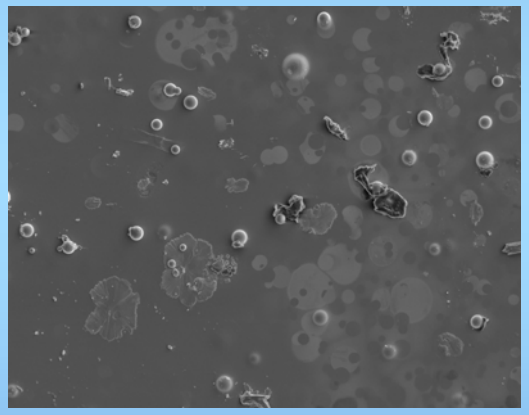
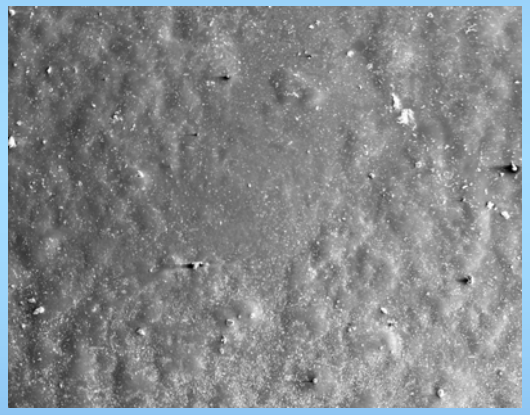
Phase Transitions in Antimony Oxychloride Glasses





