

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

PSEUDOINARY GLASSY COMPOSITIONS $(AsSe_x)_{1-y}(AsTe_x)_y$ *

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ABSTRACT

The ternary glassy composition of the general formula $(AsSe_x)_{1-y}(AsTe_x)_y$ can be considered as a pseudobinary system at $x = 1, 3/2$ and $5/2$ and $0 \leq y \leq 1$.

The results of DTA, electrical conductivity measurements, density of such glasses as well as the x-ray diffraction of the crystallized samples have been used to confirm this point of view and to explain the presence of new phases not shown in the simple binary systems As-Se and As-Te. The possibility of transformation of the glassy network from partially polymerized state MCN (molecular cluster network) to completely polymerized state CRN (continuous random network) by mixing two structural units was also discussed.

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September 1987

* To be submitted for publication.

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1. INTRODUCTION

Recently, Wells and Boolchand have studied ¹²⁹I Mossbauer emission spectroscopy ¹⁾ due to different possible sites occupied by tellerium in the pseudobinary stoichiometric glasses $(AsSe_{3/2}) - (AsTe_{3/2})$. They revealed two different sites for selenium atoms; site A corresponds to homopolar structure As-Se and site B corresponds to heteropolar structure Se-Se or As-As. As the tellerium content increases the percentage of site A increases. The authors explained these results by the presence of two different structures for the glassy state: a partially polymerized or molecular cluster network (MCN) and a completely polymerized or continuous random network (CRN). The transformations MCN + CRN can be induced by increasing the tellerium content. Such transformation plays a central role in glass forming tendency and the crystallization tendency as well as the physical properties of the obtained glasses. As was indicated in several works for $(As_2Se_3)_{1-x}(As_2Te_3)_x$ the kinetic of crystallization is so retarded that does not observe a crystallization exotherm ²⁾ $T_c = T_x$ easily in selenium rich glasses ($x \leq 0.5$). But as $x \rightarrow 1$ the glasses have high tendency toward crystallization. Similar results have been observed for other pseudobinary glasses ³⁾⁻⁵⁾. If we consider the phase diagram of the ternary system ^{6),7)} As-Se-Te (Fig.1) the systems $(AsSe) - (AsTe)$ and $(As_2Se_3) - (As_2Te_3)$ can have stoichiometric chemical structure in addition to the known system $(As_2Se_3) - (As_2Te_3)$. The proposed chemical structures are $[As(Se,Te)_{2/2}]_2$ and $As_2(Se_4Se_{2/2} - Te_4Te_{2/2})$ for the first and the second pseudobinaries respectively. The first has excess heteropolar bands As-As and the second has excess heteropolar bands Se-Se (or Te-Te). Among the three pseudobinaries the system $(As_2Se_3) - (As_2Te_3)$ has the maximum structure disorder. The process of alloying selenium-arsenic compounds by tellerium should affect to a great extent the tendency towards crystallization of such glasses. The present work reviews some physical properties namely; density electrical conductivity and kinetic study of the crystallization process using DTA for these three pseudobinaries. The resulted crystalline phases have also been studied by x-ray diffraction.

2. EXPERIMENTAL TECHNIQUE

For sample preparation stoichiometric quantities of pure arsenic (99.9999%), selenium and tellerium (99.999%) were sealed in evacuated quartz tubes. The synthesis have been carried out at $950 \pm 20^\circ\text{C}$ for 4-8 hours with periodical shaking followed by quenching in current air or in water-ice mixture to bring the materials into glassy state⁸⁾. The amorphous structure and microscopic homogeneity was examined by x-ray diffraction and other methods^{8),9)}. The density and DC electrical conductivity at different fixed temperatures for the glassy samples have been measured as described previously⁹⁾. The differential thermal analysis (DTA) was carried out for each composition using Shiniazo DT-30 thermal analysis system using different rates of heating 5-10 deg/min. The x-ray diffraction for the crystallized samples was carried out using the Philips diffractometer with $\text{Cu K}\alpha$ radiation^{6),10)}.

3. RESULTS AND DISCUSSION

The composition of the pseudobinary glasses examined are represented by the three dotted horizontal lines on the phase diagram given in Fig.1. In the same figure the phase diagrams of the binary elementary systems As-Se, As-Te and Se-Te are given^{6),7)}. The chemical compositions of the general formulas $(\text{AsSe}_x)_{1-y}(\text{AsTe}_x)_y$ for $x = 1, 3/2, 5/2$ and $0 \leq y \leq 1$ are given in Table 1.

