

Chemical ordering and topological effects in chalcogenide glass systems

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The property-composition data of several chalcogenide glass systems have been summarised. Models such as the chemically ordered network model and the topological models which have been adopted to understand the atomic arrangement in network glasses are briefly reviewed. The merits and the drawbacks of these models have been pointed out. The importance of considering the effects of both the chemical ordering and of network topology in accounting for the features observed in the property-composition data of network glasses has been indicated.

1 Introduction

Properties such as infrared transmission, switching, semiconduction and photoconductivity exhibited by chalcogenide glasses have rendered them technologically important. Some of their applications are as threshold and memory switches, as photoresists, as acoustooptic modulators, as infrared transmitting and detecting elements through various optical components and optical waveguides, particularly for the middle infrared region. Characterization of these glasses based on various physical, thermal, electronic, optical and mechanical properties is important not only for assessing these materials for various applications, but also from a fundamental point of view to understand the glassy state of matter.

In most chalcogenide glass systems, the various properties of a system are composition dependent; further, in the variation of the property with composition, features (of an extremum or change in slope or kink) are exhibited at specific compositions in the various systems. Correlation of the features observed at specific compositions with the atomic arrangement in these materials gives insight into the nature of the amorphous state in general and of the glassy state in particular. For example, studies on the composition dependence of molar volume (V), elastic properties and the glass transition temperature (T_g) are helpful in understanding the packing of atoms, the nature of bonding and their structural arrangement. In this article, the development of the various models which are adopted to understand the features observed in the property-composition dependence of chalcogenide glasses are briefly reviewed. An elaborate discussion of these models is beyond the

scope of this article and specific papers have been cited for further details.

2 Chemically Ordered Network Model

Of the two models, namely, the random covalent network model (RCNM) and the chemically ordered network model (CONM) consistent with the bonding schemes (namely, the 8- N rule) in chalcogenide network glasses^{1,2}, the CONM has been adopted to understand the features observed in the property-composition dependence of a very wide range of chalcogenide glasses³⁻²⁰.

The CONM is also referred to as the chain crossing model or as the chemically ordered covalent network model (COCN)^{4-6,15}. In the CONM, the formation of heteropolar bonds is favoured over the formation of homopolar bonds; for a glass system A_xB_{1-x} , this model envisages formation of $A-B$ type bonds only for the tie line or the stoichiometric compositions of the system which correspond to the formation of stable chemical compounds. These tie line compositions are also referred to as the chemical thresholds^{21,22} of the system as they represent compositions corresponding to the chemical compounds. With the tie line composition of the system as reference, for the A -rich compositions of the system, the CONM envisages formation of $A-B$ type and then $A-A$ type bonds; for the B -rich compositions, $A-B$ type and then $B-B$ type bonds are formed.

Due to chemical ordering, features such as an extremum or change in slope or a kink in the property-composition data are seen at the chemical threshold compositions of the system. Fig. 1 shows the variation of V , T_g and the electrical conductivity with composition for families of glasses of the Ge-Sb-Se

