

Case Study: Ab-initio Molecular Modeling of Phase Change Alloy Ge-Te

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Motivation

Phase change (PC) data storage devices are used in many modern computing applications (CD-RW, DVD-RW, Blu-ray Disc) and are good candidates for a wide range of other memory applications (SDRAM, SSD, etc.)[7]. PC memory devices take advantage of the fast (order 1 ns) and reversible transition from crystalline to amorphous phases. Bits are written by local melting of the material and subsequent quenching to an amorphous state. The crystalline and amorphous materials experience several order of magnitude contrast in both optical and electronic properties. The written bits are erased by heating the amorphous material above the re-crystallization temperature until the crystalline state is recovered.

The optical and electronic contrasts are attributed to the large structural changes seen in the amorphous phase. Although there have been experimental measurements of the local structure of the liquid and amorphous phases of various PC materials, not much is known about these structures on a component-by-component basis [4,5,8].

Atomistic simulations could elucidate the detailed amorphous structure of PC materials, which could give insights into why PC materials work so well and how they might be improved. However, no interatomic potentials exist for PC materials to perform large-scale classical Molecular dynamics simulations. Thus, the studies reviewed here use Ab-initio (quantum mechanical) molecular dynamics simulations, which require no interatomic potentials to be parameterized.

The focus of [1-3] is on the compound Ge-Te, which is an important PC material itself and is also a building block in the more widely used $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) compound. Similarities between these two compounds will be identified in [2]. The studies reviewed here are concerned with the structural changes in Ge-Te in both the liquid phase [3] and the quenched amorphous phase [1,2]. All 3 studies are performed using ab-initio molecular dynamics simulations within the Born-Oppenheimer approximation. These simulations are extremely expensive (calculations scale as the number of electrons in the system, $O(N^3)$) and are usually used when no suitable interatomic potentials exist for the material (as is the case for PC materials).

Ab-initio Molecular Dynamics

Ab-initio Molecular Dynamics refers to a class of molecular simulation techniques which derive the forces in a molecular simulation via a quantum mechanical (electronic structure) calculation. In the Born-Oppenheimer approximation, the electrons follow the nuclear

coordinates adiabatically, such that their instantaneous configuration is in the ground state. The equations of motion for Born-Oppenheimer molecular dynamics are:

$$M_I \vec{R}_I = - \frac{\partial E[c_i^k, \vec{R}_I]}{\partial \vec{R}_I} = \vec{F}_I$$

Where the subscript I indicates the coordinate of nuclei I . Here the energy is that calculated from an electronic structure simulation, which is a function of the nuclear coordinates and the electronic wavefunction. This expression is based on the Feynman-Hellman theorem, which is the quantum analogue of Newton's second law. Here the assumption is that for any general nuclei configuration, the electronic wavefunction is the ground state wavefunction. This allows the calculation of the forces on the nuclei as the derivative of the energy obtained from the electronic structure calculation with respect to the nuclear coordinates. There are many choices for calculating the ground state wavefunction for the system, but the most popular is Density Functional Theory (DFT) because of its computational efficiency. This method of force calculation makes it possible to simulate systems with widely varying composition and electronic structure without the need to parameterize interatomic potentials. Once the forces are calculated, the molecular simulation can be carried out by evolving the positions of the nuclei using any number of integration algorithms (Verlet, Runge-Kutta, etc.) in any number of ensembles (NVE, NVT, NPT, etc.).

Measurement of Structure

In [1-3], there are several measurements made to quantify the liquid and amorphous structure of Ge-Te and GST. Perhaps the most elucidating is the measurement of the Radial Distribution Function (RDF), defined as:

$$g(r) = n(r)/(\rho 4\pi r^2 dr)$$

Here, $n(r)$ is the number of atoms inside a shell of radius size r and volume $4\pi r^2 dr$ around a given atom. This is normalized by the bulk density ρ such that in the large r limit, $g(r)=1$. Measurement of $g(r)$ is done by ensemble averaging over all atoms in the system. Partial RDFs can be defined by measuring $g(r)$ around, say, Ge and counting only other Ge atoms inside the shell. For multi-species systems many partial RDFs can be defined (which are difficult or impossible to measure experimentally). These partial RDFs contain information about bonding on a species-by-species basis, and can be valuable for analysis.

In the crystal phase, RDFs display multiple well defined peaks corresponding to the first, second, and larger nearest neighbor distances. In amorphous and liquid phases, RDFs usually display a first (and possibly a second) nearest neighbor peak, after which $g(r)$ decreases sharply

to its large r limit of 1. This is an indication of a lack of long-range order, which is the signature of a disordered/amorphous structure.

