The Structure of Antimony Oxychloride Glass

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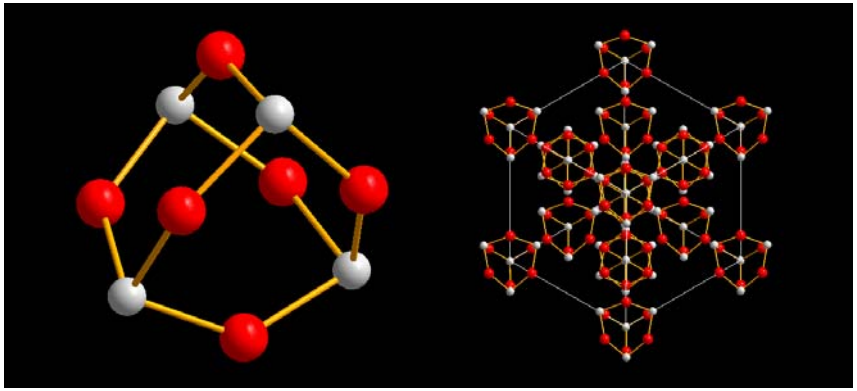
Introduction

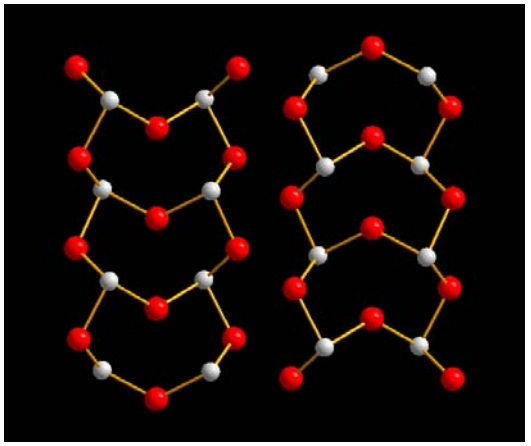
- Sb_2O_3 is a conditional glass former – there is little evidence for a pure Sb_2O_3 glass at this time.
  - Hasegawa *et al.* – 5 mol% B_2O_3 added.
  - Masuda *et al.* – 5 mol% MO or 10 mol% M_2O.
  - Bednarik and Neely – 2.5 mol% SiO_2.
  - Miller and Cody – Melted in vycor $\rightarrow$ B_2O_3 + SiO_2.
  - Johnson *et al.* – ~8 at% Cl present.
- We have continued the latter investigation into chlorine-stabilised Sb_2O_3 glasses.
- The lone pair on the antimony could lead to an interesting glass structure and possible non-linear optical properties.

Sb_2O_3 crystal structure



SENARMONTITE

Sb_4O_6 molecules in a close-packed arrangement.



VALENTINITE

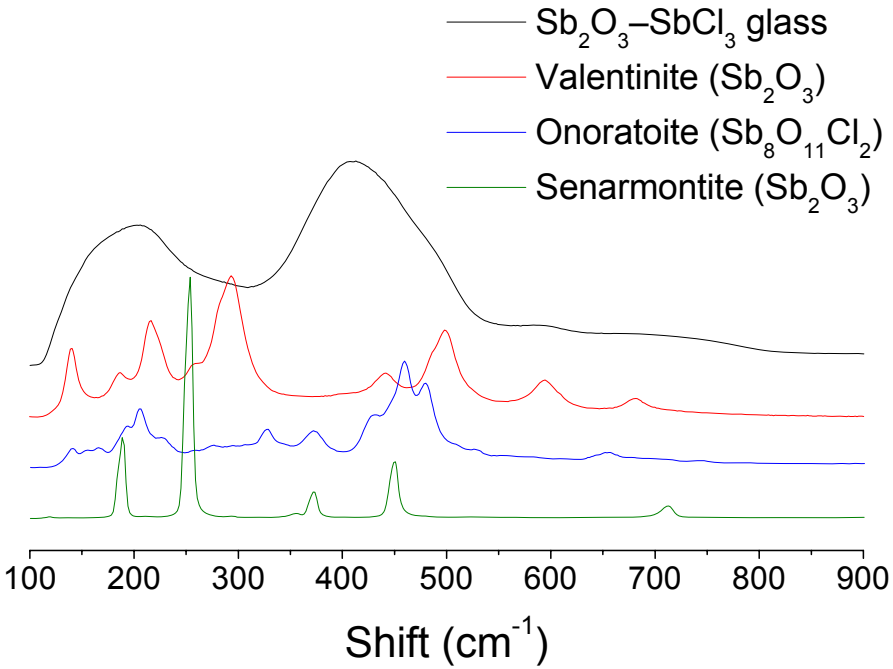
Double chains of $[SbO_3]$ trigonal pyramids arranged to form layers, with the lone pair electrons pointing into an empty layer.

