CHALCOGENIDE GLASSES: TRANSFORMATION AND CHANGE

Stephen Elliott
Department of Chemistry
University of Cambridge

sre1@cam.ac.uk

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Chalcogenides

• What are they?

• Why are they interesting?

• Photo-induced (c-c, a-c, a-a) transformations

• Some applications
Chalcogenide glasses

- Chalcogen – Gp. VI element: \{O\}, S, Se, Te, \{Po\}

- Chalcogenide – alloy of chalcogen & Gps. III, IV, V, VII…
  - eg As$_2$S$_3$, GeSe$_2$, Ge$_2$Sb$_2$Te$_5$ etc

- but glass-forming over wide composition ranges
Chalcogens: Electronic structure

Atomic coordination of chalcogens is generally 2-fold: 2 $p$-$\sigma$ bonds

-although 3-fold coordination is also possible using *dative* bonds involving $p$-$\pi$ lone-pair states
Chalcogenide glasses: Electronic structure

NB 1) Electronic structure of binary, etc, chalcogenide glasses is very similar to that of pure chalcogens: ‘LP semiconductors’

2) Electronic structure of glasses is very similar to crystals (very similar short-range atomic structures)
Atomic coordination of chalcogenide glasses: ‘8-N Rule’ \((N = \text{no. of valence electrons})\)

- **Chalcogens** ({O}, S, Se) \(= 2\) \((N = 6)\)
  
  (Te) \(= 2\) (3 dative)

- **Pnictogens** (P, As, Sb) \(= 3\) \((N = 5)\)

- ‘**Tetragens**’ (Si, Ge) \(= 4\) \((N = 4)\)

- **Halogens** (Cl, Br, I) \(= 1\) \((N = 7)\)
Phillips-Thorpe constraint theory

• Assume glass structure is a continuous network satisfying CNs, \( r_i \), of constituent elements, \( i \):
  - average CN = \( <r> \)

• Bond-stretching constraints: \( <r>/2 \)
• Bond-bending constraints: \( 2<r> - 3 \)
• Total no. of constraints: \( N_c = \{5<r>/2\} - 3 \)
  - if equals spatial dimensionality: \( N_d = 3 \)

\[ \rightarrow i.e. \text{ critical } <r_{cr}> = 12/5 = 2.4 \text{ 'optimal' CN} \]
Arsenic chalcogenides

• For stoichiometry: \( \text{As}_2\text{S}_3 \),
  \[
  <r> = \frac{2 \times 3 + 3 \times 2}{5} = 2.4 = <r_{cr}>
  \]
  \(\rightarrow\) good glass former

• For stoichiometry: \( \text{As}_4\text{S}_4 \),
  \[
  <r> = \frac{4 \times 3 + 4 \times 2}{8} = 2.5 > <r_{cr}> = 2.4
  \]
  \(\rightarrow\) \( N_c = 3.25 > N_d = 3 \)
  - ‘overconstrained’ \( \textbf{if} \) in a network structure
  \(\rightarrow\) poor glass former (or another reason...)
Chalcogenide structures: Networks or molecular aggregates?

- The low values of CNs of chalcogens (2) and of pnictogens (3) mean that glass structures can be either: 2-3D networks or 0D molecular clusters (Van der Waals-bonded).

- E.g. structure of stoichiometric As$_2$S$_3$ consists of network of corner-shared AsS$_3$ pyramidal units.

- But how are As atoms distributed in As-rich glasses – (non)randomly – and in network/molecule?

- For possibilities, refer to crystals – e.g. As-S.
c-$\text{As}_2\text{S}_3$: orpiment

2D layer structure

c-axis

a-axis

b-axis
Molecular As-S species

- Molecules are approximately *spherical*

-real-life atomic model for hard-sphere systems
c-$\text{As}_4\text{S}_4$

Nb 2 As-As homopolar bonds per molecule

\[
\begin{align*}
\alpha,\beta - \text{realgar} & & \quad \text{pararealgar} \\
(\alpha,\beta \text{ different packings})
\end{align*}
\]
c-As$_4$S$_3$

Nb 3 As-As homopolar bonds per molecule

α,β-dimorphite

‘= para-realgar – S’
c-As$_4$S$_5$: uzonite

Nb 1 As-As homopolar bond per molecule

'= \alpha,\beta$-realgar + S'
Realgar-like molecular fragment in network structure

- *Ab initio* molecular-dynamics model of a-As$_2$S$_3$

Does chemical disorder – e.g. (oriented) homopolar bond) – promote quasi-molecular formation?

How to detect molecular entities?

