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## A NEUTRON DIFFRACTION INVESTIGATION OF THE STRUCTURE OF $\text{PbO-PbCl}_2$ GLASSES

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**Résumé** - La structure de verres  $\text{PbO-PbCl}_2$  a été étudiée par diffraction neutronique, en fonction de la composition entre  $\text{PbO-PbCl}_2$  et  $9\text{PbO-PbCl}_2$ . Alors que la première distance  $\text{Pb-O}$  est bien définie, la distribution des distances  $\text{Pb-Cl}$  est beaucoup plus large, en accord avec les mesures d'EXAFS antérieures.

**Abstract** - Neutron diffraction techniques have been employed to investigate the structure of  $\text{PbO-PbCl}_2$  glasses as a function of composition in the nominal range  $\text{PbO-PbCl}_2$  to  $9\text{PbO-PbCl}_2$ . It is concluded that, whereas the first  $\text{Pb-O}$  distance is well defined, the distribution of  $\text{Pb-Cl}$  distances is much broader, in agreement with a previous EXAFS study.

### 1 - INTRODUCTION

Although neither  $\text{PbO}$  nor  $\text{PbCl}_2$  are glass-formers lead oxychloride glasses can be prepared over a wide range of composition (from 90 to 35 mole %  $\text{PbO}$ ). The continuous manner in which the composition of these glasses can be altered provides an ideal experimental system to study the co-ordination geometry and bond ionicity systematically as a function of anion substitution.

In contrast to the crystalline state, present knowledge concerning the co-ordination chemistry of  $\text{Pb}$  in glasses is rather limited. In both the red and yellow forms of crystalline  $\text{PbO}$  each  $\text{Pb}$  is covalently bonded to 4  $\text{O}$  neighbours in a tetrahedral configuration to give a layer structure with Van der Waals bonding between the layers /1,2/. The  $\text{Pb}^{2+}$  ions in crystalline  $\text{PbCl}_2$ , on the other hand, are 9-fold co-ordinated /1/, this being the highest known co-ordination for a divalent halide. The variation between  $\text{PbO}$  and  $\text{PbCl}_2$  is the result of difference in bond ionicity. The bonding in  $\text{Pb}$  oxychlorides is even more interesting in that  $\text{Pb}$  may exist with a mixed co-ordination shell. For example, Mendipite ( $2\text{PbO-PbCl}_2$ ) contains  $\text{Pb}$  atoms with both mixed 6 and 7-fold co-ordination /3/.

An X-ray diffraction study of  $\text{PbO-PbCl}_2$  glasses /4/ suggests that (a) the  $\text{Pb}$  atoms are in octahedral co-ordination over the entire composition range, (b) the octahedra incorporate two covalently bonded oxygen atoms as a necessary feature for network formation and (c) the oxygen atoms remain mostly in  $\text{OPb}_4$  tetrahedra, while the co-ordination of the chloride ion changes from 6 to 3 as the  $\text{PbCl}_2$  content increases from 10 to 50 mole %. The real space resolution of the X-ray study, however, was not high ( $Q_{\text{max}} = 7.0\text{\AA}^{-1}$ ) and the  $\text{Pb-O}$  and  $\text{Pb-Cl}$  distances were not resolved. Also, no attempt was made to model the intermediate range order. XANES and EXAFS studies at room temperature /5,6/ suggest that the local atomic configuration around  $\text{Pb}$  corresponds to  $\text{PbO}_2\text{Cl}_4$ , perhaps in the form of a distorted octahedron.

## II - OUTLINE THEORY

A full account of the theory of neutron diffraction by amorphous solids has been presented elsewhere /8,9/ and only a brief summary will be given here. The neutron interference function  $QI(Q)$  may be derived from the corrected experimental diffraction pattern  $I(Q)$ , normalised to absolute units

$$QI(Q) = Q[I(Q) - \overline{\sum_j b_j^2} \rho_j(\lambda, 2\theta)] \quad (1)$$

where  $Q$  is the scattering vector of magnitude  $(4\pi/\lambda) \sin \theta$ ,  $\lambda$  being the incident wavelength and  $2\theta$  the scattering angle.  $\overline{b_j}$  is the isotopically averaged neutron scattering length of atom  $j$  and the  $j$  summation is taken over the atoms in one composition unit.  $\rho(\lambda, 2\theta)$  is the so called Placzek correction for departures from the static approximation /10/. The real-space correlation function  $T(r)$  is obtained by Fourier transformation of the interference function.

