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POLYNARY SILICON ARSENIC CHALCOGENIDE GLASSES WITH HIGH SOFTENING TEMPERATURES

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The introduction of Ag in Si–As–Te glasses permits the incorporation of Se, otherwise volatile and/or degradable as a constituent in Si-containing chalcogenide glasses. Si–As–Ag–Te–Se glasses exhibit much higher softening ranges and glass transition temperatures than encountered in known chalcogenide systems. A glass $\text{Si}_{35}\text{As}_{15}\text{Ag}_{10}\text{Te}_{20}\text{Se}_{20}$ had the viscosity $\log \eta = 13$ at about 500°C , as compared to 370°C for the base glass $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$, the viscosity of $\log \eta = 9.8$ at about 560°C , as compared to 442°C for the base glass. Phase separation occurs in the system Si–As–Ag–Te–Se and becomes manifest in two glass transitions indicated by changes in the slopes of the expansion curves and breaks in the softening point-composition relations. The existence and behavior Si–As–Ag–Te–Se glasses suggests the possible development of higher T_g i.e. transparencies and higher T_g semiconductor glasses than described so far.

1. Introduction

The ternary system Si–As–Te has been explored in connection with the development of glasses with high temperature softening ranges for transparencies operating between 3 and $14\ \mu\text{m}$ and for amorphous semiconductors. Some Si–As–Te glasses are characterized by the highest softening temperatures among the many simple chalcogenide glasses investigated [1], if S glasses are excluded because of their limited transmittance above $10\ \mu\text{m}$. However, in practice Ge–As–Se glasses have been preferred because Si appears associated with an interfering absorption band attributable to Si–O bonds. Since in other infrared transmitting chalcogenide glasses ad-

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vanced preparation methods have eliminated oxygen impurity and because of the potential importance of the Si–As–Te system in the field of amorphous semiconductors Si–Te glasses were chosen for further study from a technological as well as scientific viewpoint [2, 3].

From first principles one may expect that chalcogenide glasses containing Si and Se would have still higher glass transition temperatures and softening ranges than those with optimized compositions containing Si and Te, or Ge and Se [4], and that they would still have sufficient long-wave i.r. transmittance. Unfortunately, experimental evidence reveals that Si–Se glasses decompose either during preparation or, after fabrication, in moist air, giving off Se [5, 6], and our own experience showed that decomposition also takes place if Se is added to, or substituted in Si–As–Te glasses, or if Ge–Sb–Se or Ge–As–Se glasses are blended with Si–As–Te glasses [2]. The main objective of the present investigation was the formulation of higher viscosity vitreous i.r. transparencies. Considerable effort had first been spent on the exploration of polynary glasses based on the ternary Si–As–Te with fourth or fifth components designed to contribute strong bonds without impairing i.r. transmission. This approach was often thwarted by crystallization.

More recently, the search has focused on understanding and influencing the rejection or acceptance of Se in glass-forming melts containing substantial amounts of Si. In this direction was seen [3] the only reasonable hope for significantly increased softening ranges, possibly on the basis of copolymeric structures in which the stronger bonds became manifest.

One hypothesis underlying experiments aimed at the promotion of Se acceptance was that the addition of group I elements might make incompatible groups more compatible and contribute to the lowering of the liquidus, facilitating vitrification of copolymers with inherently high bond strength.

Because of the high reactivity of elemental alkalis, Ag was first introduced with rewarding results. Pb was also chosen, both per se and together with Ag, because its particular electronic configuration has been associated with wide ranges of oxide glass formation [7], and because during the period of our exploration Monyhan et al. [8] and Aggarwal et al. [9] reported interesting biphasic structures, with one of the two glass transition temperatures fairly high, in the Ge–As–Pb–Se field.

2. Glass formation and structure in the field Si–As–Te

In contrast to S and Se, elemental Te does not form a glass. In general glass formation within group VI has been found to increase from O through S to Se, then to decrease to Te [10]. In the binary Ge–Te, glasses can be obtained starting from about $\text{Ge}_5\text{Te}_{95}$ and, more normally, as one approaches the eutectic near $\text{Ge}_{20}\text{Te}_{80}$. The glass transition temperature of binary Ge–Te glasses increases to a maximum for the composition GeTe_2 [11] just as in the case of GeSe_2 , strongly suggesting ordered cross-linked structures somewhat similar to those established for SiO_2 [12]. This

ordering is based on the preference for Ge–Te over Ge–Ge and Te–Te bonds. The glasses containing more Te than in GeTe_2 as well as those containing more Ge are softer.

In the latter glasses, as one approaches the composition GeTe , a different ordering scheme appears, however, not at all the structure of crystalline GeTe (coordination of Ge = 6) [13], rather another one with lower coordination (Ge = 4 or 3) characteristic of the glasses only [14–16]. In this range phase separation and sequential crystallization may occur. It may be assumed that conditions in the binary Si–Te start similarly. Indeed between $\text{Si}_{15}\text{Te}_{85}$ and $\text{Si}_{25}\text{Te}_{75}$ Hilton and Jones [5] obtained glasses quite readily, but SiTe_2 structures are less likely. There is no glass formation in the binary Si–As.

In the binary Te–As the glass transition temperature rises, but smoothly, not indicating any ordering nor any tendency to ‘saturate’ at the stoichiometric composition, As_2Te_3 [11]. As a matter of fact a glass of the composition As_2Te_3 can – in contrast to the classical glass As_2S_3 – form only under extreme quenching conditions and its structure differs entirely from that of crystalline (monoclinic) As_2Te_3 [17, 18]. In the chain structure of the crystal the As atoms show 6 and 3 coordination, the Te atoms 3 and 2 coordination. In the glass As has the coordination 3, Te the coordination 2, most likely just as in both crystalline As_2S_3 (orpiment) and vitreous As_2S_3 [19]. This disordered orpiment structure is encouraged when some Ge or Si is present.

The large region of glass formation in the ternary Si–As–Te [1] may be related

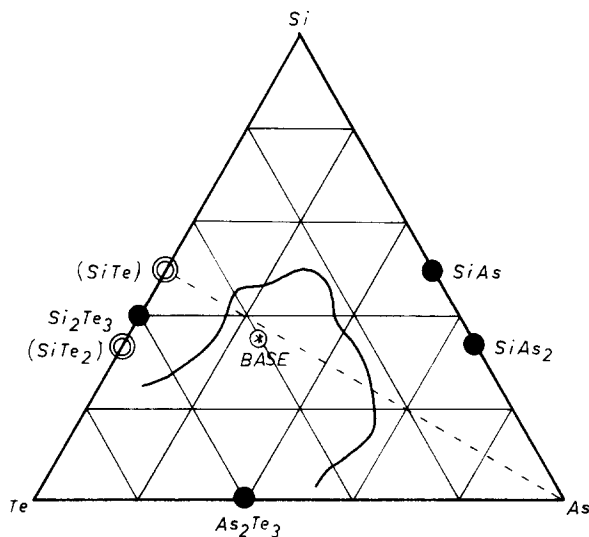


Fig. 1. Si–As–Te ternary, showing the extended region of glass formation and known binary compounds (the existence of SiTe and SiTe_2 is doubtful).

to the occurrence of compounds in the three binaries (fig. 1), using a classical experience in oxide glasses.

The highest softening ranges, and concomitant glass transition temperature, are found near $\text{Si}_{40}\text{As}_{20}\text{Te}_{40}$ on the pseudobinary joint SiTe–As. DeNeufville [12] proposes an average three-fold coordination arrangement involving Si–As bonds along this joint connecting average five electron per atom groupings as in As. GeTe and As are electronically isostructural [21, 22]. Good glasses have also been prepared from five electron per atom combinations like TlAsX_2 , AsXI ($X = \text{chalcogen}$) [20].

However, observations indicate significant differences between the Si–Te and Ge–Te binaries. While GeTe_2 structures in glasses are made plausible by T_g maxima, SiTe–X structures appear to prevail over SiTe_2 structures in the ternary glasses, making DeNeufville's [11, 12] and Krebs' [21] concepts even more applicable in the proper case.