Robin Orman

THE UNIVERSITY OF WARWICK

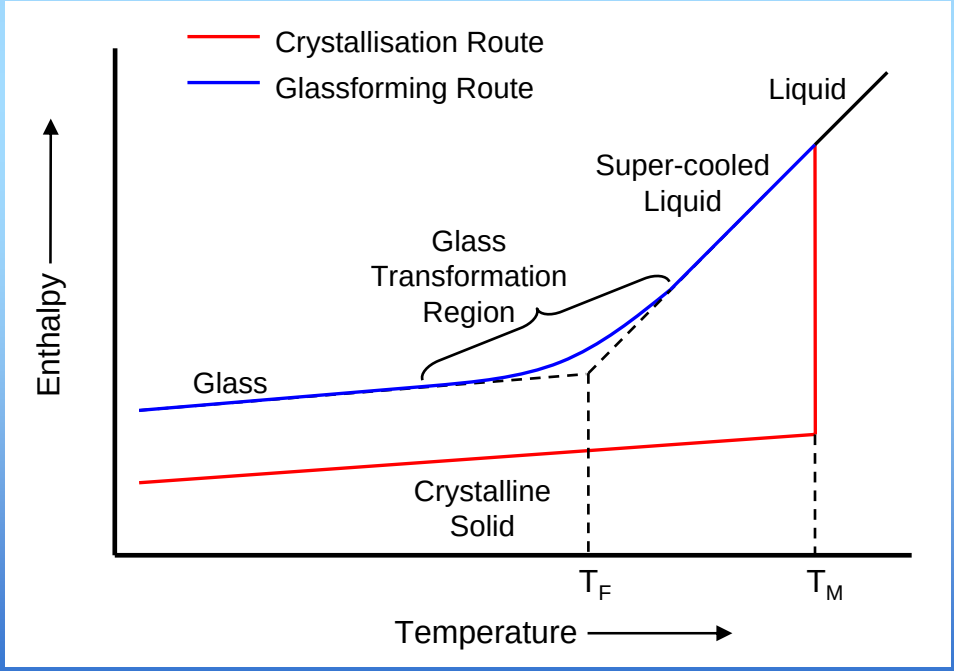
MSc Aims

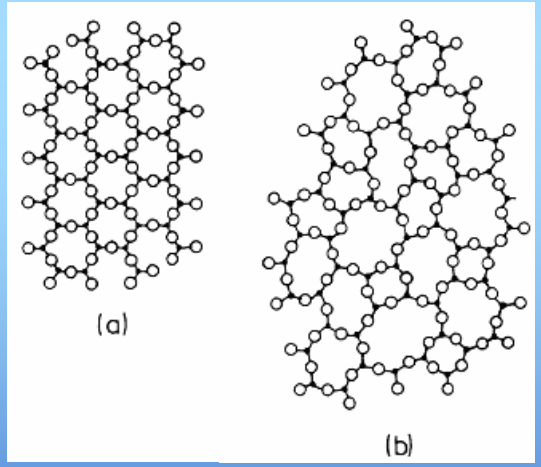
- Perform improved thermal analysis on the Sb_2O_3 polymorphs, senarmontite and valentinite, and explain the transformations observed
- Obtain Raman spectra of the oxides
- Prepare Cl-doped and H_2O-doped Sb_2O_3 glasses
- Use thermal analysis and Raman to see how the glass structures relates to those of the oxides
- Prepare and characterise the related oxychloride, onoratoite ($Sb_8O_{11}Cl_2$)

THE UNIVERSITY OF WARWICK

What is a Glass?

- A non-crystalline solid…
  - No long-range atomic arrangement
- …that experiences a ‘glass transformation region’

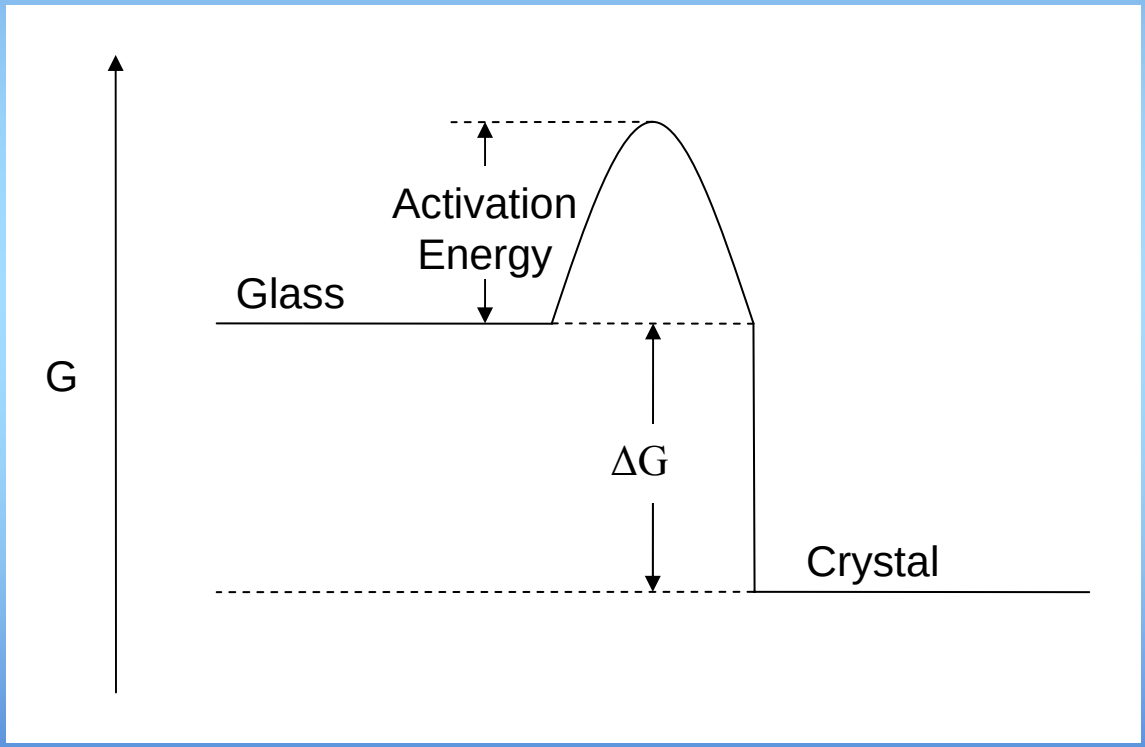




THE UNIVERSITY OF WARWICK

Glass Stability

- Glass thermodynamically less stable than a crystal
- Can prevent transformation if:
  - (a) Activation energy high
  - (b) Can cool rapidly to point where kT << activation energy