Chlorine-stabilised Sb_2O_3 glass

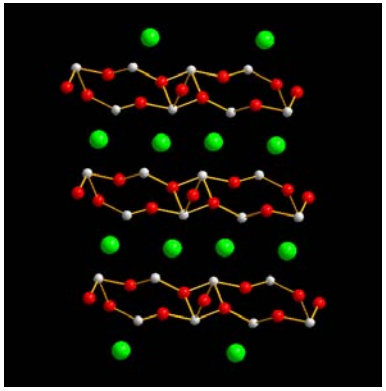
- $xSb_2O_3(1-x)SbCl_3$, x = 0.5, 0.7, 0.85.
- Alumina crucible with lid.
- 5-10 minutes at 1000°C.
- Splat-quenched between two cooled copper plates.
- x = 0.85 sample phase-separated.

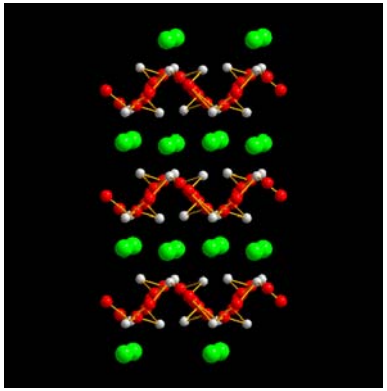
Glass analysis

- Raman spectroscopy suggests a structure based on onoratoite ($Sb_8O_{11}Cl_2$).
- The glass forms mainly onoratoite and senarmontite (α-Sb_2O_3) on crystallisation.
- EDX analysis suggests it contains a similar amount of chlorine to onoratoite.



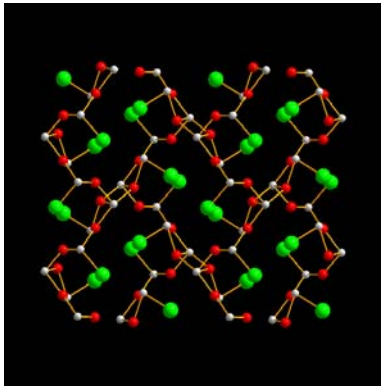
Antimony Oxychlorides

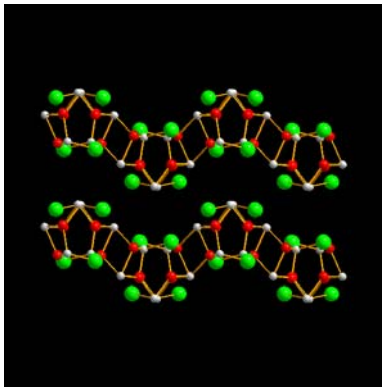




$Sb_4O_5Cl_2$

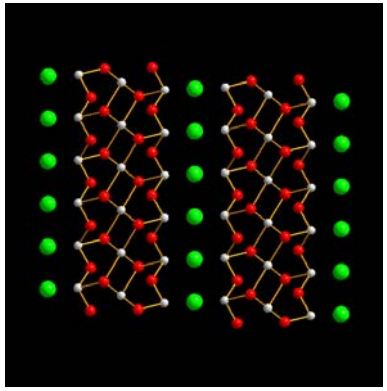
Sb–Cl = 2.9Å

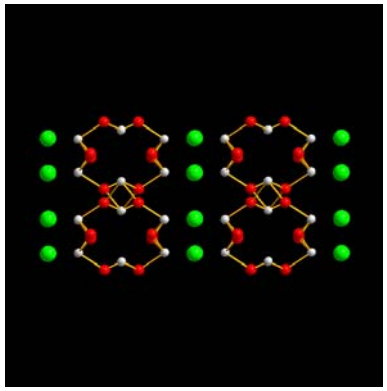




SbOCl

Sb–Cl = 2.35Å





Sb_3O_4Cl

Sb–Cl = 3.0Å

Onoratoite ($Sb_8O_{11}Cl_2$)

- The only antimony oxychloride to occur as a mineral.
- Several structural models, but generally agreed to form tubes of [SbO_4] trigonal bipyramids, interspersed with chlorine layers.
- The chlorine atoms are still unusually distant (2.9Å or more) from the closest antimony atom (Sb–Cl in $SbCl_3$ is 2.36Å).

