

Nanoscale Phase Transitions in Phase Change Materials

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Phase change (PC) materials are among the most promising candidates for the next generation of computer random access memory (RAM) and rewritable storage devices. Unlike conventional RAM, the content is not lost when power is disconnected. PC materials switch 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 remarkable that PC materials have become the basis of a whole industry while only sketchy information is available about the structures of the phases involved. We have used the IBM BlueGene/L computer to perform extensive simulations on the amorphous and ordered states of an alloy of germanium, antimony, and tellurium (Ge/Sb/Te) that is already used in DVD-RAM. These simulations provide insight into the structural units essential to the phase change process.

Computers and other electronic devices place ever-increasing demands on the density, speed, and stability of memory, and phase change (PC) materials are familiar to us as rewritable media (CD-RW, DVD-RW, DVD-RAM). Recently (January 2008), Warner Bros, the world's largest distributor of DVD films, announced that—from May this year—it would sell only the Blu-ray disc (BD) version of its products. Blu-ray discs, like commercially available DVD-RW storage devices and DVD-RAM, are based on films of 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 (~ 1 ns) laser annealing to a temperature above the melting point. Longer laser heating (~ 50 ns) to a temperature above the glass transition temperature but below the melting point leads to a metastable crystalline form. The ideal storage materials of the future will be fast (~ 10 ns switching time), dense (bit diameter $\ll 50$ nm), stable (several years per lost bit), long-lived ($> 10^{12}$ cycles per lost bit), and—naturally—with low manufacturing cost and power consumption. Such bit diameters would result in storage densities far in excess of those found in current commercial devices, such as those based on giant magnetoresistance (GMR).

PC optical memory devices have focused for over 20 years on films of semiconductors and semimetals with melting points that are low enough to allow laser-induced melting but high enough to prevent spontaneous crystallization. The materials of choice today are Ge/Sb/Te alloys [1], with particular focus on the pseudobinary compounds $\text{GeTe-Sb}_2\text{Te}_3$. One of them ($\text{Ge}_2\text{Sb}_2\text{Te}_5$, GST) is the basis of digital versatile disc-random access memories (DVD-RAM), and another ($\text{Ge}_8\text{Sb}_2\text{Te}_{11}$) is the basis of Blu-ray Disc (BD) technology.

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 to calculate in ternary alloys with a significant number (typically around 20%) of vacancies. In the case of GST, even the structure of the metastable crystalline form is a matter of debate, and the metastable nature of amorphous GST (bulk samples crystallize) has restricted experimental studies of this material. In any event, 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. A number of calculations have been performed in recent years, but the unit cells (with ~ 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. We have used the Blue Gene/L supercomputer in Jülich to extend greatly the range of density functional (DF) calculations on these and related materials. We have performed simulations on GST in a unit cell containing 460 atoms over several hundred picoseconds. We begin from 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 $\text{Ge}_{0.50}\text{Te}_{50}$. Full details are provided in Ref. [2].

Such simulations allow us to follow the motion of all atoms throughout, and we can determine pair-correlation functions for all atom types. The structures of the amorphous and crystalline phases show similarities, as the speed of the phase change be-

tween them would suggest, and the structure factors agree remarkably well with the results of scattering experiments (x-rays, neutrons) where available. 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 striking (and unexpected) result is illustrated in Fig. 1, where we highlight four-membered *ABAB* rings. Since the crystalline (rocksalt) phase comprises perfectly ordered *ABAB* squares, we can view the rapid amorphous-to-crystalline transition as a reorientation of such squares to form additional *ABAB* bonds and cubic subunits in a locally “distorted octahedral” structure. A crucial component of these materials (and essential for an understanding of their properties) are the vacancies, and our simulations provide us with their shapes and distributions as well. In Fig. 2 we show a typical medium-sized vacancy (and the neighbouring bonds) in GST. Vacancies in the disordered phase provide the necessary space for the phase transition to take place.