THE UNIVERSITY OF WARWICK

Glass Stability (2)

Activation energy high if:

(a) Strong directional bonds between atoms

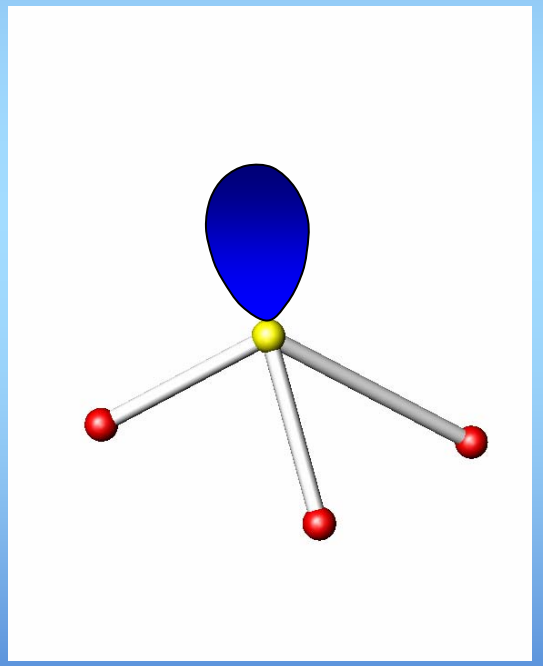
(b) Chemically complex so that atom redistribution slow

Commercial glasses based on multi-component silicates

$[SiO_4]$ - tetrahedra joined by directional Si-O-Si linkages

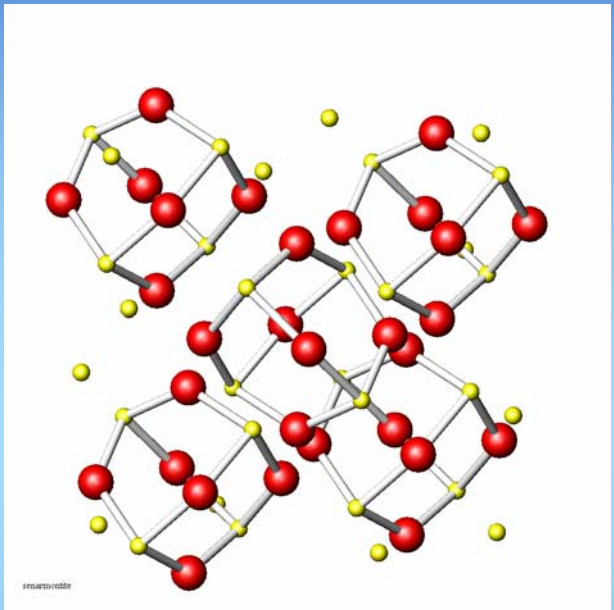
Sb_2O_3 – very simple

$[SbO_3]$ – trigonal pyramids joined by directional Sb-O-Sb linkages



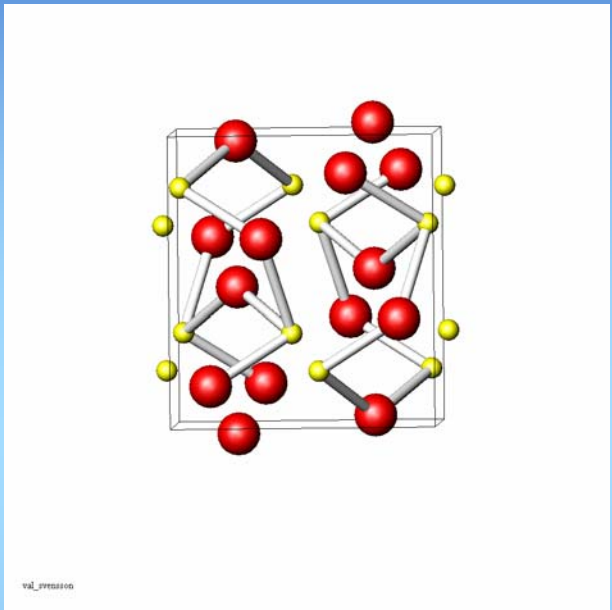
THE UNIVERSITY OF WARWICK

Crystal Structure



SENARMONTITE

Sb_4O_6 molecules in a close-packed arrangement



VALENTINITE

Double chains of $[SbO_3]$ trigonal pyramids arranged to form layers, with the lone pairs pointing into an empty layer.