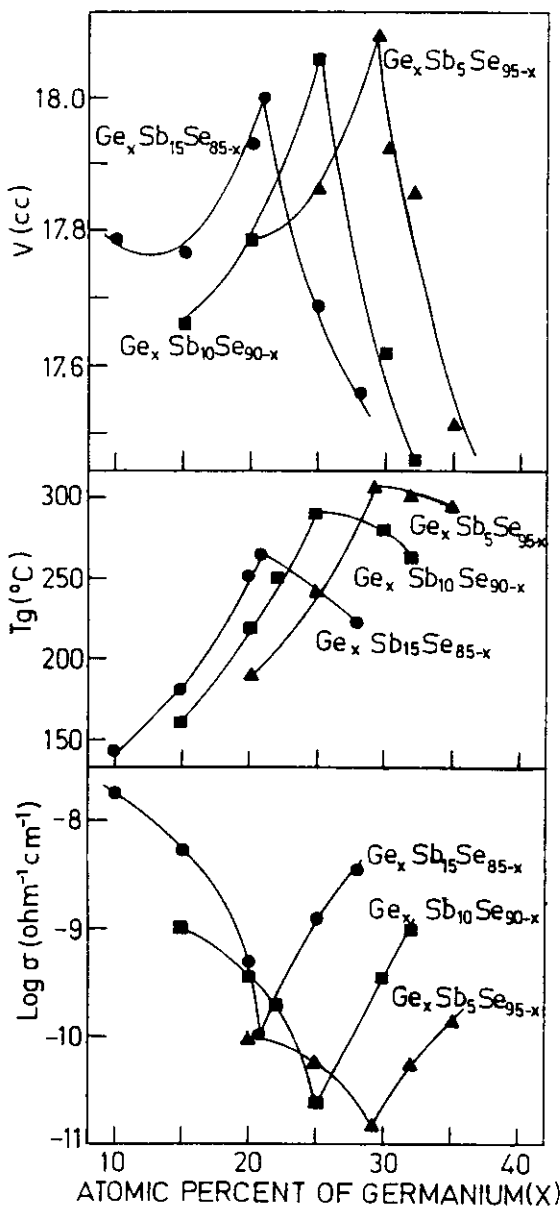


Fig. 1—Plot of V , T_g and $\log \sigma$ (electrical conductivity) versus atomic per cent of Ge for the $\text{Ge}_x\text{Sb}_5\text{Se}_{95-x}$ (▲ data points); the $\text{Ge}_x\text{Sb}_{10}\text{Se}_{90-x}$ (■ data points); and the $\text{Ge}_x\text{Sb}_{15}\text{Se}_{85-x}$ (● data points) glasses of the Ge-Sb-Se system^{10,11}

system. The features of an extrema seen at specific compositions of the various families of this system have been explained⁹⁻¹¹ using the CONM. According to this model, the glass structure can be pictured to be composed of cross linked structural units of GeSe_2 and Sb_2Se_3 with excess of Ge or Se dispersed among these units. The extrema in properties seen at the chemical threshold compositions is because these compositions are composed of cross linked units of GeSe_2 and Sb_2Se_3 only with neither Se or Ge in excess. Though Fig.1 illustrates the data for the Ge-Sb-Se system, similar

special features are seen in the physical, thermoelectronic, mechanical and optical properties several other binary and multicomponent chalcogenide glasses also; these features have been explained using the CONM³⁻²⁰.

3 Shortcomings of CONM

Though the CONM was successfully adopted to understand the features observed in the property-composition dependence of several systems, it was soon realised that aspects such as the ease of glass formation of specific compositions and the stability of certain compositions of various systems were not addressed to in this model.

With the advent of efficient preparative techniques, the glass formation region of several systems could be extended. Data on a wider range of compositions in several systems indicated additional features occurring at compositions other than those at the chemical threshold compositions of these systems^{7,23,24}. Fig.2 shows the variation of V and T_g with composition for the Ge-Se and As-Se systems. For the Ge-Se system, in addition to the maxima in V and T_g seen at the composition $\text{Ge}_{33.33}\text{Se}_{66.67}$ (i.e. the GeSe_2 chemical threshold composition), features of a minimum in V for the composition $\sim \text{Ge}_{22}\text{Se}_{78}$ and a change in slope in the T_g -composition data at the composition $\sim \text{Ge}_{17}\text{Se}_{83}$ are also seen. For the As-Se system similarly, in addition to the extrema in V and T_g seen at the composition $\text{As}_{40}\text{Se}_{60}$ (i.e. the As_2Se_3 chemical threshold composition), features of a local maximum in V for the composition $\sim \text{As}_{64}\text{Se}_{36}$ and a local peak in T_g at the composition $\sim \text{As}_{62}\text{Se}_{38}$ are also seen.

Various techniques such as X-ray and neutron diffraction, Mössbauer and nuclear magnetic resonance techniques, Raman and infrared spectroscopic techniques have all contributed to an understanding of the structure of network glasses; the results of all these studies have been summarised in a recent review²⁵. Based on these studies, it is possible to assign²⁵ three ranges of ordering for the network glasses. Ranges I and II which correspond to the formation of basic structural units and their interconnection represents the short range ordering (SRO) that is present in these materials; this extends to about 5Å in extent. Range III which represents network topology describes the medium range ordering (MRO) that exists in these materials; this extends from about 5Å to about 20Å . There is no ordering beyond 20Å . As the glasses lack long range ordering it was reasonable to expect that gross topological properties of the resulting network should determine the overall property of the glass.