Density: The results of density measurements at room temperature for the three pseudobinary glassy systems are given in Fig.2. For all the three series the density increases by increasing the tellerium content. If the density of the glasses can be considered as simple additive property depending only on the fraction of each structural units according to the equation

$$d(y) = (1-y)d(\text{AsSe}_x) + yd(\text{AsTe}_x) \quad (1)$$

where $d(\text{AsSe}_x)$ and $d(\text{AsTe}_x)$ are the density of the corresponding material, the theoretical value of the density can be calculated. The calculations have been carried out for $x = 3/2$ with values 4.490 and

5.264 gr/cm^3 for the glasses $\text{AsSe}_{3/2}$ and $\text{AsTe}_{3/2}$ respectively, and the results are given in Fig.2. The deviation of the experimental data from straight line relationship indicates that the increase of $\text{AsTe}_{3/2}$ is not a simple addition of different structural units and can be attributed to the transition from partially polymerized network (MCN) to completely polymerized and more chemically ordered network¹⁾. According to this point of view the decrease of MCN contents leads to the increase of density as it is clear from the deviation shown in Fig.2 at $0 \leq y \leq 0.4$. The general features of the change of density with y are similar for $x = 3/2$ and $5/2$ but different from that at $x = 1$.

Electrical conductivity: To investigate the electrical properties of these samples typical temperature dependence of the D.C conductivity $\sigma(T)$ for the three pseudobinary glassy systems have been measured⁹⁾. The results have been used to compute the conductivity at room temperature ($\log \sigma_{20^\circ\text{C}}$) and the thermal activation energy of the conductivity E_σ according to the equation

$$\sigma(T) = \sigma_0 \exp(E / 2kT) \quad (2)$$

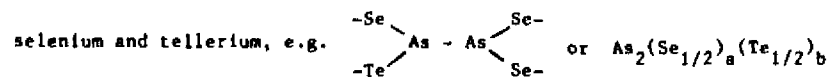
The values of $\log \sigma_{20}$ and E_σ for all values of x and y are given in Figs.3 and 4. For $x = 3/2$ the simple additive formula similar to Eq.(1) has been applied to calculate $E_\sigma(y)$ taking E_σ equals to 1.87 and 0.34 e.v. for glassy $\text{AsSe}_{3/2}$ and $\text{AsTe}_{3/2}$ respectively. The results of the calculations are given as straight lines in Fig.3. The decrease of MCN contents by increasing y leads to a deviation of $E_\sigma(\text{exp})$ from the theoretical straight line in the range $0 \leq y \leq 0.4$ as the density does.

Thermal differential analysis and x-ray diffraction: The DTA thermograms for all the samples have been recorded at different rates of heating 5-10 deg/min and sometimes 20° deg/min. The details of these thermograms as well as the kinetic calculations have been reported previously¹¹⁾. The characteristic transition temperatures T_m , crystallization temperature T_c and melting temperature T_m have been determined from the thermal spectrum. The areas of the exothermic peaks corresponding to the crystallization process have been used to study the crystallization kinetics of these glasses to determine n the parameter defining the order of crystal growth and E_{cryst} .

the activation energy of the crystallization process using Auram's equation¹²⁾. Figs. 6, 7 and 8 illustrate the dependence of T_g , T_c and T_m for the three values of x and for $0 < y < 1$. The results of the kinetic calculation are given in Table 2. Some samples show more than one characteristic temperature even by changing the rate of heating. For example at $(x = 3/2; y = 0.66)$ there are more than one T_g , at $(x = 3/2, y = 0.9, 0.5)$ and $(x = 1; y = 0.1)$ there are more than one T_c , also for $(x = 3/2, y = 0.2, 0.33, 0.57, 0.8)$ there are more than one T_m . These facts are indicated in Figs. 5, 6 and 7 by dashed areas. The samples showing more than one possible characteristic temperature have some phase separation during the crystallization process. In case there are definite two crystallization peaks, both of them have been analyzed. The calculated values of n and E_{cryst} are given in Table 2. Alternatively, if there are no more than one clear characteristic temperature or crystallization peak, it does not mean that there is no phase separation because of the possibility of overlapping or the predominancy of one phase.