THE UNIVERSITY OF WARWICK

Previous attempts

- Hasegawa et al – X-ray diffraction – interatomic distances suggest [SbO_3] pyramids, in chains, as in valentinite

  5 mol% B_2O_3 added

- Masuda et al – X-ray fluorescence – both Sb^{3+} and Sb^{5+} present

  5 mol% MO or 10 mol% M_2O

- Bednarik and Neely – infra-red [SbO_3] – trigonal pyramids similar to those in valentinite.

  2.5 mol% SiO_2

- Miller and Cody – Infra-red/Raman – 2D like v-As_2O_3

  Melted in vycor $\rightarrow$ B_2O_3 + SiO_2

- Johnson et al – neutron diffraction – [SbO_3] pyramids

  ~ 8 at% Cl present

THE UNIVERSITY OF WARWICK

Glass preparation

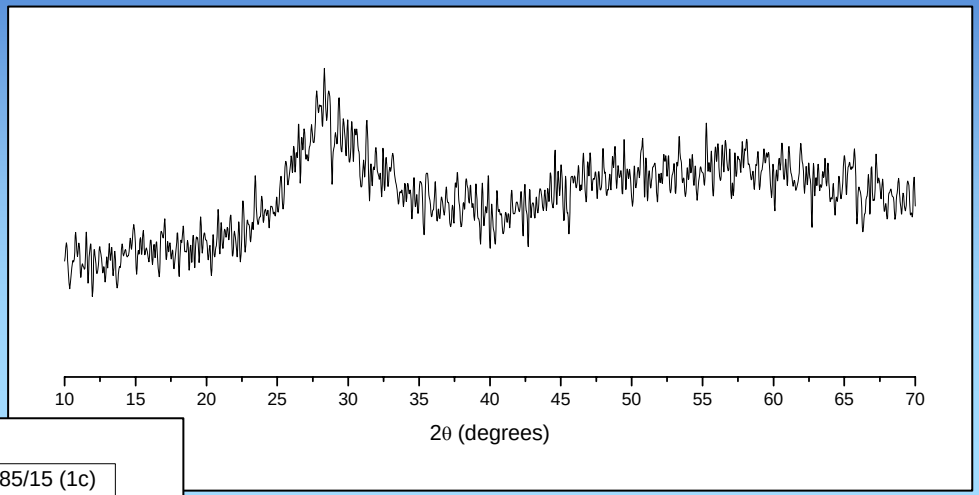
- Sb_2O_3 (99.6% Alfa Aesar), $SbCl_3$ (99% Sigma-Aldrich)
- $xSb_2O_3(1-x)SbCl_3$, x = 0.5, 0.7, 0.85