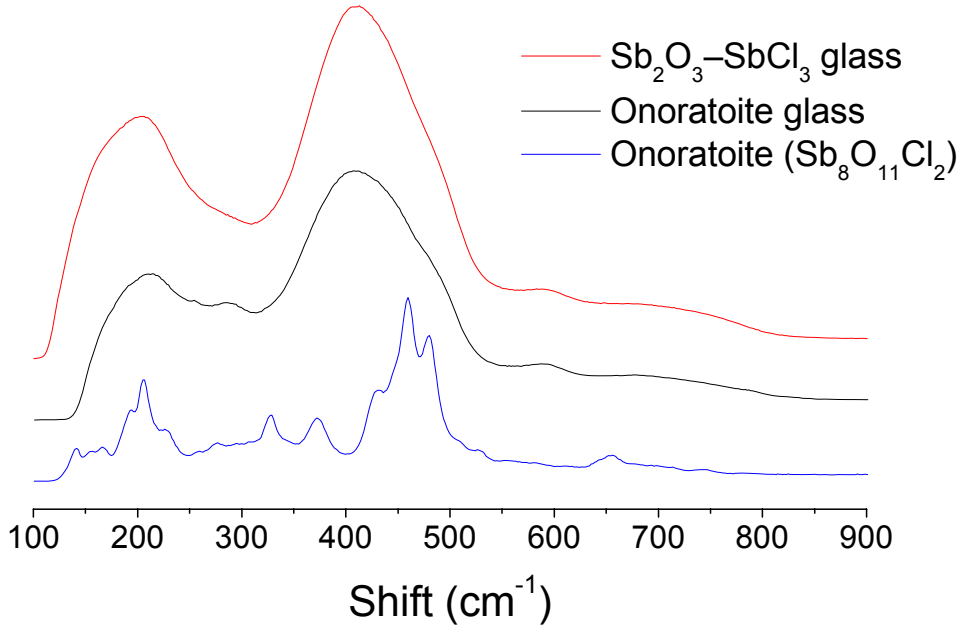
Making antimony oxychlorides[1]

- $4SbCl_3 + 5H_2O \xrightarrow{35°C} Sb_4O_5Cl_2 + 10HCl$
- $(\text{or } SbCl_3 + H_2O \xrightarrow{35°C} SbOCl + 2HCl)$
- Wash with diethyl ether and suction filter.
- Dry in an oven at 80°C.
- $(5SbOCl \xrightarrow{220°C} Sb_4O_5Cl_2 + 4SbCl_3)$
- $11Sb_4O_5Cl_2 \xrightarrow[\text{Under Argon}]{440°C} 5Sb_8O_{11}Cl_2 + 4SbCl_3$

[1] R. Matsuzaki, A. Sofue, and Y. Saeki,
Chem. Lett. **12** (1973) 1311-1314 .

