

XANES in doped radiosensitive glasses

A.L. Yusoff^{a,1}, R.P. Hugtenburg^b, D.A. Bradley^{a,*}

^a*School of Physics, University of Exeter, EX4 4QL, UK*

^b*Queen Elizabeth Medical Centre, University Hospital Birmingham B15 2TH, UK*

1. Introduction

Radiosensitive glasses can be formulated with a variety of dopants, the interest of the present group being in the thermoluminescence produced by such systems. X-ray absorption near-edge structure (XANES) allows study of the chemical state and local structure of an ion in the vicinity of K- and L-edges. Transitions to intermediate bound states within the same atom may be treated within an isolated atomic model. Given its ability to show the resonant intermediates as well as chemical shift of the K-edge energy with increasing charge, XANES can be used to determine charge state, including mixed charged states, of a given species within a material. Experiment and theory (Suortti, 1979; Nakai et al., 1998) suggest that XANES can be measured in a fluorescence mode, enabling more accurate characterisation of the sample. This is the mode of measurement employed herein.

2. Experimental methodology

Samples of Cu- and Zn-doped glass (~1.3 wt% of dopant in both cases) have been produced using the sol-gel technique, the samples being sufficiently thick (>1 mm mean free path for 9 keV photons in glass of 0.25 mm) to allow the assumption that scatter is independent of thickness to a reasonable approximation; the effect of multiple scatter can be predicted using Monte Carlo methods. Measurements have been made at the Daresbury SRS beamline 16.3 and at beamline

BM28 (the X-ray magnetic scattering beamline, XMaS) at the European Synchrotron Radiation Facility, ESRF. At both Daresbury SRS and the ESRF, fluorescence was measured using a HPGe detector (resolution better than 0.5 keV FWHM). The detector was set along the normal to the beam incident on sample direction, the sample being set at angle of 40° to the incident beam at Daresbury and 45° at the ESRF, with respective scattering angles of 80° and 90° in each case. On each occasion the fluorescence signal was measured for incident photon energies that were scanned from some 10 eV below the relevant K-absorption edge to in excess of 10 eV above the same edge.

3. Results and discussion

In Fig. 1, results for the three samples of glass have been compared to that from a ~100 nm thin Cu film vapour deposited on glass and 0.1 and 1 M solutions of CuSO₄ (i.e. Cu II) from which a calibration has been derived. Two of the glasses were Cu (I) formulations, allowing examination of uniformity of response; the third was formulated to yield Cu II. Results for the CuSO₄ have been suppressed in intensity by a factor of 10. Sensitivity to charge state is immediately apparent. The shoulder appearing on the rising edge of all but the aqueous solution of Cu is indicative of shakedown, occurring where there is covalent sharing of electrons. As an example, for Cu, the covalent atom donates an electron to a vacant 3d shell lowering its charge state and therefore transition energies. The two Cu I formulations, a result of separate sol-gel production runs, provide closely similar features and intensities.

We have also examined Zn-doped glass, looking first at the homogeneity of doping making use of the high brightness available at BM28. Fig. 2. shows results for a

*Corresponding author. Tel.: +44-1392-264085; fax: +44-1392-264111.

E-mail address: d.a.bradley@exeter.ac.uk (D.A. Bradley).

¹Also for correspondence.

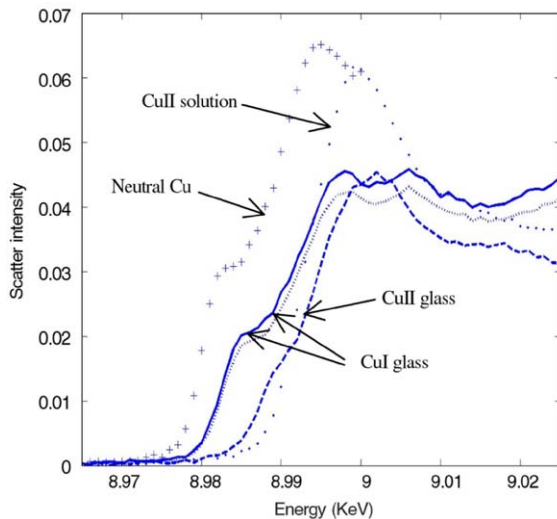


Fig. 1. XANES spectra from three samples of Cu-doped glass; two are Cu I formulations, the third yielding Cu II. Comparison has been made with results for the thin-film of neutral Cu and CuSO_4 (i.e. Cu II).

