

ON THE STRUCTURE OF $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ GLASSES

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The local structural order of glasses in the ternary system, $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$, is not well established. Using the covalent nature of the bonding, we present a model of the local structural order in these glasses. We discuss changes in the local structural order imposed by chemical preferences for specific bonds. We describe the potential importance of nano-scale phase separation and its effect on the local structural order. Finally, we discuss the effect of specific features in the local structural order on the performance of phase-change memory devices.

1. Introduction

The structures of ternary chalcogenide glasses can often be understood using the covalent nature of the bonding and the preference for certain chemical bonds. Often these two criteria conflict with one another. For example, in the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ system the covalent nature of the bonding suggests that Ge, As, and Se are bonded to four, three, and two nearest neighbors, respectively. This situation, which is sometimes referred to as the “8-N rule” [1], results because these coordination numbers provide a closed shell of eight electrons around each element by sharing electrons with nearest neighbors in covalent bonds. Also in this system, there exists a slight preference for Ge-Se and As-Se bonds over the other possibilities, Ge-As, Ge-Ge, As-As and Se-Se. Clearly this latter chemical constraint is not compatible with the 8-N rule for arbitrary compositions. In fact, the two constraints are mutually accommodated only along the pseudo-binary composition line, $\text{GeSe}_2\text{-As}_2\text{Se}_3$. For all other compositions, one of the two constraints must be violated. In the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ system, the bonding preferences are weak, and therefore the 8-N rule is the dominant factor in determining the local structural order [2]. This fact implies that the coordination numbers for Ge, As, and Se remain 4, 3, and 2, respectively, for all compositions in the glass-forming region. Off the pseudo-binary line, $\text{GeSe}_2\text{-As}_2\text{Se}_3$, these coordination numbers are maintained by forming other types of bonds, such as As-As, Se-Se, or Ge-Ge, depending on the composition.

As one goes down the periodic table in a given row, the size of the element increases and the propensity to form more metallic-like bonds also increases [3]. This fact leads to the propensity for heavier elements to have more nearest neighbors than would be expected from the covalent picture described by the 8-N rule. If the covalent nature of the bonding still plays a major role, such that one can still formally share 8 s- and p-electrons around each element even though metallic or ionic effects may influence the bonding, then one can modify the 8-N rule. Such a modification was developed independently by Liang et al. and Laderman et al. [4] and by Liu and Taylor [5,6] to explain the observed local structural order in $\text{Cu}_x\text{As}_y\text{S}_{1-x-y}$ and $\text{Cu}_x\text{As}_y\text{Se}_{1-x-y}$ glasses. In these systems the Cu is always tetrahedrally coordinated [4], and therefore the number of nearest neighbors is constrained by covalent effects even though the bonds are certainly not covalent. If one considers only s- and p-electrons, Cu behaves as a Group I element. The way that each element in these ternary systems formally obtains a closed shell of electrons by “sharing” with nearest neighbors in bonds is to increase the coordination number of the chalcogen element, thereby formally donating electrons to the Cu atoms. Effectively, the lone-pair p-electrons on the S or Se are

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converted to bonds with Cu where both electrons come from the chalcogen. This generalized 8-N rule, which is sometimes called the Formal Valence Shell Model [6], explains the structures of both crystals and glasses in these two ternary systems.

As one adds Cu to the As-Se glasses, the average coordination number of the Se increases from two to three, and for large enough Cu concentrations finally to four. As in the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ system, chemistry also plays a role, with Cu-Se and As-Se bonds preferred. There exists one pseudo-binary line along which these two constraints can hold simultaneously, namely the line $\text{Cu}_2\text{Se}-\text{As}_2\text{Se}_3$. Off this line, other types of bonds, such as As-As or Se-Se, are formed depending on the composition.

The local structural order in the $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ system is not well known, and since the elements Sb and Te are larger than As and Se, one does not know a priori which of the above described scenarios will prevail. If the ordinary 8-N rule dominates then one predicts that the Ge, Sb, and Te elements remain four-, three-, and two-fold coordinated for all glassy compositions. On the other hand, in many of the crystals in this system the Te exhibits a coordination number that is greater than two. Therefore, absent experimental evidence to the contrary, one cannot exclude the possibility that as Ge is added to the Sb-Te glasses, the average coordination number of the Te increases to provide for the chemical preference for only Ge-Te and Sb-Te bonds.

2. Structure of $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ glasses

If only s- and p-electrons are considered in the bonding, then one may calculate the average local coordination number for any given ternary glass composition if the coordination numbers of two of the three elemental constituents are known [6]. As described above, this possibility arises because the number of bonds for a given atom, n_b , is related to the number of s and p valence electrons (column number in the periodic table), N , by the equation, $n_b = 8 - N$.