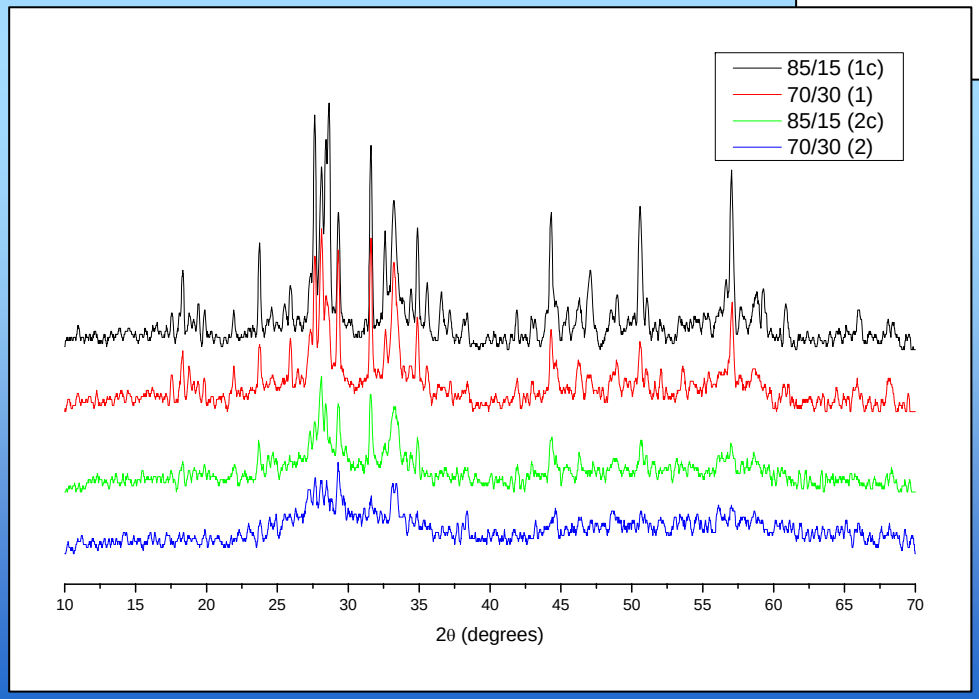
- Alumina crucible with lid
- 5-10 minutes at 1000°C
- Splat-quenched between two cooled copper plates
- x = 0.85 phase-separated

THE UNIVERSITY OF WARWICK

X-ray Diffraction

- 50/50 (x = 0.5) samples →



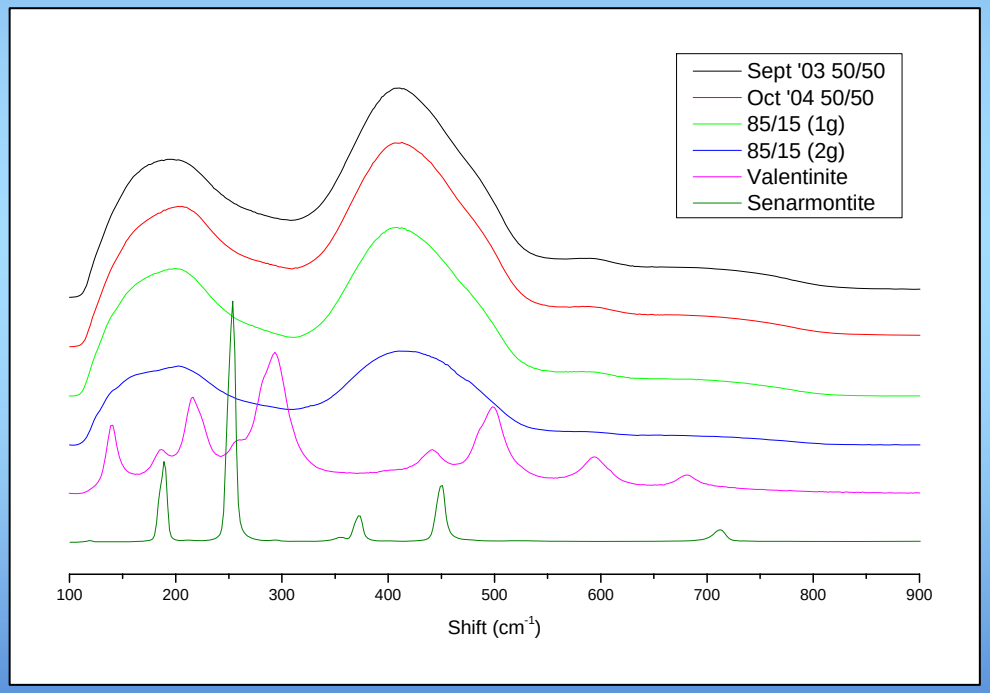


- 85/15 and 70/30 (x = 0.85, 0.7) samples ←

THE UNIVERSITY OF WARWICK

Raman Spectroscopy

- Glasses tend to give broadened Raman peaks
- Chlorine-stabilised glasses don't appear to match c-Sb_2O_3

