Crystallization of amorphous Ge$_2$Sb$_2$Te$_5$: Order from disorder

R. O. Jones,[1,2] J. Kalikka,[3] J. Larrucea,[3] and J. Akola [1,3,4]

[1]Peter Grünberg Institute PGI-1, Forschungszentrum Jülich, D-52425 Jülich, Germany
[2]Computational Materials Science, German Research School for Simulation Sciences, D-52425 Jülich, Germany
[3]Nanoscience Center, Department of Physics, P.O. Box 35, FI-40014 Jyväskylä, Finland
[4]Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101, Tampere, Finland
r.jones@fz-juelich.de,   jaakko.akola@tut.fi

ABSTRACT

The rate-limiting process in phase change (PC) optical memories is the extremely rapid (nanosecond time scale) crystallization of nanosized amorphous "marks" in a polycrystalline layer. Our knowledge of the amorphous and ordered structures of Ge/Sb/Te and Ag/In/Sb/Te alloys has improved significantly in recent years and has led to plausible pictures for the transition between them, but the simulation of the actual crystallization process is complicated by the need to study large numbers of atoms over time scales that are difficult to attain, even with modern supercomputers. We have performed density functional/ molecular dynamics (DF/MD) simulations on a sample of Ge$_2$Sb$_2$Te$_5$ (GST-225) with 460 atoms at 500 K, 600 K, and 700 K for up to 600 picoseconds. Crystallization has been promoted by fixing the structure of a crystalline "seed" (4x4x4 sites, 58 atoms, 10% vacancies). We present a progress report on the results and on a simulation of 648 atoms with a similar "seed" at 600 K.

Key words: phase change materials, crystallization, Ge/Sb/Te alloys, density functional, molecular dynamics

1. INTRODUCTION

Close interplay between theory (density functional/ molecular dynamics simulations) and experiment (particularly x-ray diffraction and EXAFS) has shown that the amorphous structure of GST-225 and other alloys of Ge, Sb, and Te can be characterized by *"ABAB alternation"* (*A*: Ge,Sb, *B*: Te) with four-membered *ABAB* rings being a dominant motif [1]. This pattern is also prevalent in the metastable (rock salt) crystalline structure, so that it is plausible that the rapid amorphous-to-crystalline transition be viewed as a re-orientation (nucleation) of disordered *ABAB* squares supported by the space provided by cavities. Knowledge of the amorphous and crystalline structures of an Ag/In/Sb/Te alloy allows us to develop a picture of crystallization in this case as well [2]. Simulations of crystallization in GST-225 have been carried out on samples with less than 200 atoms with interesting results [3,4], but small samples leave many questions unanswered. We describe here DF/MD simulations of a sample of 460 atoms at 500 K, 600 K, and 700 K for up to 600 picoseconds, where crystallization is promoted by fixing the structure of a crystalline "seed" (58 atoms, 6 vacancies) throughout. The densities were adjusted during the simulation to allow for the difference between the amorphous and crystalline forms. In addition, we simulated a larger (648-atom) system with a similar "seed" at 600 K for 600 ps. This sample is not commensurate with the crystalline unit cell and cannot crystallize completely, but it reveals interesting details of the nucleus growth.

2. METHODS

The combined DF/MD calculations were performed on GST-225 with the CPMD package [5], using the approximation of Perdew *et al.* (PBEsol) [6] for the exchange-correlation energy and scalar-relativistic Troullier-Martins pseudopotentials [7] with a plane wave cutoff energy of 20 Ry. Periodic boundary conditions

were used, with a single point (k=0) in the Brillouin zone of the cubic unit cell. The temperature (500 K, 600 K, and 700 K) was controlled by a Nosé-Hoover thermostat. More details are provided in our earlier papers [8,9]. The starting structure incorporated a 4x4x4 crystallite (13 Ge, 13 Sb, 32 Te atoms, 6 vacancies, rock salt structure with lattice constant 3.0 Å) into the amorphous structure found previously [1]. The crystallite had the rock salt structure that is often assumed for GST-225, with Te atoms on one sublattice, and randomly distributed Ge, Sb, and vacancies on the other [10]. The simulation box was adjusted to the change in density (~ 7 %) between the amorphous and crystalline densities by reducing the starting box size (24.629 Å) in five steps of 0.114 Å to the final size (24.060 Å).