In the case of the glassy system, $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$, the Ge and Sb atoms are probably 4- and 3-fold coordinated, respectively. Recent x-ray absorption fine structure (EXAFS) experiments [7,8] tend to confirm these suggestions. If the coordination number for Te is always two (the 8-N rule holds for all three elements individually), then one may calculate the average coordination number for all glasses in the system in exact analogy with the Ge-As-Se ternary system [2,6]. For simplicity we consider the normalized composition, $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$, where x and y are between zero and one.

In this case the average coordination number of all three elements, n_{av} , is

$$n_{av} = 4x + 3y + 2(1 - x - y) = 2x + y + 2. \quad (1)$$

Fig. 1 shows the ternary diagram for the Ge-Sb-Te system with three “pseudo-binary” composition lines indicated. The solid line, $\text{GeTe}-\text{Sb}_2\text{Te}_3$, contains the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ composition ($2\text{GeTe}-\text{Sb}_2\text{Te}_3$). This composition is very important because it is used in commercial rewritable digital versatile disks (DVD's) [9]. Along the dotted line, $\text{GeTe}_2-\text{Sb}_2\text{Te}_3$, if the Te is always 2-fold coordinated, then there are only Ge-Te and Sb-Te bonds. It follows from eq. (1) that if Te is two fold coordinated, then there must be some additional bonds (Ge-Ge, Sb-Sb, or perhaps Ge-Sb) along the line $\text{GeTe}-\text{Sb}_2\text{Te}_3$, which contains insufficient Te to satisfy the constraint of only Ge-Te and Sb-Te bonds. The vertical dashed line in Fig. 1 represents the compositions for which the average coordination number is the same as it is for $\text{Ge}_2\text{Sb}_2\text{Te}_5$. This line is important because in some glassy systems many properties depend only on the average coordination number and not on the exact composition [10]. This trend, which holds best when there is no strong preference for specific chemical bonds, is sometimes called the iso-coordination rule [2,10]. The region near $x = 0.2$ along the $\text{Ge}_x\text{Te}_{1-x}$ binary outlined by the solid line is the glass-forming region for materials quenched from the melt. The materials used in phase-change memory applications all fall well outside this glass-forming region.

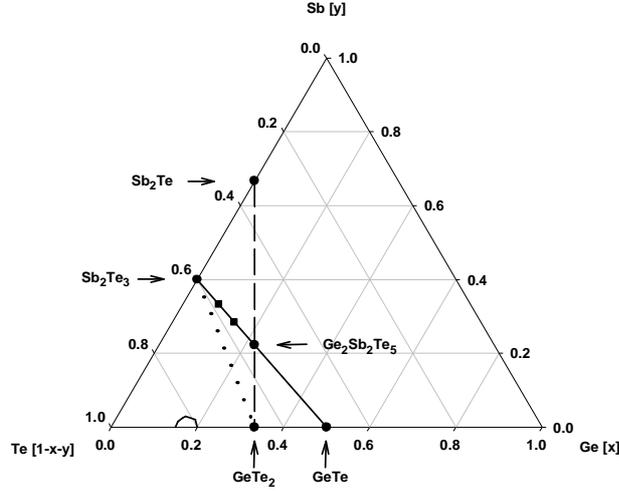


Fig. 1. Ternary diagram of the $Ge_xSb_yTe_{1-x-y}$ system. The dotted, dashed, and solid lines represent the pseudo-binary tie lines, $GeTe_2-Sb_2Te_3$, $GeTe_2-Sb_2Te$, and $GeTe-Sb_2Te_3$, respectively. The technologically important phase-change memory composition, $Ge_2Sb_2Te_5$ is also labeled. The two solid squares represent two additional phase - change memory compositions, $Ge_1Sb_4Te_7$ and $Ge_1Sb_2Te_4$. See text for details.

A second possibility for the local structural order in the $Ge_xSb_yTe_{1-x-y}$ glasses is that the coordination number of Te increases with increasing Ge and Sb concentration to insure that only Ge-Te and Sb-Te bonds occur at all possible compositions. In this case, which corresponds to a strong chemical preference for specific bonds, one may calculate the average coordination number for all glasses in the system in exact analogy with the Cu-As-Se and Cu-As-S ternary systems where the Cu is always tetrahedrally coordinated. The average coordination number is the same as that given in eq. (1) for $6x + 5y < 2$ (to the left of the dotted line in Fig. 1 or Fig. 2, which is the pseudo-binary line $GeSe_2-Sb_2Te_3$). To the right of this line the average coordination number for Te increases from two to three and the average coordination number for the glass is given by

$$n_{av} = 8x + 6y, \quad (2)$$

where the average coordination number for Te is

$$n_{av}^{Te} = \frac{4x + 3y}{1 - x - y}. \quad (3)$$

Along the line $7x + 6y = 3$, which is indicated by the long-dashed line in Fig. 2, $n_{av}^{Te} = 3$. To the right of this line the coordination of one of the elements, presumably Te, must increase further for the above model to apply. The short-dashed line in Fig. 2 represents the pseudo-binary compositions that are least likely to phase separate. The propensity for nano-scale phase separation to occur in this system will be discussed in the next section.