Our starting point in the development of higher softening range polynary Si–Te glasses, $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$ (fig. 1), happens to lie significantly close to the joint SiTe–As singled out by DeNeufville [23].

3.1. Fabrication

Glass samples were produced in carefully cleaned sealed silica type vials which had been evacuated, backfilled with H_2 , evacuated and heated with a torch prior to sealing [2]. The vials were reacted in a rocking furnace.

The raw materials utilized were of five 9's or better purity when received from the chemical suppliers. Elemental As tends to absorb oxygen on its surface and must be further purified with hydrogen gas. This process consists of placing a quantity of As in an open-ended tube through which H_2 gas is routed, and heating to 350°C . Se is purified in a sealed pyrex container that is evacuated and subsequently heated to 400°C . A portion of the container is maintained outside the furnace during the purification and there the oxides condense. Other elements such as Si, Te and Ag were used as received.

The sample vials were withdrawn from the hot furnace (975°C), held in air until a dark red color was attained, and placed in a container composed of insulating material.

3.2. Evaluation procedures

3.2.1. Stability

Samples were classified as unstable if they gave off noxious vapors believed to be H_2Se or if the glass vials in which they were stored acquired a red-brown residue, presumably SeO_2 . Additionally, samples were classified as unstable if after heating near 500°C they produced the above phenomenon.

3.2.2. Softening point analysis

The indentation system utilized for measuring relative softening points consisted of a quartz rod loaded on a sample, in a furnace, connected with a dial [2] similar to a device used by Jones and Hafner [24]. Calibration of this system was accomplished with NBS 712 glass.

Two penetration depths of the rod were correlated to viscosities. The first point corresponds to a viscosity of $10^{9.8}$ Poise, the second to a viscosity of $10^{8.4}$ Poise, in good agreement with the calibration results of Jones and Hafner [24]. These softening points are designated $T_{9.8}$ and $T_{8.4}$ in this paper.

3.2.3. Phase separation

Phase separation was observed directly by transmission electron microscopy in a Hitachi HU-11A with a cold stage (120 K) accessory.

Samples were prepared for analysis by chipping fragments from the bulk glass with a diamond file and placing them between two 75 mesh copper grids. The resulting grid-glass sandwich is then positioned on a standard compression type specimen holder.

The magnification used for this study was 43 000 X as determined by a collodion standard. All micrographs obtained represent electron transmission through thin edges.

3.2.4. Infrared transmission

Ir analysis was carried out on small lenses produced by grinding and polishing opposite sides of bulk samples to flat parallel surfaces. The lens thickness ranged between 0.8 and 2.0 mm. A Perkin-Elmer 137 spectrophotometer with a range of 3–15 μm was used for analysis. A standard lens made of the base glass ($\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$) was employed to calibrate the instrument. Transmission is reported as measured at 6 μm .

3.2.5. Dilatometry

The dilatometer used to obtain expansion data on selected compositions consisted of a tube furnace, sample container, signal transfer rod, transformer and core, and electronic recording equipment. The sample container and transfer rod were both silica. Breaks in the expansion curve were considered related to glass transition temperatures.

3.2.6. Density

Density measurements were made utilizing the Archimedes principle and converted into molar volume by dividing the normalized formula weight by the density.

3.2.7. Crystallization

Samples were tested for devitrification by X-ray analysis using a General Electric XRD-5 diffractometer. The specimens were scanned in the range $2\theta = 10^\circ$ to 50° .

4. Results

4.1. Relative chemical stability

In previous work by Hilton et al. [16] and by Sholnikov [6] chalcogenide glasses containing Si in conjunction with Se have been found chemically unstable. In the present investigation modifiers to improve the chemical stability of such glasses were to be found, because they were expected to have a significantly higher softening range. Initial investigations in the system Si-As-Se showed that a sample containing approximately equal amounts of the three constituents seemed to behave normally while hot (900°C) and in the liquid state. Under these conditions it was contained in less than half the vial volume. However, upon removal from the furnace the melt expanded and filled the entire vial. The resulting product consisted of flakes that decomposed emitting what appeared to be H₂Se [5].

Hilton et al. [25] also demonstrated that while the system Si-Sb-Se contains glasses with relatively high softening points they were unstable.

In the present investigation the glass Si₃₅As₂₅Te₄₀ was chosen as a starting point. Experiments showed that substitutions of up to only 5% Se for Te without any other compositional modification resulted in stable glasses. Modifications involving, as one might first be inclined to try, elements conducive from first principles to strong

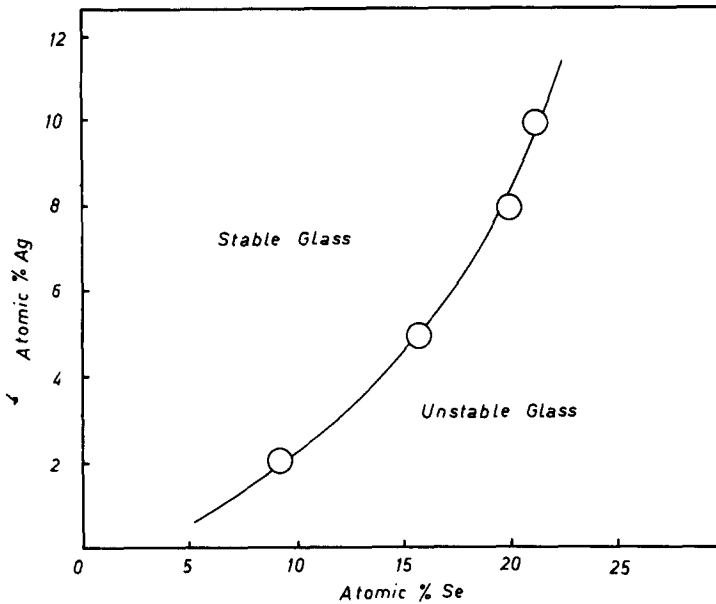


Fig. 2. Stability limits. The circles show the last stable glass in the series $Ag_x Si_{35} As_{25-x} Se_y Te_{40-y}$

Table 1
Ag-Se doped Si-As-Te glasses^{a)}

Ag	Se	Si	As	Te	Stab. b SP	Stab. a SP	$T_{9,8}$ (°C)	$T_{8,4}$ (°C)	ΔE (vis) (kcal/mol)	$\eta = 10^{13,0}$ (°C)	$\eta = 10^{14,6}$ (°C)	IR	Density (g/cm ³)	% Area phase separated
(Base)		37	30	33	+++	+++	490	523	118	424	395		4.22	0
2		35	25	40	+++	+++	442	478	95	372	348	56	4.33	0
		35	23	40	+++	+++	434	466	104	370	343	51	4.20	0
2	5	35	23	35	+++	+++	445	482	94	372	343		4.34	20-30
2	10	35	23	30	+++	+++	460	500	91	383	352		4.26	50-60
2	15	35	23	25	+++	++	479	510	122	416	389		4.17	90
2	20	35	23	20	-	-	475	510	118	406	386		4.10	
5		35	20	40	+++	+++	425	452	120	370	345		4.55	0
5	5	35	20	35	+++	+++	442	469	126	387	363	55	4.45	20-30
5	10	35	20	30	+++	+++	454	482	126	397	372	54	4.36	40-50
5	15	35	20	25	+++	++	478	504	144	424	401	50	4.28	80-90
5	20	35	20	20	+++	++	530	558	152	472	447		4.22	90
8		35	17	40	+++	+++	399	425	116	346	323	37	4.71	10-30
8	5	35	17	35	+++	+++	424	454	108	364	338	56	4.58	20-40
8	10	35	17	30	+++	+++	458	484	137	405	380	56	4.47	40-50
8	12	35	17	28	+++	+++	470	492	105	424	402	56	4.43	90
8	20	35	17	20	+++	+++	544	572	158	486	461	56	4.28	95
8	25	35	17	15	+++	+	569	597	168	511	486		4.25	
10		35	15	40	+++	+++	387	414	107	332	308		4.87	10-30
10	5	35	15	35	+++	+++	421	447	123	368	344		4.72	30-40
10	10	35	15	30	+++	+++	454	480	135	401	377	28	4.61	40-50
10	15	35	15	25	+++	+++	537	564	161	481	456	56	4.49	80-90
10	20	35	15	20	+++	+++	560	588	164	502	476	35	4.39	90
10	30	35	15	10	-	-	588	625	134	514	483		4.27	
15	25	35	10	15	-	-	574	616	115	492	456	36		

a) Stability: b SP - before softening analysis, a SP - after softening analysis; +++ no signs of reaction with atmosphere, ++ initial instability, stability after one hour, + initial instability, stability after one day, - very slow continuous deterioration, --- rapid deterioration; $T_{9,8} = T^{\circ}\text{C}$ at $\eta = 10^{9,8}$, $T_{8,4} = T^{\circ}\text{C}$ at $\eta = 10^{8,4}$; ΔE (vis) = activation energy of viscous flow; $\eta = 10^{13,0}$, $\eta = 10^{14,6}$ = extrapolated temperature at this viscosities, (see subsect. 3.2.2); IR = transmission at 6 μm .