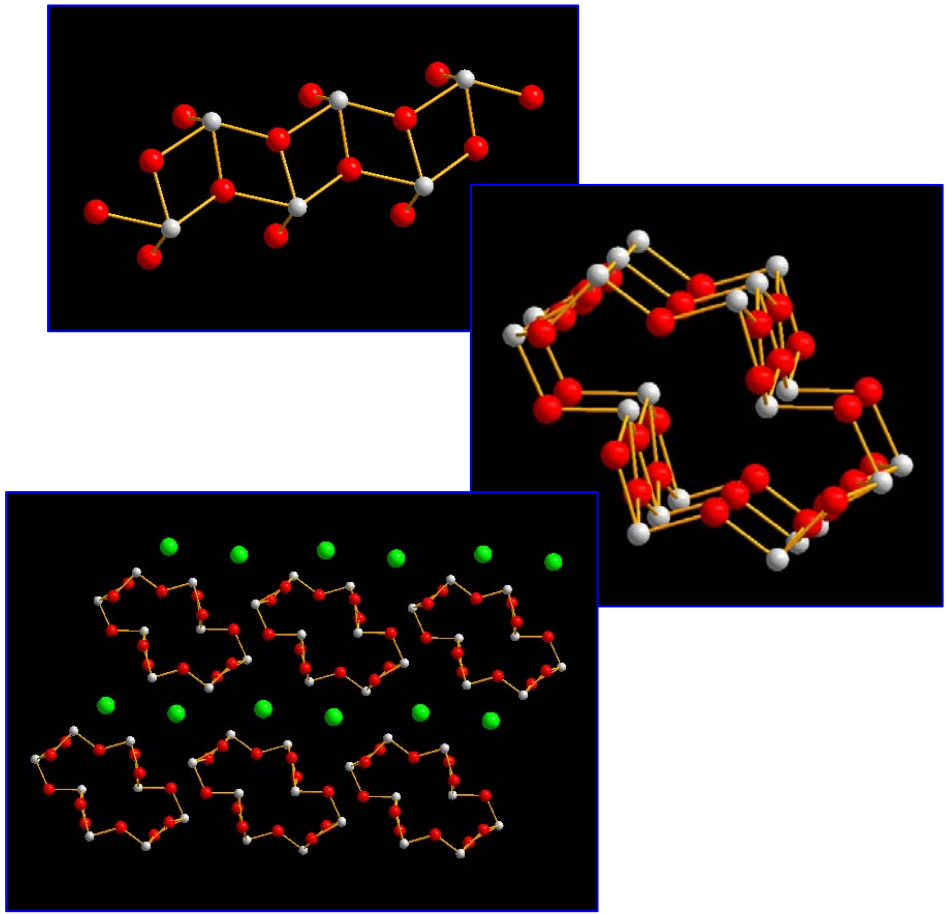
Onoratoite Glass

- Glass prepared from crystalline onoratoite.
- Melted at 1100°C in a lidded alumina crucible, then splat quenched.
- Raman spectroscopy suggests a similar structure to that of the Sb_2O_3–$SbCl_3$ glass.
- Thermal behaviour also consistent with the earlier glass.



Onoratoite: Menchetti's model[2]

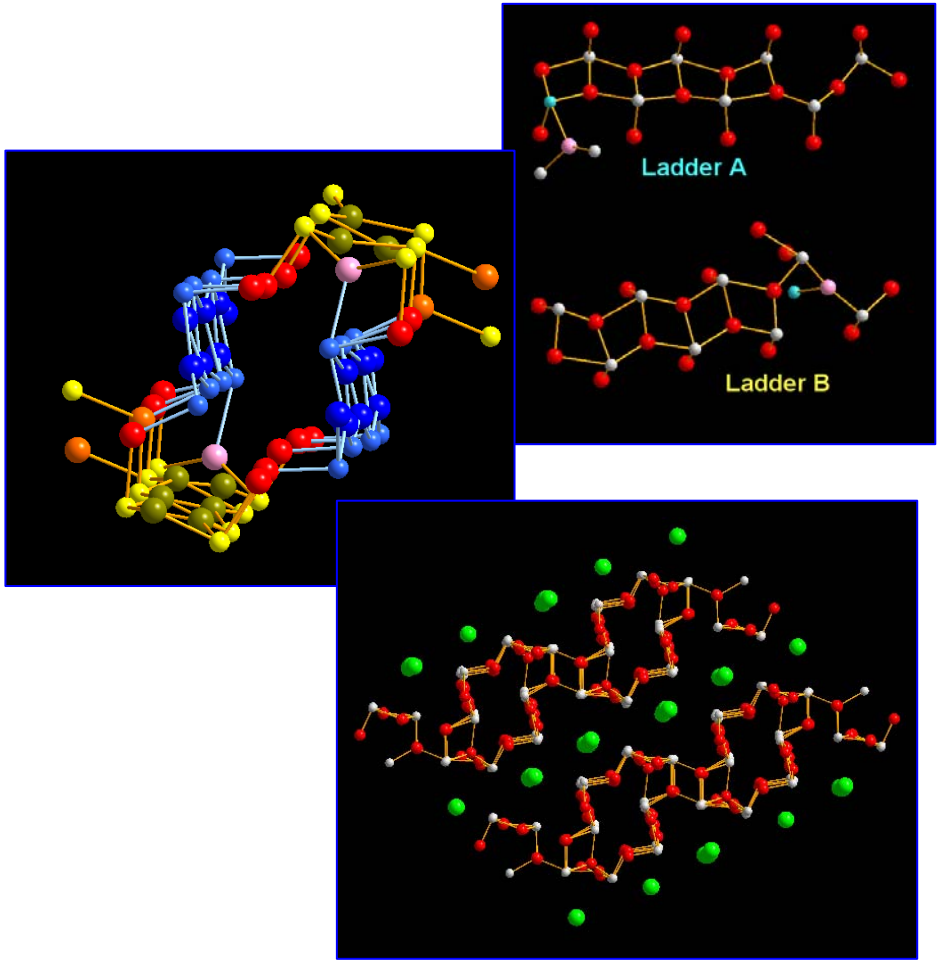
- Ladder-like chains of Sb and O linked to form tubes.
- 4 of the 6 oxygen positions are partially occupied, resulting in 3/8 Sb atoms 3-coordinated, the rest 4-coordinated.
- The resulting chemical formula is $Sb_8O_{10.54}Cl_2$
- Sb–Cl distances range from 3.2-3.8Å.
- No Sb–O links between tubes; Cl atoms the 'glue'.