X-ray diffraction analysis for the crystallized phases: The amorphous and the polycrystalline states have been examined by x-ray diffraction for powder materials. The polycrystalline forms are obtained by annealing glassy samples at temperatures between their softening and crystallization temperatures ($T_B - T_C$) determined by DTA for different soaking times. These varied from 160°C to 260°C and from 7 up to 60 hours⁹⁾. The x-ray diffraction patterns for all the amorphous $(AsSe_x)_{1-y}(AsTe_x)_y$ show a three stepped hump except for amorphous AsTe. This may be due to the presence of three different types of chemical banding leading to the contribution of diffracting atomic planes¹⁾. This is clearly absent in the case of AsTe glassy state which has completely polymerized structure (CRN).

For $x = 1$ the completely crystallized AsSe shows a single crystalline phase. However, AsTe crystallizes in two phases; one corresponds to $AsTe_{3/2}$ and most of all the other peaks are related to arsenic crystal structure. The intermediate compositions have more than one phase. In the region $0 < y < 0.2$ there are two phases; one corresponds to AsSe and the new one corresponds to a deformed AsSe phase which may be considered as As(Se, Te) phase where the structure building block contains both



where $a > b$. Increasing the tellerium contents i.e. $0.4 < y < 0.9$ a more rich tellerium phase have been developed of the type $As_2(Se_{1/2})_a(Te_{1/2})_b$ with $b > a$ but atill has the pattern of AsSe. Accordingly the system $(AsSe)_{1-y}(AsTe)_y$ in the range $0 < y < 0.9$ can be considered as pseudo-binary structure and not a ternary one. The crystallization data, however, show that there is a possibility of crystallization in two phases for $y = 0.9$ one rich selenium phase and the other rich tellerium phase. The presence of T_c in Fig. 6 confirms this point of view.

At $x = 3/2$ according to the phase diagram Fig. 1 there are two stoichiometric structures $AsSe_{3/2}$ and $AsTe_{3/2}$ corresponding to $y = 0$ and $y = 1$ respectively. For our samples the separation between the x-ray diffraction plans and the relative intensities of the diffracted peaks of both $AsSe_{3/2}$ and $AsTe_{3/2}$ are in good agreement with ASTM cards. For the compositions $(AsSe_{3/2})_{1-y}(AsTe_{3/2})_y$ in the range $0 < y < 0.5$ there is a deformed $AsSe_{3/2}$ structure due to the substitution of As-Se bands by As-Te bands i.e. the presence of mixed pyramidal structural units. In the range $0.5 < y < 0.9$ there is a deformed $AsTe_{3/2}$ crystalline structure corresponding to mixed pyramidal structure rich in tellerium. Accordingly it is not difficult to consider this system as pseudobinary in all range of y . At the same time the crystallization data show the possibility of crystallization of two phases at $y = 0.1$ and $y = 0.9$ which may correspond to rich selenium and rich tellerium phases. The presence of two T_c and T_m and T_g confirms this point of view. These two phases become very close to each other from the structure point of view at $y = 0.5$. Consequently, around $y = 0.5$, the structure of the material has the least microheterogeneity between the rich selenium and rich tellerium phases. At this point the crystallization energy is also minimum (Table 2).

For the glassy system at $x = 5/2$ there are no stoichiometric crystalline phases according to the phase diagram. Both $AsSe_{5/2}$ and $AsTe_{5/2}$ glasses crystallized into two phases; one of them is polycrystalline selenium and the other is the corresponding $AsSe_{3/2}$ and $AsTe_{3/2}$ crystalline phases. For intermediate values of y there are indications that the mixed pyramidal crystalline phases developed as in the case of $AsSe_{3/2} - AsTe_{3/2}$ ⁹⁾. As Fig. 7 shows, it is not easy to detect T_c and T_m at $y < 0.4$. The crystallization energy calculated for $0.4 < y < 0.8$ is much higher than in the case $x = 1$ or $3/2$. The pseudobinary structure

of the glasses $(AsSe_{5/2})_{1-y}(AsTe_{5/2})_y$ is the most disordered one from the chemical point of view and MCN is the most appropriate description for the structure.