bonding while still expected to maintain infrared transmission in the desired range, were leading to minimal success. These elements included Ge, P, Bi and Pb. The latter may yet be further investigated, particularly in combination with more successful modifications.

Next, group I elements were considered for modification, with the aim of increasing the compatibility of Te and Se groupings in the planned copolymer, as discussed in sect. 2. And, because of the reactivity of alkali elements, Ag was chosen as model and first constituent. It was with Ag that significant stabilization of Si-Te glasses containing Se was achieved [26]. Increasing amounts of Se substituted for Te were accommodated in stable glasses with substitutions of Ag for As in $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$ glasses (table 1, and fig. 2).

4.2. Softening point analysis

4.2.1. Ternary Si-As-Te glasses

Samples in the Si-As-Te system and related derivations were analyzed for $T_{9,8}$ and $T_{8,4}$ (as defined in sect. 3). The results obtained are listed in table 1. An activation energy was estimated from the slope between these admittedly close values.

The data taken in the ternary system Si-As-Te correspond well to Hilton's [1]. Two compositions of particular interest in this system are $\text{Si}_{37}\text{As}_{30}\text{Te}_{33}$ and $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$. $T_{9,8}$ for the first glass was 490°C and represents the highest attainable in the system. However, this composition lies in the region of the glass field that tends toward devitrification. The second composition has a $T_{9,8}$ of 442°C , but has the ability to resist crystallization when subjected to variations in fabrication temperatures of 300°C or more.

4.2.2. Modifications by Sb, P, Ge, Al, Bi, Pb and Zn

Modifications of Si-As-Te glasses involving 5% of these elements had generally lower softening points. In higher concentrations devitrification interfered frequently (subsect. 4.4). Ge, Sb, P, Zn could be substituted up to 10% yielding good glasses. But only in two cases was a somewhat elevated softening range attained:

- (1) $\text{Si}_{35}\text{Ge}_5\text{As}_{20}\text{Te}_{35}\text{Se}_5$ with $T_{9,8} = 482^\circ\text{C}$, $\log \eta = 13$ at 452°C , $\log \eta = 14.6$ at 433°C and
- (2) $\text{Si}_{30}\text{Ge}_5\text{As}_{20}\text{P}_5\text{Te}_{35}\text{Se}_5$ with $T_{9,8}$ at 463°C .

4.2.3. Si-As-Ag-Te-Se glasses

As soon as it had been realized that increasing amounts of Ag stabilize selenium in modified Si-As-Te glasses, a systematic series of Ag and Se substitutions for As and Te respectively in $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$ glass was analyzed for $T_{9,8}$ and $T_{8,4}$.

Silver substituting for As without any substitution of Se, decreases these 'softening points' by about $7^\circ\text{C}/\text{at } \%$ Ag (fig. 3). Such a decrease might have been expected, but was to be compensated by the additional substitution of Se for Te.

In a glass containing 2% Ag substituted for As replacement of Se for Te up to 17%

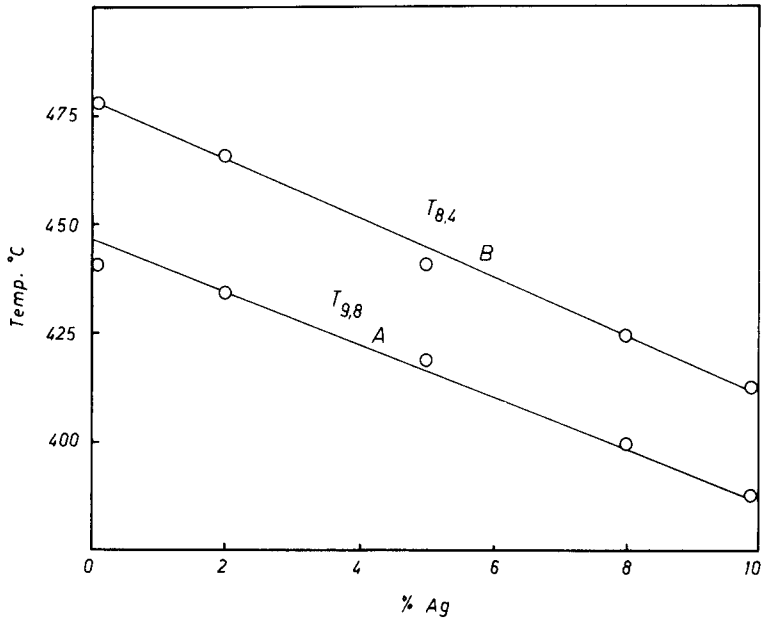


Fig. 3. Softening points of the $Ag_xSi_{35}As_{25-x}Te_{40}$ glasses versus % Ag.

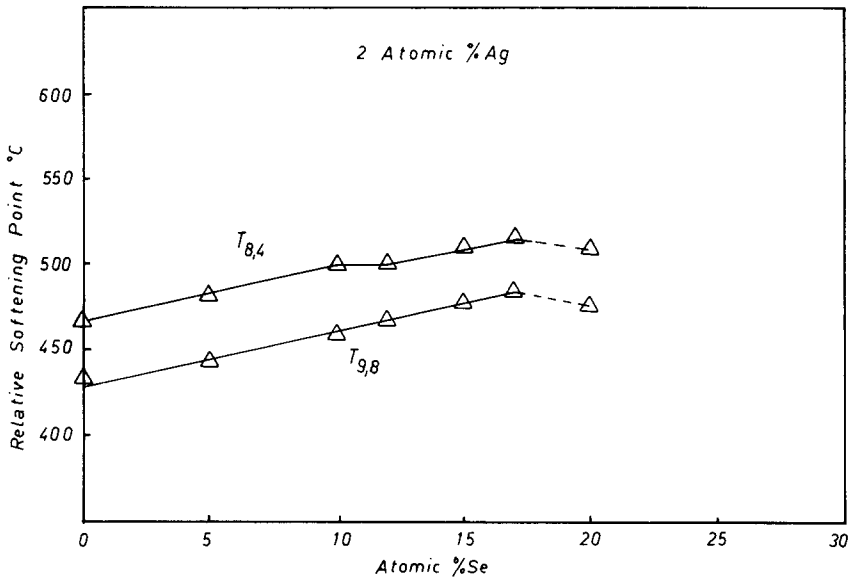


Fig. 4. Softening points of the $Ag_2Si_{35}As_{23}Se_yTe_{40-y}$ glasses versus % Se.