[2] S. Menchetti, C. Sabelli, and R. Trosti-Ferroni, *Acta Crystallogr. C* **40** (1984) 1506-1510.

Onoratoite: Mayerová's model[3]

- Describes Menchetti's model as "an average structure of a much more complex superstructure, in which the oxygen disorder is resolved…"
- Two types of ladder chains, interrupted by [SbO_3] groups.
- 5/16 of the Sb atoms are 3-coordinated.
- Sb–Cl distances of 2.95-3.20Å
- One oxygen site forms links between the tubes.



[3] Z. Mayerová, M. Johnsson, and S. Lidin, *Solid State Sci.* **8** (2006) 849-854.

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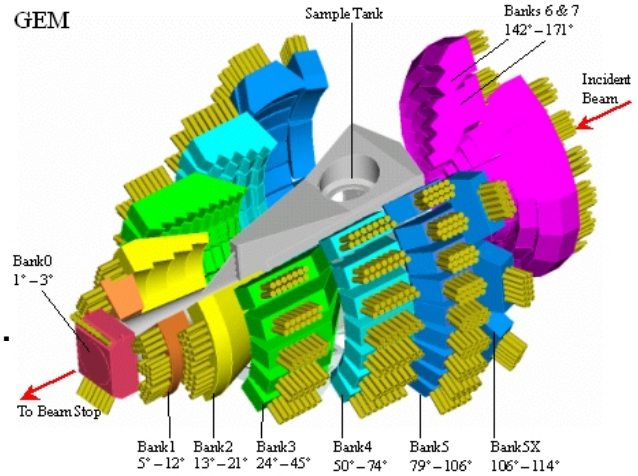
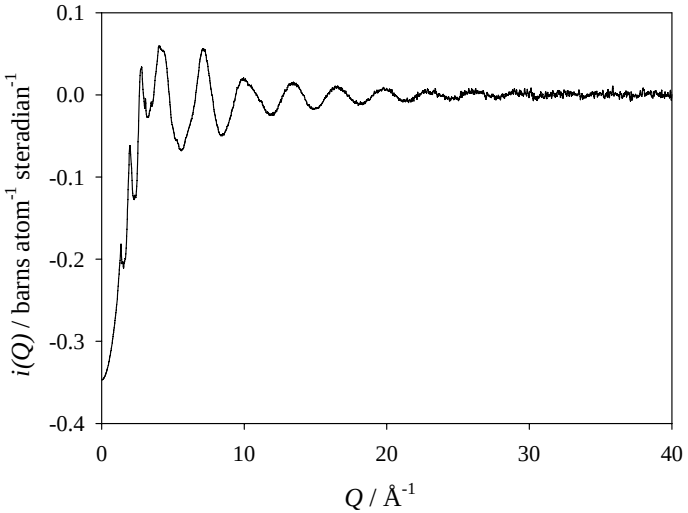
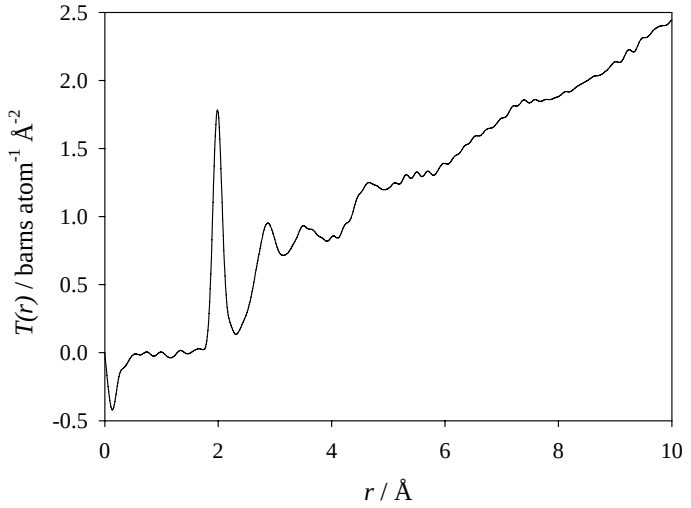
GEM

