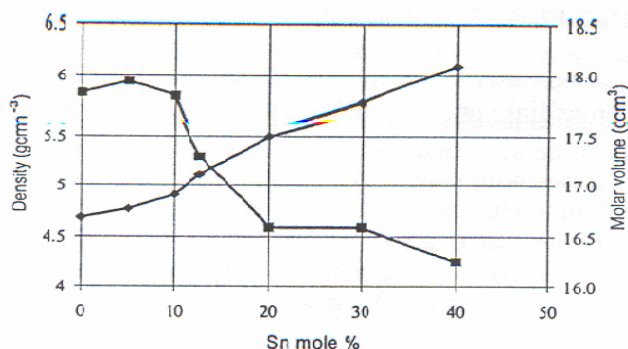


Figure 2: The measured density and its corresponding molar volume versus Sn mole % of the  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  systems.

The molar volume is the volume of a mole of the atoms present in the glass. Molar volume is a better gauge of the structure since it eliminates the effect of different mass elements and is determined by how the atoms are arranged in the glass structure [12]. The calculated molar volumes of  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  systems are plotted in Figure 2. In this Figure, the molar volume curve shows a decreasing behaviour with an increase of Sn mole %. A maximum molar volume is occurred at binary  $\text{Sb}_{10}\text{Se}_{90}$  sample. Addition of Sn mole % caused increase in the curve at  $\text{Sn}_5\text{Sb}_{10}\text{Se}_{85}$  sample. Then addition of 10-20 mole % Sn shows a rather sharp drop in the curve due to phase changes from amorphous to crystalline state. Then molar volume decreased gradually as the Sn mole % exceeding 20 and this trend continues until it reaches 40.

By removing the mass effect we can see that the structure of this glass does vary as the Sn-Se ratio is modified. As the cross-linking increases in this glass, the molar volume decreases. The cross-linking agents pulling the structures of the glasses into closer proximity than if only van der Waals forces were present between the chains can explain this general trend. However, there appears to be other effects which modify the molar volume, especially along the stoichiometric and like stoichiometric tie line such as Sn = 5, 15 mole % on binary systems.

As the samples composition approaches the Sn mole %,  $x = 5, 15$  and the stoichiometric tie line with increasing cross-linking, the molar volume does not continue to decrease. It begins to increase, and undergoes a local maximum for  $x = 10$  mole %. Similar increase behaviour was reported on Ge-Sb-Se systems by Giridhar *et. al*, (1981) [13]. They stated that this higher molar volume at the stoichiometric tie line was apparently due to the larger volume requirement for attaining the completely cross-linked network of  $\text{Sb}_2\text{Se}_3$  and  $\text{GeSe}_2$  structural unit present in these compositions compared with Ge-rich or Se-rich glasses of the corresponding family. Referring to the fraction of Sn-Se bond calculations, Sn mole % = 10, shows the same fraction of stoichiometric  $\text{SnSe}_2$  beyond it a similarity decreasing is observed in Figure 28.

This is an interesting proposal because it suggests that the glass can become "over-constrained". What this means is that there are so many bonds that must form at specific

angles that the structure no longer contracts with increasing cross-linking, but begins to expand, commonly called *stearic hindrance*. The contention that the  $\text{GeSe}_2$  and  $\text{Sb}_2\text{Se}_3$  structure are layered [13-14] could also be used to explain these finding by using the volume between the layer of this structure to cause this local maximum.

Another interesting observation was that the molar volume initially decreased more with Sn than Sb. This would be observed at the pure Se composition on  $\text{Sb} = 5$  curve since the Sn should allow more cross-linking compared to the antimony. Since, more cross-linking occurs in the structures, it can be seen that the glasses with a high antimony content reach a lower molar volume than glasses with similar Sn content. Part of this can be ascribed to the hypothesis that the like stoichiometric maximum in molar volume occurs in glass having a high Sn content. It is interesting that this low molar volume at a large Sb content extends approximately along the samples where average co-ordination number,  $m$  is less than 2.4. At  $m = 2.4$  [3] it was proposed that the number of constraints on a glass system are equal to the number of degrees of freedom.

