A mathematical model of amorphous structure of $Ge_2Sb_2Te_5$ based on crystal-like local structures

Mamoru Tanaka, Akihiko Hirata

mamoru.tanaka@wpi-aimr.tohoku.ac.jp

AIMR, Tohoku University, Japan

1 Purpose

$Ge_2Sb_2Te_5$ (GST), which is a GeTe-Sb_2Te_3 pseudobinary compound, is a phase-change recording material used in practical applications. It is well known that amorphous GST crystallizes into a metastable NaCl-type crystal structure in an allotropic manner. An early EXAFS study indicated that Ge atoms in amorphous form tetrahedral atomic configurations, which are totally different from the NaCl crystal [1]. After that, however, several experimental and theoretical works proposed the amorphous model including the NaCl-like local structures. Additionally recent angstrom-beam electron diffraction method ([2]) provided clear evidences of the presence of the NaCl-like local atomic structures in amorphous GST. Based on these results, we constructed a mathematical model that has a NaCl-like local atomic configuration.

2 Features of GST

When GST is crystal phase, its crystal structure is NaCl type. Cl-sites are occupied by Te, and Na-sites are occupied by Ge, Sb, and Vac (vacancy) randomly. In practice, Ge, Sb at Na-site are out of equilibrium position a bit randomly. Note that the pairs of the nearest neighbor atoms are only Te-Ge and Te-Sb.

When GST is amorphous phase, it is considered that its atomic configuration is similar to NaCl-type crystal structure locally, and it constructs numerous comparatively robust covalent clusters (molecules).

(i) The number of covalent bonds of Ge, Sb, and Te are 4, 3, and 2 or 3 respectively.

(ii) Major bonds are Ge-Te and Sb-Te.

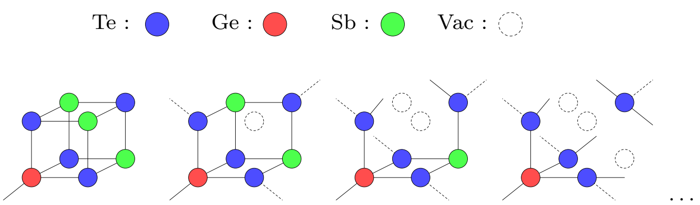
(iii) Ge-Te bonds in amorphous phase is especially shorter than it in crystal phase.

(iv) Among cycles by bonds, the proportion of four and six membered ring by Ge-Te (or Sb-Te) is high.

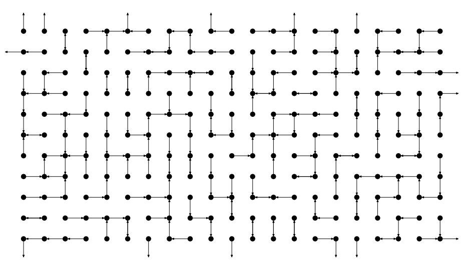
(v) The amorphous structure can be interpreted as the combinations of molecules $GeTe_4$ and $SbTe_3$.

3 Model

1. Give several types of units composed of four Te, some Ge, and some Sb following composition ratio which is not connected. The connection is determined after Step 3. The following are part of the units with only one Ge after Step 3.



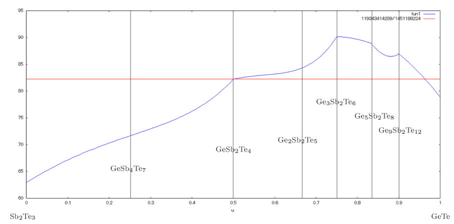
2. Locate the units on every 3-dimensional cubical lattice points randomly.
3. Give bonds between Ge in each unit and Te in some neighbor unit randomly. (The arrows represents bonds from Ge to Te in the following 2-dimensional picture. Connected components correspond covalent clusters.)



We here consider local and global bonding structures of this simple model, which is independent of small variation of atomic positions.

4 Local bonding structure

The expectation of Ge-Te and Sb-Te 4 membered rings may represent how similar to the crystal structure locally [3]. So we calculate the expectation for each ratio of GeTe and Sb_2Te_3 for our model in some cubi area.