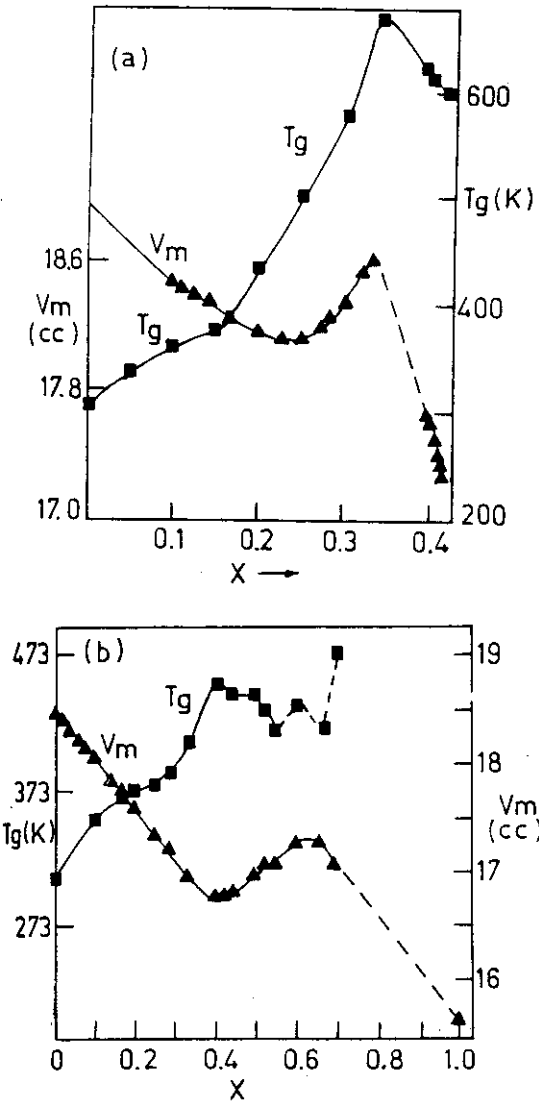


Fig. 2—Data of T_g (■ data points) and V_m (▲ data points) versus composition for (a) Ge_xSe_{1-x} and (b) As_xSe_{1-x} glasses⁷

rather than the local chemical ordering of the structural units. This idea led to the development of the topological models of glass structure.

Topological Models

In these models, one of which was developed by Phillips⁶⁻²⁹, the dynamics of the network topology has been given importance. The cross linking in covalently bonded solids is described in terms of the average coordination number, Z (symbols such as $\langle r \rangle$ or $\langle m \rangle$ are also used to denote the average coordination number, Z). The importance in chalcogenide alloys of the short range bonding interactions described by valence force fields (VFF) whose coordinates are the bond vectors connecting

the nearest neighbours was recognised by Phillips. Such interactions are of two types; one being a two body interaction associated with bond stretching and the other, a three body interaction associated with bond bending. In this VFF model, for a binary alloy A_xB_{1-x} , there exist one bond stretching $A-B$ interaction and two bond bending $A-B-A$ and $B-A-B$ type interactions. The constraints are calculated in terms of Z ; for a binary A_xB_{1-x} system, Z is given as equal to $xN_A + (1-x)N_B$ where N_A and N_B are the coordination numbers of atoms A and B . For a multicomponent chalcogenide system, Z is simply defined as the atom averaged covalent coordination of the constituents^{15,30}. In general, Z is not an integer. It can be regarded as the coordination of a hypothetical pseudoatom forming a structure whose topology is identical to that of the real system³.

Considering the short range ordering occurring in glasses and equating the number of operative constraints to the number of degrees of freedom of the network, a threshold value of $Z \sim 2.40$ has been arrived at for the percolation of glass properties²⁶⁻²⁹. At this threshold value of $Z \sim 2.40$, the glass network moves over from an elastically floppy to a rigid type²⁶⁻²⁹. The ease of glass formation and the stability of the resulting network are also associated with this value of $Z \sim 2.40$. Special features observed in the property- Z data in a large number of systems around this threshold value of Z have been attributed to this topological transition which has been probed by studying both macroscopic and microscopic properties^{7,31-48}.

The macroscopic measurements include a wide gamut of properties such as the mean atomic volume, elastics properties, refractive index, polarisability, optical gap, thermal diffusivity etc.^{7,32-35,41-44}. Studies have also been extended to include properties such as the transition pressure for the semiconductor to metal transition, the activation energy for pressure dependent conductivity and also the crystallisation behaviour of several $A^{IV}B^{VI}$ ($A = Ge, Si; B = Se, Te$) glasses⁴⁵⁻⁴⁸. The microscopic properties cover infrared, Raman and Mössbauer spectroscopic measurements. Reference 47 includes a comprehensive listing of all these studies along with the chief observations. Such studies have supported the presence of a mechanical threshold (also known as the percolation threshold) at $Z \sim 2.40$. The threshold value of Z in many instances does not occur at the theoretical value of 2.40, but occurs^{7,26,36,49,50} at Z values ranging between 2.40 ± 0.06 . This has been attributed⁵¹⁻⁵³ to the formation of over constrained clusters embedded in an under constrained matrix.

Fig.3 shows the schematic of the dependence of V on Z of several chalcogenide glass systems which has been proposed³⁰ based on the data of a few systems, namely, As-Se, Ge-Se and Ge-As-S. In the overall decrease of V with increasing Z , features of a minimum in V at $Z \sim 2.40$ and a local maximum in V and $Z \sim 2.67$ are seen. The minimum in V seen at $Z \sim 2.40$ is traceable to the topological threshold at this value of Z , wherein the most stable glass of the system can be expected to have a minimum in volume³⁰. Accounting for the feature of a local maximum in V at $Z \sim 2.67$ observed in many chalcogenide glass systems necessitated consideration of the MRO existing in these glasses. This led to the identification of yet another topological threshold. This threshold was invoked³⁰ originally for understanding the experimental features associated with the first sharp diffraction peak in diffraction experiments.