Based on Philips's constraint theory, it can be explained that the minimum molar volume occurrence at  $\text{Sn} = 12.5$ , Figure 2, in the Se rich region is due to the structure of the glass approaching to the Philip percolation threshold ( $m = 2.4$ ). At the cross-linking levels above this threshold, the structure must recognise to satisfy the increased bonding. This over-constrained structure would need a larger atomic volume to maintain the correct bond angles while maintaining a glassy structure. The molar volume decreases on the  $\text{Sn} = 12.5$  line as the Sb content increases because the composition is closer to that of the ideally constrained glass.

DTA results of incorporation of Sn into  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  are presented in Figure 3. In this Figure the DTA temperature plots for composition  $x = 0, 5, 10$  and  $15$  mole percent. The bottom curve shows DTA analysis in sample  $\text{Sb}_{10}\text{Se}_{90}$  with zero Sn mole percent. Increasing Sb mole % from 5 to 10 shows increase in the glass transition temperature, which occurred at  $160.2^\circ\text{C}$ . While the crystallisation and melting temperatures with their endothermic peak, are observed at  $217.3^\circ\text{C}$  and  $232.4^\circ\text{C}$ , respectively. Addition of 5-mole percentage Sn in  $\text{Sn}_5\text{Sb}_{10}\text{Se}_{85}$  system causes reduction in  $T_g$ , which occurred at  $123^\circ\text{C}$ . On the other hand, the crystallisation temperature decreased to  $214^\circ\text{C}$  while the melting temperature  $T_m$ , with a single endothermic peak is observed at  $222.5^\circ\text{C}$ .

Further reduction in the glass transition temperature is observed at  $115^\circ\text{C}$  when 10-mole percentage Sn is added to the system in  $\text{Sn}_{10}\text{Sb}_{10}\text{Se}_{80}$  sample. Therefore, exothermic peak that is observed at  $216.5^\circ\text{C}$  is ascribed to crystallisation temperature of the sample. Feltz, [17] stated that "an exothermic enthalpy effect is observed if the heating rate falls below the cooling rate. The system, approaching the glass transition temperature,  $T_g$  region with decrease in volume or by released of enthalpy, is transformed to a super cooled melt". This finding is in agreement with a decrease in molar volume that observed in Figure 3, of the same sample. The endothermic peak occurred at  $222.4^\circ\text{C}$  is assigned for the melting temperature. On other hand, the glass transition temperature is reduced to  $113.6^\circ\text{C}$ , when 12.5-mole percentage Sn is added. Low and broad exothermic peak is observed at crystallisation temperature  $212.2^\circ\text{C}$ , while the small endothermic peak occurred at  $221.9^\circ\text{C}$ , which is ascribed to the melting temperature.

