Determining the Structure of Antimony Oxychloride Glass

Robin Orman (Warwick), Diane Holland (Warwick), Alex Hannon (ISIS)

Abstract

Crystalline onoratoite ($Sb_8O_{11}Cl_2$) has been prepared and a portion vitrified by splat-quenching of the melt. The two samples have been compared with an earlier Sb_2O_3-$SbCl_3$ glass using Raman spectroscopy and examined using neutron diffraction. The Raman data confirms that the new antimony oxychloride glass is essentially identical to the older sample and has a structure based on that of crystalline onoratoite. The crystal neutron data suggests that a recent, complex structural model is more accurate than an older one with oxygen disorder. The glass neutron data supports the Raman data in showing that the structure is broadly similar to the crystal. Rietveld refinement and RMC techniques will be used to analyse the data further.

Introduction

Sb_2O_3-based glasses are of interest due to the lone pair of electrons on the antimony atom and the non-linear optical properties that may arise from it.

A chlorine-stabilised Sb_2O_3 glass was prepared by Johnson *et al.* [1] from the melting of an equimolar mixture of Sb_2O_3 and $SbCl_3$, and this system has been the subject of a more detailed study by Orman [2].

In Orman's work, differential thermal analysis showed that the glass exhibited similar thermal events to those of the crystalline antimony oxychloride $Sb_8O_{11}Cl_2$ (onoratoite) and Raman spectroscopy showed the structure to be similar. Energy dispersive X-ray analysis also estimated the chlorine content to be ~8.5 at.%, similar to that predicted for onoratoite (9.5 at.%).

Onoratoite: crystal and glass

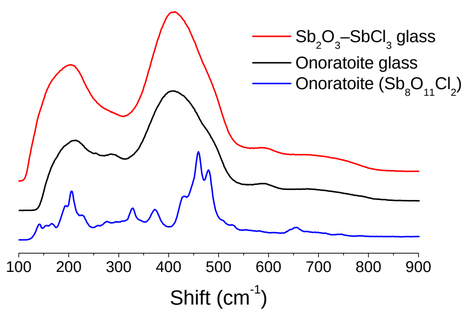


Figure 1 *– Spectra obtained at room temperature on a Renishaw Invia Raman spectrometer using a 20mW laser source of wavelength 514nm.*

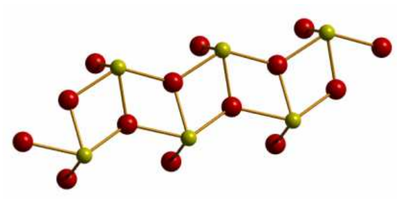
Crystalline onoratoite was prepared according to the method of Matsuzaki *et al.* [3], melted in a lidded alumina crucible and splat-quenched to form a glass.

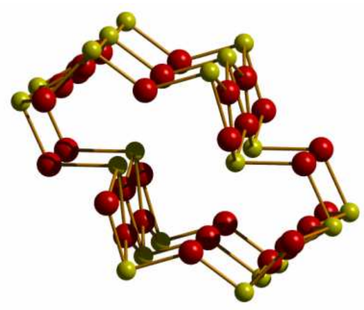
Raman spectroscopy shows the new glass to be almost identical to the earlier Sb_2O_3-$SbCl_3$ glass, and similar to the crystalline onoratoite.

Neutron diffraction of both forms of onoratoite was carried out on the GEM diffractometer at the ISIS neutron source, UK.

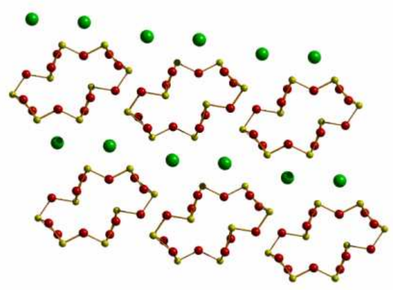
Menchetti's model

After a single-crystal XRD experiment, Menchetti *et al.* [4] proposed a model based on a simple antimony-oxygen 'ladder' structure. The chains link to form self-contained 'tubes' of atoms.

