Evidence of Self-organization in photonic materials - the case of As-S glasses

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## Periodic Table for Chalcogen Based Glasses

<table>
<thead>
<tr>
<th></th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>CN</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>CN</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
</tbody>
</table>

| CN  | 4  | 3  | 2  | 1   |

| CN  | \(s^2p^2\) | \(s^2p^3\) | \(s^2p^4\) | \(s^2p^5\) |
Applications of Chalcogenide Glasses

Schematic of dual layer blu-ray disc rewritable (50GB)

Active element is chalcogenide based phase change material (PCM). Writing: melting the PCM around followed by a rapid quench of a few nanoseconds; Erasing: heated to lower T for a duration of tens of nanoseconds.

* Friso Jedema, nature mater. 6, 90 (2007); Jochen Hellmig et. el., JJAP, 42, 848 (2003).
Applications of Chalcogenide Glasses

- AgInSbTe (CD-RW), GeSbTe (DVD-RAM, DVD-RW, DVR blue), SbTe (DVR blue), SbSe, InSe, InSbSe, InSbTe, GeSbSe, GeSbTeSe, AgInSbSeTe;
- Speed 100 Mbit/s or higher. (8x DVD, or 4x Blu-ray)

Figure adapted from Friso Jedema, nature mater. 6, 90 (2007).
Applications of Chalcogenide Glasses

- Phase-change memory – aimed to replace flash drive and PC memory.
- Can be "switched" between two states, **crystalline** and **amorphous**, with the application of heat.
- Fast (5ns), high density (3nm).

Recent versions by Intel can achieve two additional distinct states, effectively doubling its storage capacity (fragmented network, fully polymerized, partial-crystallized, crystalline ??)

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Applications of Chalcogenide Glasses

\[ P = \varepsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots \right) \]

- Nonlinearity, High \( \chi^{(3)} \) \( \rightarrow \) Kerr effect (for all-optical switching, etc.)
- \( \chi^{(2)} \) \( \rightarrow \) Second order linearity is absent in glasses in the electric-dipole approach. (no efficient second harmonic generation)
- But there are other contribution to the second-order nonlinear polarization: higher-order terms, such as quadrupole, magnetic dipole, and surface (core-cladding interface in optical fibers)
- In many chalcogenide glass systems: As-S, As-Se, As-S-Se, Ge-As-Se, Ge-As-S, etc.
Glass Transitions and structures

- Narrow $T_g$s with symmetric non-reversing enthalpies ($\Delta H_{nr}$) that age: Flexible structures.
- Reversing $T_g$ profiles ($\Delta H_{nr} \sim 0$) that do not age: Marginally rigid structures. Here we have networks that display dynamic reversibility.
- Wide $T_g$s with asymmetric $\Delta H_{nr}$ profiles that age: Rigid but stressed structures.

“Elastic Flexibility or Rigidity captures functionality of network behavior”
Bond strength scaling of $T_g$ usually occurs when network connectivity are similar. *Ge-P-Se* and *Ge-P-S*
Network packing and free volume

![Graph showing the relationship between As-fraction and VM (cm^3). The graph includes lines for As_x Se_{1-x} glass, g-As_x S_{1-x} (exp.), g-As_x S_{1-x} (predicted), c-As_2 S_3, and c-As_2 Se_3. Key points indicate 10% reduction in glass and 15% reduction in crystal.]
Modulated DSC on $\text{As}_x\text{S}_{1-x}$ glasses

For $x=15\%$:
- $T_g = 35^\circ\text{C}$
- $T_m = 139^\circ\text{C}$
- $\Delta C_p = 37 \text{ mcal/g}^\circ\text{C}$
- $\Delta C_p_{x} = 16 \text{ mcal/g}^\circ\text{C}$

For $x=10\%$:
- $T_g = 60^\circ\text{C}$
- $T_m = 148^\circ\text{C}$
- $\Delta C_p = 32 \text{ mcal/g}^\circ\text{C}$
- $\Delta C_p_{x} = 16 \text{ mcal/g}^\circ\text{C}$

For Pure S:
- $T_m = 117.95^\circ\text{C}$
- $3.26 \text{ cal/g}$ or $3.5 \text{ kJ/mol}$
- $12.8 \text{ cal/g}$ or $13.7 \text{ kJ/mol}$

Heat Flow (cal/g°C)

$T(\circ\text{C})$
Reversibility windows in \( \text{As-S} \) and \( \text{As-Se} \) glasses compared.
First principles (DFT) cluster calculations by Dr. Jackson

(i) the symmetric and asymmetric stretch of PYR units have nearly the same frequency;
(ii) such is not the case for QT units;
(iii) One expects a high frequency mode corresponding to the As=S stretch.

$T_g(x)$ change little in the RW where we have largely a connected backbone, and few $S_8$.

One observes a reversibility window in the $22.5% < x < 29.5%$ range.

One observes a local minimum in molar volumes in the reversibility window.
Concluding Remarks

- Reversibility windows in chalcogenides can be reconciled in terms of four isostatic local structures; Group V based PYR and QT units and group IV based CS and ES units.

- Group V- sulfides represent examples in which $S_n$ chain fragments usually demix from the backbone. Sulfide glasses are usually not fully polymerized.

- Compositional trends in $T_g$ and molar volumes, in addition to the $\Delta H_{nr}$ term provide crucial insights in network connectivity of chalcogenides.
$Ge_xP_xSe_{1-2x}$ glasses