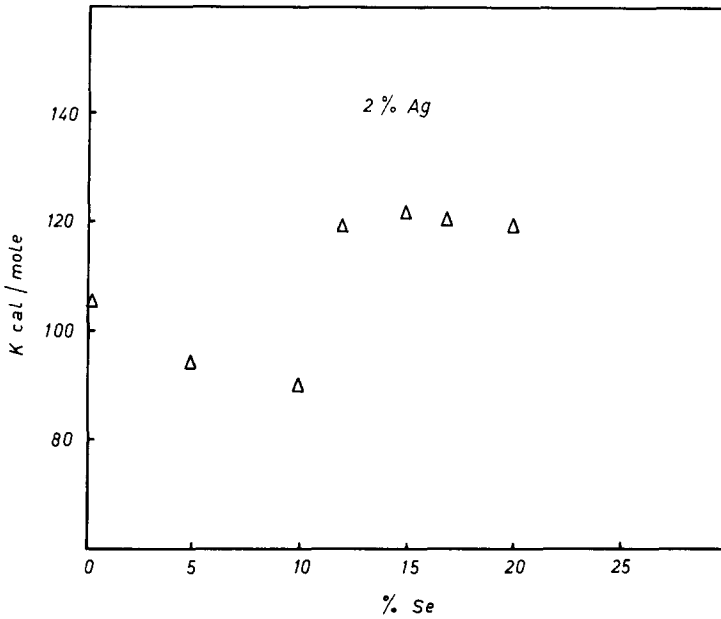


Fig. 5. E_{vis} of the $Ag_2Si_{35}As_{23}Se_yTe_{40-y}$ glasses versus % Se. The activation energy of viscous flux was calculated from the data of fig. 4.

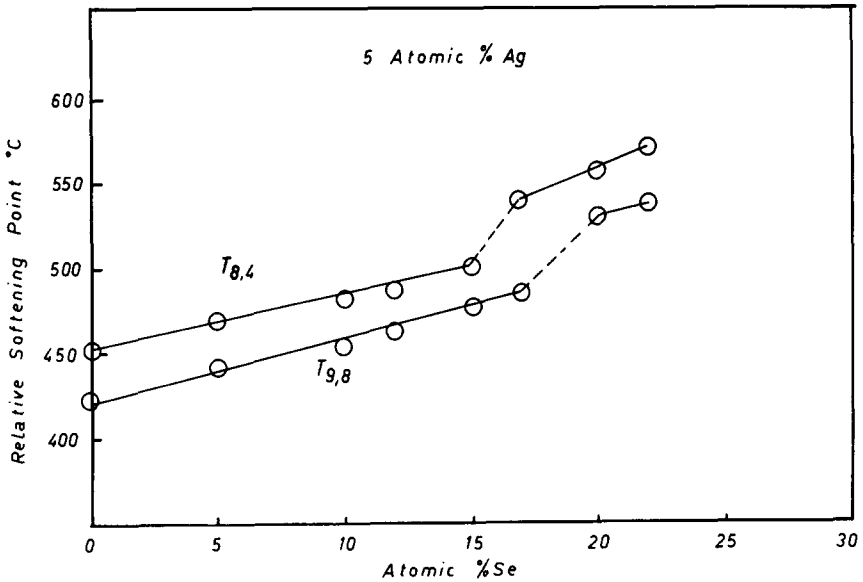


Fig. 6. Softening points of the $Ag_5Si_{35}As_{20}Se_yTe_{40-y}$ glasses versus % Se.

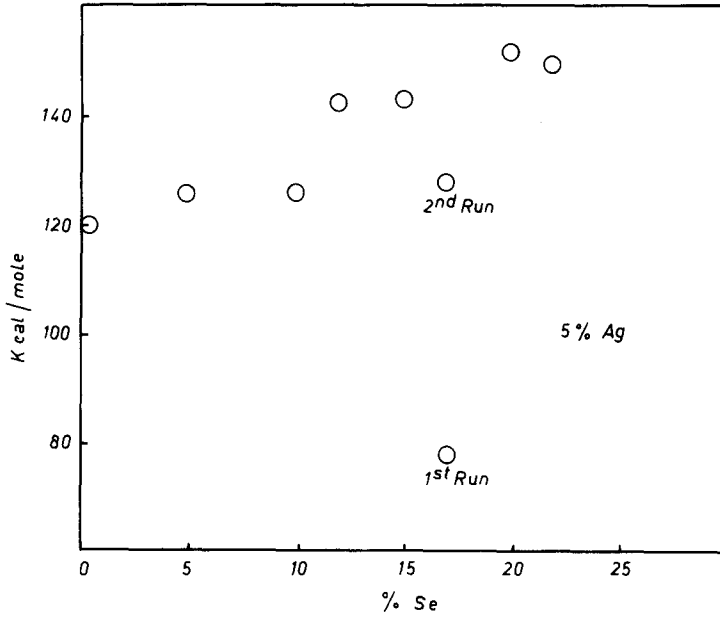


Fig. 7. E_{vis} of the $Ag_5Si_{35}As_{20}Se_yTe_{40-y}$ glass versus % Se. For 1st and 2nd run see the text.

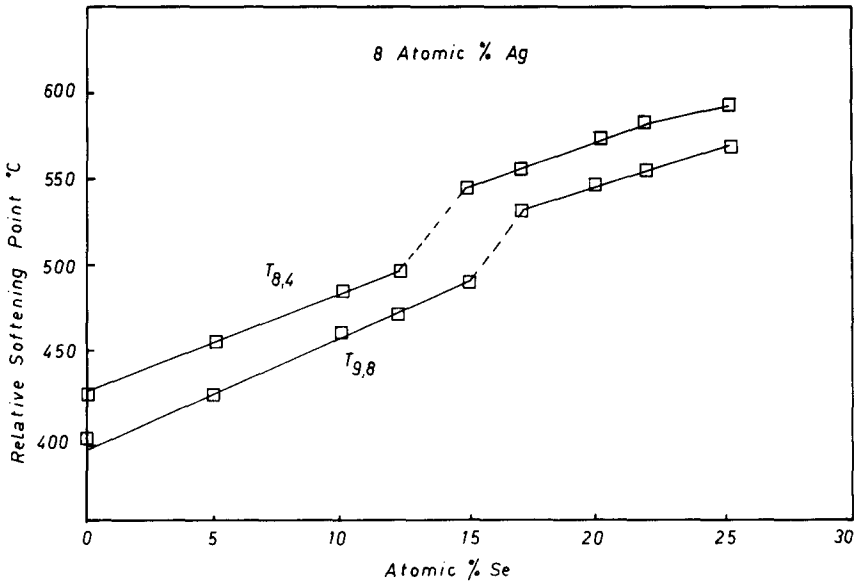


Fig. 8. Softening points of the $Ag_8Si_{35}As_{17}Se_yTe_{40-y}$ glasses versus % Se.

caused a moderate increase of 'softening points'. Additional Se was detrimental to the softening characteristics of the 2% Ag glass. Also, after softening analyses glasses containing 12 and 15% Se show instability. The softening behavior of the 2% Ag series can be seen in fig. 4. The energy of activation for viscous flow showed an increase of about 20 kcal/mol near 12% Se (fig. 5).

A series of glasses containing 5% Ag substituted for As showed increasing 'softening points' with increasing Se (fig. 6). In the vicinity of 17% Se a break is evident. A re-run of the 17% Se glass resulted in a rise of $T_{9.8}$ from 485°C to 510°C and of $T_{8.4}$ from 536°C to 542°C. The energy of activation for viscous flow in this series shows a break of about 30 kcal/mol around 12% Se. These observations represent the first indication of a possible change in glass structure within a series of fixed Ag content.

In samples containing 8% Ag progressive replacements of Se for Te further increased 'softening points'. The highest $T_{9.8}$ and $T_{8.4}$ measured were 551°C and 576°C in a stable 20% Se glass, and 569°C and 597°C in the highest (25%) Se glass (fig. 8). Here a break in the data was observed around 15% Se. A re-run of this sample resulted in changes of $T_{9.8}$ from 494°C to 532°C and of $T_{8.4}$ from 545°C to 559°C. A plot of the estimated activation energy for viscous flow shows a discontinuity of about 40 kcal/mol at 12% Se (fig. 9).