- Neutron diffraction data collected on the GEneral Materials (GEM) diffractometer at the ISIS facility.
- GEM has a large detector array that covers a large area and a wide range of scattering angles.
- Neutron diffraction will give better data on the oxygen positions than single-crystal XRD.





Fourier transform



Neutron scattering lengths

Sb = 5.57 fm O = 5.803 fm Cl = 9.577 fm

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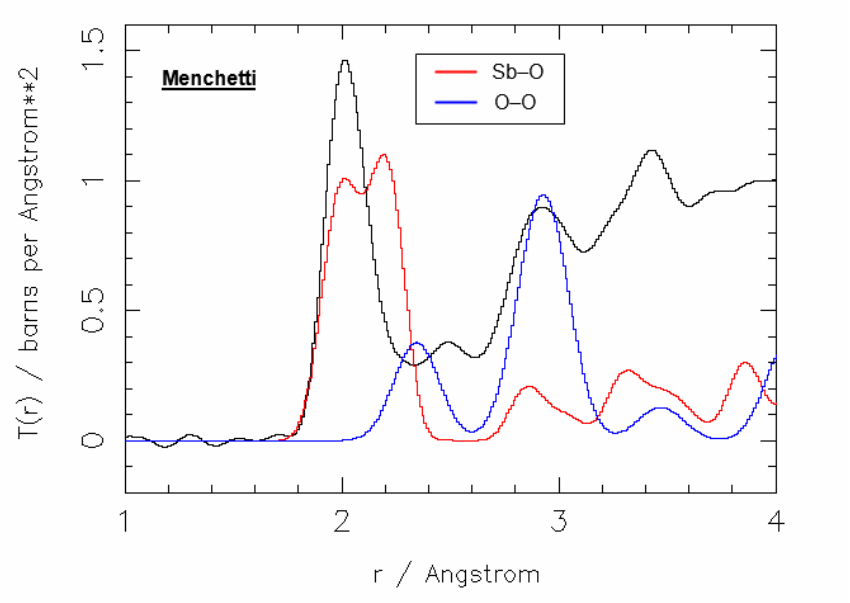
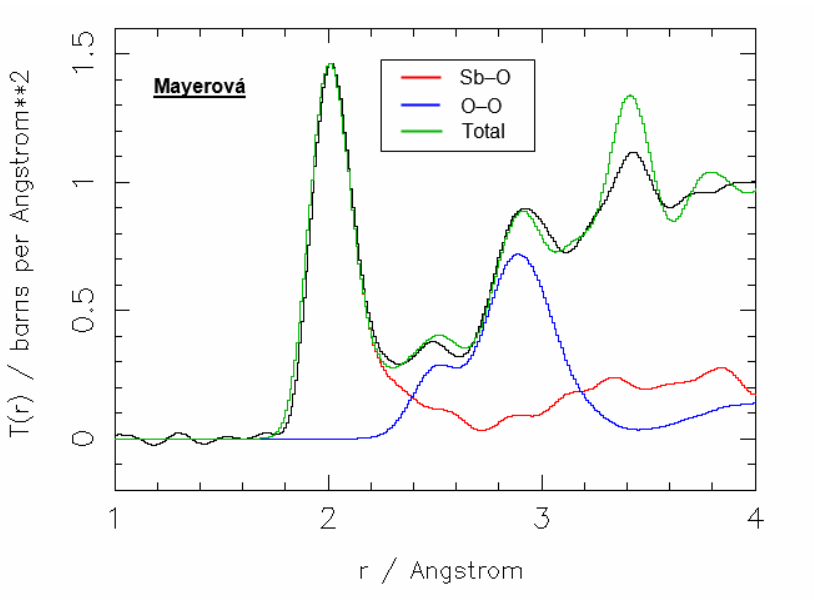
Neutron Data (1)