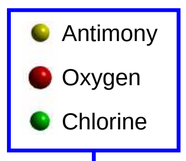




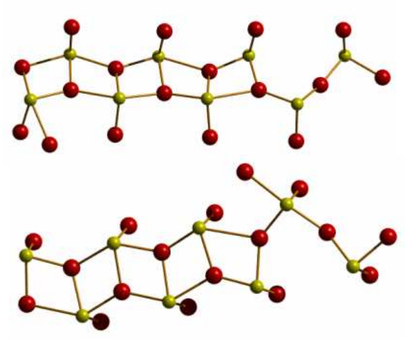
The tubes form alternating layers with the chlorine atoms, giving rise to unusually wide Sb–Cl separations (3.2-3.8 Å).



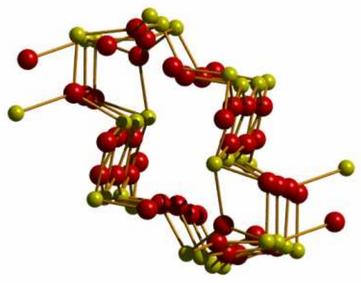
4 of the 6 oxygen positions are partially occupied, resulting in 3/8 of the antimony atoms being 3-coordinated, the rest 4-coordinated.



More recently, Mayerová *et al.* [5] conducted a new X-ray diffraction study and developed their own model – a more complex version of Menchetti's.

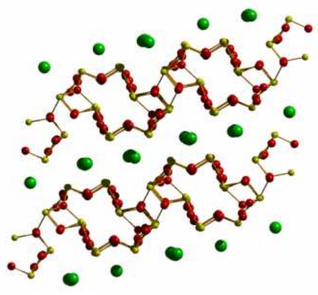


Mayerová's model



This new model has two types of ladder chain, each one interrupted by [SbO_3] groups. One oxygen site also forms links between the tubes within each layer.

5/16 of the Sb are 3-coordinated and Sb–Cl distances are 2.95-3.20Å – shorter than in the Menchetti study but still unusually long.



Which model is more accurate? (1)

Simulated correlation functions for the two models of crystalline onoratoite (generated using the XTAL program [6]) have been compared with the neutron data.

Menchetti's model (Fig. 2) shows a noticeable deviation from the observed data. The model predicts half of the Sb–O separations to be 2.2 Å (the links along the 'ladder') whilst the perpendicular Sb–O 'rungs' of the ladder are 1.9-2.1 Å. This leads to roughly equivalent peaks in the correlation function at 2.0 Å and 2.2 Å – however, the data shows that a large majority of the Sb–O separations are of the shorter variety, with only a small proportion of longer bonds. The shortest O–O distance predicted by Menchetti, arising from the oxygen atoms in the plane of the ladder, is also noticeably shorter than that actually observed.

Which model is more accurate? (2)

A comparison of the data with Mayerová's model is more favourable (Fig. 3). Both the Sb–O and the O–O contributions reproduce the observed data with a high degree of accuracy; the small discrepancy in the position of the first O–O peak may be attributable to a less-than-perfect merging of the information from different detector banks, or due to small inaccuracies in oxygen positions in the model.

It is noticeable from the previous work [5] that the Bond Valence Sum (BVS) parameters for the chlorine atoms in this structural model are of the order of 0.2-0.25 (i.e. significantly lower than the expected value of 1.0). The antimony and oxygen atoms have, approximately, their expected BVS values (3.0 and 2.0, respectively).

Glass and crystal comparison

The data from the neutron diffraction appears to support the Raman data in that the onoratoite glass structure seems to exhibit similar atomic correlations to the crystal. The absence of intensity at ~2.1 Å in the glass probably indicates shorter and more uniform Sb–O bonds than in the crystal, perhaps due to the relaxation of the requirement for long-range atomic ordering.

We plan to use Rietveld refinement to improve the structural model of crystalline onoratoite – previous studies have used X-ray diffraction, so the neutron data should provide better information on the lighter atoms – and Reverse Monte Carlo modelling to determine the glass structure.