$$\begin{aligned} T(r) &= T^0(r) + D(r) \\ &= \sum_j \sum_k \overline{b_j} \overline{b_k} \int_0^\infty t_{jk}(r') [P(r-r') - P(r+r')] dr' \end{aligned} \quad (2)$$

where

$$T^0(r) = 4\pi r \rho^0 \left[ \overline{\sum_j b_j} \right]^2 \quad (3)$$

and

$$D(r) = \frac{2}{\pi} \int_0^{Q_{\max}} QI(Q) M(Q) \sin rQ \, dQ \quad (4)$$

$M(Q)$  is the modification function due to Lorch /11/ and  $\rho^0$  the average number of composition units per unit volume. The  $k$  summation is taken over atom types and  $t_{jk}(r)$  is the component correlation function

$$t_{jk}(r) = 4\pi r \rho_{jk}(r) \quad (5)$$

$\rho_{jk}(r)$  being the number density of  $k$  type atoms a distance  $r$  from origin atom  $j$ . The reduced neutron peak function  $P(r)$  defines the experimental resolution in real space and is the Fourier cosine transform of  $M(Q)$ .

## III - EXPERIMENTAL RESULTS AND DISCUSSION

PbO-PbCl<sub>2</sub> glasses have been prepared with nominal composition PbO·PbCl<sub>2</sub>, 2PbO·PbCl<sub>2</sub>, 4PbO·PbCl<sub>2</sub> and 9PbO·PbCl<sub>2</sub>. PbCl<sub>2</sub> and yellow PbO were mixed in the appropriate molar quantities and heated in vitreous silica tubes in an oxyacetylene flame. A brown melt of considerable fluidity was produced and held in the molten state at a temperature of 600-900°C for 1 to 3 minutes. Drops were then quenched between polished metal plates /7/ to give pale yellow glasses which are stable in air and insensitive to atmospheric humidity. Neutron diffraction data have been obtained for the four glass compositions, using the DIDO CURRAN powder diffractometer (A.E.R.E., Harwell) at an incident wavelength of 1.04Å ( $Q_{\max} = 9.8\text{Å}^{-1}$ ), and the corrected, normalised diffraction patterns are shown in fig.1 together with that for a partially devitrified sample nominally of the Mendipite composition. Each pattern is normalised to the nominal composition  $x\text{PbO} \cdot \text{PbCl}_2$ .