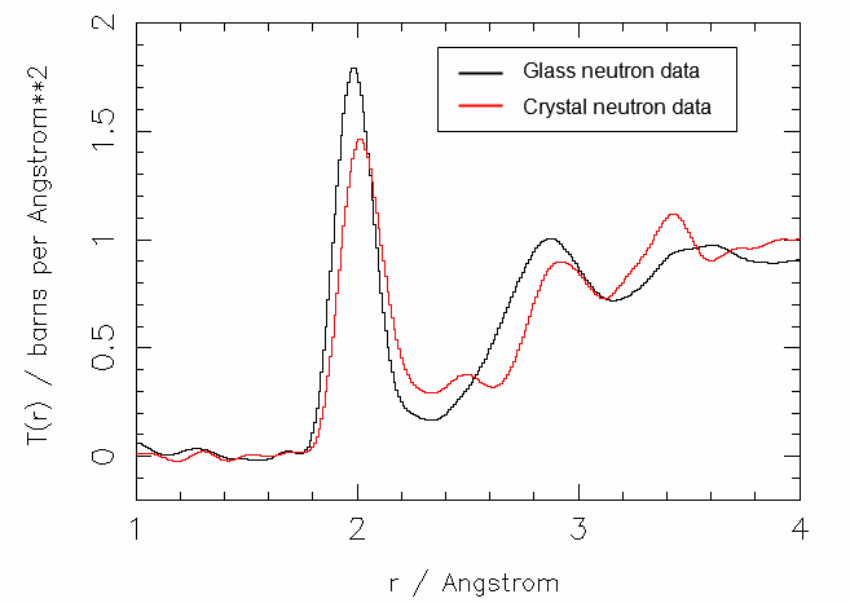


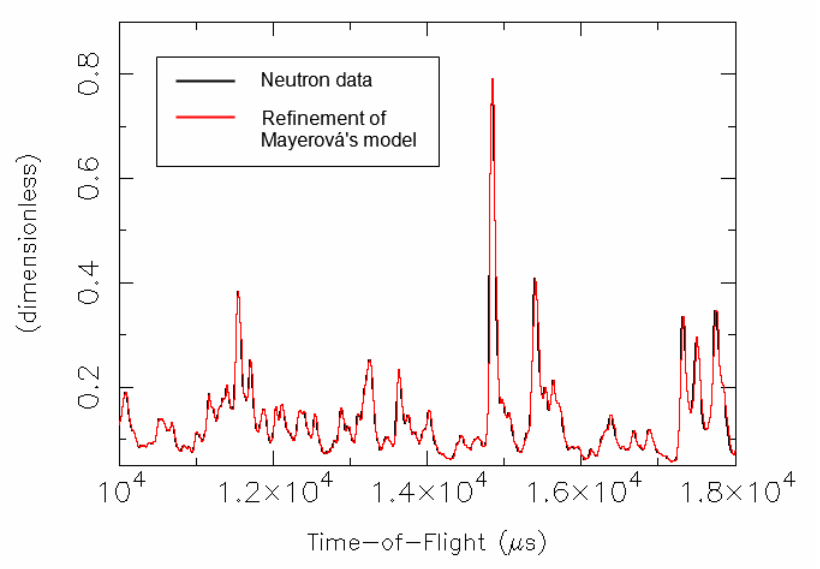


- Menchetti's model is not consistent with the observed neutron diffraction pattern…

- …but Mayerová's model is.
- This suggests a more complex, but more ordered, crystal structure.

Neutron Data (2)





- The onoratoite glass data is suggestive of a structure based closely on the crystal.
- The Sb–O distance appears to be shorter in the glass than the crystal.

- Rietveld refinement is being performed on Mayerová's structure to match the observed crystal data, prior to analysing the glass.
- R (weighted) = 0.19

Conclusions

- Mayerová's improvement of Menchetti's model of the onoratoite structure appears to be confirmed by the new neutron diffraction data.
- The structure of the glass formed from onoratoite appears to be related to the crystal structure.
- Further information (coordination numbers, refined crystal structure, glass structure…) yet to come.
- With the loosely-bonded Cl atoms, could there be the potential for ionic conductivity in these materials?

Acknowledgements

- Emma Barney at the University of Warwick for her assistance in analysing the neutron data.
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Thanks for listening!

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