The existence of the first sharp diffraction peak (FSDP) in many chalcogenide glasses and the variation of the FSDP intensity are now explicable in the framework of a two dimensional layered structure for these network glasses for Z values upto ~ 2.67 (Ref.30). In this model, the FSDP is interpreted as the peak diffracted from stacks of layers held together by intermolecular bonds consisting of van der Waals forces. The increase in V for Z between ~ 2.40 to ~ 2.67 is traced to the increase in interlayer separation brought about by compositional changes.

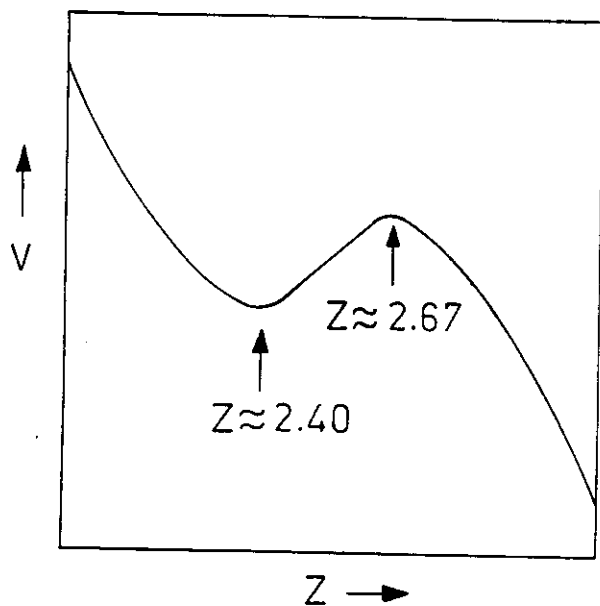


Fig. 3—Schematic showing the dependence of V on Z of chalcogenide glasses

Considering the MRO and a two dimensional structure and equating the number of operational constraints to the degrees of freedom, gives a value $Z = 2.67$ for the other topological threshold³⁰. For Z greater than ~ 2.67 , the layer structure undergoes a transition to a three dimensional network progressively increasing cross linking with increasing Z . The local maximum seen in V at $Z \sim 2.67$ in several systems is thus attributed³⁰ to a structural transition occurring in network glasses where a transition to a three dimensional cross linked arrangement from an essentially layered arrangement occurs for compositions with Z greater than ~ 2.67 .

The occurrence or otherwise of features at both the topological thresholds depends on the property that is being investigated. The mean atomic volume V is sensitive to both the SRO and MRO that occurs in these materials³⁰. Therefore, features of a minimum in V at $Z \sim 2.40$, a local maximum in V at $Z \sim 2.67$ with V increasing as Z changes from ~ 2.40 to ~ 2.67 is exhibited in the V - Z plot of many chalcogenide glass systems. The compositions which exhibit features in the V and T_g (Fig.2) data of the Ge-Se and the As-Se systems have Z values of ~ 2.40 and ~ 2.67 , close to the two topological thresholds. The electrical conductivity, the activation energy for electrical conductivity and the semiconductor to metal transition pressure observed⁵⁴ in $\text{Ge}_x\text{Se}_{100-x}$ glasses exhibit features at compositions corresponding to both the topological thresholds of $Z \sim 2.40$ and ~ 2.67 .

In systems containing elements from group V and VI (those containing P, As, Sb, S, Se, Te) the chemical threshold corresponding to the formation of A_2B_2 type structural units occurs at $Z = 2.40$, coinciding with one of the topological thresholds. In systems containing elements from group IV and VI (those containing Ge, Si, S, Se, Te) the chemical threshold corresponding to the formation of AB_2 type structural units occurs at $Z = 2.67$, coinciding with the other topological threshold. The CONM can account for only one of the features observed in V-VI and IV-VI systems. The topological models on the other hand can account for features at both the Z values. It was therefore, thought³⁰ that the topological models are of a more general nature and therefore these models began to get wider acceptance in understanding the features observed in the property-composition dependence of chalcogenide network glasses.

5 Inadequacies of Topological Models

Though the topological models found wide acceptance, some aspects still remained unanswered