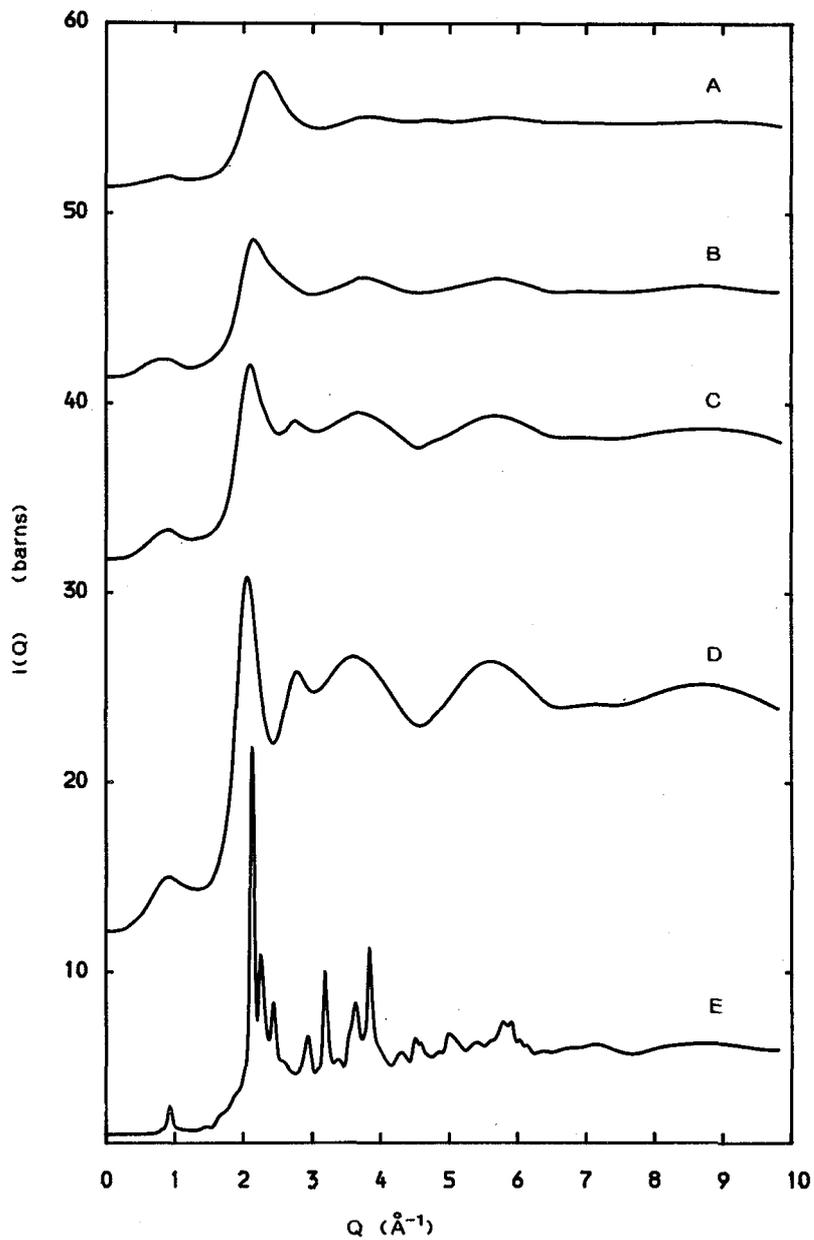


Fig. 1 - Corrected normalised diffraction patterns  $I(Q)$  for A vitreous  $\text{PbO} \cdot \text{PbCl}_2$ , B vitreous  $2\text{PbO} \cdot \text{PbCl}_2$ , C vitreous  $4\text{PbO} \cdot \text{PbCl}_2$ , D vitreous  $9\text{PbO} \cdot \text{PbCl}_2$  and E devitrified  $2\text{PbO} \cdot \text{PbCl}_2$ .

