Structure of liquid phase change material AgInSbTe from density functional/molecular dynamics simulations

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The liquid phase of the AgInSbTe phase change material Ag5.5In3.5Sb75.0Te17.7 has been studied using molecular dynamics/density functional simulations. The calculated structure factor and total pair distribution function agree very well with high-energy x-ray diffraction measurements. We find that: (a) there are signs of medium-range order, (b) Ag and In prefer to be near Te rather than Sb atoms, and promote octahedral coordination in association with Te, (c) Ag is the most mobile element, has the shortest bonds (2.8–2.9 Å) and the highest coordination (5.5), and is anionic with the largest effective charge, and (d) there are few cavities (4% of volume).

Phase change materials involve the rapid and reversible change between nanoscale amorphous (α-) and crystalline (c-) spots in a polycrystalline film, and play central roles in rewritable media and nonvolatile computer memory. Two families of chalcogenide alloys dominate practical applications: (a) GeTe-Sb2Te3 (GST) pseudobinary alloys, and (b) AgInSbTe (AIST) alloys near the SbTe eutectic composition (Sb70Te30). DVD-RAM and Blu-ray Disc are examples of the former, CD-RW and DVD-RW represent the latter. Understanding the phase change mechanisms is impossible without structural information, and there has been much speculation about the structure of the different alloy phases. Although these are complicated by the presence of three and four elements, respectively, significant progress has been made recently in both chalcogenide families.

A reverse Monte Carlo analysis of high-energy x-ray diffraction (HEXRD) data from the prototype GST material a-Ge2Sb2Te5 (Ref. 4) indicated that the structure was dominated by ring structures also found in the crystal. Extensive density functional (DF) calculations5–7 on liquid (ℓ-) and a-GST extended this picture and showed that medium-ranged order exists among Te atoms, and that cavities and ABAB squares (A: Ge/Sb, B: Te) characterize these materials and their phase changes. Of particular interest is the time-resolved x-ray diffraction study of crystallization in Ge2Sb2Te5 and Ag5.3In3.5Sb75.0Te17.7.8 The results are consistent with the different crystallization mechanisms: nucleation and subsequent growth in GST, growth of the surrounding crystalline edge in AIST.9 The amorphous marks in AIST films are more sharply defined along the crystal boundary, resulting in higher stability at elevated temperatures, lower jitter, and faster crystallization than in GST.9 Crystallization is the rate-limiting step in a write/erase cycle, and the addition of small amounts of Ag and In to SbTe alloys increases both crystallization temperature8,10 and thermal stability.11

The liquid structures of phase change materials12 are crucial to amorphization and crystallization. The former results from quenching the liquid and the latter via an undercooled liquid state, but little is known about the structures involved. Here we perform DF calculations with molecular dynamics (MD) to study liquid Ag3.5In3.5Sb75.0Te17.7, which has been investigated previously below the melting point,8,13 and compare the results with HEXRD measurements.14 DF calculations are particularly valuable in AIST alloys, because the atomic radii (and bond lengths) and atomic numbers (47–52) of the components are similar. X-ray scattering methods do not discriminate well between them, and the neutron scattering lengths of Ag, Sb, and Te differ by less than 10 %.15

Combined MD/DF calculations5 were performed with the CPMD package,16 using the PBEsol approximation17 for the exchange-correlation energy. The initial structure contained 640 atoms (23 Ag, 25 In, 480 Sb, and 112 Te) distributed randomly in a cubic cell (size 27.087 Å) appropriate to the density of the liquid (0.032 20 atoms/Å3).18 The 4d levels in Ag and In are relatively shallow and must be included in the “valence” configuration. Convergence of the calculation then requires a higher kinetic energy cutoff of the plane wave basis (60 Ry) than used in our work on GST alloys (20

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the phase change mechanism. The calculated structure factor $S(Q)$ and the total pair distribution function (PDF) $g(r)$ were determined from 13 snapshots of structures taken at 850 K. The agreement between theory and the XRD data is very good for $S(Q)$ [Fig. 2(a)] and $g(r)$ [Fig. 2(b)]. The minor deviations in $g(r)$ near the first peak (maxima at 2.94 and 3.02 Å, respectively) and the second maximum at 4.2 Å suggest that the calculated coordination numbers may be slightly larger than the experimental estimates. Seven partial PDFs $g_{ij}(r)$ are shown in Fig. 3. Ag–Ag, Ag–In, and In–In PDF are given in the SI, where we also tabulate the dependence of coordination number on the choice of cutoff.

