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Chemical order, molecular clusters, and topological transitions in chalcogenide network glasses

R. Aravinda Narayanan*
Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

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A simple variant of the chemically ordered covalent network model, in which the presence of homopolar bonds are also considered, explains a maximum in physical properties in Ge-As-S chalcogenide network glasses observed close to a mean-coordination number of atoms $\langle r\rangle = 2.60$, which was originally thought to be due to a topological transition connected with a change in the dimensionality of the network. The model reproduces the observed trend in the extremum as a function of Ge:As ratio with good accuracy, and in the process helps to identify and explain related instances found in the literature. Also, the physical significance of topological thresholds in the context of glass forming ability of materials is posited.

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This Brief Report focusses on several aspects of some recent[1–3] data on chalcogenide network glasses, which bears on a long-standing issue[4,5] concerning the existence of a topological transition proposed by Tanaka,[6] and chemical threshold based on the chemically ordered covalent network model[7] (COCN), both of which are predicted to occur around $\langle r\rangle = 2.67$.

In chalcogenide glass literature, commonly, three different topological thresholds are discussed, around which many physical properties such as molar volume,[6,8] Mössbauer site intensities,[9] and electrical switching field[10] have been found to vary anomalously. These thresholds are rigidity percolation threshold, Tanaka transition, and chemical threshold. Rigidity percolation threshold: Phillips and Thorpe proposed the constraint counting theory,[11,12] which predicts a floppy to rigid transition at $\langle r\rangle = 2.40$, in a random covalent network, assumed to be the case in chalcogenides. Physically, at $\langle r\rangle = 2.40$, the network is supposed to be optimally coordinated to yield the best glass in the system. Both macroscopic[13] and microscopic[14] evidence is available for the random covalent nature of a chalcogenide network. For example, in Ge-As-Se glasses, the glass transition temperature T_g has a universal dependence on $\langle r\rangle$ in the range $2.0 \leqslant \langle r\rangle \leqslant 2.50$; and beyond that due to chemical effects T_g exhibits a composition-specific behavior. Tanaka transition: Since chalcogens have a propensity to form low-dimensional structures, applying constraint theory to a two-dimensional chalcogenide network embedded in three-dimensions, Tanaka showed[6] the possibility of a topological transition from two-dimensions to three-dimensions around $\langle r\rangle = 2.67$. Chemical threshold: It is the stoichiometric composition in the system, in which only heteropolar bonds are present and therefore, it is the glass with maximum chemical order. In V-VI (e.g., As-Se) and IV-VI (e.g., Ge-Se) systems, chemical threshold occurs at $\langle r\rangle = 2.40$ (As_2Se_3) and 2.67 ($GeSe_2$), respectively.[15] In a IV-V-VI (e.g., Ge-As-Se) glass system, it is supposed[8] that the threshold can occur, anywhere in the tie line joining As_2Se_3 and $GeSe_2$, which is between $\langle r\rangle = 2.40$ and 2.67 depending on the atomic concentration of the elements.

However, in a majority of the glass systems,[8,10,15] thus far, chemical threshold has been found pretty close to $\langle r\rangle = 2.67$, perhaps owing to the way the compositional tie line were chosen, and it has not helped in clarifying the issue[5] of existence of Tanaka transition and chemical threshold. This situation has been rectified, recently, by Aitken and coworkers who have systematically investigated three series of $Ge_xAs_yS_{1-x-y}$ glasses, where x, y, $(1-x-y)$ are the atomic percentages of Ge, As, and S. The difference between the glasses in the three series is in terms of their Ge:As ratio, which are 1:2, 1:1, 2.5:1. The coordination numbers[1] of Ge, As, and S are 4, 3, and 2, respectively, and therefore, the mean coordination of atoms can be calculated using the formula

$$\langle r\rangle = 4x + 3y + 2(1-x-y). \tag{1}$$

In their study, when molar volume, thermal expansion coefficient, and Raman intensities[2] are plotted against $\langle r\rangle$, a broad maximum is seen centered around $\langle r\rangle = 2.60$. More precisely, they find that as Ge:As ratio decreases, the maximum in molar volume (Fig. 1 of Ref. 2), shifts from an $\langle r\rangle$ of 2.64 to 2.60. They suggest[2,3] that this extremum pertains to the Tanaka transition, although it is also recognized that this maximum varies with Ge:As ratio. Furthermore, these compositional dependencies are attributed to the presence of arsenic containing molecular clusters. Interestingly, in this data there is no signature of a rigidity percolation at $\langle r\rangle = 2.40$.