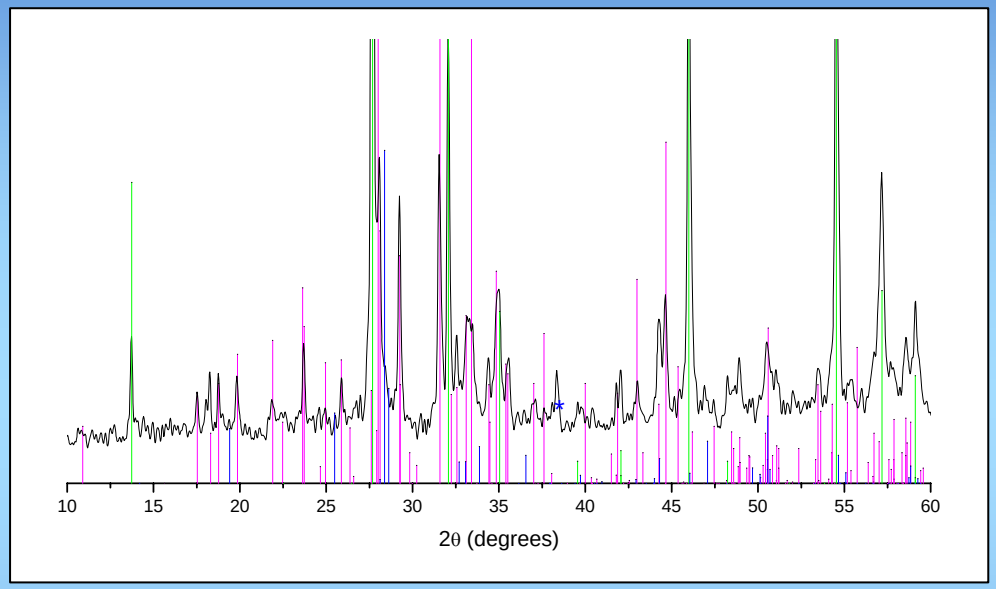


THE UNIVERSITY OF WARWICK

Glass Crystallisation

- Glass after crystallisation at 390°C
- Forms senarmontite and onoratoite, with some valentinite

•H_2O-treatment: crystallises to valentinite



Green = Senarmontite (Sb_2O_3)

Blue = Valentinite (Sb_2O_3)

Magenta = Onoratoite ($Sb_8O_{11}Cl_2$)