Given the above discussion, there are two possibilities for bonding in the commercially important alloy, $Ge_2Sb_2Te_5$. First, if eq. (1) holds, then the Te is 2-fold coordinated and either 1/3 of the Ge bonds are Ge-Ge bonds, or 1/2 of the Sb-bonds are Sb-Sb bonds, or some mixture of these two possibilities, and $n_{av} = 2.67$. (From EXAFS measurements, there is experimental evidence for the presence of Ge-Ge bonds and against the presence of Ge-Sb bonds [8].) Second, if n_{av}^{Te} increases to keep the constraint of only Ge-Te and Sb-Te bonds, then $n_{av}^{Te} = 2.8$ and $n_{av} \cong 3.1$.

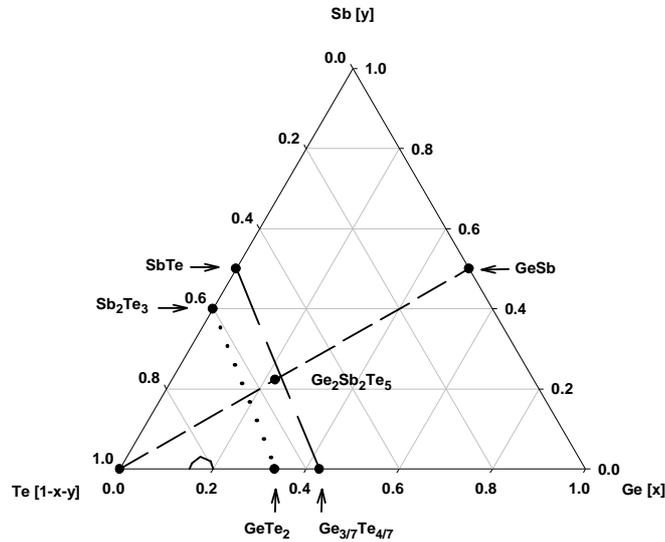


Fig. 2. Ternary diagram of the $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ system. The dotted, long-dashed, and short-dashed lines represent the pseudo-binary tie lines, $\text{GeTe}_2\text{-Sb}_2\text{Te}_3$, $\text{Ge}_3\text{Te}_4\text{-SbTe}$, and GeSb-Te , respectively. The technologically important phase-change memory composition, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is also labeled. See text for details.

Experimental evidence is currently insufficient to decide between these two possibilities. If the Te remains 2-fold coordinated, then the local structural order is determined by the covalent nature of the bonding with the chemical preference for specific bonds playing only a minor role. If the Te is essentially 3-fold coordinated, then the local structural order is determined by the chemical preference for Ge-Te and Sb-Te bonds. Finally, it is entirely possible that both effects are important and the coordination of the Te is between two and three.

Some facts are, however, clear. In the two crystalline phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, the Ge, Sb, and Te are essentially octahedrally coordinated [11,12,13,14]. The coordination numbers for all three elements in the glass are considerably smaller. The Ge is four-fold (tetrahedrally) coordinated and the Sb is three-fold (pyramidally) coordinated. Even though the exact coordination of the Te is questionable, it is clearly less than or equal to three [7,8].

3. Nano-scale phase separation in glassy $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$

In the binary system, $\text{Ge}_x\text{Te}_{1-x}$, Boolchand and Bresser have suggested that phase separation occurs on a nano-scale for values of x greater than about 1/3 [15]. This phase separation was inferred from Raman scattering spectra and glass transition temperature data [15]. The interpretation is that for Ge concentrations that exceed the stoichiometric GeTe_2 composition, the glass phase separates into Ge-rich regions and GeTe_2 regions. There is no evidence that this phase separation is macroscopic. First, no phase separation is observed in electron microscopy. Second, two distinct glass transition temperatures are not observed. Therefore, the authors [15] suggest that the phase separation occurs on a nano-scale.

Boolchand et al. [2] have generalized these ideas to ternary chalcogenide systems containing Ge. In some ternary systems, such as $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$, no phase separation is observed, and the GeSe_4 tetrahedral and AsSe_3 pyramidal units mix on a molecular scale. Like-atom bonds, such as Ge-Ge, As-As, and Se-Se, occur depending on the composition, but they also do not cluster. This behavior is consistent with the situation described in the previous section where we found that there is little preference for specific chemical bonds in determining the local structural order.

