Ab Initio Study of the Mechanical, Electronic, Thermal and Optical Properties of $\text{Ge}_2\text{Sb}_2\text{Te}_5$

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Outline

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• Methods and Calculations
• Discussion
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Introduction

Chalcogenide alloys \((\text{GeTe})_m(\text{SbTe})_n\)

Reversible switching between crystalline and amorphous states

Optical data storage: DVD

Electronic non-volatile memory: PCM
**Ge$_2$Sb$_2$Te$_5$ (GST)** most widely applied and studied

Excellent and fast transition between crystalline and amorphous states (~50 ns)

Subject of this first principles study
Large difference in properties between the two phases (crystal - metallic amorphous - semiconducting)

Reflectivity changes by 30%: DVD

Resistivity changes by 3 orders of magnitude: PCM

Transition induced by heating (joule or laser irradiation)

Two-state system: possibility of storing a “0” or a “1” bit
Schematic of PCM cell

- Active region: a small drop within GST film undergoes the phase transition

- Heating via Joule effect

Concept first proposed by Ovshinsky in 1968

Despite phase change materials being functional and commercially available, many of their fundamental properties are not yet fully understood and are still the subject of intense debate.

Calculation of the structural, electronic, optical and thermal properties of crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$ from first principles
PCMs faster with better scalability than flash

April 2010

Numonix (now bought by micron) commercialized 90 nm PCM device. Research center based in Agrate Brianza (Milano-Italy)

April 2011

First mobile phone with PCM inside commercialized by Sumsung

July 2012

Micron: 45 nm PCM devices produced
Methods and Calculations

Two crystalline phases: hexagonal and face-centered cubic (rock salt-like)

Hexagonal Phase

P-3m1 symmetry and 9 atoms per unit cell stacked in 9 layers along the c-axis in the sequence:

Te - Ge - Te - Sb - Te - Te - Sb - Te - Ge

Rock salt-like phase

Approximated by an equivalent hexagonal lattice

Atoms stacked along the c-axis ([111] direction in fcc) in the sequence: Te-Ge-Te-Sb-Te-v-Te-Sb-Te-Ge repeated 3 times, where v denotes vacancy

27 atoms per unit cell

Calculations performed within the framework of DFT as implemented in Quantum ESPRESSO package with $E_{xc}$ in the LDA of Perdew and Zunger (PZ) and norm-conserving pseudo-potentials.

In generating the pseudo-potentials, only the Ge 4s$^2$4p$^2$, Sb 5s$^2$5p$^3$ and Te 5s$^2$5p$^4$ orbitals were considered for the valence states.

A kinetic energy cutoff of 50 Ry was used for both hexagonal and rock salt-like GST.

Brillouin zone integration was performed over an 8×8×2 Monkhorst-Pack mesh for both hexagonal and rock salt-like GST.
Discussion

Energy versus volume data fitted to Murnaghan EOS

Large % deviations between theoretical and experimental lattice constants

Exclusion of Te 4d orbitals from valence states


<table>
<thead>
<tr>
<th></th>
<th>This Study</th>
<th>Experiment</th>
<th>Others</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td><strong>Hexagonal GST</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>7.81</td>
<td>8.034\textsuperscript{a}</td>
<td>8.091\textsuperscript{c}, 8.072\textsuperscript{e}</td>
<td>2.8%</td>
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<tr>
<td>c</td>
<td>31.38</td>
<td>32.647\textsuperscript{a}</td>
<td>32.722\textsuperscript{c}, 33.819\textsuperscript{e}</td>
<td>3.9%</td>
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<tr>
<td>c/a</td>
<td>4.02</td>
<td>4.064\textsuperscript{a}</td>
<td>4.044\textsuperscript{c}, 4.19\textsuperscript{e}</td>
<td>1.1%</td>
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<tr>
<td>$V_0$</td>
<td>1720.30</td>
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<td></td>
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<tr>
<td>$B_0$</td>
<td>50.5</td>
<td></td>
<td>44\textsuperscript{g}</td>
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</tr>
<tr>
<td>$B'_0$</td>
<td>6.21</td>
<td></td>
<td>4\textsuperscript{g}</td>
<td></td>
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</tbody>
</table>

|                |            |            |                    |       |
| **Cubic GST**  |            |            |                    |       |
| a              | 7.80       | 8.053\textsuperscript{b} | 8.11\textsuperscript{d}, 8.072\textsuperscript{f} | 3.1%  |
| c              | 95.64      | 98.544\textsuperscript{b} | 100.38\textsuperscript{d}, 104.121\textsuperscript{f} | 2.9%  |
| c/a            | 12.26      | 12.237\textsuperscript{b} | 12.38\textsuperscript{d}, 12.899\textsuperscript{f} | 0.19% |
| $V_0$          | 5190.92    |            |                    |       |
| $B_0$          | 55.3       |            | 39\textsuperscript{e}    |       |
| $B'_0$         | 4.74       |            | 4\textsuperscript{g}      |       |
Fitted energy versus volume curves

Hexagonal GST slightly more stable than rock salt-like GST?
Phonon dispersion: Density Functional Perturbation Theory (DFPT)

Hexagonal GST
+ve frequencies: dynamically stable

Cubic GST
-ve frequencies: dynamically unstable
Isochoric heat capacity: calculated within the framework of the Quasi-Harmonic Approximation

Heat capacity is larger than the classical Dulong-Petit limit in the high-temperature region

Attributed to chemical disorder and point defects

Electronic Band Structure at Ground-State Conditions

Hexagonal GST: Behaves like a semi-metal.

Cubic GST: No band gap measured.
DFT is known to underestimate the electronic band gap

Electronic band gap is also a function of lattice constants

Hexagonal GST  
Cubic GST
Optical absorption spectra: Time Dependent Density Functional Theory (TDDFT)

Hexagonal GST
First main absorption peak at 0.475743 eV

Cubic GST
First absorption peak at eV 0.689834 eV

Response charge density

Indicates where in space absorption takes place

Localized in the subsystem where absorption is happening

Absorption peaks are the result of contributions from the subsystems

Rock salt-like GST

Hexagonal GST
The End
Acknowledgements