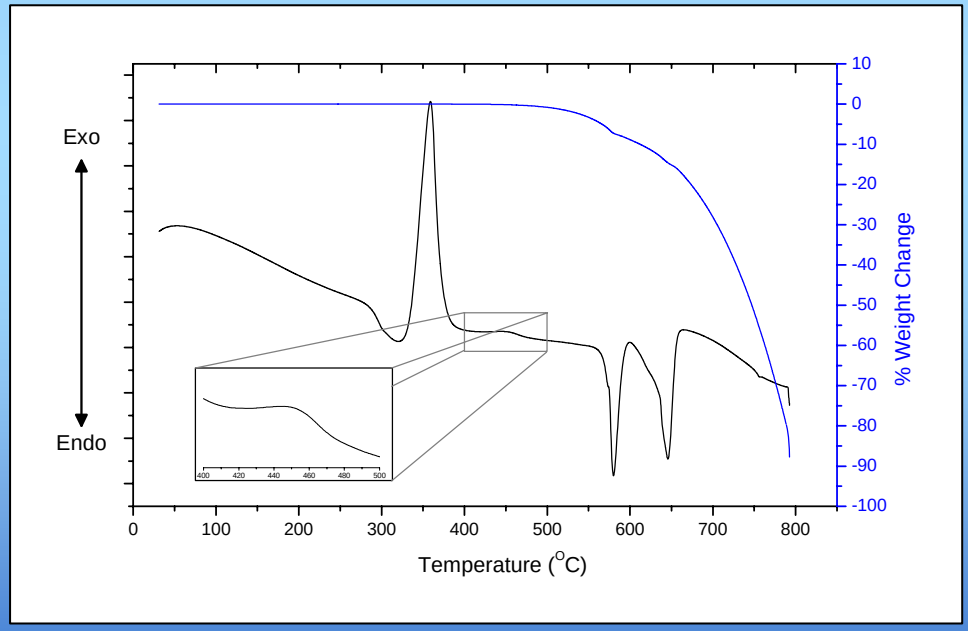
THE UNIVERSITY OF WARWICK

Thermal Analysis

- T_g = 297±3°C (85/15, 70/30)
- T_g = 286±3°C (50/50)
- T_c = 334±3°C

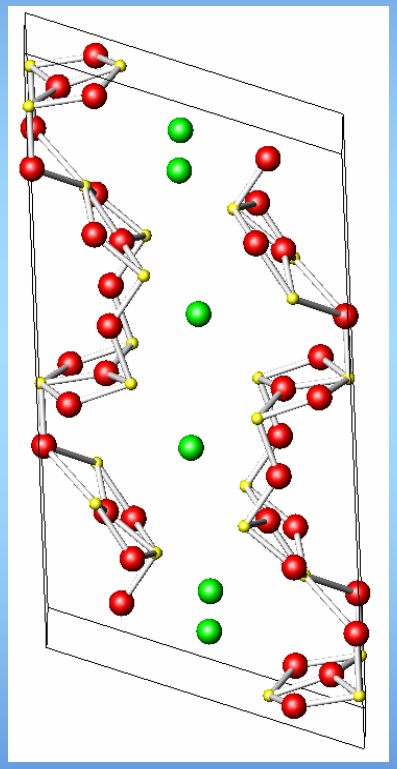
❖ Small feature: depressed valentinite-senarmontite transition

❖ Later peaks… onoratoite?

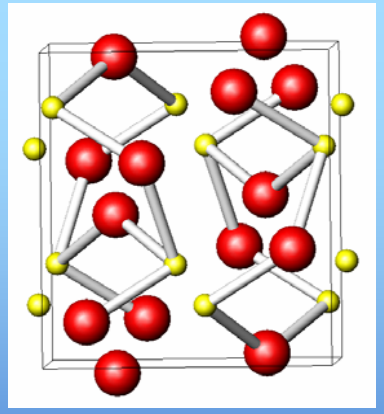


THE UNIVERSITY OF WARWICK

Onoratoite compared to Glass



Onoratoite ($Sb_8O_{11}Cl_2$)



Valentinite (Sb_2O_3)

- EDX analysis suggests chlorine content is similar to onoratoite

Sample	at.% Cl (±2.0)
85/15 (1g)	7.5
85/15 (2g)	8.2
50/50 (Sept. '03)	6.0
50/50 (Oct. '04)	6.9
Onoratoite (predicted)	9.5

THE UNIVERSITY OF WARWICK

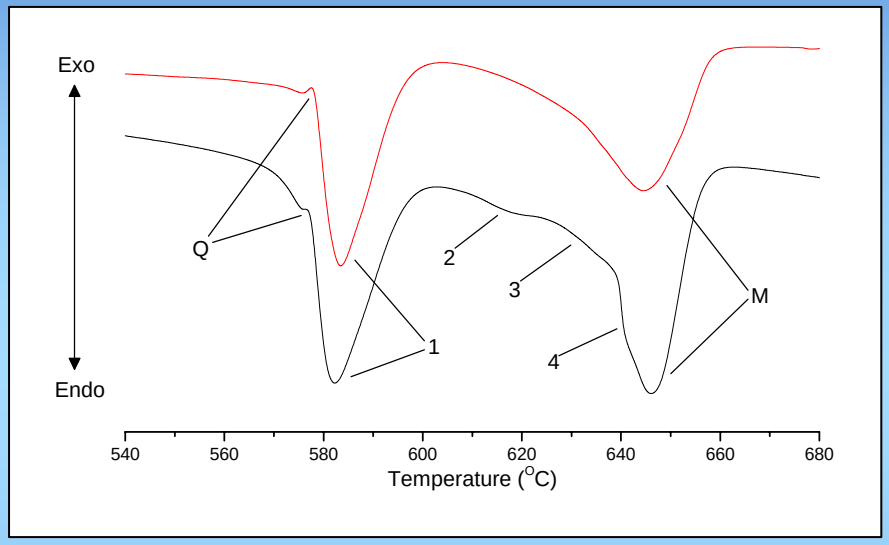
Onoratoite preparation

- $SbCl_3$ (99.6% Sigma-Aldrich)
- 20g hydrolysed in 200ml water at 35°C
- Washed with ethyl ether
- Precipitate held at 420°C under argon for 1 hour
- Based on Matsuzaki *et al.*'s prep

THE UNIVERSITY OF WARWICK

Thermal Analysis (2)

- Peak 1: Onoratoite decomposition
- Peaks 2-4: Three-stage senarmontite-valentinite transition?