This raises several important questions: (1) If the extremum occurring at $\langle r\rangle = 2.60$, is indeed Tanaka transition, why is it shifted from the theoretically predicted value of $\langle r\rangle = 2.67$?; (2) how does one reconcile with the observed shifting of this extremum to lower $\langle r\rangle$ values as Ge:As ratio decreases?; (3) in general, glasses near the Tanaka transition are not good glass formers, then why do the extremum compositions in the Ge-As-S glasses nearly lie in the middle of their glass forming region in the ternary phase diagram? (Fig. 6 of Ref. 2)

In this article, we concentrate on the variation of molar volume with $\langle r\rangle$ (other properties can be similarly explained), and explicitly show that the extremum occurring around $\langle r\rangle = 2.60$ is due to a ‘‘peculiar’’ chemical threshold, in which chemical order coexists with arsenic homopolar bonds. We present calculations, which considers the presence of arsenic molecular clusters and reproduce the observed trend in the chemical threshold as a function of Ge:As ratio.

Also, we argue that chemical threshold and Tanaka transition have a common origin. Furthermore, we explain how the topological thresholds bear upon the general question of glass forming ability of these materials.

Let us first qualitatively understand the property variation in the Ge-As-S glasses. Towards this we use Boolchand's model[16] to describe glass networks on the basis of specific molecular fragments. Raman spectroscopic measurements suggest the presence of the following molecular units[2,3] in the glass: $\mathrm{Ge(S_{1/2})_4}$, $\mathrm{As(S_{1/2})_3}$, $\mathrm{As_4S_4}$, $\mathrm{As_4S_3}$. Of these $\mathrm{Ge(S_{1/2})_4}$ and $\mathrm{As(S_{1/2})_3}$ units aid in forming an extended network. In the $\mathrm{As(S_{1/2})_3}$ network, rigidity percolation and chemical threshold coincide at $\langle r\rangle = 2.40$; and in $\mathrm{Ge(S_{1/2})_4}$ they occur separately at $\langle r\rangle = 2.40$ and 2.67, respectively.[11] On the other hand, the molecular clusters of $\mathrm{As_4S_4}(\langle r\rangle = 2.50)$ and $\mathrm{As_4S_3}(\langle r\rangle = 2.57)$ affect only the chemical order. It is thus obvious that in the present system, chemical order is possible at $\langle r\rangle = 2.40$, 2.50, 2.57, and 2.67. In general, molar volume displays a minimum near the rigidity percolation and a maximum near the chemical threshold.[8] This means that in Ge-As-S system, molar volume would indeed have a broad maximum in the range $2.40 < \langle r\rangle < 2.67$, but the relative concentrations of the different molecular units would vary depending on the Ge:As ratio, and the peak value of this broad maximum would shift accordingly: The peak would lie closer to $\langle r\rangle = 2.67$ when the atomic concentration of Ge is greater than As, and if it becomes less than that of As it is likely to move towards $\langle r\rangle = 2.40$. Also, it is understandable that the first-order chemical ordering effects at $\langle r\rangle = 2.40$ and 2.50 would overwhelm the second-order rigidity percolation effects at $\langle r\rangle = 2.40$, and consequently, the effect of rigidity on molar volume would not be visible.