4. CONCLUSIONS

i) The compositions $(AsSe_x)_{1-y}(AsTe_x)_y$ where $x = 1, 3/2, 5/2$ in glassy state can be considered as pseudobinary alloys.

ii) From the point of view of chemical banding the ratio of disordered network (MCN) to an ordered one (CRN) increases as x increases and as y decreases.

iii) The glass formation tendency increases as x increases and as y decreases.

iv) The glassy system $(AsSe_{5/2})_{1-y}(AsTe_{5/2})_y$ has the highest tendency to glass formation and highest E_{cryst} .

v) $(AsSe_{3/2})_{0.5}(AsTe_{3/2})_{0.5}$ in glassy state has the least microheterogeneity and can be considered as ideal material to be described by CRN structure.

ACKNOWLEDGEMENTS

One of the authors (M.K.E.M.) would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

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TABLE 1

Composition	Composition	
	x = 3/2	x = 5/2
AsSe	AsSe _{3/2}	AsSe _{5/2}
(AsSe) _{0.6} (AsTe) _{0.4}	(AsSe _{3/2}) _{0.9} (AsTe _{3/2}) _{0.1}	(AsSe _{5/2}) _{0.8} (AsTe _{5/2}) _{0.2}
(AsSe) _{0.5} (AsTe) _{0.5}	(AsSe _{3/2}) _{0.8} (AsTe _{3/2}) _{0.2}	(AsSe _{5/2}) _{0.6} (AsTe _{5/2}) _{0.4}
(AsSe) _{0.3} (AsTe) _{0.7}	(AsSe _{3/2}) _{0.67} (AsTe _{3/2}) _{0.33}	(AsSe _{5/2}) _{0.5} (AsTe _{5/2}) _{0.5}
(AsSe) _{0.1} (AsTe) _{0.9}	(AsSe _{3/2}) _{0.5} (AsTe _{3/2}) _{0.5}	(AsSe _{5/2}) _{0.2} (AsTe _{5/2}) _{0.8}
AsTe	(AsSe _{3/2}) _{0.43} (AsTe _{3/2}) _{0.57}	AsTe _{5/2}
	(AsSe _{3/2}) _{0.2} (AsTe _{3/2}) _{0.8}	
	AsTe _{3/2}	

TABLE 2

Composition	First Peak		Second Peak	
	n	E _{cryst.} K.Cal./mole	n	E _{cryst.} K.Cal./mol
AsSe	2.0	27	-	-
(AsSe) _{0.6} (AsTe) _{0.4}	2.4	28	-	-
(AsSe) _{0.5} (AsTe) _{0.5}	2.8	31	-	-
(AsSe) _{0.3} (AsTe) _{0.7}	2.4	17	-	-
(AsSe) _{0.1} (AsTe) _{0.9}	2.8	45	3.8	65
AsTe	-	-	-	-
AsSe _{1.5}	-	-	-	-
(AsSe _{3/2}) _{0.9} (AsTe _{3/2}) _{0.1}	3.6	60	3.5	107
(AsSe _{3/2}) _{0.67} (AsTe _{3/2}) _{0.33}	2.6	55	-	-
(AsSe _{3/2}) _{0.5} (AsTe _{3/2}) _{0.5}	2.8	36	-	-
(AsSe _{3/2}) _{0.43} (AsTe _{3/2}) _{0.57}	3.2	44	-	-
(AsSe _{3/2}) _{0.34} (AsTe _{3/2}) _{0.66}	2.9	50	-	-
(AsSe _{3/2}) _{0.2} (AsTe _{3/2}) _{0.8}	3.2	90	2.5	26
AsTe _{3/2}	-	-	-	-
AsSe _{5/2}	-	-	-	-
(AsSe _{5/2}) _{0.8} (AsTe _{5/2}) _{0.2}	-	-	-	-
(AsSe _{5/2}) _{0.6} (AsTe _{5/2}) _{0.4}	2.3	85	2.4	100
(AsSe _{5/2}) _{0.5} (AsTe _{5/2}) _{0.5}	4.2	102	1.6	66
(AsSe _{5/2}) _{0.2} (AsTe _{5/2}) _{0.8}	3.0	166	1.5	80
AsTe _{5/2}	-	-	-	-