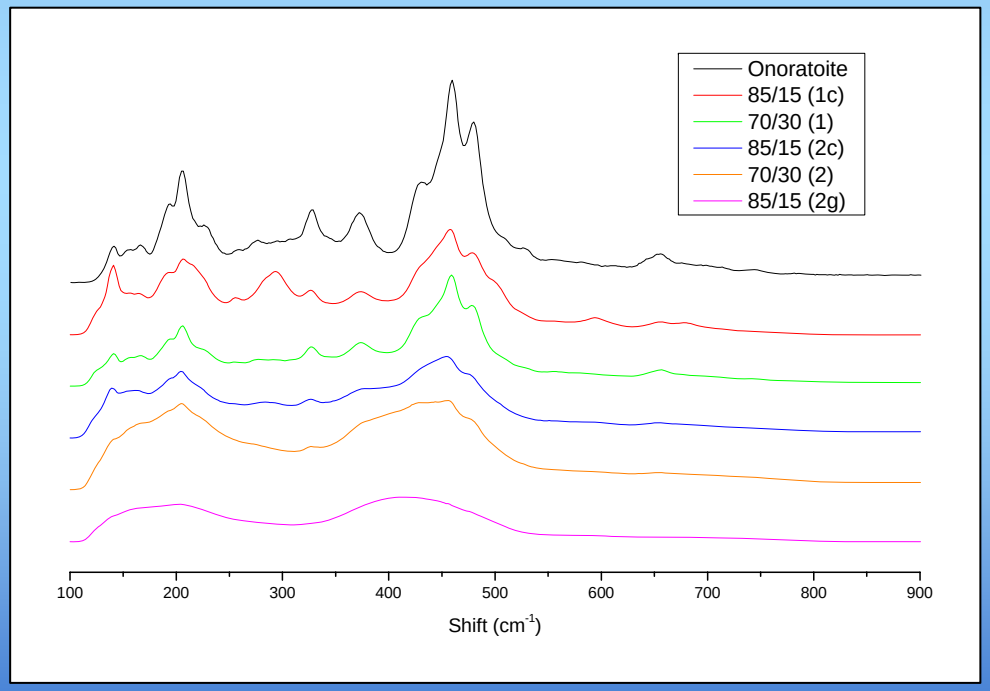
Black = Glass

Red = Onoratoite ($Sb_8O_{11}Cl_2$)

THE UNIVERSITY OF WARWICK

Raman Spectroscopy (2)

- Glass Raman spectra similar to onoratoite



Black = Onoratoite ($Sb_8O_{11}Cl_2$)

Red = 85/15 (1c) sample

Green = 70/30 (1) sample

Blue = 85/15 (2c) sample

Orange = 70/30 (2) sample

Magenta = 85/15 (2g) glass

THE UNIVERSITY OF WARWICK

Conclusions

- Glass appears to be based on onoratoite structure:
  - Crystallisation (by heating)
  - Crystallisation (by water)
  - Raman Spectroscopy
  - Chlorine content
- Subsequent transitions probably affected by the presence of chlorine?

THE UNIVERSITY OF WARWICK

Future Work

- High-temperature XRD, Raman or neutron diffraction spectroscopy to examine ‘3-stage’ transition
- Effects of water on the transitions?
- Kinetic studies using DSC techniques

THE UNIVERSITY OF WARWICK

Acknowledgements

- Dr Diane Holland
- Keith Briggs and Dave Hammond
- Ben Parkinson
- Dr Mark Newton and Robin Cruddace
- Prof Frank Berry & Xiaolin Ren at the OU

THE UNIVERSITY OF WARWICK