The order in the sample was studied using several measures: First, "crystalline'' atoms were identified with the aid of the order parameter of Steinhardt, Nelson, and Ronchetti [11], which has proved to be of value in discussing bond orientation order in disordered systems:

$$\bar{q}_l\left(i\right) = \sqrt{\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|\bar{q}_{lm}\left(i\right)|^2},$$

$$\bar{q}_{lm}\left(i\right) = \frac{1}{N_b\left(i\right)}\sum_{k=0}^{N_b(i)}q_{lm}\left(k\right); \quad q_{lm}\left(i\right) = \frac{1}{N\left(i\right)}\sum_{j=1}^{N(i)}Y_{lm}\left(\vec{r}_{ij}\right)$$

The sum over k runs over atom i and its neighbours, and the sum over j involves spherical harmonics Y_{lm}, so that angular correlations between an atom and its nearest neighbours can be identified. We define atom i as "crystalline'' if the order parameter $q_4\left(i\right) \geq 0.6$. Second, the clustering of such atoms allows us to analyze the individual structures for "percolation". If we assume a maximum bond length 3.2 Å, a cluster "percolates" if there is a path connecting an atom to its replica in the neighbouring unit cell. Finally, we have studied the changes that occur in the (partial) pair distribution functions, the numbers of "wrong bonds" and *ABAB* squares, the electronic density of states, and the mean square displacement of the atoms. We shall present details elsewhere. Essential to the present work has been the development of a new graphical user interface for following the evolution of nanosized cavities in crystalline and disordered materials and calculating their volumes, surface areas, and other properties [12].

3. RESULTS & DISCUSSION

Crystallization in the 460 atom sample occurred at both 600 K and 700 K. This is evident in Fig. 1, where we show the total potential energy, number of crystalline atoms, and the number of *"ABAB* squares*"* in the structures as the simulations proceed. Crystallization proceeds readily at 700 K, with dramatic changes in all quantities after around 200 ps. The changes are less dramatic at 600 K, but crystallization occurs and is complete before 500 ps. The situation is different at 500 K and in the larger (648-atom) simulation at 600 K. While all parameters show the trends apparent at higher temperatures, crystallization is not complete after 600 ps. The unit cell chosen in the 648-atom simulation was not commensurate with the crystalline unit cell, and this appears to hinder the process.