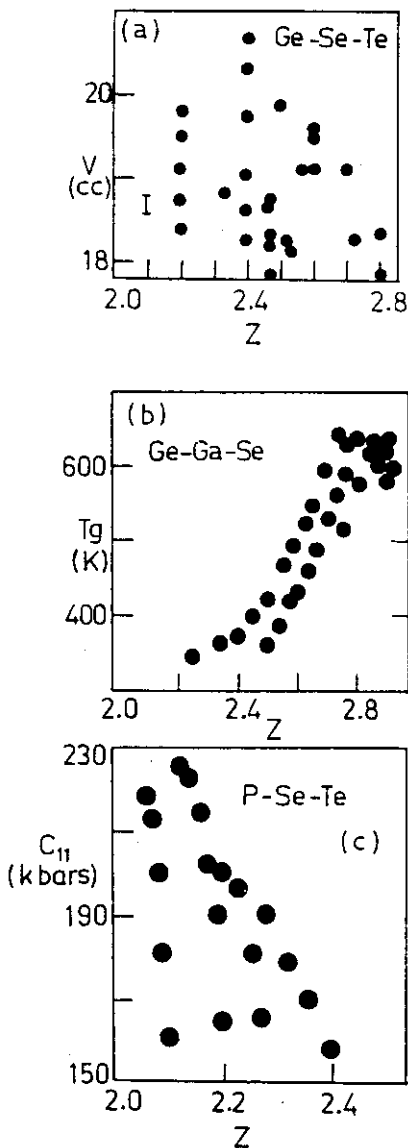


Fig. 4—Data of (a) V versus Z for the Ge-Se-Te (Ref. 68, 69) (b) T_g versus Z for the Ge-Ga-Se⁶⁶ and (c) elastic moduli C_{11} versus Z for the P-Se-Te glasses²²

The formation of structural units (generally of those of the stable chemical compounds of the respective system) during melt quenching of chalcogenide glasses has been established from various spectroscopic techniques and other measurements^{3-20, 55-65}. In the topological models, the role of an atom in contributing to Z only is considered, but the stereochemical aspect of the structural unit formed by these atoms has been ignored.

The other problem of the topological models is their inability to account for the multiple values observed in the property- Z data at several Z values in many chalcogenide glasses. In the variation of V ,

T_g , elastic moduli and several other properties of many chalcogenide glass systems, multiple values of these properties occur at several Z values^{22, 66, 67}. The V - Z , T_g - Z and elastic moduli C_{11} - Z data of glasses of Ge-Se-Te, Ge-Ga-Se and P-Se-Te systems are depicted in Fig. 4 wherein it is seen that the occurrence of multiple values at several Z values render it difficult to discern any specific dependence of the property on Z .

The occurrence of multiple values, as already discussed^{66, 70} is due to the effect of chemical ordering which is also present in these glasses. In binary systems consisting of elements from different groups, each composition has a unique value of Z ; therefore, multiple values of any measured property at several Z values does not occur in these systems. In ternary and higher multicomponent systems however, it is possible for a large number of different compositions to have the same specified value of Z , i.e. while a specified composition has a unique value of Z , a specified Z value can be obtained by a large number of compositions over the glass forming region. Different compositions of the system can be expected to have different V (or any other property) because of differences in their structural arrangement, even though they may have the same value of Z . Different fractions of the various types of structural units present in these various compositions (which may have the same value of Z) thus renders the property (such as V , T_g , elastic moduli etc.) being different for each composition thereby giving a spread in the value of the property at various Z values. The importance of considering at a time the data points of specific families of a system, rather than considering the data points of the system in totality or at random has also been pointed out in these papers⁶⁶⁻⁷⁰.

6 Coexistence of Chemical Ordering and Topological Effects in Network Glasses

Individually, the topological models or the CONM are not able to account for all the features exhibited by a wide range of chalcogenide glass systems. It is, therefore, reasonable to expect that these effects coexist in network glasses with their distinct influences on the property under consideration. In systems containing elements from group IV, V and VI (i.e. systems with P, As, Sb, Ge, Si, S, Se, Te) it is not possible to discern the features due to these effects individually because the chemical thresholds in these systems coincide with one or the other of the topological thresholds. In IV-III-VI systems however, the chemical thresholds of some families occur at Z values other than the topological threshold values. This is because, while the topological

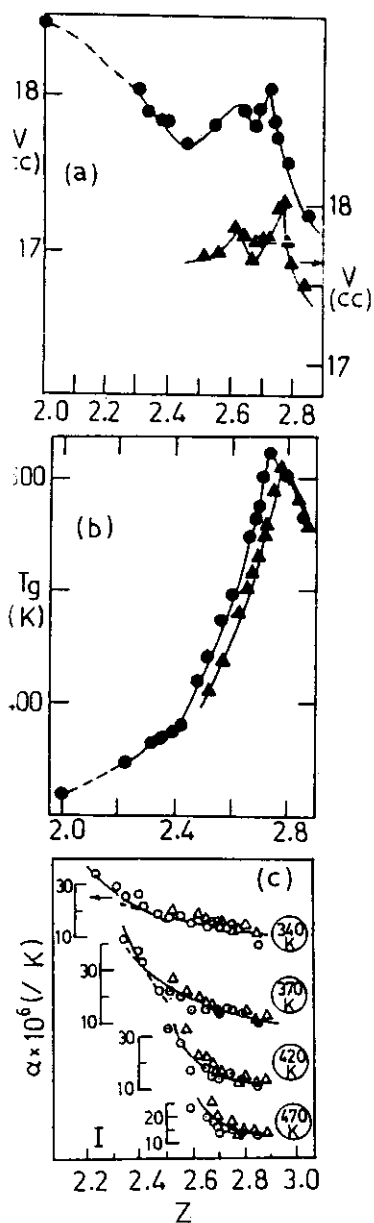


Fig. 5—Data of (a) V - Z (Ref.50) (b) T_g - Z (Ref.71) and (c) α - Z (Ref.73) for the $\text{Ge}_x\text{In}_5\text{Se}_{9.5-x}$ (● data points) and the $\text{Ge}_x\text{In}_8\text{Se}_{9.2-x}$ (○ data points) glasses of the Ge-In-Se system