FIGURE CAPTIONS

- Fig.1 The phase diagram for the elements As-Se-Te.
- Fig.2 The densities of the three systems at $x = 1, 3/2$ and 2 as a function of y . The straight line is the theoretical value for $x = 3/2$.
- Fig.3 The values of $(-\log a_{20}^0)$ as a function of x and y .
- Fig.4 The values of E_0 as a function of x and y . The straight line is the theoretical value for $x = 3/2$.
- Fig.5 The values of the characteristic temperatures T_g, T_c and T_m for $x = 3/2$ as a function of y .
- Fig.6 The values of the characteristic temperatures T_g, T_c and T_m for $x = 1$ as a function of y .
- Fig.7 The values of the characteristic temperatures T_g, T_c and T_m for $5/2$ as a function of y .

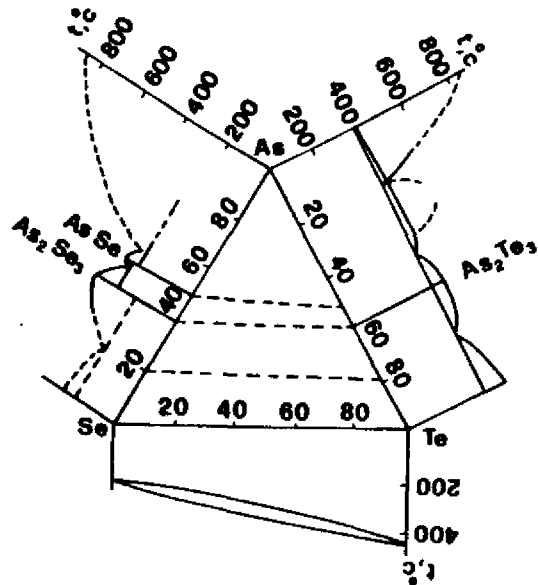


Fig.1

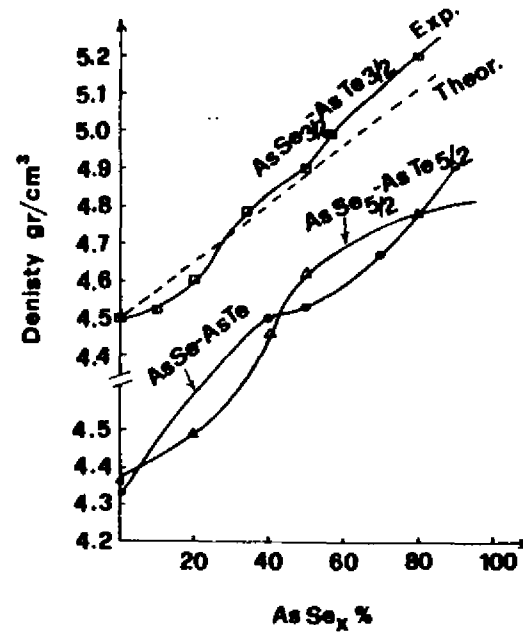


Fig.2

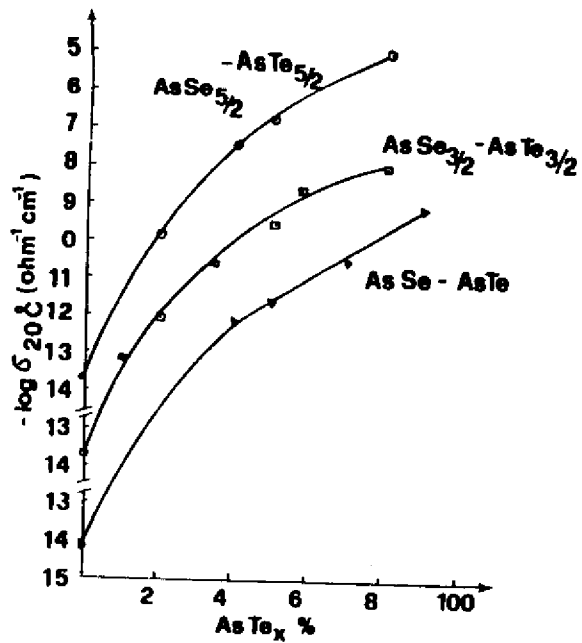


Fig. 3

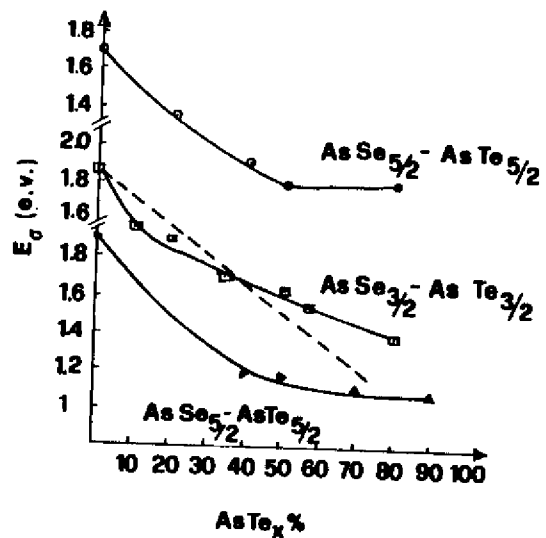


Fig. 4

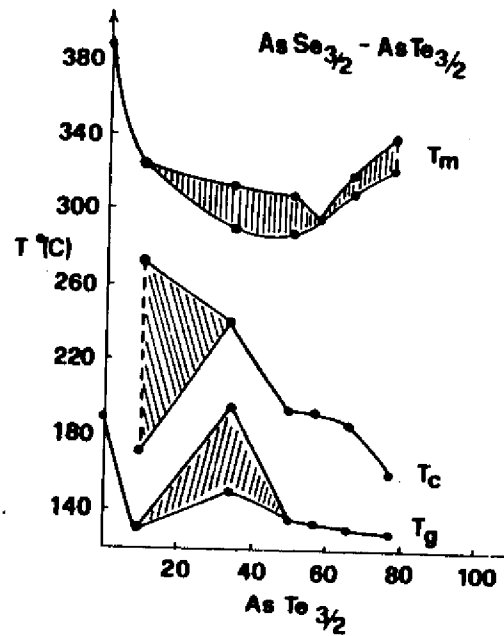


Fig. 5

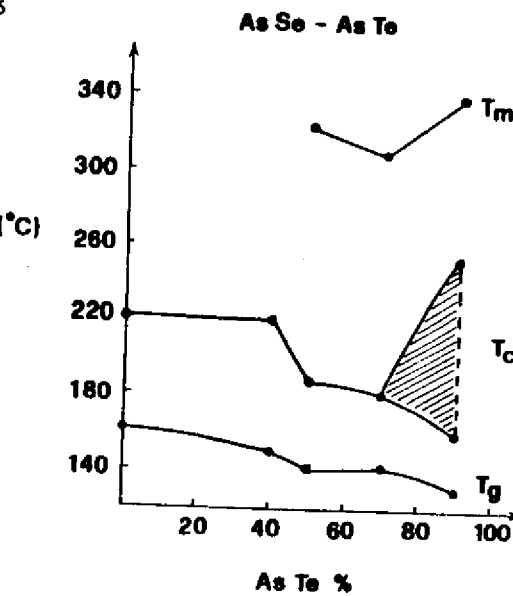


Fig. 6

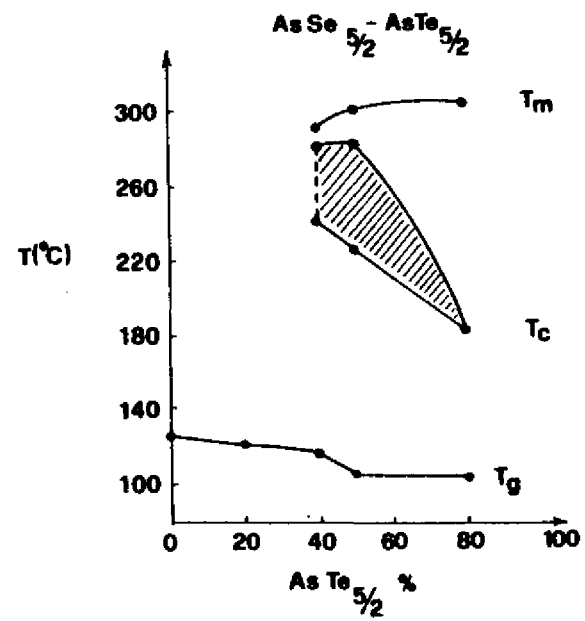


Fig. 7