Liquid Phase Simulation

Simulation Details

The liquid simulations in [3] we carried out in an NVT ensemble using the Langevin thermostat. Data collection was taken in an NVE ensemble. The forces were calculated using DFT and pseudo-potentials within the local density approximation (LDA). The system contained 64 atoms of Ge-Te in a cubic supercell of side length 12.4 Angstroms to reproduce the experimental liquid density (0.0335 atoms/Angstroms³). A time step size of 7.2 fs was used to “thermalize” a liquid at 6000K for 3 ps to remove memory of the initial crystal phase. The system was cooled to the melt temperature of 1000K in 3 ps where data was taken for another 3 ps.

The entire melt process (from crystal to liquid at the melt temperature) was performed over (roughly) 8 ps, which is (at least) 2 orders of magnitude less than the entire experimental quench process from crystal to amorphous phase. Here one must trust that the author’s tested to ensure that the results did not depend on this short melting time. Also, the size of the system is only 64 atoms, and the simulation cell contains only 2 repeat units of the distorted rocksalt bond alternation present in the crystal phase.

Results

The simulation results are compared with neutron-diffraction measurements of the liquid phase Radial Distribution Function (RDF) in Fig. 1 (6). Only the total RDF is available experimentally, and the simulation is in good agreement (top Fig. 1). One sees an overall shortening of bond lengths in the liquid phase (2.85, 3.15 Angstrom bond lengths in crystal) to 2.72 Angstroms. With the simulation results, partial RDFs were measured to show that Ge-Te and Ge-Ge experience much shorter bonding (2.72 and 2.6 Angstroms, respectively) than in the crystal phase (2.85/3.15 and 4.3, respectively). The coordination for Ge-Ge is also larger than Te-Te, while Te atoms repel each other outside the first coordination shell of the crystal phase ($r < 3.15$ Angstroms). This leads the authors to reject the proposal that the liquid phase should show tetrahedral order [6], although the total coordination is close to 4. Overall, much shorter bonding is present in the liquid phase.

Criticism

The author’s claim that the Peierl’s distortion (characterized by alternating short and long bonds) that is present at low temperature in the crystal phase, reenters in the liquid phase.

There are serious questions about the validity of this claim considering that the simulation cell used contains only 2 repeat units of the distorted rocksalt unit. The Peierl's distortion is dependent on the broken rocksalt symmetry which opens a gap at the Fermi surface. This gap opens at the Fermi wavevector, which is only (roughly) a factor 2 larger than the wavenumber of the simulation cell size. This brings up serious questions about the effect of periodicity on the simulation results, particularly with regards to electronic structure.

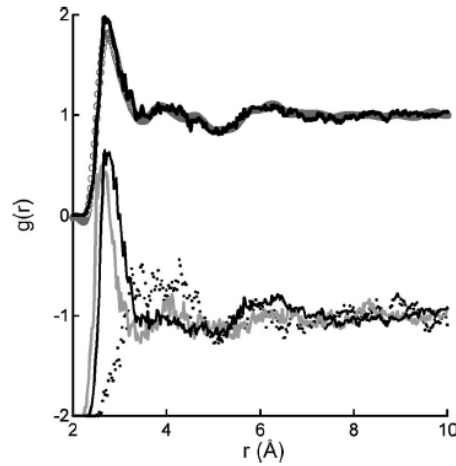


FIG. 6. Calculated total pair correlation function $g(r)$ at 1000 K (plain line) compared with neutron diffraction $g(r)$ at 1173 K (symbols). Bottom: the partial $g(r)$ (g_{GeTe} , thick line; g_{GeGe} , gray line; g_{TeTe} , dots). The partials are shifted for clarity.

Figure 1: Total and partial pair RDFs from the neutron diffraction experiment and simulations.

Amorphous Phase Simulation of Ge-Te

Simulation Details

The simulations in [1] cover the entire crystal-liquid-amorphous quench cycle. The author's study both Ge-Te and the eutectic composition $\text{Ge}_{15}\text{Te}_{85}$. There are several sharp changes to the eutectic composition upon melting, including a semiconductor to metal transition, deviations from linearity in the sound velocity, and an anomalous density increase (all of which are not seen in Ge-Te). The authors are concerned with identifying the structural differences between Ge-Te and the eutectic composition to account for these discrepancies.