The right panels of Fig. 1 show the change in the partial pair distribution functions in the 460-atom simulation at 600 K. We plot averages over the last 20 ps prior to the density changes. Bragg peaks of the crystalline seed at 3.00, 4.24, 5.20, 6.00, 6.71, and 7.35 Å become more pronounced as the simulation proceeds. The growth of these and other maxima is most pronounced between 300 and 500 ps, corresponding to the period when more than 50 % of the atoms change from amorphous to "crystalline''. The most rapid growth at 700 K is between 100-200 ps, where again ~50 % of the atoms change to crystalline.
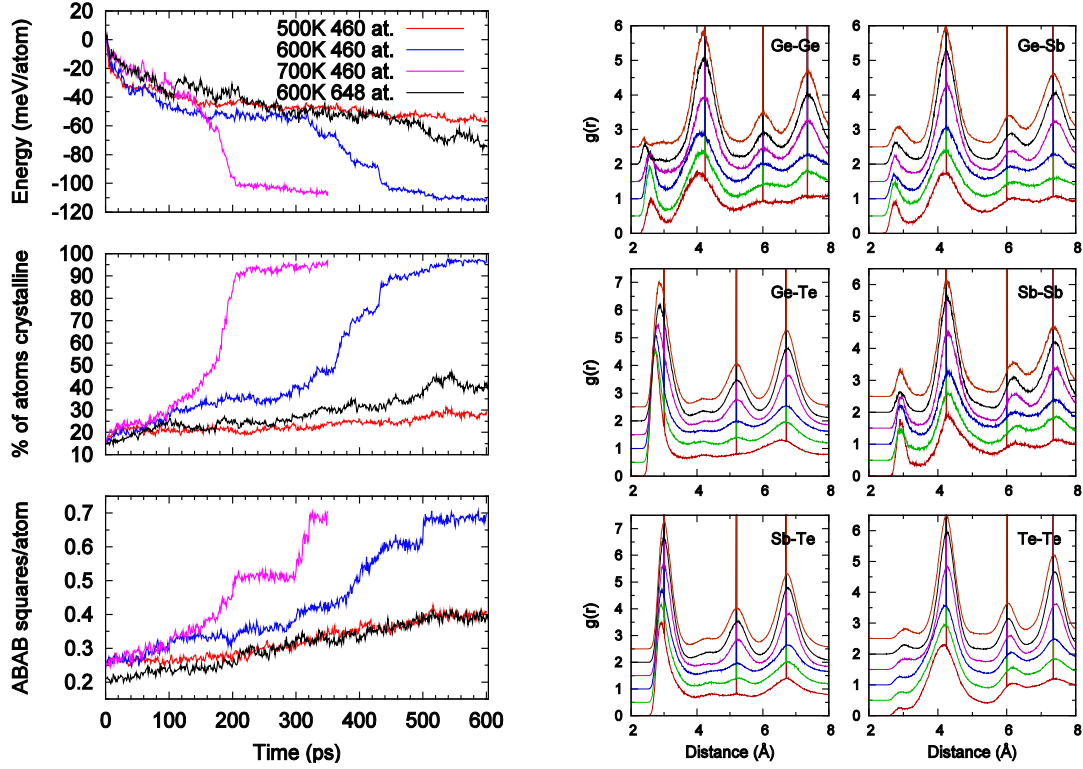
Figure 1: (Left) Time-dependence of total energy, percentage of crystallized atoms, and number of *ABAB* squares for the four simulations described. (Right) Change in partial PDF in 600 K simulation averaged over 20 ps ranges. Red: 80-100 ps, green: 180-200 ps, blue: 80-300 ps, magenta: 380-400 ps, black: 480-500 ps, orange: 580-600 ps.
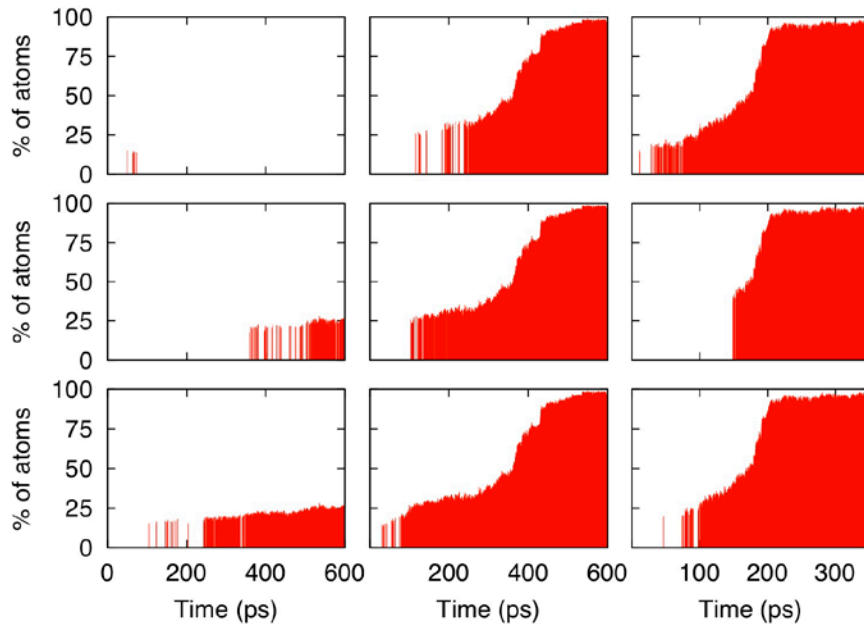

Figure 2: Size of percolating crystalline cluster as a function of time. Left, centre, right: 500 K, 600 K, and 700 K, respectively. Top, centre, and bottom rows denote percolation along the x, y, and z axes, respectively.

