Nanoscale phase transitions in phase change materials: What's new?

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Phase change (PC) materials are the leading candidates for the next generation of computer random access memory (RAM) and rewritable storage devices. The past year has emphasized this, when the Blu-ray Disc (BD) became the de facto standard as the successor to the digital versatile disk (DVD). The recording medium of all BD products comprise PC materials. A write/erase cycle involves the switching between amorphous and ordered states when an electric current or laser pulse is applied, and the state can be determined by monitoring the optical or electrical properties. It is astonishing that materials based on *structural* phase changes now support a mature industry, while at the same time only sketchy information is available about the *structures* involved. We have used the BlueGene/L and BlueGene/P supercomputers to extend our simulations of the amorphous and ordered states of a range of alloys used in PC memory and storage materials. There have been some unexpected and exciting results.

The demands placed by computers and other electronic devices on the density, speed, and stability increase without any sign of saturation. Phase change (PC) materials are familiar to us all as rewritable media (CD-RW, DVD-RW, DVD-RAM), but 2008 brought the announcement that Blu-ray Disc (BD) was the only survivor of the battle to succeed the DVD. The BD standard focuses mainly on the aperture and wavelength (405 nm) of the laser, but the recording materials in use are all of the PC variety and often alloys of Ge, Sb, and Te. The basis of their function is the rapid and reversible transition between the crystalline and amorphous forms of nanoscale bits ($\lesssim$ 100 nm), which arise from quenching after a localized and short ($\sim$ 1 ns) laser annealing to a temperature above the melting point. Longer laser heating ($\sim$ 50 ns) to a temperature above the glass transition temperature but below the melting point leads to a metastable crystalline form. The diameters of the amorphous marks ("bits") currently possible yield storage densities far in excess of those found in current magnetic memory devices.

Many of the materials of choice for PC storage and memory materials [1] can be seen in Fig. 1. GeTe was the first system to show (1986) real promise as a PC material, and alloys along the tie-line between GeTe and Sb_2Te_3 are in widespread use today. $Ge_2Sb_2Te_5$ (GST), in particular, is used in DVD-RAM and is viewed as the prototype PC memory material. Prominent alloys used in BD applications also belong to this family, an example being $Ge_8Sb_2Te_{11}$.

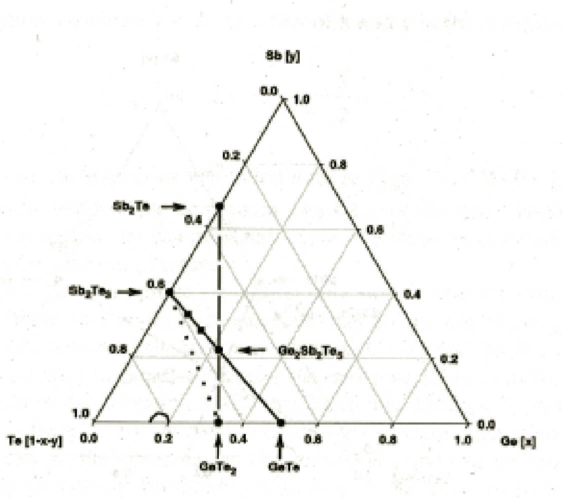

FIG. 1: Alloy diagram for $Ge_xSb_yTe_{1-x-y}$.

To understand the properties of these materials it is essential to know the atomic arrangement ("structure") in the phases involved, but these are difficult to measure or calculate in ternary alloys with a significant number of vacancies. The analysis of experiments often requires wide-ranging assumptions about the atomic arrangements, an example being the widespread use of reverse Monte Carlo methods to find structural information from measured x-ray and neutron scattering experiments. Several calculations have been performed in recent years, but the unit cells (with $\sim$ 60 atoms) are usually too small to describe structural details, and the simulation times (typically a few picoseconds) are too short to describe vibrational and other thermodynamic properties reliably. There are also several "models" of the structural phase changes that have survived stubbornly in the literature regardless of new developments. As we mentioned last year, we have used the Blue Gene supercomputers in Jülich to extend greatly the range of density functional (DF) calculations on these and related materials. We have performed simulations with hundreds of atoms in the unit cell over several hundred picoseconds, beginning with a high temperature liquid in order to avoid bias towards particular structural types. In addition to the liquid and amorphous materials (at 900 K and 300 K, respectively), we have simulated rock-salt (ordered) structures of GST and states of the prototype PC material $Ge_{0.50}Te_{50}$. Full details are provided in Ref. [2].