Presently, we shall quantitatively comprehend the observed chemical threshold. By definition, chemical threshold is the composition at which all the bonds are heteropolar. This condition would be satisfied when the valence requirements of the chalcogen is completely met by Ge and As atoms. But in the present Ge-As-S glasses there is an additional complication borne out of detailed[1] Ge and As *K*-edge x-ray absorption fine-structure spectroscopy that they have As homopolar bonds at low and intermediate levels of sulphur deficiency, which is supposedly reflected in the formation of molecular clusters[2,3] of $\mathrm{As_4S_3}$ and $\mathrm{As_4S_4}$ which are made of As—As and As—S bonds.[17] While it seems that lack of sulphur alone forces the formation of As—As bonds, a look at the relevant bond energies[18] in the system and a few other experimental results[19] suggests a deeper explanation: The bond energy of Ge—S ($551\ \mathrm{kJ\,mol^{-1}}$) > As—As ($382\ \mathrm{kJ\,mol^{-1}}$) > As—S ($379.5\ \mathrm{kJ\,mol^{-1}}$), which defines the order of the probability of bond formation. From this we can see that As homopolar bonds are at least as probable as the As heteropolar bonds. As a result of which in arsenic containing chalcogenides, even stoichiometric compounds such as $\mathrm{As_2S_3}$ and $\mathrm{As_2Te_3}$ (which have sufficient chalcogen content) have arsenic homopolar bonds.[19] In view of the above facts, we propose the following model: In the Ge-As-S system, as mentioned previously, Raman spectroscopy has revealed[2] the presence of $\mathrm{AsS_{1.5}}$, $\mathrm{AsS_{1.0}}$, $\mathrm{AsS_{0.75}}$ molecular units.[2,3] Now, in the COCN model where one considers average coordination to understand the evolution of physical properties is a mean-field approach. In this tradition, we take the average of the three units, which is $\mathrm{AsS_{1.08}}$. This is close to $\mathrm{As_4S_4}$, in which of the three bonds emanating from each arsenic atom, one is an As—As bond.[17] Using this logic in $\mathrm{Ge}_x\mathrm{As}_y\mathrm{S}_{1-x-y}$ glasses, of the possible $3y$ As bonds, on the average y of them would be homopolar and therefore, only the remaining $2y$ bonds would be available to satisfy the valence requirements[20] of S. Expressed mathematically,

$$2(1-x-y) = 4x + 3y - y; \tag{2}$$

which on rearrangement, gives

$$3x + 2y = 1. \tag{3}$$

Using this we now calculate the chemical threshold in each of the three series of $\mathrm{Ge}_x\mathrm{As}_y\mathrm{S}_{1-x-y}$.

(A) $x:y = 2.5:1$. That is, $x = 2.5y$. Substituting this in Eq. (3), we get $y = 2/19$. Using Eq. (1), we find that this corresponds to $\langle r\rangle = 2.63$.

(B) $x:y = 1:1$. So, $x = y$ and inserting this in Eq. (3), we get $y = 1/5$. This is equivalent to an $\langle r\rangle = 2.60$.

(C) $x:y = 1:2$. That is, $x = 0.5y$. Substituting this again in Eq. (3) gives $y = 2/7$. This pertains to $\langle r\rangle = 2.57$.

Thus, through these calculations we explicitly show that the maximum in the plot of molar volume versus $\langle r\rangle$ is due to chemical ordering that is accompanied by arsenic clustering. This also fairly well reproduces the experimentally observed shift in the extremum to lower $\langle r\rangle$ values as Ge:As ratio decreases. The above bond counting procedure which is a simple extension of the COCN model, to take into account the presence of homopolar bonds, also clarifies a controversy[21] which is several years old, concerning the possibility of a chemical threshold at $\langle r\rangle = 2.50$ in IV-VI alloys: Molar volume measurements on the $\mathrm{As}_x\mathrm{Se}_{1-x}$ glass system, reveal a maximum at $\langle r\rangle = 2.50$, and it had been suggested that this anomaly could be due to As clustering. Following the same arguments that were used for Ge-As-S glasses the condition [Eq. (2)] for chemical threshold can be written as $2(1-x) = 3x - x$. Solving which we get $x = 0.50$, which indeed corresponds to $\langle r\rangle = 2.50$. The above model also helps us to rationalize other similar instances in the literature.[16,22,23]

As mentioned earlier, the proposal[6] for a rigidity transition at $\langle r\rangle = 2.67$, by Tanaka, for a two-dimensional network is based on the constraint counting theory. For pedagogical value we shall now derive it for Ge-As-S glasses. The following is the formula for counting the constraints[24] on the atoms when their coordination number r is greater than $(n_d - 1)$, where n_d is the covalent network dimension, which in the present case is assumed to be 2.

$$n_{co}(r,n_d) = (r/2) + (1/2)(n_d - 1)(2r - n_d), r \geqslant n_d - 1 \tag{4}$$