Glass compositions containing 10% Ag substituted for Ag again show increased 'softening points' as Te is systematically replaced by Se. The overall behavior is illus-

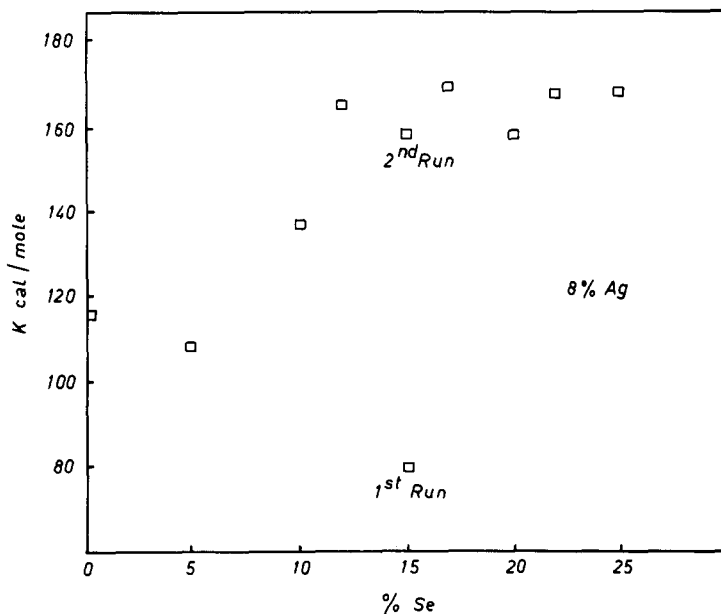


Fig. 9. E_{vis} of the $Ag_8Si_{35}As_{17}Se_yTe_{40-y}$ glasses versus % Se. For 1st and 2nd run see the text.

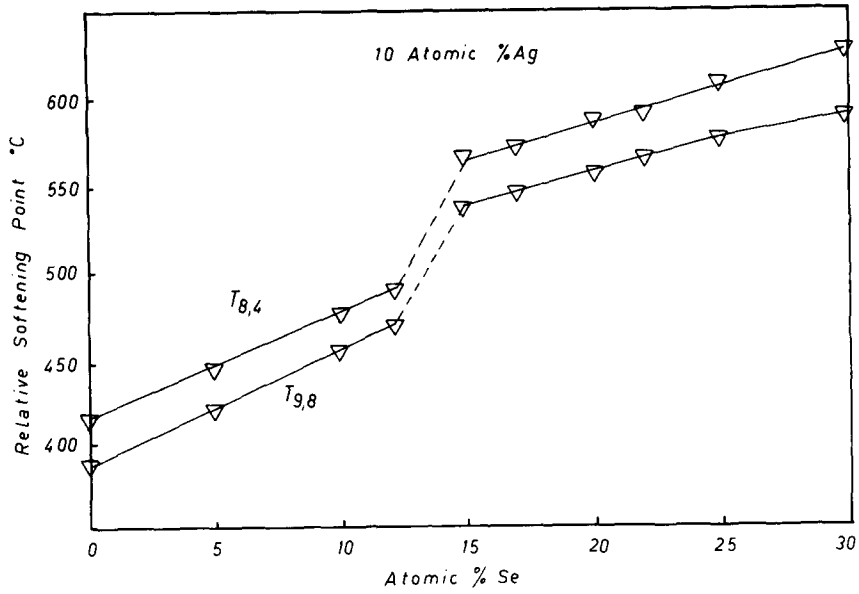


Fig. 10. Softening points of the $Ag_{10}Si_{35}As_{15}Se_yTe_{40-y}$ glasses versus % Se.

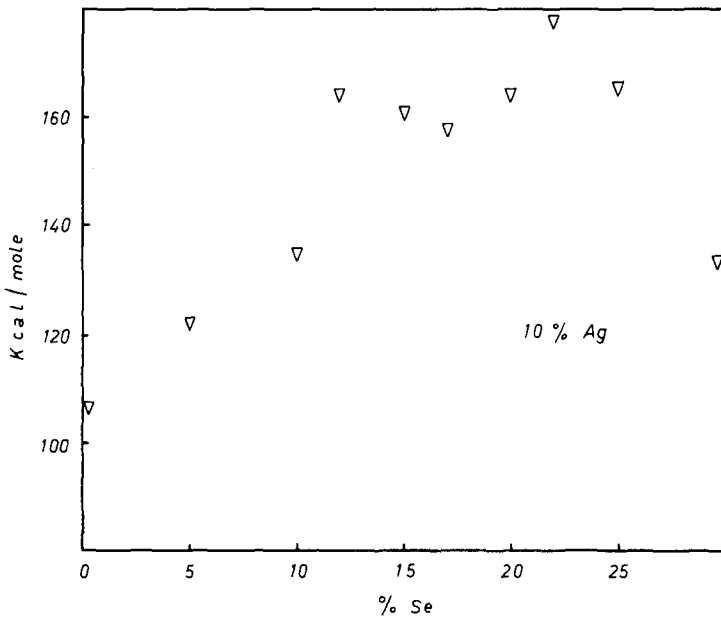


Fig. 11. E_{vis} of the $Ag_{10}Si_{35}As_{15}Se_yTe_{40-y}$ glasses versus % Se.

trated in fig. 10. The highest $T_{9.8}$ and $T_{8.4}$ were 560°C and 588°C in the stable 20% Se glass and 588°C and 625°C in the 30% Se glass. Furthermore, the break now occurs between 12 and 15% Se. The activation energy for viscous flow again shows a break of about 40 kcal/mole at 12% Se (fig. 11).

Additional explorations with 13, 15 and 20% Ag substituted for As were conducted with 25 and 30% Te replacing Se. Some of these glasses exhibited exceedingly high 'softening points' as shown in table 1. However, all samples were highly reactive with the atmosphere.

4.2.4. Glasses containing Pb

Pb-modified Si-As-Te glasses as already stated possess reduced 'softening points'. However in glasses containing 3% Pb plus 5% Ag in the place of As substitution of Se for Te produced higher $T_{9.8}$. The abnormally high $T_{8.4}$ softening point in these glasses is caused by crystallization evidenced by X-ray investigation. Other Pb-modified glasses containing 7 and 10% Ag and more than 20% Se were partly crystallized as quenched.

4.3. Extrapolated and dilatometric glass transition data

Evaluations of T_g have been proven of great value for the understanding of the relations between composition, structure and properties of chalcogenide glasses [23, 27].

The estimation of the temperatures for viscosities $10^{14.6}$ ('strain point') and $10^{13.0}$ ('annealing point') may provide an estimate for the glass transition temperature pending direct evaluations.

Our estimation was made by the extrapolations from the (admittedly close) temperatures for viscosities of $10^{8.4}$ and $10^{9.8}$ to those at 10^{13} and $10^{14.6}$. The increase in those 'glass transition temperatures' with Se content is indicated in the trend registered in fig. 12 for the 10% Ag glass. The extrapolated values go from 370°C for the $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$ base, down to about 332°C for the 10% Ag substituted glass, and up to above 518°C for the high selenium glasses. These data compare with temperatures at the breaking points of the dilatometric curves. These breaks are believed to correspond closely to the glass transition temperature of the participating phases.

Glasses containing 0 and 5% Se and the base glass exhibited a single low temperature 'glass transition' (fig. 13). Other compositions ranging from 10 to 15% Se produced a high and a low temperature 'glass transition'. Samples containing 17 and 20% Se show either one high temperature or two high temperature transitions.

Glass compositions exhibiting a high and low temperature 'glass transition' are in the vicinity of the discontinuities in 'softening points' reported in subsect. 4.2.3 (figs. 6, 8 and 10). In addition a glass composition containing 8% Ag with 15% Se was tested and it also produced a high and a low temperature 'glass transition'. This composition also lies at that discontinuity.