These simulations allow us to follow the motion of all atoms throughout. Amorphous GST shows long-range ordering (at least to 10 Å) of Te atoms and a high degree of AB alternation (A: Ge, Sb; B: Te). This is also true in the case of GeTe [2], which is much less attractive than GST for these purposes. More recently we have studied the eutectic alloy $Ge_{0.15}Te_{0.85}$, i.e. the binary Ge/Te alloy with the lowest melting point (650 K) [3]. There is no Te segregation at the eutectic composition, where the material resembles neither GeTe nor Te.

The alloy $Ge_8Sb_2Te_{11}$ is used by some manufacturers as the recording medium in Blu-ray Disc applications. The choice of alloys on the pseudobinary line GeTe-Sb_2Te_3 requires compromise: near the GeTe end there is good contrast between the optical properties of the amorphous and ordered phases, but the crystallization process is too slow. At the other (Sb_2Te_3) end the reverse is true: short crystallization times, but poor optical contrast. $Ge_2Sb_2Te_5$ was viewed as a satisfactory compromise, but alloys nearer to GeTe appear to be even better. We have performed a simulation of $Ge_8Sb_2Te_{11}$ (the ratio of GeTe to Sb_2Te_3 is 8:1) with 630 atoms in the unit cell over 400 picoseconds. [4] A comparison of the results (structure, valence density of states, ...) with those for GeTe and $Ge_2Sb_2Te_5$ showed remarkable similarities to the latter, although GeTe is much closer on the plot of Fig. 1. It appears that GeTe is a singular case (this is also evident in the structures of the crystalline phases), and that *other* members of this pseudobinary family have much more in common.

Optical storage media are not limited to these pseudobinary alloys. Alloys of Sb and Te with compositions near the eutectic ($Sb_{70}Te_{30}$) are used for CD-RW and DVD-RW applications, usually with small amounts of Ag and In present. The crystallization of amorphous marks in a thin film proceeds by growth from the edge (rather than nucleation, as in the GST alloys), and this leads to some advantages. We have simulated a common composition of this alloy as well [5], and we shall present the results in next year's Report. These are among the most extensive such simulations that we have performed to date (640 atoms in the unit cell, more than 200 ps).

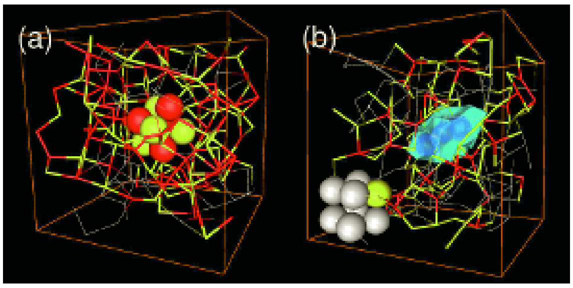

FIG. 2: (a) Simulation box of a-GeTe (18.6 Å, 216 atoms) with $ABAB$ squares highlighted. An $ABAB$ cube is also shown. Red: Ge, yellow: Te. (b) Simulation box of $Ge_{0.15}Te_{0.85}$ (19.7 Å, 216 atoms) with Ge and Ge-coordinating Te atoms highlighted. A multivacancy and a cubic Te subunit are shown.

This continues to be an exciting area in which to work. Do look at the references for more details, and we expect you to return again next year for the latest developments! Better still, why not contact us for more information in person or by e-mail?

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[1] M. Wuttig and N. Yamada, Nature Mater. **6**, 824 (2007) provide a review of the history of these materials.

[2] J. Akola and R. O. Jones, Phys. Rev. B **76**, 235201 (2007); J. Phys.: Condens. Matter **20**, 465103 (2008).

[3] J. Akola and R. O. Jones, Phys. Rev. Lett. **100**, 205502 (2008).

[4] J. Akola and R. O. Jones, submitted.

[5] J. Akola and R. O. Jones, submitted.