The two terms on the right-hand side of the above equation correspond to the α and β constraints in the valence force field models.[11] Using Eq. (4), we calculate the constraints on Ge, As, S as 5, 7/2, and 2, respectively. Therefore, the total number of constraints per atom in $\mathrm{Ge}_x\mathrm{As}_y\mathrm{S}_{1-x-y}$ is,

$$n_{co}(\mathrm{Ge}_x\mathrm{As}_y\mathrm{S}_{1-x-y}) = x \times n_{co}(r_{\mathrm{Ge}}) + y \times n_{co}(r_{\mathrm{As}}) + (1-x-y) \times n_{co}(r_{\mathrm{S}}) \qquad (5)$$

So, $n_{co}(\mathrm{Ge}_x\mathrm{As}_y\mathrm{S}_{1-x-y}) = 5x + 7/2y + 2(1-x-y)$. The network is supposedly optimized when the n_{co} equals the embedding dimension, which is 3. This leads to the equation

$$6x + 3y = 2, \qquad (6)$$

from which the Tanaka transition for $x{:}y = 2.5{:}1$, $1{:}1$, and $1{:}2$, can be shown to occur universally, using Eq. (1), at $\langle r \rangle = 2.67$. This result as such proves that the occurrence of the Tanaka transition is independent of the chemical constituents, contrary to suggested explanation for the experimental observation.[2,3] Recently, the present author showed that rigidity percolation threshold can be shifted from the predicted value of $\langle r \rangle = 2.40$, due to noncovalent interactions in the network in some tellurium containing chalcogenide and oxide glasses.[20,25] A similar shift of the Tanaka transition is unlikely in the case of the strongly covalent Ge-As-S glasses.

The reason for a maximum in molar volume when there is maximum chemical order, is the following: Consider the stoichiometric compositions of GeS_2 and $\mathrm{As}_2\mathrm{S}_3$. These are layered compounds, with covalent bonding in the layer and van der Waals bonds between the layers. In glasses of nonstoichiometric compositions, this arrangement is marred by the presence of homopolar bonds, which affects the gap between the layers and consequently the molar volume decreases. Therefore, in IV-VI and IV-V-VI chalcogenide glassy alloys, the transition from a two-dimensional to three- dimensional network around $\langle r \rangle = 2.67$ is likely to be accompanied by chemical ordering; and as to which of the two aspects is discerned depends on the experimental technique: For example, in $\mathrm{Ge}_x\mathrm{Se}_{1-x}$ glasses, the composition dependence of anomalously large low-energy Raman scattering intensities, indicates[26] a percolative transition from two- to three-dimensional fractal morphology near $\langle r \rangle = 2.70$, while density goes through a minimum[15] around $\langle r \rangle = 2.67$.

By definition, in any system, good glass formers are to be found near the rigidity percolation threshold; and poor glass formers near the chemical threshold and hence, Tanaka transition is also found among poor glass formers. In this sense, Tanaka transition is *not exactly* another rigidity percolation threshold. The above definitions hold true in Ge-rich systems[11,23] but fail in As-rich systems,[23,27] as we find in the present Ge-As-S glass system that glasses near the chemical threshold are found in the middle of their glass forming region[2] and we believe that this is mainly due to the unusual chemical order posited in this paper. That is, in As-based systems at the chemical threshold, As homopolar bonds are present which interrupts long-range ordering of atoms. Also, unlike Ge, As has a lone pair of electrons. Lone-pair interaction among the As homopolar bonds and with those from the chalcogen causes the formation of a lone-pair electronic band above the bonding band. This lone-pair band acts as a structural buffer and prevents the excitation of electrons from the bonding band, which otherwise would lead to easy rearrangement of the bonds, and consequently lead to crystallization.[28]

In conclusion, we suggest a modification to the chemically ordered covalent network model to include homopolar bonds and accurately understand chemical ordering in Ge-As-S and other As-rich chalcogenide glass systems. Sometime ago, Thorpe suggested[12] that presence of rings in the atomic network could shift the percolation threshold. Perhaps, arsenic molecular clusters play a similar role and the extremum composition around $\langle r \rangle = 2.60$ can also be understood in terms of constraint theory.

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*Electronic address: araghava@anl.gov

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In this classic work on Ge-As-Se glasses where two series of glasses of high and low arsenic concentration are considered, a similar shifting of chemical threshold, from $\approx\langle r\rangle = 2.70$ to ≈ 2.50, can be discerned, as the arsenic content is increased. However, glasses were not chosen from a specific composition tie-line of fixed Ge: As ratio. Please see Fig. 1(b) of Ref. 16 as well.

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