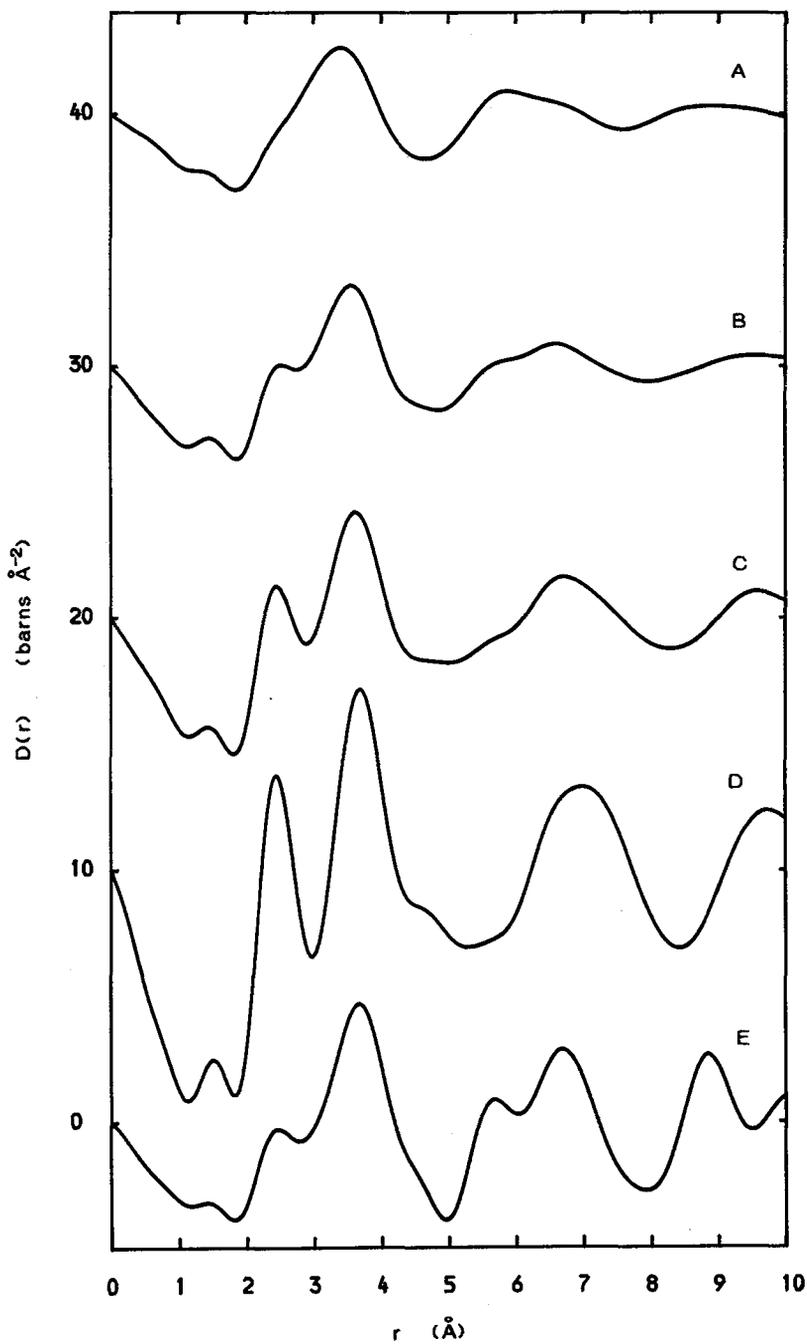


Fig. 2 - Differential Correlation functions,  $D(r)$ . Key as fig. 1.

The diffraction pattern for vitreous  $\text{PbO} \cdot \text{PbCl}_2$  is relatively featureless except for the peak at  $2.3\text{\AA}^{-1}$ . With increasing PbO content, however, sharper peaks arise at 2.06 and  $2.78\text{\AA}^{-1}$  and the structure at higher Q increases together with the small peak at  $\sim 0.9\text{\AA}^{-1}$ . Note that the scattering lengths are such ( $b_{\text{Pb}} = 0.942$ ;  $b_{\text{O}} = 5804$  and  $b_{\text{Cl}} = 0.9605$  in units of  $10^{-14}\text{m}$  /12/) that the diffraction pattern for vitreous  $\text{PbO} \cdot \text{PbCl}_2$  is dominated by the  $\text{PbCl}_2$  component. It is apparent from curve E in fig.1 that the devitrified sample is only partially crystalline and that the resulting Bragg peaks are superimposed on a residual glassy background.

Differential correlation functions obtained from the intensity data of fig.1 are given in fig.2. Again the structure in the curves for the four glass samples increases with increasing PbO content. In particular two relatively sharp peaks arise at 2.46 and  $3.70\text{\AA}$ , the first of which is a Pb-O distance and the second probably an O-O distance within  $\text{PbO}_4$  tetrahedra. (At high PbO contents not all the Pb can exist as the  $\text{PbO}_2\text{Cl}_4$  units of the type identified by EXAFS /5/). A small peak is also observed at  $\sim 1.6\text{\AA}$  which is almost certainly due to a Si-O distance caused by contamination from the  $\text{SiO}_2$  melting tube /13/. The peaks in the correlation function for the devitrified sample correspond in position to those in the parent glass for  $r \sim 8\text{\AA}$  but are much more pronounced, suggesting that the glass structure is similar to that of the crystal but disordered. It should, however, be noted that the devitrified sample still contains a significant fraction of glassy material.

#### IV - CONCLUSION

The relative weightings for PbO and  $\text{PbCl}_2$  in the correlation function are such that the 1:1 composition should reflect mainly the Pb-Cl and Cl-Cl correlations. It may therefore be concluded that there is a broad distribution of Pb-Cl distances in agreement with the results of the EXAFS study /5/. The Pb-O co-ordination shell on the other hand is much more precisely defined, the first Pb-O peak at  $2.46\text{\AA}$  being not much broader than the experimental resolution. Since the present data indicate contamination by  $\text{SiO}_2$  further analysis must await a detailed chemical analysis. High Q intensity data have also been obtained with the Harwell Linac total scattering spectrometer and will be combined with the present data to improve their real space resolution. The results of this analysis will be reported elsewhere.

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