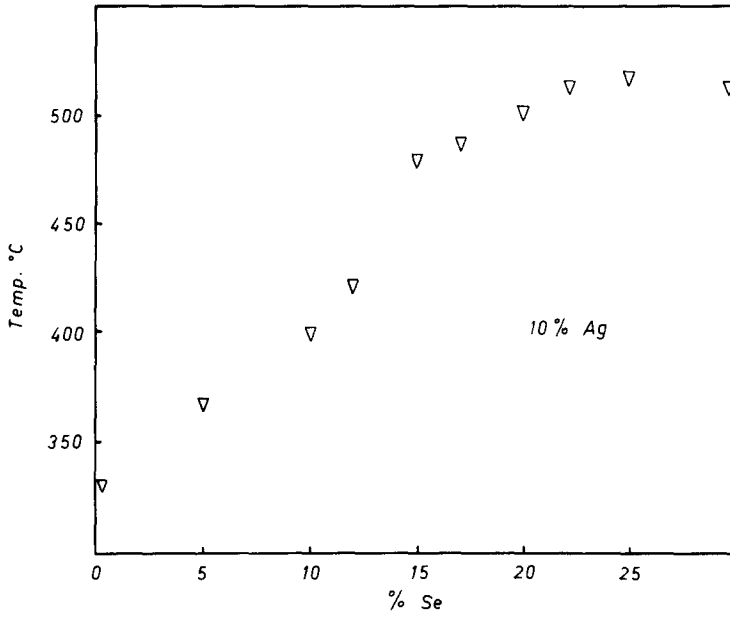


Fig. 12. Extrapolated anneal points of the $Ag_{10}Si_{35}As_{15}Se_yTe_{40-y}$ glasses versus % Se. For the method see the text.

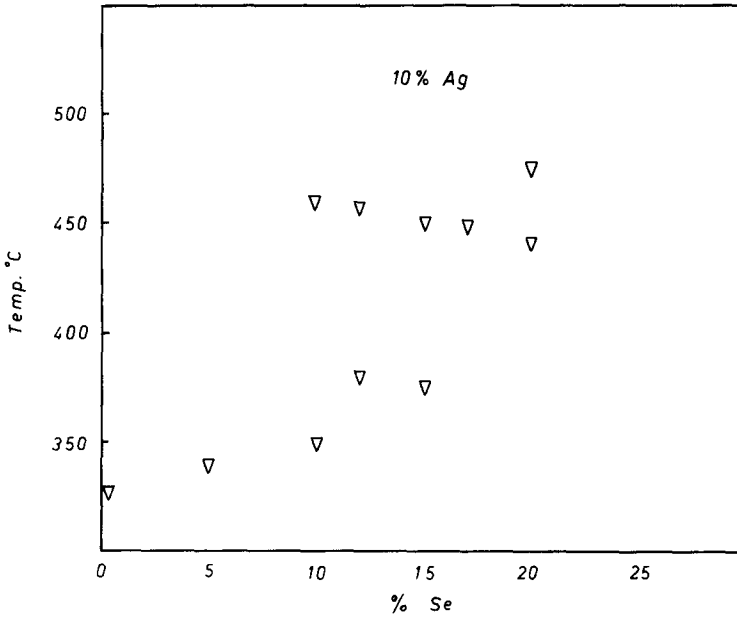


Fig. 13. Dilatometer break points versus % Se as measured for the $Ag_{10}Si_{35}As_{15}Se_yTe_{40-y}$ glasses.

These few dilatometric experiments suggest the appearance of a stronger grouping in the silver glasses containing 10% Se or more.

4.4. Devitrification analysis

The base glass ($\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$) and Ag–Se modified glasses showed no signs of crystallization.

All samples containing Pb in conjunction with Se or Te devitrified during softening analysis. The crystalline phase in the Pb modified Si–As–Te base glass was identified as PbTe. Identification of the crystalline phase in the Pb–Ag–Se doped glasses

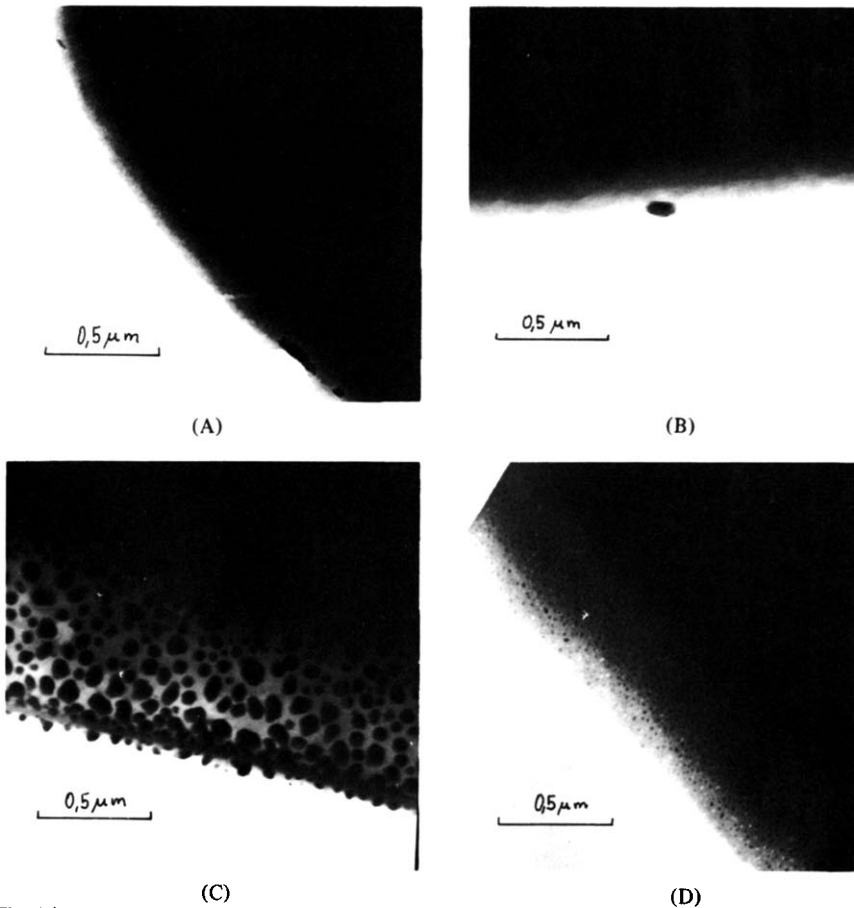


Fig. 14. Direct transmission micrographs, taken on a cold stage (-120°C) of (A) $\text{Si}_{35}\text{As}_{35}\text{Te}_{40}$, (B) $\text{Ag}_5\text{Si}_{35}\text{As}_{20}\text{Te}_{40}$, (C) $\text{Ag}_5\text{Si}_{35}\text{As}_{20}\text{Te}_{38}\text{Se}_{12}$, (D) $\text{Ag}_5\text{Si}_{35}\text{As}_{20}\text{Te}_{20}\text{Se}_{20}$. Magnification $43\,000\times$, explanation in the text.

was not accomplished. Among the other elements, added Ge, B, Sb, P, Pb, Bi and Zn, Bi showed the highest tendency towards crystallization. No composition containing Bi, alone or with Pb, showed glass formation. With up to 2.5% Pb and 2.5 %Se a good glass was obtained. The tendency towards crystallization was not as pronounced when B was introduced, however, the stability upon Se substitution for Te decreased. Glasses in which 5% Ge, Sb, P or Zn were introduced did not devitrify.