The simulations were performed using Born-Oppenheimer molecular dynamics with a Nose-Hoover thermostat. The forces were derived from a DFT electronic structure calculation using the generalized gradient approximation (GGA) of PBE for the exchange-correlation functional. The simulation contained 216 atoms with a cubic simulation cell size corresponding to the experimental liquid densities of Ge-Te (18.61 Angstroms, 0.0335 atoms/Angstrom³) and $\text{Ge}_{15}\text{Te}_{85}$ (19.70 Angstroms, 0.02827 atoms/Angstrom³). Starting with the distorted rocksalt

crystal, the Ge-Te system was superheated (in a similar way to [3]) to 5000K. It was then cooled to the melt temperature (1000K) in 50 ps, where data was then collected for 29 ps. The amorphous phase was then produced by quenching to 300K in 115 ps, where data was collected for 26 ps. Finally the temperature was lowered to 100K (96 ps) and the structure was optimized. A similar procedure was performed for the eutectic composition, and the RDF results for the amorphous phase are shown in Fig. 2 (1).

Results

The results for the liquid phase RDFs are qualitatively similar to the liquid phase results in [3]. For the Ge-Te composition, the Ge-Te and Ge-Ge RDFs show much shorter bond lengths (2.8 and 2.7 Angstroms, respectively). This is consistent with the experimental measurements of the total RDF of the amorphous phase of Ge-Te [4, 5] The Te-Te amorphous bond lengths are comparable to the bonding in the crystal phase (4.1 Angstroms versus 4.3 Angstroms). For the eutectic composition, the Te-Te bonding is much shorter (3.0 Angstroms), owing to the reduced Ge composition.

Order in the amorphous phase is quantified by the order parameter α , which is a ratio of concentrations and coordinations of the species in the system [2]. The parameter α can range from -1 (segregated species) to 0 (completely random mixture) to +1 (perfect Ge-Te alternation). Amorphous Ge-Te is shown to be semi-ordered ($\alpha > 0.5$), and even the liquid shows significant Ge-Te alternation ($\alpha > 0.3$). The author's observe that this order in the liquid tends to increase as simulation times proceed, which could explain the lower order parameter ($\alpha < 0.3$) measured in [3]. However, this also brings into question the simulation time used in [1], which could have affected the order parameter results for the same reason.

Criticism

The small number of atoms (216) used in the simulations calls into question the finite system size and its role in the calculation of the order parameter. Also, the entire melt/quench process was performed over (roughly) 225 ps, which is a factor of 5 less than the experimental melt/quench cycle. This is, however, a much more realistic time span than that used in [3]. The results in [1] show the Ge-Te amorphous phase has the same qualitative bonding as the liquid phase; shortened Ge-Te and Ge-Ge bonds and long Te-Te bonding similar to the crystal phase.

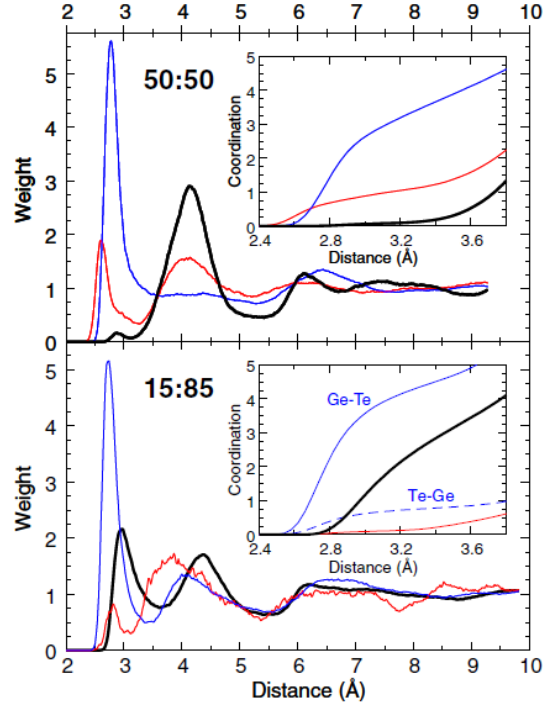


FIG. 1 (color online). Partial RDF of a -GeTe and a -Ge_{0.15}Te_{0.85} at 300 K. Black (thick) line, Te-Te; blue (peaked) line, Ge-Te (Te-Ge); red (middle) line, Ge-Ge. Insets: Coordination numbers as a function of cutoff distance (here 3.2 Å).

Figure 2: Total and partial pair RDFs of the quenched amorphous phase for Ge-Te and the eutectic composition.

Amorphous Phase Simulation of Ge-Te and GST

Simulation Details

Finally, the study in [2] compares the amorphous phases of Ge₂Sb₂Te₅ (GST) and Ge-Te. GST is the more popular PC material, which is composed of building blocks of Ge-Te and Sb₂Te₃. The results will show qualitatively similar bonding between the two alloys.