• **Raman scattering** from vibrational modes

Cross-section is very large for ‘molecular’ modes – e.g. breathing modes

Raman shift → vibrational frequencies

Inelastic light scattering

virtual energy levels (below electronic first excited state)

excited vibrational energy levels

electronic and vibrational ground state
Raman spectra of AsS

Molecular modes

- As$_{50}$S$_{50}$ glass
- As$_4$S$_4$ melt
- $\beta$-As$_4$S$_4$
- $\alpha$-As$_4$S$_4$
Glass formation of AsS

- As$_4$S$_4$ (para-) realgar-like molecules, etc, are near-spherical

- Van der Waals interactions between molecules are spherically symmetrical
  → low-viscosity molecular melts

→ bad glass-formation ability (ambient pressure)
  (limit normally 43% As)
  (c.f. rare-gas/ Lennard-Jones systems)
Glass formation of AsS

*High-pressure* melt quenching (Brazhkin et al 2009)

![Graph showing viscosity vs. pressure](graph.png)
Molecular vs. network As-S glasses

As$_2$S$_3$ pyramid stretch modes

Molecular modes

As$_{50}$S$_{50}$ glass
Molecular character of a-As-S films

Molecular species are stable in precursor vapour for evaporated films

Nb Thermal annealing destroys molecular character → ‘network’ glass

Nemanich et al 1978
Photo-transformations in chalcogenides

Reasons why chalcogenides are photo-sensitive:

• Bandgap photons excite electrons from the top of the VB – i.e. lone-pair electrons
• Optical excitation can cause changes in weak van der Waals ‘intermolecular’ interactions
• Low atomic coordination number of chalcogens favours local structural rearrangements – without necessarily breaking covalent bonds
• Similar (~octahedral 3/4-fold) coordination geometry of a-/c-phases in telluride glasses → ps/ns changes
Photo-induced c-c transformations: β-realgar $\rightarrow$ para-realgar

X-phase is intermediate, involving $\text{As}_4\text{S}_5$

Bonazzi et al 1996
Photo-induced $a$-$c$ transformation of $\text{As}_4\text{S}_4$ glass

VdW ‘bond’-breaking $\rightarrow$ molecular reorientation  
Bond-breaking $\rightarrow$ molecular reforming

α,β-realgar

para-realgar

S Samulski
Chalcogenide glasses: Semiconductors

Bandgaps, $E_g$, range from <1eV to >3eV:
- $E_g$ of chalcogenides is in order: Te < Se < S << O

Optical absorption

Mott & Davis 1979

As$_2$Te$_3$  As$_2$Se$_3$  As$_2$S$_3$
Photo-induced a-a phenomena in chalcogenide glasses

- Bandgap-illumination changes can be:
  - metastable or transient
  - reversible or irreversible
  - scalar (isotropic) or vectoral (anisotropic)
  - structural
  - optical ($\Delta \alpha, \Delta n$)
  - chemical (etching rate)…..
A-a photo-induced changes

Photodarkening – redshift of optical absorption edge

Irreversible change from as-deposited state - then reversible change from annealed state to new ‘photo-state’
Photo-induced optical changes

- Refractive-index changes of $\Delta n \sim 0.1$ can be produced by bandgap illumination
- ‘direct’ laser writing (no post-processing) → ‘buried’ optical waveguides
- Or photo-induced changes in chemical-etching rate can be used to produce ‘ridge’ optical waveguides after etching
Evanescent waveguide sensor on a chip

- Chalcogenide glass (ChG) offers excellent transparency, from visible to mid-IR
- Enhance refractive-index difference ($\Delta n$) by selective etching
- Smooth the waveguide surface by thermal annealing
  (Rowlands, Su, SRE, ChemPhysChem 11, 11, 2303 (2010))

- Before etching: $\Delta n \approx 0.05$; optical loss 7dB/cm
- After etch + annealing: $\Delta n \approx 1.5$; optical loss down to 0.1dB/cm

Achieved low transmission loss for straight and bent waveguides, including 24 cm serpentine waveguide
Evanescent waveguide sensor on a chip

- Low-loss planar optical waveguide devices can be made in the lab

- Sensor on a chip can be implemented by using evanescent-wave sensing, surface-plasmon resonance (SPR) sensors, etc.

(a) Waveguide writing; (b) laser coupling via optical fibre; (c) Top view of our waveguide interferometer; (d) Output at our Y splitter; (e) Evanescent-wave sensing; (f) Sensor on a chip system
Interferometric patterning of SERS substrates

1. Write Bragg grating (parallel-line pattern)         2. Rotate sample by 90°
3. Write 2nd Bragg grating 4. Develop ‘checker-board’ image using etchant (diisopentylamine in dimethyl sulfoxide)
5. Sputter on overlying Au film to make SERS substrate
Surface-enhanced Raman scattering (SERS) substrates using chalcogenide glasses (ChG)

Spacing between features on SERS substrate can be controlled by changing $\lambda$ and $\theta$ of inscription laser


(a) and (b) are SEM images of an SERS substrate in ChG at different magnifications; (c) is the AFM image of the same SERS substrate.
Chalcogenide-resist SERS sensor

- Experiment shows that strong surface-plasmon resonances can be effectively excited on our SERS substrates at very large (grazing) angles of incidence

(a) Two-beam interference system; (b) SERS substrate; (c) SERS spectra of R6G; (d) Angle-resolved absorption spectra; (e) Cuts on map (d)  
(Su et al 2009)
Current chalcogenide research

- Phase-change materials, PCMs (eg Ge-Sb-Te)
- Non-volatile memory with DRAM-like speeds
- In-memory logic devices
- Effect of doping (e.g. N)
- Materials ‘design’ search for new, better PCMs

- *Ab initio* computer simulations + experiments
CONCLUSIONS

- Chalcogenides can exhibit a wide range of:
  - Atomic structures
  - Physical & chemical behaviour: ‘*photo-states*’
  - Applications
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