As in $\ell$-GST, there are signs of medium-range order and very few Te–Te contacts. Bonds between In and Sb/Te are longer (by 0.2–0.3 Å) than bonds between Ag and Sb/Te, and the first broad peak in the In PDF extends beyond 4 Å. Both minority (dopant) atoms Ag and In prefer Te neighbors over Sb, a behavior also observed in EXAFS measurements of amorphous Ag$_3$In$_3$Sb$_6$Te$_3$. However, the effect on total coordination is countered by the much higher Sb concentration. There are very few bonds among minority atoms Ag and In (Ag–Ag, Ag–In, and In–In). The total coordination numbers (Table I) indicate that Ag and In increase the overall coordination, and they tend to form bond angles of 90° when associated with Te. Te atoms also enhance the octahedral character around Sb, including some nearly linear Te–Sb–Te configurations ($\approx 180^\circ$).

DF calculations lead to electron density distributions and to energy eigenvalues that reflect the underlying band structure. The calculated density of states of the valence electrons (Fig. 4) shows Sb/Te $\sigma$- and $\pi$-bands separated by a gap at $-6.5$ eV, and there are contributions from the minority atoms at $-14.5$ (In 4$d$) and $-4.5$ eV (Ag 4$d$ and In 5$s$). The In 4$d$ orbital is close to the $\sigma$-band (Sh/Te) starting at $-13$ eV, which justifies our assignment of the 4$d$ levels of Ag and In as valence electrons. There is neither a band gap nor a pronounced minimum at the Fermi energy, although band gaps

![Figure 2](image2.png)

**FIG. 2.** (Color online) (a) Structure factor $S(Q)$ in $\ell$-AIST. (b) Total PDF $g(r)$ (XRD weights). Red (gray, oscillating at low r): XRD (862 K), using $Q_{\text{max}}=25$ Å$^{-1}$ in the Fourier transform, blue (black): present simulation (850 K).

![Figure 3](image3.png)

**FIG. 3.** (Color online) Partial PDF in AIST at 850 K. Black: Sb–Sb, blue: Sb–Te, and red: Te–Te. Inset: Ag–Sb, Ag–Te, In–Sb, and In–Te.

**TABLE I.** Coordination numbers $n_x$ (cutoff 3.3–3.5 Å, see SI), bond distances with Sb ($r_{x-Sb}$), effective charges $q_{eff}$ and corresponding atomic volumes $v_{at}$, and diffusion constants $D$. Standard deviations in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>$n_x$</th>
<th>$r_{x-Sb}$ (Å)</th>
<th>$q_{eff}$ (e)</th>
<th>$v_{at}$ (Å$^3$)</th>
<th>$D$ ($1 \times 10^{-5}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>5.5</td>
<td>2.88</td>
<td>-0.35 (0.18)</td>
<td>27.5 (1.8)</td>
<td>7.330 (0.006)</td>
</tr>
<tr>
<td>In</td>
<td>5.4</td>
<td>3.15</td>
<td>+0.09 (0.23)</td>
<td>32.3 (2.3)</td>
<td>4.295 (0.004)</td>
</tr>
<tr>
<td>Sb</td>
<td>4.3</td>
<td>3.00</td>
<td>+0.04 (0.08)</td>
<td>30.7 (2.1)</td>
<td>4.122 (0.001)</td>
</tr>
<tr>
<td>Te</td>
<td>3.6</td>
<td>3.02</td>
<td>+0.11 (0.03)</td>
<td>32.8 (2.2)</td>
<td>4.806 (0.002)</td>
</tr>
</tbody>
</table>
are commonly underestimated by DF calculations. The charges on the ions (Table I) are close to those of the constituent atoms: only the Ag anion differs significantly, and In is an electron donor.

The time-dependence of the mean square displacements of the elements leads to the diffusion constants $D$ in Table I. The enhanced mobility of Ag atoms is also evident in the angular distributions, where Ag has a wide variety of configurations. The vibrational density of states of the liquid shows little structure, apart from a broad peak at $\sim 14.5$ eV. Vertical dashed line: Fermi energy.

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14T. Usuki, personal communication.
18The density of Sb$_{66}$Te$_{29}$ [K. J. Singh, R. Satoh, and Y. Tsuchiya, J. Phys. Soc. Jpn. 72, 2546 (2003)] was adjusted for the sizes of Ag and In, and the energetics checked with short MD sequences at 850 K at different volumes. This density is close to the measured value of Ag$_{1.103}$Sb$_{2.4}$Te$_{10.6}$ at 830 K [T. Matsunaga and N. Yamada, Jpn. J. Appl. Phys., Part 1 43, 4704 (2004)].