thresholds occur at $Z \sim 2.40$ and at $Z \sim 2.67$ for all the systems, the Z values at which chemical thresholds exist vary from one type of system to another and also from one family to another within a specified system. Investigations on IV-III-VI systems such as Ge-In-Se, Ge-Ga-Se, As-Al-Te indicated^{50,66,71-73} occurrence or features at the chemical thresholds of these systems in addition to those at the topological thresholds.

The V , T_g and the thermal expansion coefficient (α) data of the Ge-In-Se system are depicted in Fig.5. It is seen (Fig.5) that V exhibits features at both the

topological thresholds and also at the chemical thresholds of the respective families; the results are similar for the Ge-Ga-Se glasses⁶⁶. The V - Z data of individual families of the Ge-Sb-Se and Ge-Ga-Se glass systems have features which can be rationalized^{66,67} taking the influence of both topological and chemical ordering effects into account. Being a fundamental structure sensitive property, data of V has been studied extensively for a large number of systems such as Ge-Se^{7,33,74,75}, As-Se^{7,33,75}, As-S^{76,77}, Ge-As-Se^{78,79}, Ge-As-S⁸⁰, Ge-Sb-Se^{11,15,19,20,81,82}, Ge-Sb-S⁸³ and several other multicomponent glasses. All the data display a minimum in V at $Z \sim 2.40$. In addition, local maxima occur at the tie line compositions of the various systems^{50,66,67,79} due to which the other maxima at $Z \sim 2.67$ may not always be distinctly seen.

In the T_g - Z data of the Ge-In-Se glasses (Fig.5) a change in slope is seen at the topological threshold of $Z \sim 2.40$ and peaks in T_g are seen at Z values corresponding to the respective chemical thresholds of the two families, but no feature is clear at the other topological threshold of $Z \sim 2.67$; the T_g - Z data of Ge-Sb-Se, Ge-As-Se, Ge-Ga-Se systems also show^{66,67} a similar behaviour.

In the α data of Ge-In-Se glasses, features are seen (Fig.5) at the two topological thresholds of $Z \sim 2.40$ and $Z \sim 2.67$, but not at the chemical thresholds of the two families. In the α data of Ge-Sb-Se and Ge-As-Se glasses^{78,84} a change in slope is seen in the α -composition data at the respective chemical threshold compositions of the various families of these systems.

In the elastic moduli data over a limited range of Z from 2.25 to 2.50 for the As-Sb-Se glasses⁸⁵ features are seen at $Z = 2.40$; this value of Z coincides with the chemical threshold composition of this system. The peaks in density and sound velocities observed for $\text{As}_x\text{Se}_{1-x}$ glasses at $Z = 2.40$ has been attributed⁸⁶ to chemical ordering than to percolation effects. In the Ge-Sb-Se, Ge-As-S and Ge-Sb-S systems the elastic moduli are found to be sensitive to the medium range ordering in their networks. This results in a steep increase in the moduli for compositions with Z greater than ~ 2.67 ^{83,87,88}. The elastic property data of $\text{Si}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$ glasses also show features at $Z \sim 2.67$ than at the percolation threshold of $Z \sim 2.40$ (Ref.89,90).

It can be concluded, therefore, that the occurrence or otherwise of the features at the two topological thresholds and also at the chemical thresholds of the system depends not only on the system that is being investigated but also on whether the property that is being considered is sensitive to any or all of the short