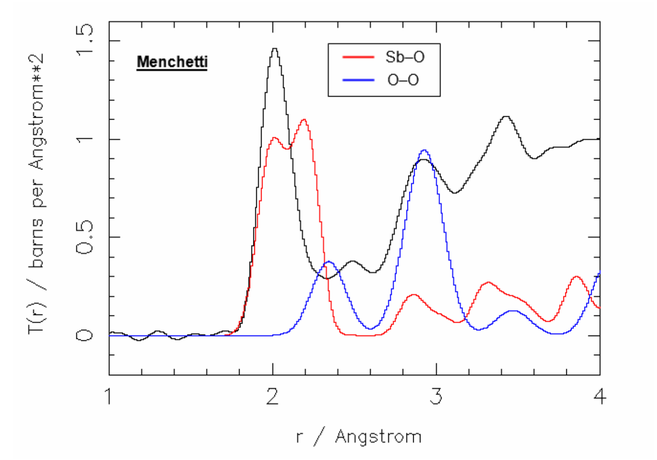


Figure 2 *– Simulated partial correlation functions for Menchetti's model compared with the neutron data (partial correlation functions not shown do not influence the total below 2.9 Å). Simulated thermal parameters for the Sb–O and O–O correlations have been adjusted to give the best fit with the data.*

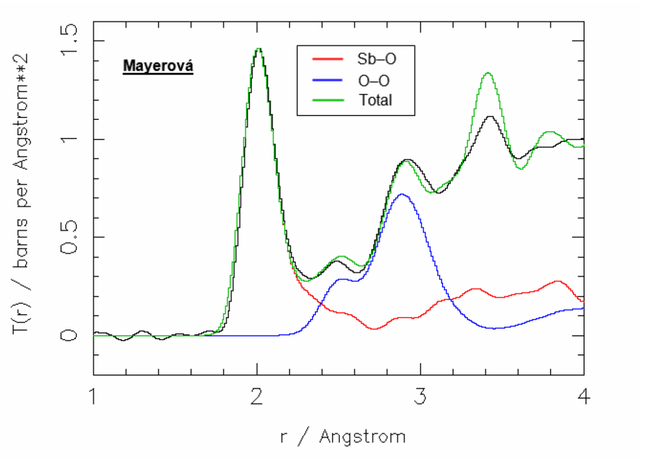


Figure 3 *– Simulated correlation functions for Mayerová's model compared with the neutron data (partial correlation functions not shown do not influence the total below 2.9 Å). Simulated thermal parameters for the Sb–O and O–O correlations have been adjusted to give the best fit with the data.*

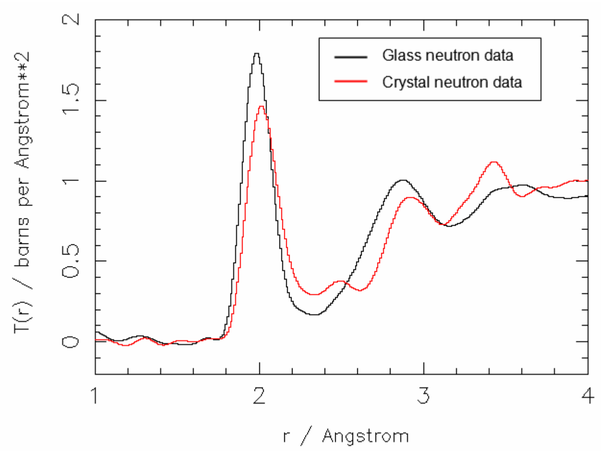


Figure 4 *– A comparison of the onoratoite glass and crystal neutron diffraction data.*

Conclusions

From the analysis of the neutron diffraction data to date, it appears that Mayerová's model of the onoratoite crystal structure is more accurate than Menchetti's. This will prove useful in determining the structure of the glass since there is evidence from Raman spectroscopy that the glass structure is strongly related to that of the crystal.

References

1. J. A. Johnson, D. Holland, J. Bland, C. E. Johnson, and M. F. Thomas, *J. Phys.: Condens. Matter* **15** (2003) 755-764.
2. R. G. Orman, MSc Thesis, University of Warwick, 2005.
3. R. Matsuzaki, A. Sofue, and Y. Saeki, *Chem. Lett.* **12** (1973) 1311-1314.
4. S. Menchetti, C. Sabelli, and R. Trosti-Ferroni, *Acta Crystallogr. C* **40** (1984) 1506-1510.
5. Z. Mayerová, M. Johnsson, and S. Lidin, *Solid State Sci.* **8** (2006) 849-854.
6. A.C. Hannon, *XTAL: A program for calculating interatomic distances and coordination numbers for model structures*, Rutherford Appleton Laboratory Report RAL-93-063, 1993.

Acknowledgements

RGO would like to thank EPSRC for a studentship.

THE UNIVERSITY OF WARWICK

EPSRC Engineering and Physical Sciences Research Council

ISIS