The simulations were performed using Born-Oppenheimer molecular dynamics with a Nose-Hoover thermostat. The forces were derived from a DFT electronic structure calculation using the generalized gradient approximation (GGA) of PBE for the exchange-correlation functional. The GST system contained 460 atoms (512 atomic sites) at the metastable crystal (6.35 g/cm³) and the amorphous (5.88 g/cm³) densities. The Ge-Te system contained 216 atoms with a cubic simulation cell size corresponding to the experimental liquid density of 5.61 g/cm³. A similar melting procedure to [1] was used for both GST and Ge-Te, and the entire melt/quench

cycle was performed in 297 ps (GST) and 340 ps (Ge-Te). The RDF results for the amorphous phase are shown in Fig. 3 (2) for both GST and Ge-Te.

Results

From the Fig. 3(1) (a), one sees long range order of the Te-Te bond in both GST and Ge-Te, and a bond length (4.1 Angstrom) which is close to the crystal value (4.3 Angstrom). Again, this is in agreement with [1,3] which show long Te-Te bonds in amorphous and liquid Ge-Te. The Te-Te RDF shows long range order (up to 10 Angstroms), which indicates the importance of large simulation cell sizes for these systems. For GST, Ge-Te and Sb-Te show shorter bonds (2.8 and 3.1 Angstrom) in the amorphous phase, which is qualitatively similar to the shortened Ge-Te and Ge-Ge bonds in amorphous Ge-Te.

Criticism

The same questions about finite system size and simulation time length can be asked about this study. However, the results seem to be in good agreement with both experiment and previous simulations [1,3]. Also, the results seem consistent from Ge-Te to GST. However, to probe more interesting (experimental) properties one would like a simulation size of (roughly) 10s nm and 10s ns.

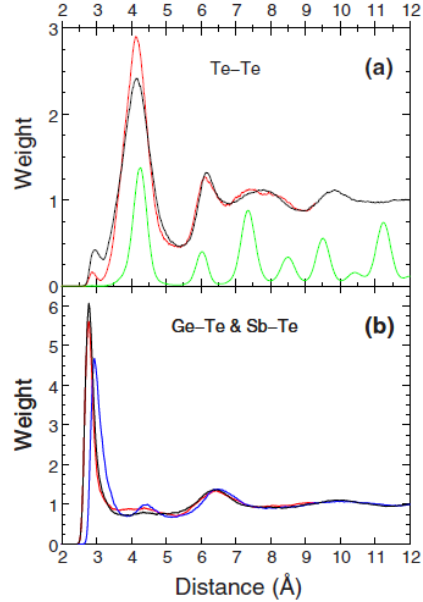


FIG. 2. (Color online) Radial distribution functions of *a*-GST and *a*-GeTe at 300 K. (a) Te-Te [black, *a*-GST; red, *a*-GeTe; and green (scaled by 0.25), metastable GST crystal at 300 K]. (b) Partial RDF (black, Ge-Te bonds in *a*-GST; red, Ge-Te bonds in *a*-GeTe; and blue, Sb-Te bonds in *a*-GST).

Figure 3: amorphous phase RDFs of Ge-Te and GST, showing partial pair RDFs.

Summary

The simulations performed in [1-3] show a qualitatively similar trend in the liquid and amorphous phases of Ge-Te, and also GST. Within the DFT framework, both LDA [3] and GGA [1,2] exchange-correlation functionals were used, and the results between the two seem to be consistent. Thus, there is little concern for the validity of the results (at least within DFT). These ab-initio molecular simulation methods are versatile and can be easily generalized to systems with diverse composition.

There are stark structural differences in the crystalline and amorphous phases which are characterized by shortened Ge-Te and Ge-Ge bonds and long, crystalline-like Te-Te bonds with long-range order in the amorphous phase. This type of bond shortening is also observed experimentally [4,5,8], providing further validity to the simulations. This type of bond shortening is also seen in GST, where the Te-Te bond lengths remain crystalline-like. Thus, ab-initio simulations were able to identify the species which is responsible (Ge) for the large amorphous structural changes.

The effects of finite simulation size and short simulation times are exemplified in the short range order seen in [1], which is reduced in the shorter and smaller simulations in [3]. The simulations carried out in [1-3] are also several orders of magnitude smaller (in both time and space) than the experimental scales. This prohibits simulation of these materials under experimental conditions, which limits how informative atomistic modeling of PC materials can be. Thus, there is a great need for more efficient simulation techniques to study PC materials.

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