In this model, $Ge_3Sb_2Te_6$ has the most 4-rings.

5 Global bonding structure

By the feature (iii), it has been believed that the constitution of Ge-Te covalent bonds plays an important role in the stabilization of the amorphous structure. So we are interested in the expected value of cluster size and the ratio of GeTe and Sb_2Te_3 which give an infinite cluster. To investigate it, we should develop percolation theory ([4]) for our model.

Let $G = (V, E, o)$ be an infinite, oriented vertex-transitive d-regular graph with the origin $o \in V$ such that $(u, v) \in E$ iff $(v, u) \in E$. For example, the D-dimensional cubical lattice $\mathbb{L}^D$ with appropriate edges and d-regular oriented trees T_d satisfy these conditions. Let $p_0, p_1, \ldots, p_d$ be non-negative numbers with $p_0 + p_1 + \cdots + p_d = 1$, and $\mathbf{p} = (p_0, p_1, \ldots, p_d)$. Step 2 and Step 3 is the procedure that, at each site $v \in V$, connect v to k sites $v_{i_1}, \ldots, v_{i_k}$ around v with probability $p_k/\binom{d}{k}$. (At Step 1, the probabilities $p_0, p_1, \ldots, p_d$ are determined.) We denote by $P_{\mathbf{p}}$ the Probability measure, by $\mathbb{E}_{\mathbf{p}}$ the expectation, by C the connected component containing the origin o, by $|C|$ the number of the sites in C.

Theorem 1. *If $\mathbb{E}_{\mathbf{p}}(|C|) < \infty$, then there exists $\alpha_1(G, \mathbf{p}) > 0$ and $\alpha_2(G, \mathbf{p}) > 0$ such that*

$$P_{\mathbf{p}}(o \leftrightarrow \partial B(n)) \leq 2e^{-n\alpha_1(G,\mathbf{p})}, \quad P_{\mathbf{p}}(|C| \geq n) \leq e^{-n\alpha_2(G,\mathbf{p})}$$

for any sufficiently large n, where $\partial B(n)$ is the boundary of the ball with radius n.

Theorem 2. *If $G = \mathbb{L}^D$, $p_1, p_2 > 0$ and $P_{\mathbf{p}}(|C| = \infty) > 0$, then the infinite cluster is only one with probability 1.*

If the graph is planar, we can estimate $P_{\mathbf{p}}(|C| = \infty) > 0$ as follows:

Theorem 3. *If $G = \mathbb{L}^2$, $p_0 + p_1 = 1 - p$, $p_2 + p_3 + p_4 = p$, then $P_{\mathbf{p}}(|C| = \infty) > 0$ if $p \geq 0.7829$.*

Theorem 4. *Let $G = (V, E)$ be the triangular lattice. If $p_0 + p_1 = 1 - p$ and $p_2 + p_3 + p_4 + p_5 + p_6 = p$, then $P_{\mathbf{p}}(|C| = \infty) > 0$ if $p \geq 0.79302$.*

Theorem 5. *If $d > 2$, and $p_1 = 1 - p$, $p_2 = p$, then $P_{\mathbf{p}}(|C| = \infty) > 0$ if and only if*

$$p > p_c(T_d) := \frac{1}{(d^2 - d - 1) + \sqrt{(d^2 - d - 1)^2 - (d - 1)^2}} \approx \frac{1}{2d^2},$$

which is a decreasing function in d satisfying $0 < p_c(T_d) < 1$.

Conjecture 1. *If $p_2 = \cdots = p_d = 0$, then $P_{\mathbf{p}}(|C| = \infty) = 0$.*

References

[1] A.V. Kolobov and J. Tominaga, Chalcogenides: Metastability and Phase Change Phenomena (Springer Series in Materials Science), (Springer, Berlin, 2012).

[2] A. Hirata et al., Nature Mater. 10, 28 (2011).

[3] S. Kohara et al., Appl. Phys Lett. 89, 201910 (2006).

[4] G. Grimmett, Percolation, Grundlehren der Mathematischen Wissenschaften, vol. 321, Springer-Verlag, Berlin, 1999.