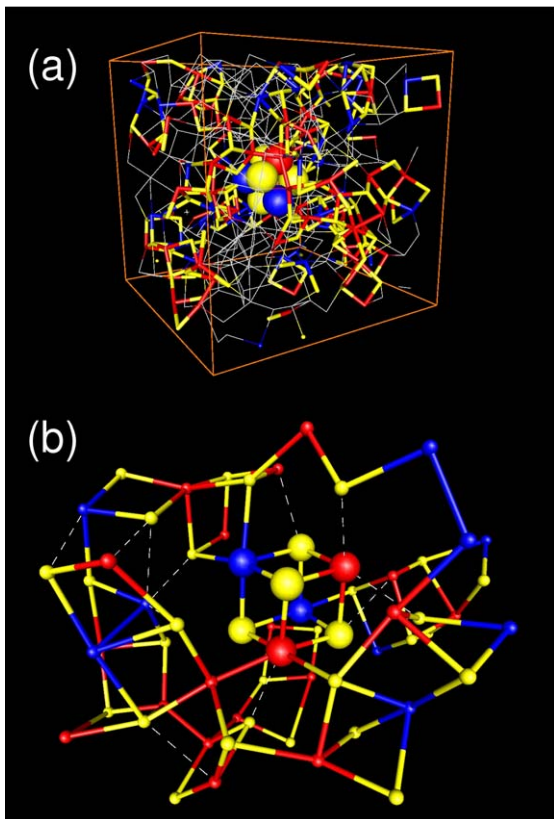


FIG. 1: *ABAB* squares and cubes in amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$. (a) Simulation box (24.6 Å, 460 atoms) with atoms and bonds of *ABAB* squares and cube highlighted. Red: Ge, blue: Sb, yellow: Te. (b) Local environment of an *ABAB* cube.

GST is just one of numerous Ge/Sb/Te alloys that are used in the world of phase change memories. In Ref. [2] we also provide a detailed discussion of GeTe and explain why it is much less attractive than GST for

these purposes. More recently we have studied the eutectic alloy $\text{Ge}_{0.15}\text{Te}_{0.85}$, i.e. the binary Ge/Te alloy with the lowest melting point (650 K) [3]. We have found that there is no Te segregation at the eutectic composition, where the material resembles neither GeTe nor Te. By good fortune we have chosen the Blu-ray alloy $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ as our next system to study. It is natural to ask: Just what is it about the structure of this alloy that makes it the material of choice for the next generation of DVD? It will surprise many that the *de facto* future standard is a material whose structure is essentially unknown. We are confident that the results we present in next year’s report will change this situation. In addition, our simulation trajectories and the well-equilibrated structures that result also allow us to calculate vibration frequencies. This provides us with another window into the properties of these materials, because there are good prospects that measured vibrational spectra of these materials will soon become available.

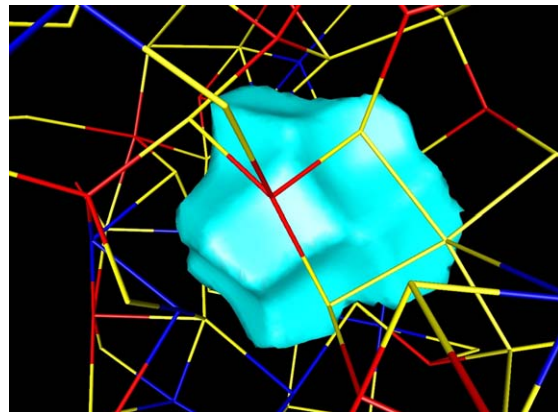


FIG. 2: A medium-sized cavity in $\text{Ge}_2\text{Sb}_2\text{Te}_5$.

This is a fascinating area in which to work. Do look at Ref. [2] for more details, and you must certainly return to these pages next year for the latest developments!

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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).
 - [3] J. Akola and R. O. Jones, submitted.