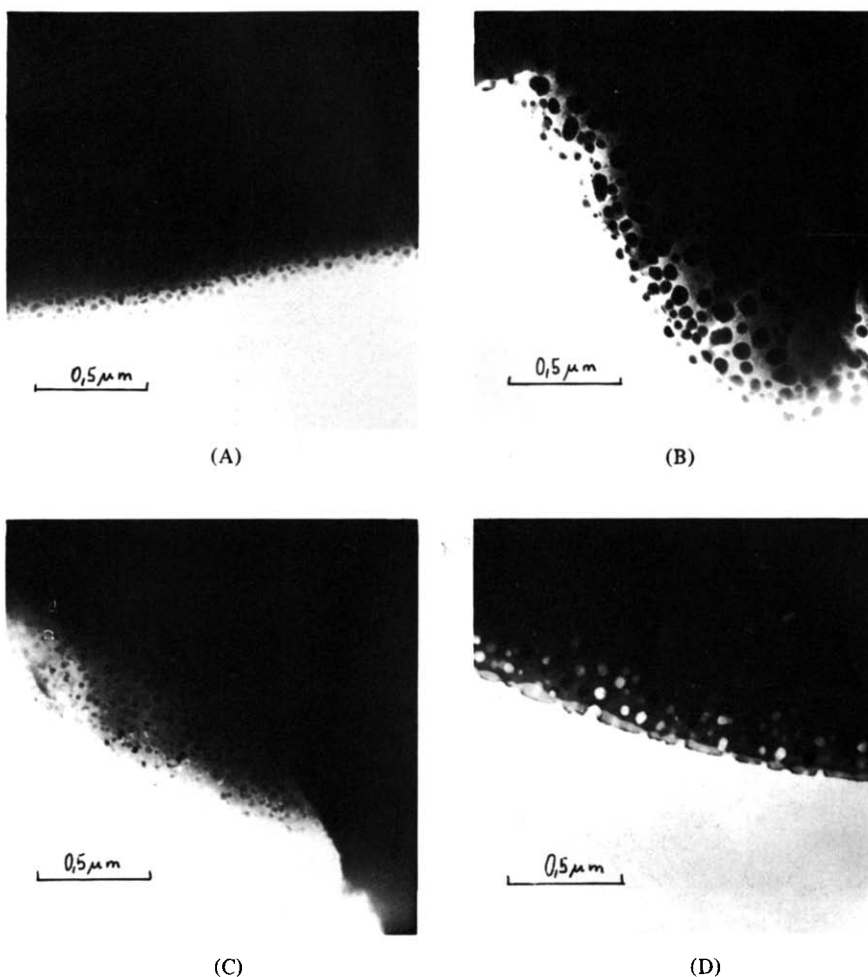


Fig. 15. Direct transmission electron microscope pictures of (A) $\text{Ag}_8\text{Si}_{35}\text{As}_{17}\text{Te}_{40}$, (B) $\text{Ag}_8\text{Si}_{35}\text{As}_{17}\text{Te}_{35}\text{Se}_5$, (C) $\text{Ag}_8\text{Si}_{35}\text{As}_{17}\text{Te}_{15}\text{Se}_{15}$, (D) $\text{Ag}_8\text{Si}_{35}\text{As}_{17}\text{Te}_{18}\text{Se}_{22}$. Magnification 43 000 \times , explanation in the text.

4.5. Phase separation

Electron transmission microscopy has revealed phase separation of varying degree and size in the Ag–Se modified Si–As–Te glass system. This separation appeared to vary with both Ag and Se content. The base glass ($\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$) did not appear to be phase separated. Electron transmission micrographs can be seen in figs. 14–16.

Glass compositions containing 2 and 5% Ag substituted for As were monophasic. Increasing substitutions of Se for Te in the four Ag modified systems revealed a trend toward larger phase size. Additionally this same systematic increase in substitutions (Ag for As and Se for Te) increased the percent of areas observed on any

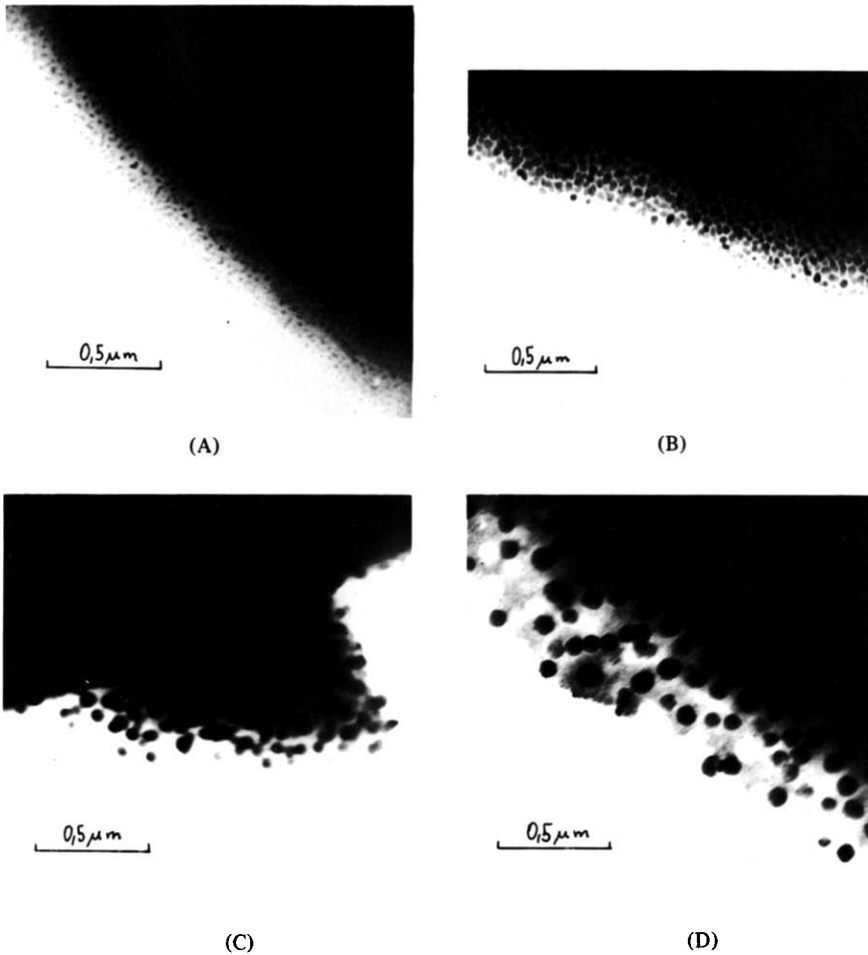


Fig. 16. Direct transmission views of (A) $\text{Ag}_{10}\text{Si}_{35}\text{As}_{15}\text{Te}_{40}$, (B) $\text{Ag}_{10}\text{Si}_{35}\text{As}_{15}\text{Te}_{88}\text{S}_{12}$, (C) $\text{Ag}_{10}\text{Si}_{35}\text{As}_{15}\text{Te}_{23}\text{Se}_{17}$, (D) $\text{Ag}_{10}\text{Si}_{35}\text{As}_{15}\text{Te}_{15}\text{Se}_{25}$. Magnification 43 000 \times , explanation in the text.

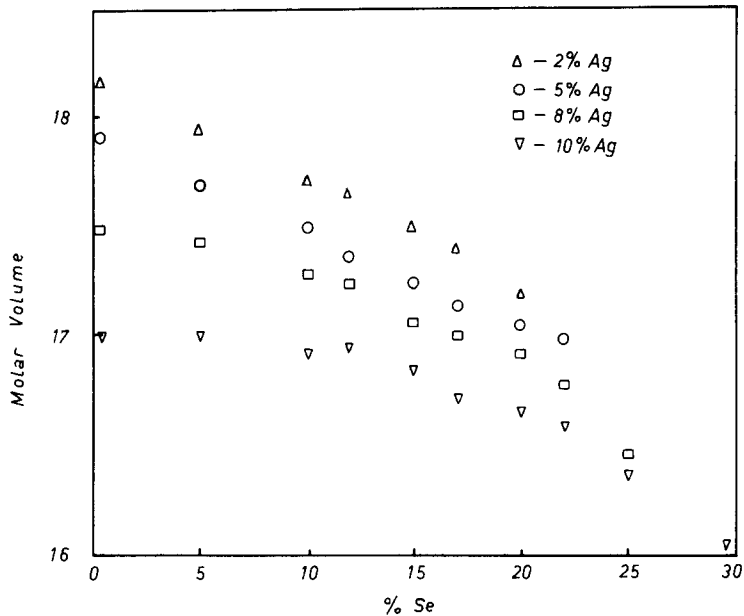


Fig. 17. Molar volume of the $\text{Ag}_x\text{Si}_{35}\text{As}_{25-x}\text{Se}_y\text{Te}_{40-y}$ glasses versus % Se. The curves for compositions containing 8 and 10% Ag show a break around 12% Se.

sample exhibiting separation. In the 8 and 10% Ag glass systems a change in phase motif appeared to exist near the compositions centered near the softening point data breaks.

Compositions in the 5, 8 and 10% Ag series extending beyond the stability limit of Se substitution appeared to possess voids. These voids correspond in size to the noncontinuous phases present.