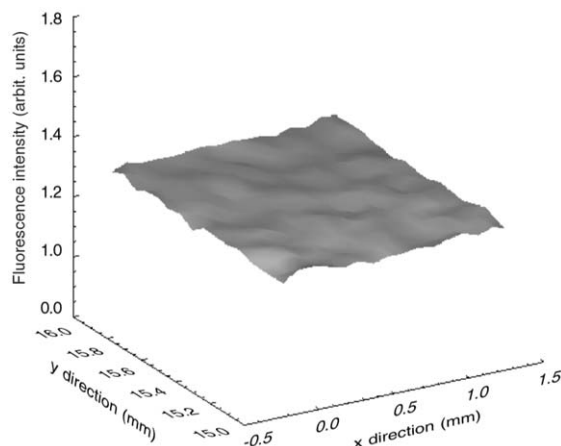


Fig. 2. XRF surface scan for a Zn-doped sample.

Zn-doped sample, using a scanning stage to obtain a $100 \times 66 \mu\text{m}^2$ array of X-ray fluorescence (XRF) measurements acquired over a field of $1.5 \times 1.0 \text{mm}^2$. Using an excitation energy of 9.7102 keV, the Zn K_α fluorescence was detected at 8.6 keV. Uniformity of $\sim \pm 2\%$ is obtained across the sampled area.

Fig. 3. shows the XANES spectra for a Zn-doped sample, comparing this with results from a ZnCl_2

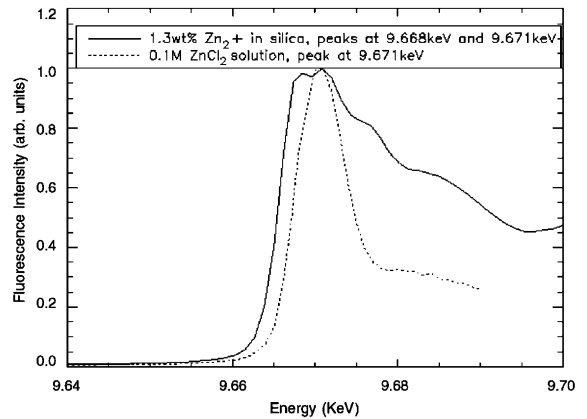


Fig. 3. XANES spectra for a Zn-doped sample.

solution. It is apparent that the double peaked feature indicates the presence of a both a charge state of 2+ and another state lower than 2+. For Zn, the $1s-4p$ transitions energies and oscillator strengths can be obtained from the HEX code of Liberman et al. (1971), adopted in the RTAB database (Kissel, 2000) with a Dirac–Slater exchange potential and a Latter tail. Use of this shows there to be a 3 eV separation between 1+ and 2+, as observed.

4. Conclusion

Measurements of XANES from Cu atoms and ions have been obtained for a variety of environments in an attempt to understand features in the intensity profile, at the atomic level and to seek possible exploitation of atomic information including charge-state and valence structure in analysis.

References

- Kissel, L., 2000. RTAB: the Rayleigh scattering database. *Radiat. Phys. Chem.* 59, 185–200.
- Liberman, D.A., Cromer, D.T., Weber, J.T., 1971. Relativistic self-consistent field program for atoms and ions. *Comput. Phys. Commun.* 2, 107–113.
- Nakai, I., Numako, C., Hayakawad, S., Tsuchiyama, A., 1998. Chemical speciation of geological samples by micro XANES techniques. *J. Trace Microprobe Tech.* 16, 87–98.
- Suortti, P., 1979. Scatter of X-rays near the K absorption edge I. *Phys. Stat. Sol.* 91, 657–666.