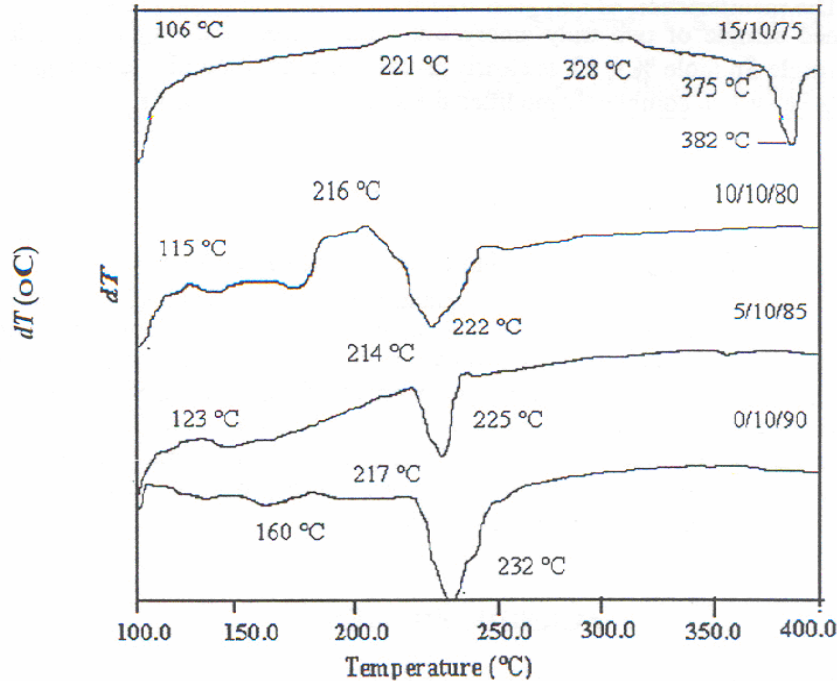


Figure 3: Differential Thermal Analysis on  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$ , where  $x = 0, 5, 10, 12.5$  and  $15$  mole %.

In crystalline sample  $\text{Sn}_{15}\text{Sb}_{10}\text{Se}_{75}$ , the curve shape changed and the glass transition temperature is reduced. While three fluctuations in the curve occurred at  $106\text{ }^\circ\text{C}$ ,  $221.8\text{ }^\circ\text{C}$ ,  $328\text{ }^\circ\text{C}$ ,  $375\text{ }^\circ\text{C}$  and  $382.0\text{ }^\circ\text{C}$ , which are assigned for double glass transition, crystallisation and melting temperature, respectively.

DTA data clearly reveals that alloying of Sn, Sb and Se in  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  system shows change in glass transition temperature by increasing Sn content from 5 to 15. Increasing the Sn% in large concentration completely modified the structure of the network. However, It appears that to induce chemical modification in the host network by the addition of Sn %, which incorporate in the glass region assuming 4, 3 and 2 co-ordination of Sn, Sb and Se respectively.

The trend can be explained in [13] argument as a function of the structural units in the glass. It was believed that the structure of the glass could be modelled with  $\text{Sn-Se}_4$  tetrahedral and  $\text{Sb-Se}_3$  trigonal units distributed in the glass, along with other components. At the stoichiometric or half-stoichiometric tie line the structure is composed completely of these structure units, and the most rigid structure would exist. This can explained the steep fall in the  $T_g$  with excess Se to be due to the 2-co-ordinated Se forming a "loose" structure. The drop in  $T_g$  with additional of Sn is suspected to be due to the weaker Sn bonds.

Appearance of double glass transition temperature was reported by [16] in amorphous  $(\text{Ge}_{42}\text{S}_{58})_{100-x}\text{Bi}_x$  and  $\text{Ge}_{20}\text{S}_{80-x}\text{Bi}_x$  carried out using DTA. His finding was interesting of DTA data, which a few of chalcogenide glasses were known to exhibit a double glass transition temperature. The manifestation of two glass transition temperatures indicates the retention in the as quenched sample of two truly amorphous phases. Upon his explanation, the DTA analysis, on sample Sn mole % = 10, is clearly revealed that addition of a large concentration of Sn to the Sb-Se system completely modified the structure of the network.

### CONCLUSION

It was found that  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  samples exhibited amorphous state for  $x = 0, 5, 10, 12.5$ , and crystalline structures for  $x = 15, 20, 30, 40$ . A quantitative analysis from XGT proved that the compositions of the as-prepared samples were maintained, based on both theoretical and measured values of the weight percentages of each element. This suggested that no excessive evaporation loss of the chalcogen or additive components. Density of  $\text{Sn}_x\text{Sb}_{10}\text{Se}_{90-x}$  increased with an increase of  $x$  while the molar volume showed a decreasing mode. The glass transition temperature, crystalline temperature and melting temperature were found to be a function of Sn mole %,  $x$ . Double values of these quantities were observed in the case of Sn/Sb/Se = 10/10/80 where the samples were predominantly amorphous.

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