The results of the percolation analysis are shown in Fig. 2. Although the starting structure was the same in each case, percolation proceeded differently. The growth of the crystallite was not isotropic, but there was no single preferred direction for crystal growth. At 600 K, percolation proceeded along the z-axis, followed by y and z, while the order at 700 K was x, z, y. The 500 K simulations did not crystallize fully, but percolation is clearly evident in the y and z directions.

"Wrong bonds" in a disordered or ordering structure are bonds that do not occur in the model structure proposed by Yamada [10], where Te atoms form one sublattice of the rock salt structure, and Ge, Sb, and vacancies are randomly distributed on the other. Such bonds are evident in the pair distribution functions as weak maxima near 3 Å. While they decrease in importance as the simulation proceeds, they show no signs of vanishing. This is also evident in Fig. 3, where the evolution of different types of wrong bonds is shown for all four simulations. There are again differences between the results after crystallization at 600 K and 700 K: Ge-Sb bonds are more prevalent than Sb-Sb bonds in the former, while the reverse is true in the latter. Te provides more than half of the atoms, and it is not surprising that Te-Te bonds are the most prevalent wrong bonds after crystallization.
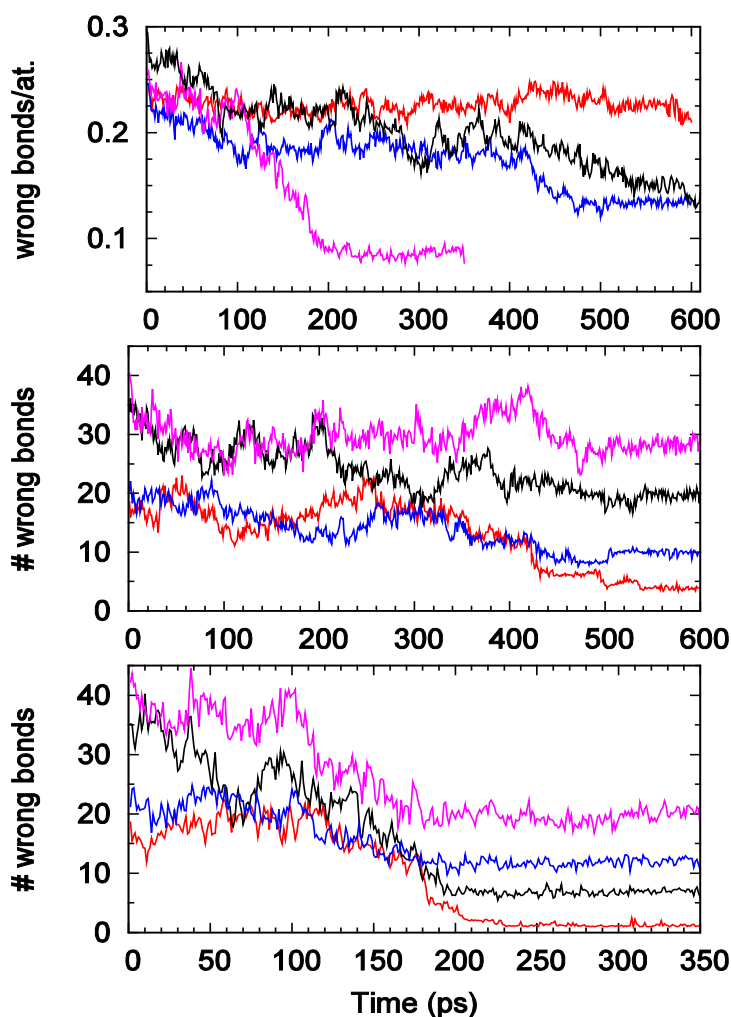

Figure 3: Evolution of the number of "wrong bonds". (Top) average number of wrong bonds per atom for all simulations. Red: 500 K, blue: 600 K, magenta: 700 K, black: 648-atom simulation at 600 K. (Centre and below) 600 K and 700 K simulations: red: Ge-Ge, black: Gs-Sb, blue: Sb-Sb, magenta: Te-Te bonds.