4.6. Density

The density data obtained during this investigation yielded the most readily interpretable information when converted to molar volume. A plot of molar volume versus percent selenium for the four silver systems (fig. 17) shows that no sharp breaks in the data occurred for the ranges of Se tested. However, a tailing off of the data for the 8 and 10% silver system is apparent (table 1).

4.7. Infrared transmission

Infrared analysis of Si-As-Te glasses showed that transmission characteristics for these samples were in good agreement with data published by Hilton [1]. The parasitic oxygen bands at 10.4 and 14.0 μm identified by Hilton [16] as well as

Savage and Nielsen [28] as Si–O and Te–O vibrations respectively, were present. Substitutions of Ag and Se in the manner previously described brought about the appearance of an additional oxygen absorption band at $13.6\mu\text{m}$. This band was believed to be attributable to Se–O vibrations [28]. In the region of the spectrum between 3 and $9\mu\text{m}$, where no absorption bands were present, transmission remained good for all compositions containing up to 8% Ag. However, samples analyzed showed a deepening of the Si–O band with increasing Se content. This was believed to be caused by oxygen spoiled Se introduced during fabrication which subsequently reacted with the Si.

Compositions containing 10% Ag in conjunction with various amounts of Se show optimal transmission around 15% Se.

Pb-modified glasses containing 5% Ag showed good transmission, when incorporated in a sample. Higher concentrations of Ag in conjunction with Pb rendered the glass opaque to i.r. All Pb-modified glass which were subjected to heat treatments were opaque.

The percent transmission at $6\mu\text{m}$ for selected glasses can be seen in table 1.

5. Discussion

In principle bonds formed between Si and Se should be stronger than those formed between Si and Te or Ge and Se. This prediction is based on the fact that a Si–Se pair possesses both a smaller average atomic radius and a greater electronegativity difference than the other two pairs.

A Si–As–Se glass would be ideal for both i.r. transmission and thermal strength. However, instability in this system excluded such glasses unless a modifier is found which allows incorporation of maximum percentages of Se in a Si–As–Te glass. This investigation has demonstrated that Ag has the ability to act as this modifier. Selected Ag–Se modified Si–As–Te glasses exhibit dual viscosity characteristics and are biphasic. The fact that such glasses when high in Se and Ag exhibit extrapolated annealing points ($\eta = 10^{13}$) up to about 150°C higher than that attributable to the base glass $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$ appears to be related to this rheology. Since glass transition temperatures (T_g) are usually not too far from temperatures corresponding to $\eta = 10^{13}$, these compositions also will have T_g 's about 150°C higher than a Si–As–Te base.

The analysis of softening characteristics of the 5% Ag system modified with increasing amounts of Se (subsect. 4.2.1) demonstrates a considerable increase in $T_{9.8}$ and $T_{8.4}$ above 17% Se. At 17% a discontinuity in softening characteristics is apparent, and paralleled by phase separation of increasing extent and particle size (subsect. 4.5). Similarly, a modest increase in 'softening points' can be observed already in the 2% Ag system, but the discontinuity in the activation energy of viscosity observed at 12% Se, is only small. Phase separation in these glasses appears less pronounced. It seems plausible that concentrations substantially below 5% Ag in con-

junction with Se are insufficient to allow a second high temperature phase to gain the extent necessary to allow some predomination of its viscosity properties.

The 8% Ag modified series exhibits viscosity properties similar to those of the 5% Ag glasses. The discontinuity now occurs near 15% and the softening points beyond this concentration show larger increases. Additionally, the activation energies for the high viscosity temperature glass compositions are greater. At this point it appears plausible that the strong glass phase is mostly controlled by Ag and Se.

Further evidence for this possibility is seen in the 10% Ag glass system. Here the general behavior of the 5% and 8% Ag glasses is repeated, but now the discontinuity in the viscosity plot occurs between 12 and 15% Se and the activation energy increases by 40 kcal/mole.

This model involving gradual changes in phase concentrations as the mechanism for attaining increased thermal strength is complemented by molar volume data (subsect. 4.6). The four silver series show continual decreases in molar volume as the Se content increases with a slight break in the data near 12% Se. This break becomes more apparent with increasing Ag content. This would seem to imply that the structure of these glasses within the two phases remains essentially the same. Only in the 8 and 10% Ag series for high Se concentrations beyond the stability limit does the molar volume show obvious deviations from the previously defined trend. This could be a possible indication of a gross structural change in one of the glass phases with the result that bonding between the phases is weakened. It is interesting to note that in the unstable glasses containing too little Ag or too much Se the two phases appear to be incompatible; the one high in Se must have volatilized, as evidenced by the fact that voids similar in size and shape to one of the phases are present.

In many respects this specific evidence supports certain generalizations regarding the development of maximum thermal strength in sufficiently infrared transmitting chalcogenide glasses, i.e., those free of S. The maximum thermal strength in terms of maximum softening temperatures in the simple ternaries Ge–As–Se and Si–As–Te is about equal and found near the pseudobinary joins GeSe–As and SiTe–As. The castable glass selected here ($\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$) as the base glass is an example. The simplest account for the improved thermal strength of the Se-substituted glasses is, of course, the one introducing this section: stronger bonding of Se, compared to Te, the former possessing smaller average atomic radius and being more electronegative.

The necessary condition for this is the introduction of Se into a stable glass. The working hypothesis underlying the introduction of group I alkali elements, somewhat simulated by the less reactive Ag, still holds in part. Other additions tried may have permitted the stable incorporation of Se, too, for instance Pb or Bi. However, such glasses crystallize easily. Silver would be expected, as group I elements would, to decrease the liquidus temperature relative to average bond strength which is an important prerequisite for glass formation best presented in the form of the Turnbull–Cohen [29] or Uhlmann [30] criteria. This combination of the acceptability of Se in an Ag-modified Si–As–Te glass and the specific effect of Se concentration

on average bond strength is a primary explanation for the high viscosity obtained in these glasses. It is interesting and encouraging to note that Goriunova et al. [31] find the largest glass forming regions in As–Se–Z glasses for Z = Ti, Ge and Ag, much larger than for Hg, Cu, Pb and Au. Also the compound Ag_3AsS_3 exists (Bragg).

However, the observation of breaks in viscosity-composition relations and the concomitant observations of phase separation make this explanation just a necessary but not a sufficient one. The increasing separation and viscosity of the Se-rich phase in this system supplements the conditions for maximum thermal strength chalcogenide glasses in the system studied.

It will be necessary to devote attention to the composition and evolution of these phases and their T_g 's using, e.g. the techniques of scanning microscopy. Ahead of these required studies, it is interesting to return to Dembovsky's [20] mentioning of other '5 electron' glasses than the DeNeufville [23] SiTe–As family, namely the TlGeX_2 (X = chalcogenide) and AsXI glass phases. But copolymerization details as well as microstructure will have to be considered, when more data are available, for a more fruitful interpretation. Polymer theory as exercised for organic glasses will be found increasingly useful as progress is made in the structural and compositional analysis of complex phase separated materials (Das et al. [32], Chen et al. [33]).

6. Conclusions

(1) Chalcogenide glasses with significantly higher softening ranges than those known to date exist and can be exemplified by glasses in the system Si–As–Ag–Te–Se based on the simultaneous partial substitution of Ag for As, and Se for Te.

(2) Among the glasses with highest softening ranges, the relative gain is 120°C for a $\text{Si}_{35}\text{As}_{15}\text{Ag}_{10}\text{Te}_{20}\text{Se}_{20}$ glass if compared to $\text{Si}_{35}\text{As}_{25}\text{Te}_{40}$ (442°C). The gain increases with selenium content, and at a characteristic discontinuity of effect with reaction temperature.

(3) Selenium retention in Si–As–Ag–Te–Se glasses is conditioned by silver doping.

(4) Phase separation tends to increase with increasing selenium content in these Si–As–Ag–Te–Se glasses, until it seems to impair transmittance. Two T_g 's (as estimated from selected expansivity data) become apparent because of this separation.

(5) The reported experiments demonstrate that the limitations imposed on the simple design of compositions from basic atomic arrangements can be overcome by formulation of complex components capable of inducing copolymerisation and microstructure.

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