On the other hand, Boolchand et al. [2] suggest, based on measurements of the glass transition temperatures as a function of composition [16], that nano-scale phase separation does occur in the ternary system, $\text{Ge}_x\text{Sb}_y\text{Se}_{1-x-y}$. These glasses are assumed to phase separate into Sb_2Se_3

regions and GeSe_z regions whenever $z < 2$. In terms of x and y in the normalized compositions this constraint becomes

$$2x > 1 - x - \frac{5}{2}y. \quad (4)$$

From eq. (4), one easily obtains the dotted lines in Figs. 1 and 2 ($6x + 5y = 2$) where there are only Ge-Se and Sb-Se bonds if the Se remains two-fold coordinated. To the right of this dotted line nano-scale phase separation can, but need not, occur. As mentioned above, there is evidence for phase separation in the $\text{Ge}_x\text{Sb}_y\text{Se}_{1-x-y}$ system.

In the $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ system phase separation only occurs near the two binary edges (Ge-Se and As-Se) [2,17]. Given this result, we speculate that in the $\text{Ge}_x\text{Sb}_y\text{Se}_{1-x-y}$ system, the phase separation is most pronounced near the two binary edges (Ge-Te and Sb-Te). Therefore the short-dashed line (GeSb-Te tie line) in Fig. 2 represents the best possibility to avoid phase separation for compositions to the right of the intersection with the dotted line (GeTe₂-Sb₂Te₃ tie line).

Whether or not there is a propensity for nano-scale phase separation in the $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ system, and in particular in the composition $\text{Ge}_2\text{Sb}_2\text{Te}_5$, is presently unclear. This question is important because any propensity for phase separation in the glass provides a potential failure mechanism for the phase-change memory devices. The composition $\text{Ge}_2\text{Sb}_2\text{Te}_5$ does lie along the line where one would least expect phase separation, but since most applications of phase-change memory devices require many reversible switching operations [18], any propensity for phase separation is potentially damaging.

Several compositions along the GeTe-Sb₂Te₃ tie line, other than $\text{Ge}_2\text{Sb}_2\text{Te}_5$, are potentially important for phase-change memory applications, notably two other compositions that form stoichiometric crystals, $\text{Ge}_1\text{Sb}_4\text{Te}_7$ and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ [19]. These two compositions are shown as solid squares in Fig. 1. Another potentially interesting phase-change memory material that lies along the GeTe₂-Sb₂Te₃ tie line is $\text{Ge}_2\text{Sb}_2\text{Te}_7$. This composition lies at the intersection of the line with the least propensity to phase separate (short-dashed line in Fig. 2) with the line separating homogeneous glasses from those that can potentially phase separate (dotted line in Fig. 2). It is unclear experimentally whether any of these three compositions is subject to nano-scale phase separation.

As mentioned above, the basic experimental evidence that suggests the onset of nano-scale phase separation is a composition above which there exists a decrease in the glass transition temperature as the average coordination number increases. Normally, the glass transition temperature increases with the average coordination number because the network becomes more rigid as n_{av} increases. Anomalous behavior is presumed to occur because the glass phase separates into two phases [2], each having lower n_{av} because the chalcogen atoms remain two-fold coordinated. It will be very difficult to measure the glass transition temperatures in the $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ system because of the propensity of these materials to crystallize. This fact makes the EXAFS measurements on Te the best hope for probing the propensity to phase separate. If for example, in glassy $\text{Ge}_2\text{Sb}_2\text{Te}_5$ the Te is predominantly three-fold coordinated, then nano-scale phase separation after many switching operations is a possibility. In principle, Te K-edge EXAFS experiments can monitor nano-scale phase separation on switching by observing a decrease in the average coordination number for Te from three to two after many switching cycles.

4. Summary

The local structural order in glasses of the system $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ is not presently known. EXAFS experiments suggest that the Ge is tetrahedrally coordinated and that the Sb is probably three-fold coordinated, but the coordination of the Te is unclear. Models of the local structural order suggest two possibilities as the Ge and Sb concentrations increase. First, the Te can remain two-fold coordinated, a scenario that in general requires the presence of like-atom bonds. Second, the Te can increase its coordination number from two to three and maintain the presence of only Ge-Te and Sb-Te bonds over a fairly wide range of compositions. A third possibility is that the glasses can phase separate on a nano-scale to lower the average coordination number of the Te. To understand failure

mechanisms in phase-change memory devices it may be important to determine which of these three possibilities exists.

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