The mean-square deviation (MSD) of the atomic coordinates from the starting configuration slows down and ultimately stops as crystallization proceeds, but it provides valuable information about the mobility of different elements and their dependence on location and crystallization temperature. Finally, we have studied changes in the electronic densities of states (DOS) during crystallization. GST-225 remains a small band gap (≤ 0.5 eV) semiconductor throughout. As expected, the gap between the two s-valence bands increases during crystallization. Cavities make up ~10 % of the total volume and were analyzed with current version of pyMolDyn [12] using the scheme described in Ref. [8]. Modulation in the volume and spatial distribution of cavities prior to the onset of crystallization indicates that they play a vital role in the process. Full details will be presented elsewhere.

4. CONCLUDING REMARKS

Crystallization occurs in most disordered systems on time scales that are far beyond the scope of density functional based calculations. Phase change materials in widespread use as optical storage and computer memory are exceptional in that the time scale (some nanoseconds) is within the reach of modern supercomputers and could provide insight into crystallization processes beyond the particular materials in question. DF/MD simulations on a nanosecond time scale remain a great computational challenge, however, and earlier simulations of crystallization in GST-225 have been restricted to samples of less than 100 [3] and 200 [4] atoms, respectively. Here we have studied the early stages of crystallization in this prototype material using samples with 460 atoms (500 K, 600 K, 700 K) and 648 atoms (600 K). In all cases, crystallization has been promoted by inserting a small (58 atoms, 6 vacancies) crystallite in the cell. Crystallization occurs at 600 K and 700 K in the 460 atom sample, and we have been able to follow the process in detail. We emphasize that the crystalline structures contain many "wrong bonds", and Te atoms are located on *both* rock salt sublattices. The commonly accepted picture of a structure with a perfect Te sublattice and random occupancy of Ge, Sb, and vacancies on the other is a substantial oversimplification.

The extent to which the inserted crystallite promotes the process is not yet known, and it is unclear whether a 460-atom sample is large enough to overcome the finite size effects inevitable in small unit cells. To answer these questions, we are carrying out simulations *without* a crystallite and are planning simulations of GST-225 with 900 atoms. The former simulation shows percolation and other signs of crystallization after 700 ps, but we are continuing the simulation and will report the results elsewhere.

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Biographies

R. O. Jones obtained his B.Sc. Hons (Physics) at the University of Western Australia in Perth and his Ph.D. at the University of Cambridge, England under Volker Heine. He spent three years as a Post-doctoral Associate at Cornell University before joining the Forschungszentrum Jülich. His main focus for over 30 years has been on density functional theory and its applications to many ordered and disordered systems (solids, surfaces, atomic clusters, molecules, polymers, biological molecules, …).

J. Kalikka studied Physics at the University of Jyväskylä, Finland, obtaining his Master's degree in 2008. He will complete the work for his Ph.D. (under Jaakko Akola) in 2012. The main focus has been on phase change materials, particularly simulations of crystallization.

J. Larrucea obtained his Master's degree in Physical Chemistry from the University of Oulu, Finland, under Kari Laasonen and his Ph.D. in 2009 in the group of Jesus M. Ugalde at the University of the Basque Country. After a postdoctoral position at the University of Jyväskylä with Jaakko Akola, he moved in June 2012 to the University of Bremen, Germany, to work with Lucio Columbi on hybrid materials.

J. Akola studied Physics at the Universities of Helsinki and Jyväskylä, Finland, obtaining his Ph.D. at Jyväskylä under Matti Manninen. After five years as a Post-doctoral Researcher at the Forschungszentrum Jülich, Germany, he returned in 2005 to the Nanoscience Center in Jyväskylä. He is currently Academy Research Fellow in the Tampere University of Technology, Finland, where he heads the Molecule and Materials Modeling (MMM) group. His fields of interest include classical, tight-binding, and density functional simulations of materials, nanoparticles, and biological systems.