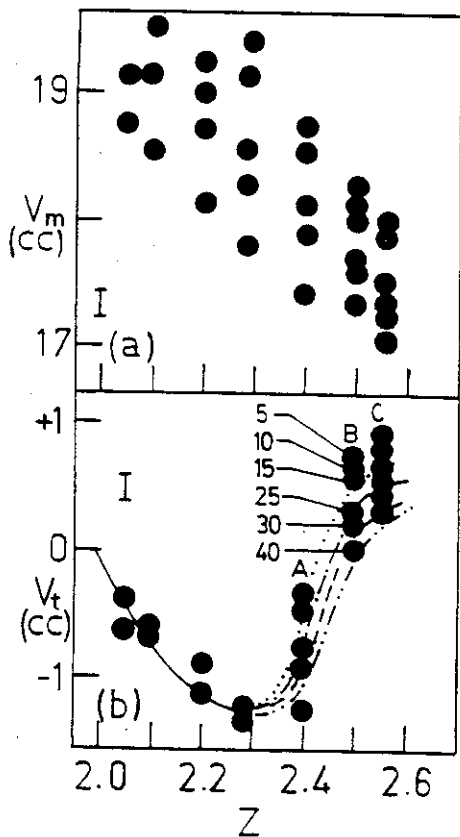


Fig. 6— V_m - Z and V_t - Z plots for the As-Se-Te glasses⁷⁰, symbols 5, 10, --- 40 refer to families with 5, 10, --- 40 atomic per cent of Se [See reference 70 for details]

range ordering, the medium range ordering or the chemical ordering present in these systems. Discussion¹⁵ of the property-composition data of a large number of chalcogenide glasses corroborate this conclusion

7 Topological Effects in Volume of Chalcogenide Glass Systems

In a recent analysis⁷⁰, by considering the measured mean atomic volume V_m as the sum of a component V_{co} which take into account the effects of chemical ordering and a component V_t due to topological effects, the V_t - Z dependence has been inferred for several chalcogenide systems. Taking the formation of structural units due to chemical ordering into account, V_{co} is evaluated as equal to $\sum M_i V_i$, where M_i and V_i are the mole fraction and the volume of individual structural units and elements of which the composition is comprised of; the summation is carried out over the various types of structural units and then excess, if any, of the elements in the various compositions.

The data for the As-Se-Te and the As-Te and P-Se systems have been reproduced in the Figs 6 and 7. The

V_m - Z data of As-Se-Te system exhibits multiple values of V_m at several Z values. In the corresponding V_t - Z data however, the expected topological feature of a minimum in V_t at $Z \sim 2.40$ is clearly seen. In the monotonic dependence of the V_m - Z data of the As-Te and P-Se systems, the effects of topology and of chemical ordering camouflage each other; in the V_t - Z data, the expected topological features are seen. The method has been tested for several systems⁷⁰ with varied V_m - Z behaviour. In these systems also, while the topological features are smudged out in the V_m - Z plots, they are clearer in the respective V_t - Z plots. By a simplistic approach, it is thus possible to bring out the topological features from the measured V_m - Z data. The multiple values seen in other properties such as T_g - Z , elastic moduli- Z data of chalcogenide glass systems are also due to the combined effects of chemical ordering and topology. However, separating their contributions in these properties is more involved, than that compared to V .

8 Electronic Structure and p to n Type Transition in Chalcogenide Glasses

In the discussions so far (sections 1 to 7), though several properties are mentioned, the emphasis has

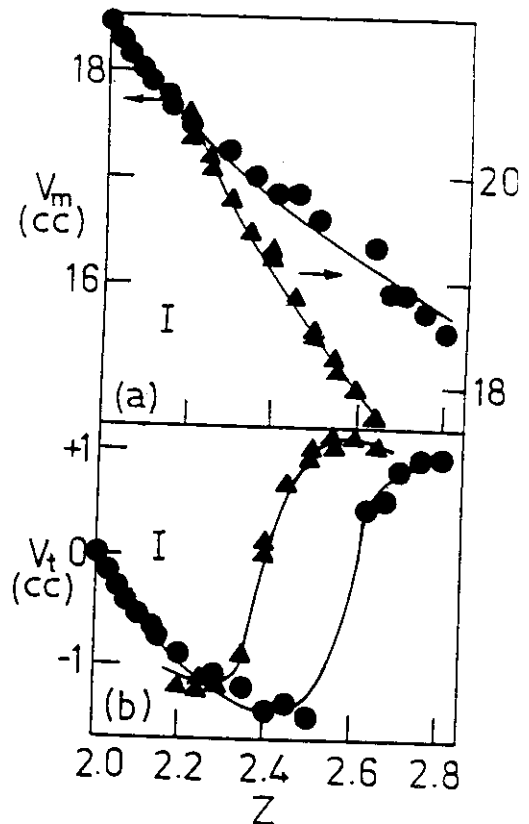


Fig. 7— V_m - Z and V_t - Z data for glasses of the As-Te (data points) and the P-Se (● data points) systems⁷⁰

been mainly on the mean atomic volume, V . This is primarily because data on V for a wide range of compositions in large number of systems are available. Also, being a fundamental structure sensitive property, V lends itself as a probe for checking the validity of various models proposed for the structure of the glassy state.

Though references to the dc electrical conductivity (σ) and the activation energy for electrical conduction (ΔE) have been made, there has been no attempt in this article to discuss the electronic structure of this class of materials. Gross features observed in the electronic properties such as the variations of σ and of ΔE with composition can be rationalised using the topological or the chemically ordered network models.

Other interesting electronic effects observed in chalcogenide glasses are, the role of various metals (Such as Cu, Ag, Tl, In, Ga etc.) as dopants in small amounts, 'Chemical modification' of several chalcogenide glasses by the introduction of larger quantities of certain metals, and the transformation in the type of electronic conductivity from p type to n type, observed on addition of metals such as Bi, Pb etc., in certain chalcogenide glasses. An understanding of these effects involves a knowledge of the electronic structure of these materials in terms of the charged defect states⁹¹⁻¹⁰¹. Except for a brief mention of the developments in these directions, along with key references for further reading, a discussion of these aspects is beyond the scope of this review article.

In amorphous semiconductors, the localised states in the gap are known to form discrete energy levels^{3,91-97}. Further, these states are either positively charged (denoted as C_3^+) or negatively charged (denoted as C_1^-) or neutral (denoted as C_2^0). The charged defects are formed according to $2C_2^0 \rightleftharpoons C_3^+ + C_1^-$ (in the Mott, Davis, Street (MDS) model) or $2C_3^0 \rightleftharpoons C_3^+ + C_1^-$ (in the Kastner, Adler, Fritzsche (KAF) model), depending on whether the neutral chalcogenide is two fold or three fold coordinated^{93,94}. As in the usual notation, the subscripts denote the coordination and the superscripts, the charge state. These defects C_3^+ and C_1^- can either be isolated or bound and are formed during glass formation from the melt. The isolated defects are active in the transport process.

Both the MDS and the KAF models make similar predictions as to the influence of charged impurities or dopants on the densities of the charged defects C_3^+ and C_1^- of the parent glass^{95,96,98,99}. The C_3^+ and C_1^- defects of the parent glass act respectively as electron and hole traps. Presence of a positively charged impurity I^+ during glass

formation from the melt at T_g enhances the C_1^- density, the enhancement being proportional to I^+ . Law of mass action predicts that the defect density C_3^+ decreases in proportion to I^+ (Ref.93,94). Depending on the nature, charge state and concentration of the dopant, corresponding changes in the concentration, location of the gap states and the resulting band gap can be envisaged. In addition to changing the density of existing traps, the dopant atoms may also introduce new trapping levels and/or modify the transport hopping channel^{98,99}. The resulting σ is thus modified according to the changes brought about by the introduced dopants on the trapping sites C_3^+ and C_1^- , and the density and location of hopping sites.

The effects of various metals as 'dopants' discussed above is confined to low concentrations, generally up to ~ 1 atomic percent (at. %), in many chalcogenide systems. At higher concentrations, these metals become regular constituents of the respective systems. In the case of certain additives (particularly the transition metals, indium etc.), which are added in larger amounts, it is possible to achieve what are termed as 'chemically modified' chalcogenide glasses¹⁰²⁻¹⁰⁴. In these materials, the localised gap states that control the conductivity differ from those of both the matrix and the modifier and they exhibit both positive (p -type) and negative (n -type) thermopower.

Chalcogenide glasses generally exhibit p -type conductivity. However, it has been observed¹⁰⁵⁻¹⁰⁹ that several compositions of glasses of the $Ge_{20}Bi_xM_{80-x}$ ($M = S, Se, Te$) system and the $Pb_{20}Ge_{21}Se_{59}$ glass exhibit n -type conductivity; the transformation from p -type to n -type conductivity occurs at Bi contents of 11 at.%, 7 at.% and 3.5 at.% for the S, Se and Te systems respectively. Various mechanisms such as (i) formation of a large number of chemical bonds of a preferred-type (Bi-Se bonds in the specific instance) in lieu of the original (Se-Se) bonds (ii) charge compensation by the introduced impurity (Bi or P in these cases) of the charged defect states (which act as electron or hole traps) resulting in the unpinning of the Fermi level (iii) existence of two micro separated phases in the glass with clusters of one phase embedded in the background matrix (which is pliable for reconstruction of n -type defects below Z value of 2.40) which moves over from an under constrained to an over constrained state at $Z \sim 2.40$, (iv) presence of a 'percolation' threshold at the composition which shows p -type to n -type transition, have all been proposed^{51,105-110} to account for the n -type conductivity observed. While

any of these mechanisms is plausible, further experimental work on a wider range of systems will help in identifying the cause for the appearance of n-type conductivity.

9 Conclusions

Models that have been developed to understand the nature of chalcogenide network glasses have been briefly reviewed. The importance of both the stereochemical properties of the constituents which result in chemical ordering and the gross network topological properties which impart stability to the resulting glass network has been pointed out. Consideration of both these effects is important in understanding the features observed in the property-composition data of network glasses.

The occurrence or otherwise of specific features at the two topological thresholds and at the chemical thresholds depends not only on the system that is being investigated but also on whether the property that is being considered is sensitive to any or all of the short range ordering, the medium range ordering or the chemical ordering present in these glasses.

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